

École polytechnique de Louvain

Dynamics of supramolecular entangled polymeric assemblies based on linear telechelic chains and metal-ligand interactions

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Contents

Introduction	5
I State of the art	7
1 Supramolecular polymers	8
1.1 Definition	8
1.2 Supramolecular polymers based on hydrogen bonding	10
1.3 Supramolecular polymers based on ionic interactions	13
1.4 Supramolecular polymers based on dipolar interactions	16
1.5 Supramolecular polymers based on multiple non-covalent interactions . . .	17
1.6 Supramolecular polymers based on metal-ligand interactions	18
2 Molecular rheological models	21
2.1 Coarse-grained models	22
2.2 Rouse model for unentangled polymers	23
2.3 Tube model	27
2.4 Rouse model for entangled polymers	29
2.5 Reptation	30
2.6 Contour Length Fluctuations	33
2.7 Constraint Release process	36
2.8 Cates' model	37
II Materials and methods	42
3 Materials	43
4 Sample preparation	46
5 Experimental method	48
5.1 Rheometry	48
5.1.1 Linear viscoelasticity	48
5.1.2 Boltzmann superposition principle	49
5.1.3 Oscillatory shear measurements	50
5.1.4 Time-Temperature Superposition (TTS) principle	53
5.2 Experimental determination of the storage and loss moduli	54
5.2.1 Dynamic Time Sweep	54

5.2.2	Dynamic Strain Sweep	54
5.2.3	Dynamic Frequency Sweep	55
III	Experimental results	56
6	Viscoelastic properties of metallo-supramolecular linear polymers: Relaxation times and Failure of the TTS principle.	57
6.1	Failure of the Time-Temperature Superposition	58
6.2	Second plateau and aggregates	58
6.3	Variations of the crossover frequency	59
6.3.1	Influence of the ion density	60
6.3.2	Influence of the metal ion nature	61
6.3.3	Influence of the temperature	62
7	Viscoelastic properties of metallo-supramolecular linear polymers: Influence of the reversible bonds on the sample elasticity	63
7.1	Qualitative observations	63
7.2	Second plateau and aggregates	64
7.3	Quantitative analysis of the storage modulus	65
7.3.1	Influence of the ion density	65
7.3.2	Influence of the ion nature	66
7.3.3	Influence of the temperature	67
8	Comparison with star samples	68
IV	Modeling	71
9	Model based on the Time Marching Algorithm	72
9.1	Description of the TMA Model	72
9.2	TMA model applied to the reference sample	76
9.2.1	Log-normal distribution	76
9.2.2	Results	78
10	TMA model applied to the metallo-supramolecular polymers	80
10.1	Flory distribution	80
10.2	Aggregates	82
10.3	First version of the model: the associated chains are stable	85
10.3.1	Construction of the matrix LI	85
10.3.2	Results	86
10.3.3	Conclusion	97
10.4	Second version of the model: the associated chains can break before being relaxed	99
10.4.1	Modification of the model	99
10.4.2	Results	101

11 Discussion	116
11.1 Probability of association p_{ass}	116
11.1.1 Deviation from the association probability expected from the sample preparation	116
11.1.2 Variation of p_{ass} with the temperature	118
11.1.3 Variation of p_{ass} with the ion density	119
11.1.4 Variation of p_{ass} with the ion nature	120
11.2 Association time τ_{ass}	120
11.2.1 Variation of τ_{ass} with the temperature	120
11.2.2 Variation of τ_{ass} with the ion density	121
11.2.3 Variation of τ_{ass} with the ion nature	122
11.3 Dissociation time τ_{free}	123
11.4 Formation of aggregates	124
11.4.1 Influence of the ion nature	124
11.4.2 Influence of the temperature	125
Conclusion	126
Acknowledgements	128

Introduction

This master's thesis focuses on the rheology of supramolecular linear polymers based on metal-ligand interactions. It is a continuation of the research performed by Dr. Flanco Zhuge, which concerned the synthesis and the study of the dynamics of metallo-supramolecular polymeric assemblies. Supramolecular polymers are a class of material that is attracting a great deal of attention in the field of material science, thanks notably to their dynamic properties and high versatility. They are therefore the subject of numerous researches. However, many questions still need to be addressed in order to fully exploit their potential.

More specifically, in this work, the dynamics of entangled supramolecular assemblies based on linear telechelic chains is investigated from a rheological point of view. The metal-ligand interactions involved consist of the complexation of terpyridine ligands with transition metal ions, forming a highly directional non-covalent bond. All the samples investigated are based on the same entangled poly(n-butyl acrylate) precursor functionalised at both ends by a terpyridine group. Two types of ions, zinc and copper ions, were added in different quantities to the samples. Furthermore, a blend of zinc and copper was also used in order to combine the two dynamics within the same sample. When complexes are formed between ligands and ions, the building blocks become associated, creating long linear assemblies. The objective is then to investigate the rheological behaviour of these supramolecular assemblies, and to understand the influence of temperature, ion density, and ion nature on their dynamics. The role played by the aggregates which can possibly appear in specific conditions is also investigated and discussed.

To this end, Dynamic Frequency Sweep tests are performed thanks to a rotational rheometer, and the experimental data obtained are analysed. The first observations resulting from the examination of the curves are then tested by means of the tube-based model developed at UCL, called the Time Marching Algorithm. We modify this last one and combine it with statistical tools in order to account for the dynamics of our telechelic chains. More precisely, two versions are developed, each one relying on different assumptions, in order to better capture the complexity of the behaviour of these polymers. By looking at the dependence of the modelling parameters in function of the polymer characteristics and temperature, we extract important information on the sample dynamics.

This document is structured as follows: in the State of the Art (Part I), the notion of supramolecular polymer is explained, along with examples focusing on telechelic linear supramolecular polymers found in the literature, and all the relevant rheological models are presented. Then, the Part II describes the materials investigated and the rheological methods used for this purpose. The experimental results obtained are presented after in

the Part III. Finally, the Part IV includes everything related to the modelling. It begins with a description of the model used. Then the two versions of the model developed are presented along with the results obtained, and it ends with a discussion on these results.

Part I

State of the art

Chapter 1

Supramolecular polymers

1.1 Definition

Supramolecular polymers are a class of polymeric materials based on non-covalent interactions. A definition given by Meijer[1] that is now quite widely used to describe them is the following: supramolecular polymers are "polymeric arrays of monomeric units that are held together by highly directional and reversible non-covalent interactions, resulting in polymeric properties in solution and bulk". On the basis of this definition, it is possible to identify the main characteristics of a supramolecular polymer.

Firstly, we need monomeric units bearing functional groups. Thanks to these groups, the monomeric units will be able to form non-covalent bonds with each other. The non-covalent nature of the bonding is essential to create supramolecular polymers. Indeed, as there is no sharing of the electrons as for covalent bonds, a non-covalent bond is reversible. This property makes the polymer a dynamic array. In the absence of permanent bonding, there is a constant association and dissociation between the functional groups, hence two monomeric units do not stay connected indefinitely. It is thanks to this characteristic that supramolecular polymers are said to be "self-healing".

Secondly, supramolecular polymers are created by self-assembly. When the monomeric units are brought into contact, they will automatically interact with each other, and thus create a polymeric array. There is no need for an initiator, a catalyst, or anything else as for a common polymerisation reaction. There are in fact only two parameters that control the growth of the supramolecular polymers: the association constant K_a and the concentration of monomer $[M]$. It must also be noted that the monomer concentration dependence is linked to the number of functional groups present on one monomeric unit. The degree of polymerisation DP is then linked to these parameters by the following equation [2], and this relationship is also illustrated on Figure 1.1 :

$$DP \propto (K_a \cdot [M])^{1/2} \quad (1.1)$$

The notions of conversion or extent of the reaction are thus not applicable for supramolecular polymers. It is due to the self-assembly phenomenon, and it makes their processing very easy.

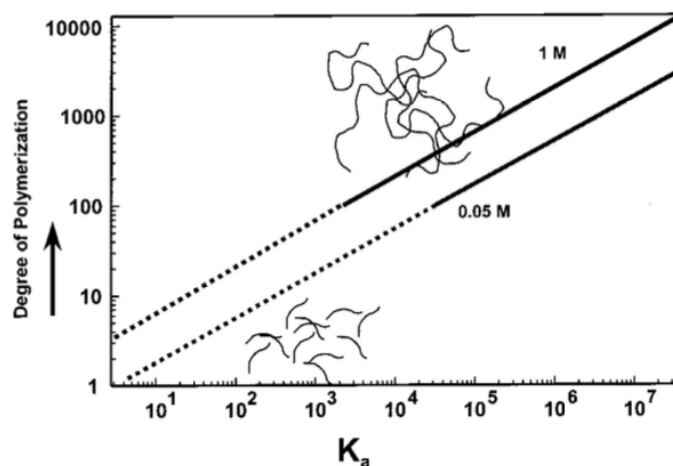


Figure 1.1: Theoretical relationship between the degree of polymerisation of the supramolecular polymer and its constant of association K_a . The two lines correspond to two different monomer concentrations $[M]$, illustrating that DP also increases with $[M]$ [1].

Thirdly, a large range of non-covalent interactions exists: van der Waals interactions, hydrogen bonding, metal-ligand coordination, aromatic stacking, host-guest interactions, ionic interactions, halogen bonding,... Supramolecular polymers can be created by a lot of different means. The only limitation is that the interactions must be highly directional. Otherwise, the bonding between the monomeric units is too weak, and it leads to a material that does not have the desired polymeric properties. Indeed, on the one hand, self-assembly is not efficient, and on another hand, the time of association between the functional groups is excessively short. However, even with this limitation, there is still a wide variety of non-covalent interactions that can be used, each one having its own characteristics, namely its own constant of association. Hence, it is possible to have a very fine tuning of the final properties of the polymer.

Finally, the nature, the size, and the architecture of the polymer composing the monomeric units does not affect the creation of a supramolecular polymer. Indeed, it relies only on the functional groups and their ability to interact non-covalently. It means that any polymer can be used, and the later may also have functional properties. For instance, optical properties, stimulus responsivity,... [4]. That leads to a very broad range of properties available for the supramolecular polymers.

Thanks to their reversible and dynamic properties, as well as their high tunability, supramolecular polymers have attracted a lot of attention, and they have been the subject of several studies. As this work is focused on supramolecular polymers based on linear telechelic chains, only the studies regarding this kind of polymers will be reviewed here. For the same reason, more attention will also be drawn to polymers in bulk than in solution.

1.2 Supramolecular polymers based on hydrogen bonding

In 1999, Meijer et al. investigated the rheological comportment of chains of poly(dimethylsiloxane) functionalised at both ends with ureidopyrimidine (UPy) [3]. The central polymer chain is apolar, while the UPy groups are able to form four hydrogen bonds with each other.

A hydrogen bonding is a dipole-dipole interaction between a hydrogen atom and an electronegative atom, namely oxygen, nitrogen, and fluorine. The strength of such a bond is quite low (between 5kJ/mol and 30kJ/mol for one hydrogen bond [4]). Creating supramolecular polymers based on simple hydrogen bonds would lead to chains of low degree of polymerisation, and thus to polymers with low mechanical properties. This is why Meijer et al. used these UPy end groups that are able to form a quadruple hydrogen bond, as it allows to increase the strength of the bonding. The sequence of donor and acceptor groups on the ureidopyrimidine was chosen as donor-donor-acceptor-acceptor (DDAA) by Meijer et al, the association constant for this functional group being equal to $10^6 M^{-1}$. This sequence is important with respect to the strength of the bond, as attractive secondary electrostatic interactions must be taken into account. This was first shown by Jorgensen et al. for triple hydrogen-bonded complexes [5]. He found that, despite having the same number of hydrogen bonds, a DAA-AAD array has a higher binding constant than an ADA-DAD array, because of these attractive secondary interactions. They are represented for the two tautomers of the UPy functional group on Figure 1.2. It proves that the DDAA sequence leads to higher association strength, as there are more attractive secondary interactions than for the DADA sequence.

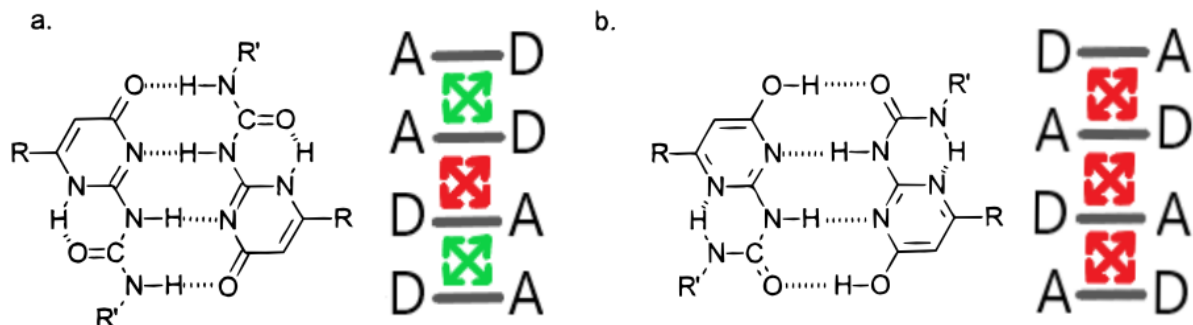


Figure 1.2: Keto tautomer (a) and enol tautomer (b) of the ureidopyrimidine functional group. Each one leads to a different bonding sequence: DDAA for the keto tautomer, and DADA for the enol tautomer [3]. On the right of each tautomer, the secondary electrostatic interactions are drawn, in green if they are attractive and in red if they are repulsive. Even if the number of hydrogen bonding is the same, the association constant of the keto tautomer will be higher than the one of the enol tautomer, as the secondary interactions are more attractive for the DDAA sequence.

In their paper, Meijer et al. compared two types of precursors: on one hand, some had a short spacer in between the UPy end groups, containing only two monomer units, hence they were oligomers. On the other hand, others had a long spacer of 100 monomer units, hence we can already talk of polymer chains.

When hydrogen bonds are created in between the UPy groups, the chain ends are linked to one another, which makes longer chains: it is like a second polymerisation occurring. That is possible because one UPy group reacts only with one other UPy group: as the interaction is directional there is a dimerisation of the end groups, but no clusters are created. Moreover, hydrogen bonds are a kind of non-covalent interactions, so this second polymerisation is reversible and dynamic.

Both chains (short and long spacers) were compared to their analogue having their end groups capped with benzyl groups in order to prevent the creation of hydrogen bonds. Concerning the oligomer, the results of the viscosity and rheology measurements are the following: firstly, they saw a large increase of the viscosity as shown on Figure 1.3. And while the analogue had a too low viscosity and thus couldn't provide reliable rheological data, viscoelastic properties appeared for the oligomer with reactive chain ends when performing a dynamic oscillatory shear measurement (see Figure 1.4). It proves that there is really a kind of polymerisation happening. As they could observe a narrow rubbery plateau, the chains should be longer than M_e , the length of the chain between two entanglements. With this information, they were able to estimate that the degree of polymerisation of the chains created was greater than 100.

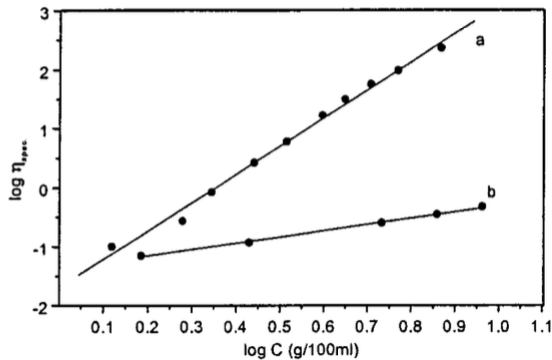


Figure 1.3: Specific viscosity of the oligomer associated through hydrogen bonds (a) versus its non-reactive analogue (b) [3].

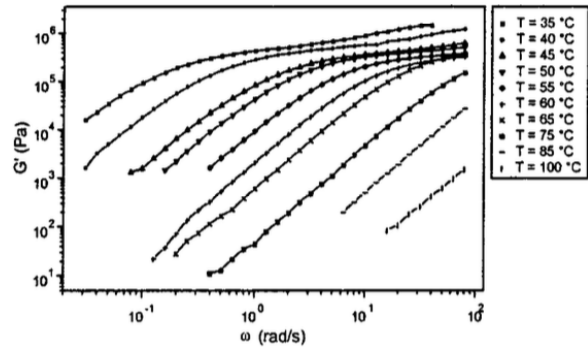


Figure 1.4: Storage modulus of the reactive oligomer at several temperatures. Apparition of a plateau at low temperatures [3].

They also performed the dynamic oscillatory shear measurement on the chains with a long spacer, and on their unreactive analogue. The later had a fluid-like behaviour at all frequencies, while for the reactive chains they could observe the crossover of G' and G'' , which shows the transition from rubbery behaviour at high frequencies to viscous behaviour at low frequencies. They estimated that the average degree of polymerisation of these chains with a long spacer was around 20.

In conclusion, Meijer et al. have been able to obtain an amorphous supramolecular polymer based on telechelic chains linked through multiple hydrogen bonds.

Another supramolecular polymer based on hydrogen bonding has been investigated by Rowan et al.[6]. The monomer units have a poly(THF) backbone, end-capped by a nucleobase derivative. They used two nucleobases: one monomer unit was terminated with an adenine derivative and the other was terminated with a cytosine derivative. These

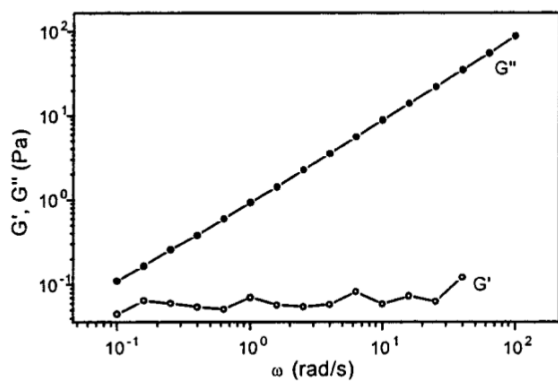


Figure 1.5: Storage and loss moduli of the unreactive analogue of the chain with a long spacer [3].

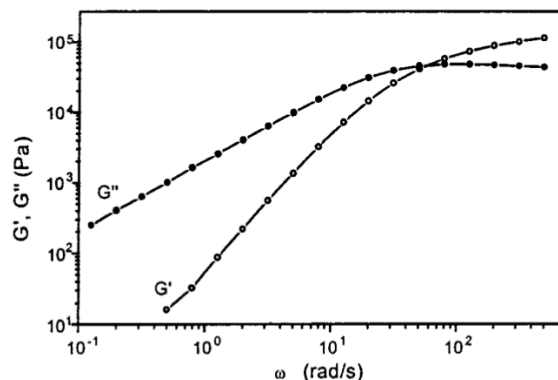


Figure 1.6: Storage and loss moduli of the reactive chain with a long spacer [3].

nucleobases are able to form hydrogen bonds between one another, and that way, longer chains can be created. However, the association constant is quite low: around $1.5M^{-1}$ for the adenine and around $5M^{-1}$ for the cytosine. Hence, it is not enough to give polymeric properties to the material.

Nonetheless, they observed a change of material properties for both types of chains when adding the nucleobase derivatives at the chain ends. The melting temperature increases from 20°C for the precursor to 135°C with adenine and 126°C with cytosine. They were also able to obtain polymeric-like films with these, while the precursor was a soft and waxy material. This large change of material properties cannot be explained by the hydrogen bonds alone. In fact, there is also a phase separation occurring: on one hand the soft poly(THF) matrix, and on the other hand, a hard semi-crystalline phase formed by the end-groups (see Figure 1.7). In this second, hard phase, the nucleobase derivatives are stacked and held together thanks to $\pi - \pi$ interactions.

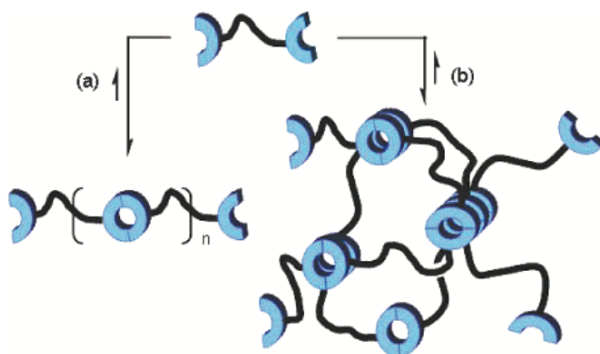


Figure 1.7: Supramolecular polymer formed by (a) linear assembly of the nucleobases through hydrogen bonding, (b) phase segregation and linear assembly through hydrogen bonding.

As there are two different mechanisms involved, the hydrogen-bonding and the phase separation, the rheological behaviour of this supramolecular polymer is complex. At low temperature, a polymer-like behaviour is observed. But at higher temperatures, G' and G'' become parallel to each other, which is characteristic to a gel. This behaviour could

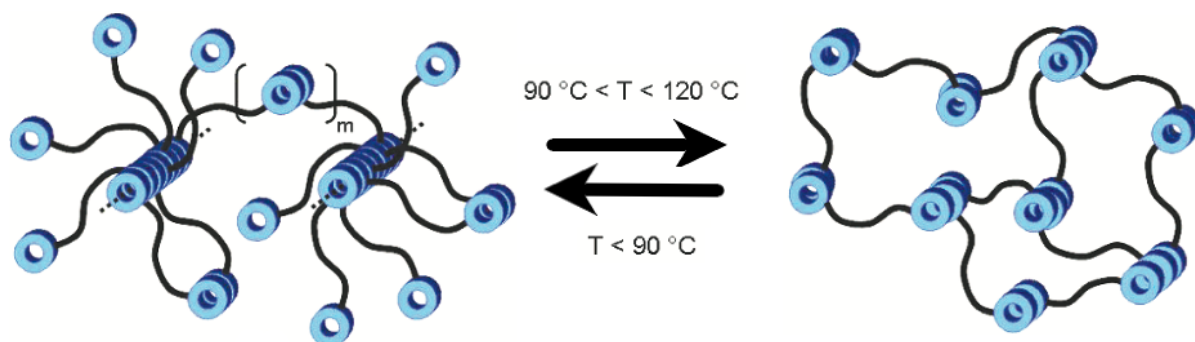


Figure 1.8: Transition of the structure of the supramolecular polymer upon a change of temperature. When heating above 90°C, the stacks become smaller and more numerous, the free ends disappear, and the percolation threshold is reached [6].

be explained as such: at low temperature, the hard phase is composed of big stacks of nucleobases, and some chain ends are still free, without hydrogen bonding. At this stage, the stack concentration is below the percolation threshold, and the material has polymeric properties. Upon heating, the stacks become smaller, therefore more numerous, and the hydrogen-bonds are increased, there are no more free chain ends. That way, the stacks are all linked to each other, and the percolation threshold is reached: a gel is obtained. This transition is depicted on Figure 1.8. Finally, when reaching the melting point, the solubility of the hard phase in the matrix increases, hence the phase separation disappears, there are no more polymer-like properties.

Finally, in this study, they were able to obtain a supramolecular network thanks to weak hydrogen-bondings, and with the help of a phase separation between the chain ends and the polymer backbone. This phase separation is driven by another non-covalent interaction: $\pi - \pi$ interaction between the nucleobase derivatives. These polymers are also very sensitive to the temperature, as their mechanical properties change from polymer-like, to gel-like upon heating.

1.3 Supramolecular polymers based on ionic interactions

Bailly et al. studied the rheological behaviour in the bulk of a supramolecular polymer created by ionic interactions [7]. The building blocks had a backbone made of polybutadiene, which is apolar, and were terminated at both ends by a carboxyl group, which is polar and acidic. Their molecular weight was equal to 7.4kg/mol, which is quite low. This acid precursor was then neutralised with an alkali metal hydroxide, which is a base. They used several different hydroxides, based namely on lithium, sodium, potassium and rubidium. When neutralised, they could confirm thanks to FT-IR measurements that an ionic salt of type $\text{COO}^- \text{M}^+$ is created.

Regarding the structure of the polymer obtained, they observed a phase separation between the polar backbone and the ionic groups. The ionic groups form clusters inside an amorphous matrix.

They first investigated the influence of the carboxyl end groups on the rheology. To this end, they compared the precursor $\text{PBd}(\text{COOH})_2$ with $\text{PBd}(\text{COOEt})_2$, which is a non-acidic equivalent of the precursor. These polymers were not neutralised with the alkali metal cations. The terminal relaxation time of the acid precursor appeared larger than the one of the esterified analogue by about one decade, and the plateau modulus G_N^0 was also larger, as shown by Figure 1.9. These effects indicate that there is a dimerization of the acid groups through H-bonds, which is not possible after esterification. This association already creates a weak network. And when comparing the acid precursor to a sample neutralised, both G_N^0 and the relaxation time increase a lot, which shows that a much stronger network is created with the alkali metals (see Figure 1.10).

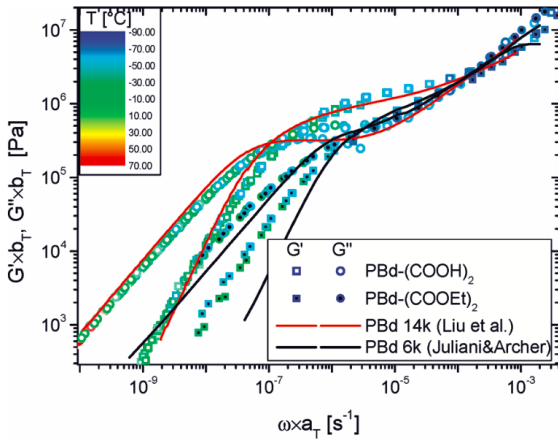


Figure 1.9: Storage and loss moduli of the acid precursor, its esterified version, and linear PBd chains of different masses [7].

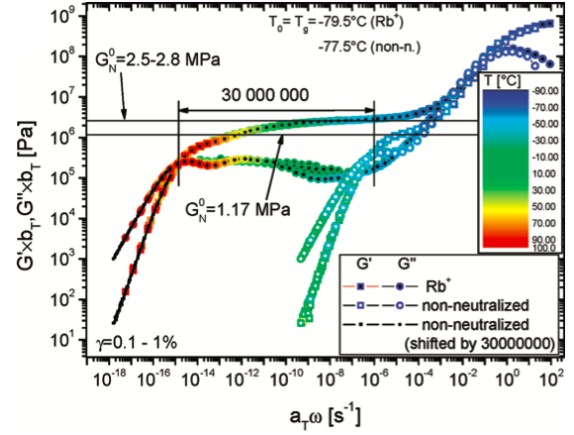


Figure 1.10: Storage and loss moduli of the acid precursor and of the sample neutralised with Rubidium [7].

Then, for the neutralised samples, they showed that the rheological properties depended on a certain equilibration time, which is the time needed for the clusters to reach a more ordered state. When resetting the supramolecular structure of a sample, some time is needed for the rheological properties to reach their equilibrium value. For example, they could observe a shoulder on the loss modulus, which is sharper for the reset sample than for the equilibrated one, as shown on Figure 1.11. This shoulder can be attributed to the presence of clusters. The plateau modulus also increases when reaching the equilibrium. In addition, the terminal relaxation does not follow a single Maxwell mode. It can be explained by considering the combination of two relaxations mechanisms: firstly the destruction of the clusters, followed by relaxation by reptation. These results are true for all metal ions, but when the mass of the ion increases, the equilibration time increases, as well as the terminal relaxation time and the plateau modulus.

Finally, on Figure 1.12, they compared the shift factors arising from the Time-Temperature Superposition principle for the different samples. Usually, these shift factors follow an Arrhenius relationship with respect to the temperature, which means that by plotting the logarithm of the shift factor $\log(a_T)$ versus $1/T$, a straight line is obtained. That is indeed the case for the non-neutralised acid precursor and the esterified analogue. On

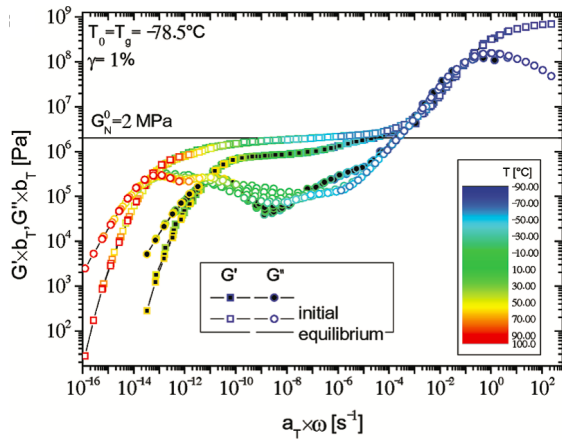


Figure 1.11: Storage and loss moduli of the sample neutralised with potassium hydroxide, in the initial state ($t = 300$ sec, filled dots), and in the equilibrium state ($t = 2.4 \cdot 10^8$ sec, empty dots) [7].

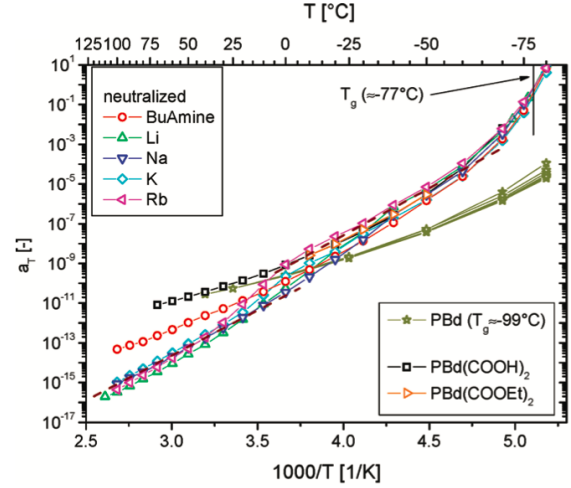


Figure 1.12: Arrhenius plot: shift factors as a function of the temperature for normal PBd, the acidic precursor, its esterified version, and the different neutralized samples [7].

the contrary, for the metal neutralised samples, above a certain temperature, the shift factors deviate from this straight line, they do not follow the same trend as the acidic precursor. This behaviour can be explained if the clusters created by the secondary ionic interactions are considered as crosslinkers. At low temperature, these clusters are stable and really behaves as crosslinkers, the shift factors follow indeed the Arrhenius law. While at higher temperatures, the clusters are less and less stable, they are too weak to act as crosslinkers. This is why the temperature dependence becomes stronger. It can be considered that the clusters have their own glass transition temperature T'_g , below which they behave as crosslinkers, and above which the chains can move freely inside the cluster. This T'_g can be linked to the shoulder in the loss modulus, which represents this secondary relaxation process. The T'_g also appears to increase when the sample passes from a reset to an equilibrated state, which means that the clusters become more and more ordered when reaching the equilibrium. With heavier counterions, the deviation from the Arrhenius law takes place at higher temperatures, because they allow forming clusters highly ordered, thus more stable, than those formed with lighter ions. These more perfect clusters have a strong crosslinking effect, leading to a higher G_N^0 , but they are also more difficult to form, which explains the longer equilibration time.

To conclude, in this study, the carboxyl end groups form clusters through secondary ionic interactions with alkali metal counterions. These clusters act as crosslinkers below their glass transition temperature. And above that temperature, they become weaker, which allows the chain ends to move. This is a secondary relaxation process. The creation of these clusters is also dependent on the equilibration time and the mass of the counterion ion: at longer times and with heavier counterions, the cluster is better ordered, and thus more stable.

1.4 Supramolecular polymers based on dipolar interactions

Another type of supramolecular polymer has been studied by van Ruymbek et al. [8]. This polymer has a polyisoprene backbone, which is apolar and is end-capped with phosphorozwitterionic groups, that are polar. Driven by strong dipolar interactions, these end-groups self-assemble to form clusters. Consequently, a transient network is created. In this study, the building blocks are rather long and well entangled. This article investigated not only telechelic linear chains but also telechelic star chains. However, only the results concerning the linear chains are presented here.

The rheology measurements performed were dynamic frequency sweep experiments. It revealed that the plateau modulus of the supramolecular polymer was increased compared to the unfunctionalised polymer, which is due to the presence of clusters. The relaxation is also slower, as the chain is not able to relax as long as its ends are trapped into the clusters. Hence, the relaxation is dependent on the probability of an arm to escape from the junctions. Moreover, as this polymer is entangled, when a chain end dissociates from a junction, the time before it associates again in a junction is too short for the chain to relax completely. Hence, several dissociation-association events are needed before reaching the complete relaxation of the chain.

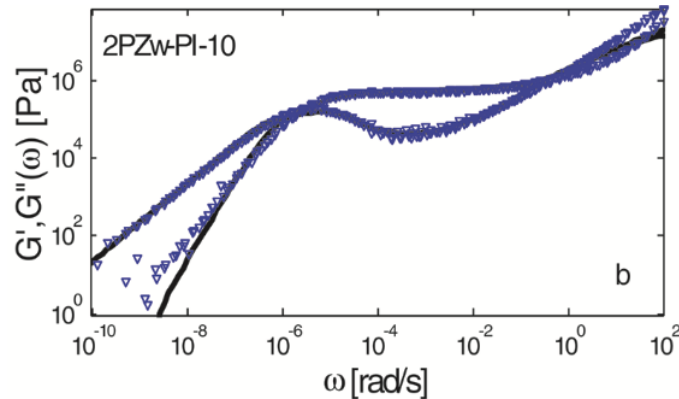


Figure 1.13: Experimental data for the storage and loss moduli of the linear telechelic chains (blue triangles) compared to the simulation obtained from a TMA model (dark lines) [8].

The authors could successfully model their data by using a tube-based time marching algorithm. To do that, they made several assumptions. As the probability for a telechelic linear chain to have its both ends free at the same time is small, they considered that the relaxation mechanism is only the contour length fluctuations (CLF) and not the reptation. They assumed that the average time during which a chain end is associated in a cluster $\tau_{associated}$ is much larger than the time during which it is dissociated from the cluster τ_{free} and also larger than the fluctuation time τ_{fluc} . They also considered that the average number of associated chain ends stays always the same. Finally, the results are shown on Figure 1.13, where it can be seen that the model is in good agreement with the experimental data. The parameters used are $\tau_{associated} = 10^5$ sec and $\tau_{free} = 100$ sec.

1.5 Supramolecular polymers based on multiple non-covalent interactions

Most often, supramolecular polymers are based on only one type of non-covalent interaction, but it is also possible to combine several non-covalent interactions at the same time. This has been done by Schmuck et al, where they used three different interactions to create a supramolecular polymer [9]. Their monomeric unit is very small, it has no polymeric backbone, it is made of a terpyridine ligand connected to a guanidiniocarbonyl pyrrole carboxylate zwitterion. On one hand, two terpyridine ligands are able to form a bond through metal-ligand interactions when adding a metal ion. And on the other hand, the zwitterion is self-complementary, two zwitterions can form strong bonds through ion pairing and hydrogen bonds. That way, long linear chains can be created. It must also be noted that this supramolecular polymer is in solution.

The dimerization can be controlled externally for both end groups. Firstly, for the terpyridine, there is no bonding until a metal ion, here Fe^{2+} , is added to the monomer units. And with the further addition of HEEDTA, which is a competing ligand, this bonding can be broken. Secondly, the zwitterion is only present in solutions having a pH between 5 and 7. Outside this range, the self-assembly of the zwitterion end-groups is not possible. These different reactions are illustrated on Figure 1.14. Finally, both stimuli favouring the dimerisation of the end-groups must be present to obtain long linear chains, hence polymeric properties.

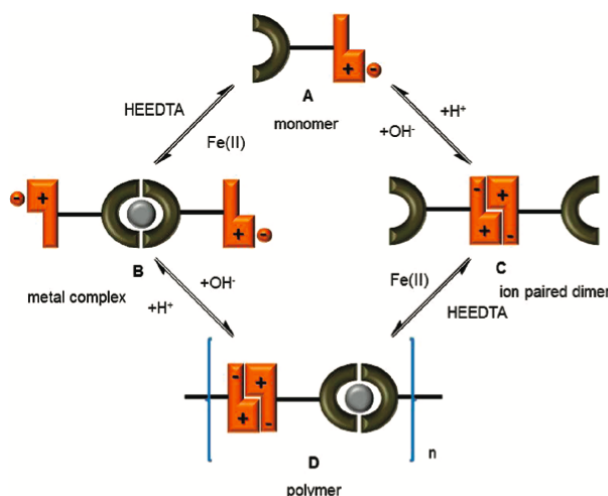


Figure 1.14: Transformation of the monomer into the polymer (and inversely) through the intermediate reactions allowing the creation (and breaking) of the various non-covalent bonds [9].

In order to probe the polymerisation of the monomer units, they measured the viscosity of the solution, the results being represented on Figure 1.15. They first observed an increase of the viscosity with an increasing content of metal ions Fe^{2+} , until they reached a concentration of 0.5 equivalent, where the viscosity becomes constant. It is due to the fact that one ion is needed for two terpyridine ligands. The value of 0.5 equivalent represents the stoichiometric amount, for which all terpyridine ligands are linked with another ligand through one ion. Hence, above 0.5 equivalent, additional ions won't create new bonds.

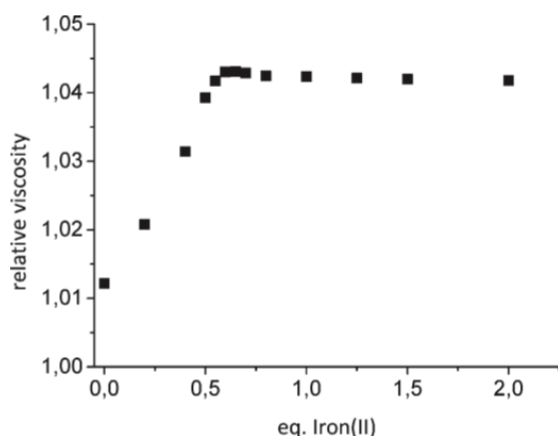


Figure 1.15: Evolution of the relative viscosity of the supramolecular polymer upon increase of the ion density, with Fe^{2+} used as metal ion [9].

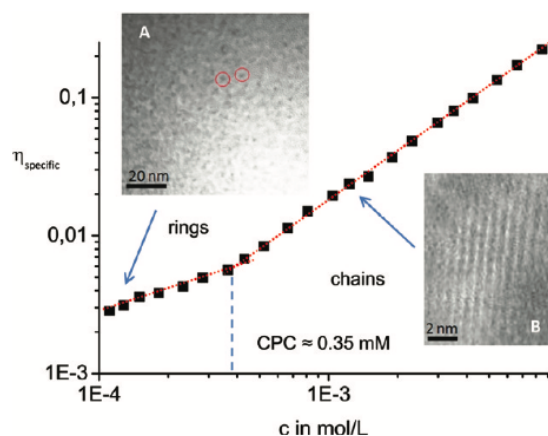


Figure 1.16: Evolution of the specific viscosity upon increase of the monomeric unit concentration in the solution. Image obtained from a TEM at 0.1mM (A) and 1mM (B) [9].

Finally, they also measured the viscosity of the solution containing different concentrations of the monomer. It appeared that the viscosity increases linearly with the concentration. But the slope is lower at low concentration than at high concentration, and these two lines intersect at the critical polymerisation concentration (CPC). Thanks to images obtained with a transmission electron microscope, they could observe oligomeric rings at low concentration, and that these rings become linear chains above the CPC. This polymerisation process is called a ring-chain polymerisation mechanism. So, not only they were able to create a supramolecular polymer through different covalent bonds, but they were also able to identify the polymerisation process.

1.6 Supramolecular polymers based on metal-ligand interactions

Zhugue et al. investigated the rheological properties of supramolecular polymers based on metal-ligand interactions [10, 11]. This type of supramolecular polymer is called "metallo-supramolecular polymer" (MSP) [4]. Several MSPs with different architectures were studied by Zhugue et al.: linear mono-functional chains, linear telechelic chains, and star chains with four arms. All of these monomeric units are composed of a long, entangled poly(*n*-butyl acrylate) (PnBA) backbone end-terminated by tridentate terpyridine ligands. When adding metal ions, complexes are formed between two terpyridine ligands and one ion. This associating unit is called a sticker, and this coordination is reversible and dynamic. Upon the formation of the complexes, either longer chains are created from the linear precursors as shown on Figure 1.17, or a network from the star precursors. They also used different metal ions to observe their effect on relaxation. The monomeric units have a molecular mass above M_e , the mass of the segment between two entanglements. Hence, as these MSPs are entangled, both the entanglements and the stickers will have an influence on the relaxation dynamics. They performed oscillatory frequency sweeps in the

linear regime to investigate the rheological behaviour of their polymers. Only the results concerning the linear telechelic chains are reviewed here.

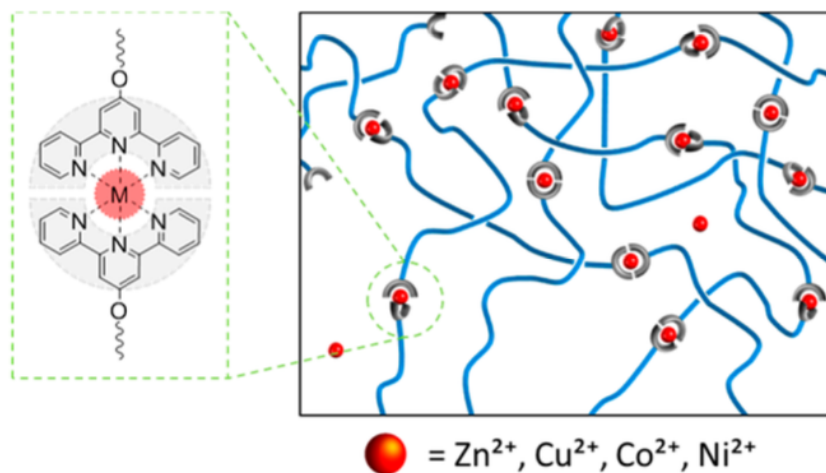


Figure 1.17: Schematic drawing representing the entangled supramolecular polymer created by association of the metal-ligands units in between the linear telechelic chains. On the left, the details of the stickers are revealed. It is composed of two tridentate terpyridine groups, each one corresponding to a different chain end, and the connection between the two is made by a divalent metal ion (Zn^{2+} , Cu^{2+} , Co^{2+} , Ni^{2+}) [10].

Regarding the linear telechelic chains, they observed that at 25°C , the crossover of G' and G'' was shifted towards a lower frequency when comparing the sample without ions to the samples with ions. And it is shifted even further when using less labile ions. Indeed, less labile ions create stickers that are more stable, the relaxation is thus delayed. This effect can be seen on Figure 1.18. They could classify the ions as such, from more to less labile: $\text{Zn}^{2+} > \text{Cu}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+}$. It proves that the nature of the ion has an influence on the dynamics. When performing the same frequency sweep measurements at different temperatures ranging from -20°C to 60°C , they saw that the Time-Temperature Superposition Principle couldn't be used for the MSPs (see Figure 1.19). It is due to the fact that the temperature has an impact not only on the dynamics of the polymer chains, but also on the dynamics of the stickers, and the latter are not taken into account into the TTS principle. More precisely, when increasing the temperature, the sticker's lifetime is reduced, and so is its probability of association with the terpyridine groups.

In addition, they noticed some unexpected effects on Figure 1.18. Firstly, for the sample with cobalt, the moduli G' and G'' are proportional to $\omega^{1/2}$ at lower frequency, while this relationship is usually seen for relaxation by a Rouse process at high frequency. Secondly, with nickel ions at low frequencies, a second plateau appears for G' . Their two hypotheses that could explain these effects are the following: either entangled polymer loops are created through the self-assembly of the building blocks, that can only relax when dissociated. Or the metal-terpyridine complexes could form aggregates by phase-separating from the polymer matrix. However, they couldn't verify which of these hypotheses was the correct one.

In conclusion, apart from these remaining unexplained results, they were able to observe the influence of several parameters on the relaxation dynamics. Firstly, when adding metal

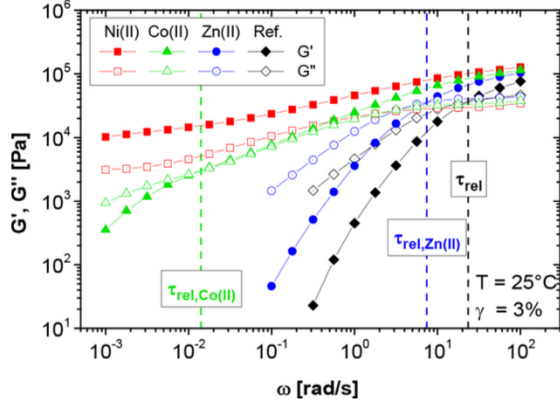


Figure 1.18: Storage and loss modulus of the linear telechelic polymer PnBA-tpy₂ without ions (reference sample in black) and with different transition metal ions [10].

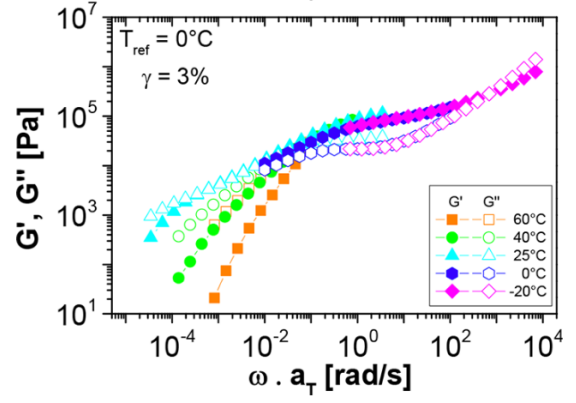


Figure 1.19: TTS applied on the curves G' and G'' of PnBA-tpy₂ mixed with Co²⁺. The curves at different temperatures do not superimpose, the TTS does not work [10].

ions, the final relaxation is always delayed, but depending on the nature of the ion used, this delay can be more or less important, as the metal-ligands complexes are more or less stable. Secondly, the increasing temperature lowers the stability, and consequently the lifetime, of the stickers. Finally, the chain architecture has also an influence on the relaxation dynamics. Indeed, a linear chain can always relax by reptation and CLF even when associated, while a star chain forms a network once ions are added, and the relaxation is possible only when the arms are free, hence when the stickers are dissociated.

Chapter 2

Molecular rheological models

By definition, rheology is the science of deformation and flow of materials. Rheology is particularly interesting for polymers as they are non-Newtonian fluids, and therefore viscoelastic. It means that when a polymer undergoes a stress τ or a deformation γ , it does not react as a viscous liquid, nor as an elastic solid, but it has an intermediate behaviour, which is dependent on the time scale. The Deborah number is useful to understand that time dependency. It is a dimensionless number defined as the ratio between the characteristic relaxation time of the material and the time of the experiment.

$$De = \frac{\tau_{rel}}{\tau_{exp}} \quad (2.1)$$

At short times, $De \gg 1$, the response of the polymer will be the one of a solid: the stress and the deformation are proportional, with G the elastic modulus which is constant.

$$\tau = G\gamma \quad (2.2)$$

At long times, $De \ll 1$, its response will be the one of a liquid: the stress is proportional to the rate of deformation, with η the constant viscosity.

$$\tau = \eta\dot{\gamma} \quad (2.3)$$

And at intermediate times, $De \sim 1$, its response is more complex, it is a combination of the viscous and the elastic responses. The elastic modulus and the viscosity are no longer constant.

$$\tau = G(t, \gamma)\gamma \quad (2.4)$$

$$\tau = \eta(t, \dot{\gamma})\dot{\gamma} \quad (2.5)$$

The variable that is most used to describe the rheological properties of these viscoelastic materials is the modulus $G(t)$, which is also called the relaxation function, or relaxation modulus. If a small deformation is applied, this function does not depend on the amplitude of deformation, and the corresponding stress increases linearly with gamma. This defines the linear regime of deformation.

In order to understand the complex behaviour of non-Newtonian fluids, several rheological models have been developed. Molecular models constitute a category of models that allow establishing an expression of the relaxation modulus $G(t)$ that is very close to experimental

data. Molecular models are not the only ones existing that are effective for this purpose. For instance, the Maxwell and Kelvin-Voigt models, as well as all the models made by a combination of Maxwell and Kelvin-Voigt elements, provide a very good estimation of the relaxation function of viscoelastic materials. However, the advantage of the molecular models is that they allow to describe very accurately the motions of a polymer chain during relaxation, there is a real physical meaning behind them. For the Maxwell and Kelvin-Voigt models, it is also possible to link the model parameters to some properties of the material, but it is not as straightforward as for molecular models [12, 13].

Each of the molecular models that will be presented here describes a different relaxation process, valid only within a certain time window and for a specific polymer chain or fraction of polymer chain. Thanks to all these models put together, one can find an expression for the relaxation modulus $G(t)$. Within these models, at equilibrium and for small deformation (that is in the linear regime), $G(t)$ is interpreted as a measure of "how the orientation of each molecular segment is correlated with their initial orientation through time [12]". In other words, at the initial time, the chain has a certain conformation. And this chain will be considered as completely relaxed when its conformation has completely changed, that is, there are no more correlations with the initial one. As the chain relaxes, the stress measured by the rheometer, $G(t)$, will decrease. Hence $G(t)$ shows how decorrelated are the chain conformations, or how relaxed is the chain. More details about the relaxation modulus $G(t)$, the rheological experiments conducted to measure it and more generally about rheometry are given in chapter 5.

The rheological models presented in the following sections will be used later, in order to analyse the results and to construct the Time Marching Algorithm model that allows a numerical simulation of the relaxation modulus.

2.1 Coarse-grained models

In order to use the molecular models, it is necessary to first simplify the representation of the polymer chain. Indeed, keeping all the atomic details of the chain is not useful and would lead to very complicated molecular models for the relaxation. The simplified representation of the chain used here is a kind of coarse-grained model based on the Dumbbell model [12]. In a coarse-grained model, all the chemical details of the polymer chain are ignored, only its general shape is kept. By doing that, the number of bonds considered is significantly decreased, and the limitations of conformations due to the interactions between the monomers at a short range can be ignored. It leads to a simple string made of n Kuhn segments, also called "freely-jointed chain". A Kuhn segment is not a monomer, it is composed of several monomers, and its characteristics are the following:

- All the Kuhn segments have the same length, noted b .
- The angle between two Kuhn segments can take any value.
- There are no interactions between the Kuhn segments.

It results from these properties that the Kuhn segments are completely independent of each other, there is no excluded volume between them. Hence, in the coarse-grained model,

the chain can be considered as ideal, in analogy with ideal gases. The freely-jointed chain behaves like a Gaussian chain, its conformation can be described by a 3D random walk, and the Kuhn segment is the smallest sub-molecule that is Gaussian. Within this model, the end-to-end distance of the chain is computed thanks to Equation 2.6.

$$R^2 = nb^2 \quad (2.6)$$

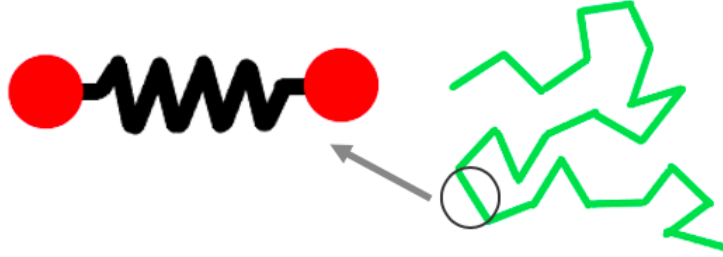


Figure 2.1: Representation of a chain according to a coarse-grained model based on the Dumbbell model.

Then, in the Dumbbell model, each chain is represented as a dumbbell. The dumbbell is made of two beads, linked to each other with a spring. The spring represents the entropic elastic force in the polymer chain, and the two beads bring the friction, the viscosity. However, this representation of the chain is slightly too simplified, because knowing the behaviour of only parts of the chain is also very important in order to understand the relaxation of the chains. Consequently, each Kuhn segment from the coarse-grained model is represented as a dumbbell, as shown on the Figure 2.1. This can be done because, at the level of the Kuhn segment, any sub-chain can be described by a Gaussian just like the entire chain.

2.2 Rouse model for unentangled polymers

The Rouse model is based on the representation of the polymer chain as depicted by the Dumbbell model. It describes well the dynamics of dilute solutions of polymers. Within the Rouse model, the diluted polymer is exposed to a velocity gradient in a flow which will cause the two beads to be drawn away from each other. Thereafter, the relaxation of the chain occurs by diffusion through Brownian motions [12, 14, 13].

The spring of the dumbbell represents the elastic force inside a polymer coil, whose origin is entropic and arises from Brownian motions. The action of stretching a chain decreases the number of possible conformations, which decreases its entropy. As a result, the chain wants to reduce its end-to-end distance $\underline{R}$ in order to seek a more random conformation where its free energy will be minimised. In reaction to the flow that tends to separate the two beads, the dumbbell will undergo this entropic force that will bring the beads closer to each other. The expression for the entropic elastic force in the dumbbell is the following:

$$F_{entropic} = -\frac{3kT}{nb^2}R \quad (2.7)$$

This force is proportional to the end-to-end distance, and the term before R can be interpreted as the spring constant.

The two beads represent the internal friction in a polymer, due to the interactions of the chain with the neighbouring chains or with the solvent. Under the flow, the friction force created by the two beads will oppose the motion created by the entropic elastic force.

$$F_{friction} = n\zeta_0 \frac{dR}{dt} \quad (2.8)$$

The friction force is proportional to the length of the chain, thus proportional to n . The friction also brings the viscosity in the polymer, this is why ζ_0 , the friction coefficient of one Kuhn segment, that is one dumbbell, appears in the equation of the friction force. For a chain composed of n dumbbells, the total friction for the whole chain is then $\zeta_R = n\zeta_0$. And the Einstein relationship gives the diffusion coefficient of the chain:

$$D = \frac{kT}{\zeta_R} \quad (2.9)$$

The friction force $F_{friction}$ acts against the entropic force of the spring $F_{entropic}$. When equilibrium is reached, these two forces are equal, they cancel each other:

$$F_{entropic} = F_{friction} \Leftrightarrow -\frac{3kT}{nb^2} R = n\zeta_0 \frac{dR}{dt} \quad (2.10)$$

From the Equation 2.10, it is possible to get an expression for the elongation of the chain over time, with $R(0)$ the initial end-to-end distance of the chain.

$$\frac{R(t)}{R(0)} = \exp(-t/\tau_R) \quad (2.11)$$

with

$$\tau_R = \frac{n^2 b^2 \zeta_0}{3kT} \quad (2.12)$$

In this last equation, Equation 2.12, τ_R is the characteristic time for an unentangled chain in solution to come back to an equilibrium state, and it is also called the Rouse time. It can also be described as the time needed for a chain in solution to change its initial conformation.

Another way to find the expression of this Rouse relaxation time is based on the Einstein relationship for the diffusion coefficient of the chain as shown on the Equation 2.9. Here, it is assumed that, for the chain to be relaxed, one of its extremities must have diffused to the other extremity. It occurs through a one-dimensional diffusion process of one chain end over a distance equal to the end-to-end distance R . The chain is Gaussian, so the motion of its extremity can be described by a random walk. It is as likely to move to the right or to the left, so its average displacement is null: $\langle r \rangle = 0$. However, its variance is not zero, it is proportional to the diffusion coefficient multiplied by the time: $\langle \Delta r^2 \rangle \propto D\Delta t$. In the case of the diffusion of one extremity towards the other, the diffusion distance is R , thus $\langle \Delta r^2 \rangle = R^2 = nb^2$. It gives:

$$\Delta t = \frac{\langle \Delta r^2 \rangle}{D} \quad (2.13)$$

$$\tau_R \approx \frac{R^2}{D} = \frac{nb^2}{kT/n\zeta_0} = \frac{\zeta_0 b^2}{kT} n^2 \quad (2.14)$$

Except for the factor $1/3$, the equations 2.12 and 2.14 are exactly the same, the dependency on the square of the molar mass appears again through the proportionality $\tau_R \propto n^2$.

The Rouse relaxation time is the time needed for a whole polymer chain to relax through a Rouse process. However, it is also possible to only focus on the relaxation of a fraction of the chain instead of its entirety. As already mentioned, the smallest submolecule is equal to one Kuhn segment. In that case, $n = 1$, and the Rouse time of one Kuhn segment, noted τ_0 , will be defined as:

$$\tau_0 \approx \frac{\zeta_0 b^2}{kT} \quad (2.15)$$

The Rouse relaxation time can then be rewritten as a function of τ_0 : $\tau_R \approx \tau_0 n^2$. The Equation 2.15 can be generalised for any fraction of the chain composed of n/p segments. These are the Rouse relaxation modes. The Rouse relaxation time for each of these modes is noted τ_p and is defined in the Equation 2.16. In this equation, the parameter p is an integer of value comprised between 1 and n , which leads to $\tau_1 \approx \tau_R$ and $\tau_n \approx \tau_0$. Hence, τ_p is the time needed to relax a submolecule of n/p Kuhn segments. The Rouse relaxation modes are illustrated on the Figure 2.2.

$$\tau_p \approx \tau_0 \left(\frac{n}{p} \right)^2 \quad (2.16)$$

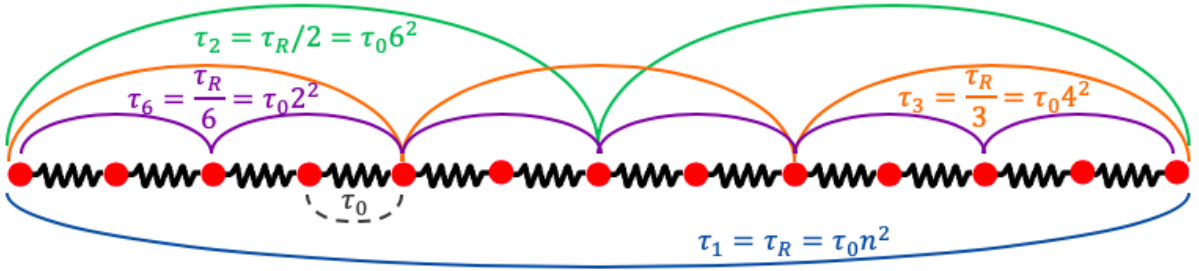


Figure 2.2: Rouse relaxations modes for a chain composed of $n = 12$ Kuhn segments. A smaller fraction of the chain will need less time to change its conformation than a larger segment: $\tau_0 < \tau_6 < \tau_3 < \tau_2 < \tau_1$. The relaxation time of each mode is proportional to the square of the number of Kuhn segment contained in each fraction of the chain.

These modes show that the chain in solution does not relax all at once. At $t = \tau_p$, the number of unrelaxed modes is equal to p , and then it decreases over time. Hence, at the initial time, the number of unrelaxed modes is equal to n , the number of Kuhn segments. Over time, the Kuhn segments relax, the number of unrelaxed modes decreases and the size of the non-relaxed segments increases. The chain now consists of fewer, larger dumbbells. This process is depicted on Figure 2.3.

The entropic elasticity of a chain is driven by the thermal motions, hence, at equilibrium, the total stress is equal to kT per segment able to carry a stress, that is per unrelaxed segment. The general formula for the total stress is shown by the Equation 2.17, with ν the number of segments able to carry a stress. At time τ_p , the number of unrelaxed segments corresponds to the p unrelaxed modes. Hence, as the different modes get relaxed,

the stress decreases, as shown on Figure 2.3.

$$\underline{\tau} = \nu k T \underline{I} \quad (2.17)$$

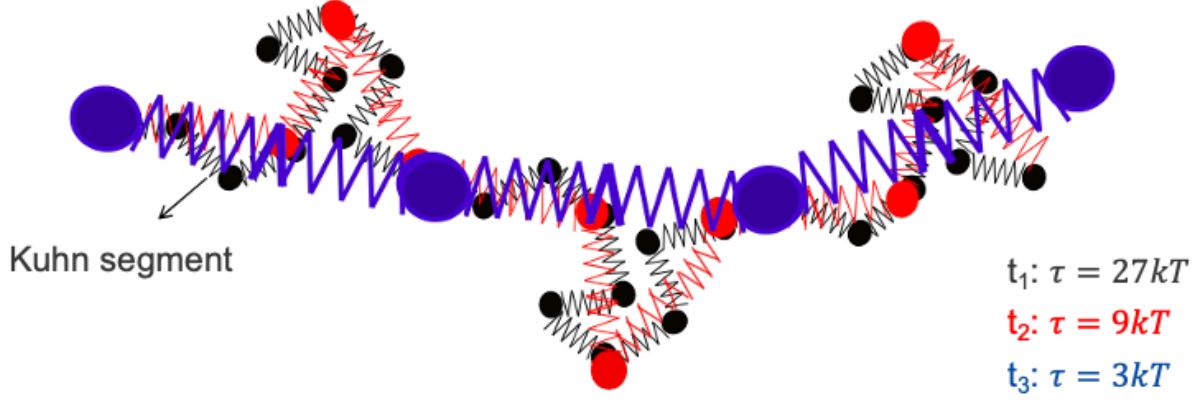


Figure 2.3: Evolution of the stress for different Rouse relaxation modes. At the initial time t_1 , one unrelaxed mode is equal to a Kuhn segment. There are many unrelaxed modes, the total stress being equal to kT per non-relaxed segment, the stress is high. Afterwards, at longer times t_2 and then t_3 , the number of unrelaxed modes becomes smaller, the dumbbells become larger and larger. At the same time, the total stress in the chain decreases. Figure retrieved from [12].

From the Equation 2.17, one can find an expression for the relaxation modulus that uses the concept of the Rouse relaxation modes. In this Equation 2.18, ν represents the number density of active chains.

$$G(\tau_p) \approx kT\nu p \quad (2.18)$$

Assuming that $t = \tau_p$, one can express p as follows:

$$t \approx \tau_0 \left(\frac{n}{p} \right)^2 \Leftrightarrow p \approx \left(\frac{t}{\tau_0} \right)^{-1/2} n \quad (2.19)$$

Introducing this result in the Equation 2.18, it gives:

$$G(t) \approx kTn\nu \left(\frac{t}{\tau_0} \right)^{-1/2} \quad (2.20)$$

This Equation 2.20 is only valid for $\tau_0 < t < \tau_R$. However, it is possible to generalise this equation for all times $t > \tau_0$ by considering that the stress $G(t)$ always tend to zero at long times. To this end, an exponential factor is added in the Equation 2.20 to obtain the Equation 2.21.

$$G(t) \approx kTn\nu \left(\frac{t}{\tau_0} \right)^{-1/2} \exp \left(\frac{-t}{\tau_R} \right) \quad (2.21)$$

The Equation 2.21 is an approximate Rouse result, but it is very close to the exact solution of the Rouse model given by the Equation 2.22, as shown on Figure 2.4.

$$G(t) = \frac{\rho RT}{M} \sum_{p=1}^n \exp \left(\frac{-t}{\tau_p} \right) \text{ with } \tau_p = \frac{\zeta_0 b^2 n^2}{6\pi^2 k T p^2} \quad (2.22)$$

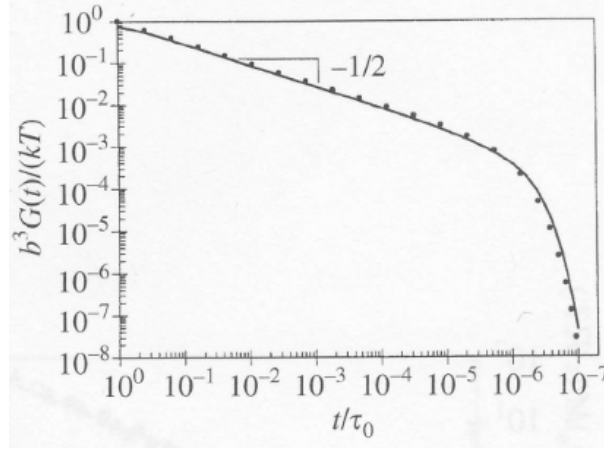


Figure 2.4: Relaxation modulus as given by the exact solution of the Rouse model (Equation 2.22) in full line, and as given by the approximate solution of the Rouse model (Equation 2.21) for the dotted line. Retrieved from [12].

Although the Rouse model was originally developed for dilute solutions of polymers, it is also valid for unentangled polymer in the melt. These two kinds of chains can relax entirely through the Rouse process. However, the Rouse model cannot be used as such for entangled polymers. It has to be adapted within the tube model in order to be valid for entangled polymers.

2.3 Tube model

Unlike an unentangled chain or a chain in solution, an entangled chain is surrounded by all its neighbours, with which it is entangled. This environment hinders the motions of the chain, which cannot move as freely as the unentangled chain. The tube model gives a representation of the chain that allows taking these constraints into account.

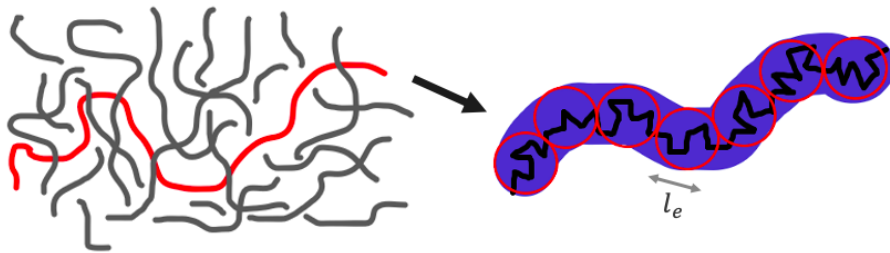


Figure 2.5: Tube model for an entangled chain in the melt. The circles in red highlight the segments between two entanglements. The length of a segment between two entanglements is noted l_e .

According to the tube model, the volume occupied by a chain and in which it can move freely can be approximated by a tube. An example is provided on Figure 2.5. Within the tube, the chain is also blocked by the entanglements, which are located at the intersections of the red circles on Figure 2.5.

The different parameters of interest are the following (some of them being represented on Figure 2.6):

- a is the diameter of the tube.
- l_e is the length of a segment between two entanglements, and its mass is M_e .
- n_e is the number of Kuhn segments between two entanglements.
- n is the total number of Kuhn segments.
- b is the length of one Kuhn segment.
- Z is the number of segments between two entanglements, and it can be computed as $Z = M/M_e = n/n_e$.
- L_{eq} is the length of primitive path of the chain, which is constructed by the segments between two entanglements:

$$L_{eq} = Z \cdot l_e = \frac{n}{n_e} l_e \quad (2.23)$$

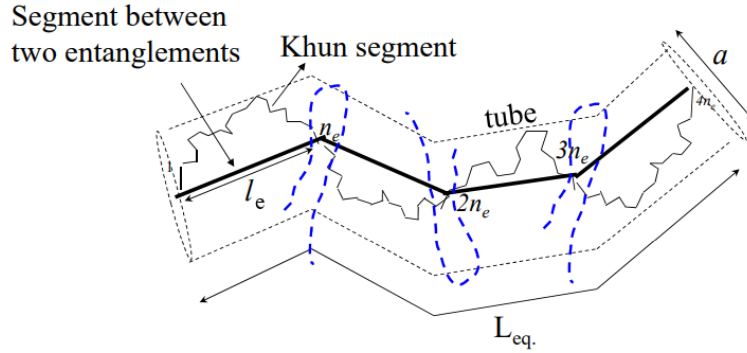


Figure 2.6: Tube model for an entangled chain with 3 entanglements. Retrieved from [12].

As the chain is Gaussian, we can use the same equation as the Equation 2.6 for the distance between two entanglements.

$$l_e \approx n_e b^2 \quad (2.24)$$

Moreover, L_{eq} is also the equilibrium length of the chain, for which the potential of energy, represented at the Figure 2.7, is minimised. The Equation 2.25 describes this potential $U(L_{chain})$.

$$\frac{U(L_{chain})}{kT} = cste - \frac{3nb^2}{a^2} + \frac{3}{2nb^2} L_{chain}^2 \quad (2.25)$$

The value of $U(L_{chain})$ is minimised when

$$L_{eq} \cdot a \approx nb^2 = R^2 \quad (2.26)$$

With the three equations 2.23, 2.24 and 2.26 together, one finds that the diameter of the tube is equal to the length between two entanglements l_e .

$$l_e \approx a \quad (2.27)$$

Finally, within the tube model, for the chain to be relaxed, it must come out of the tube completely. When this happens, the chain has lost all correlation between its current position and the initial orientation of the chain.

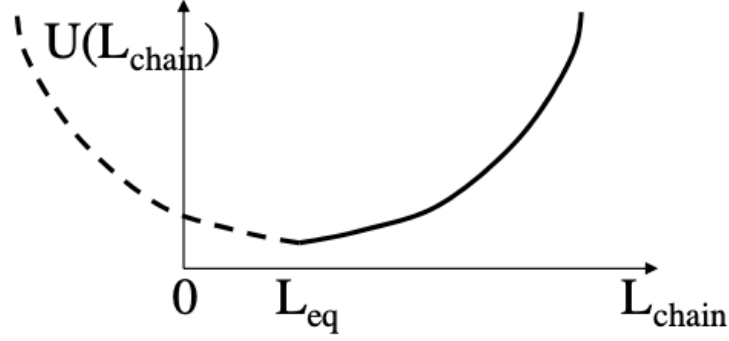


Figure 2.7: Potential of energy for a polymer chain. This potential is minimum at L_{eq} , which is the most probable length of the chain [12].

2.4 Rouse model for entangled polymers

An unentangled chain is able to relax by the Rouse process only. However, it is not the case for an entangled chain, because it is constrained by the tube and the entanglements. Inside the tube, the chain can move very locally, thanks to thermal energy: it is a relaxation corresponding to the Rouse model. The longest segment that can relax by a Rouse process is the one of weight M_e , which is the mass of the section of length l_e between two entanglements. With the notation defined in the section 2.3, the Rouse relaxation time for this segment M_e can be written as

$$\tau_e = \tau_0 \left(\frac{n}{n/n_e} \right)^2 = \tau_0 (n_e)^2 \quad (2.28)$$

After the time τ_e , the segment of mass M_e has lost the correlation with its initial position, but the chain begins to feel the limitations of the tube, the relaxation is thus blocked. The modes longer than l_e cannot relax by a Rouse process. The Rouse model is no sufficient for the complete relaxation of the polymer. Therefore, additional relaxation processes are needed for the chain to leave the tube. This is at this moment that the rubbery plateau is reached.

In consequence, for the entangled chain, the equation of the relaxation modulus of 2.22 must be adapted. Instead of having a sum over all the relaxation modes, $G(t)$ is divided into two terms. On the one hand, there are all the modes that can still relax by the same Rouse process as the unentangled chains. These modes correspond to chain sections smaller than l_e and their p value is comprised between $Z + 1$ and n , with $Z = n/n_e$. Their contribution to the stress, noted $G_{Rouse}(t)$, is similar to 2.22 as the underlying mechanism is the same: only the unrelaxed modes at time t contributes to the stress at time t .

$$G_{Rouse}(t) = \frac{\rho RT}{M} \sum_{p=Z+1}^n \exp\left(\frac{-t}{\tau_p}\right) \text{ with } \tau_p = \frac{\zeta_0 b^2 n^2}{6\pi^2 k T p^2} \quad (2.29)$$

On the other hand, there are all the Rouse modes that are blocked by the tube and that cannot relax. It corresponds to chain sections larger than l_e , and they always fully contribute to the stress. Hence, they can be taken out of the sum of exponential, because their contribution to $G(t)$ is always equal $1 \times \frac{\rho RT}{M}$. The height of the plateau modulus will

be determined by the number of these modes, which is Z .

$$G_N^0 = \frac{\rho RT}{M} Z = \frac{\rho RT}{M_e} \quad (2.30)$$

Finally, when adding Equation 2.29 and Equation 2.30, one finds the relaxation modulus:

$$\begin{aligned} G(t) &= G_N^0 + G_{Rouse}(t) \\ &= G_N^0 + \frac{\rho RT}{M} \sum_{p=Z+1}^n \exp\left(\frac{-t}{\tau_p}\right) \text{ with } \tau_p = \frac{\zeta_0 b^2 n^2}{6\pi^2 k T p^2} \end{aligned} \quad (2.31)$$

The main steps of the relaxation of a polymer melt are identified by numbers on Figure 2.8. At very short times, the number 1 corresponds to the glassy region: the polymer is frozen and nothing moves. Then, the polymer starts to relax by the Rouse process, designated by the number 2. There, the two curves become separated: the blue curve, which is the relaxation modulus of the unentangled polymer, continues to decrease with the same slope because it can always relax by the Rouse process. While the red curve representing an entangled polymer stops decreasing to reach the rubbery plateau of value G_N^0 : this is shown by the number 3. The stress will only take a value lower than G_N^0 when the chains confined in their tube will be able to leave the tube thanks to other relaxation processes. This last step is called the final relaxation and is indicated by the number 4 on Figure 2.8.

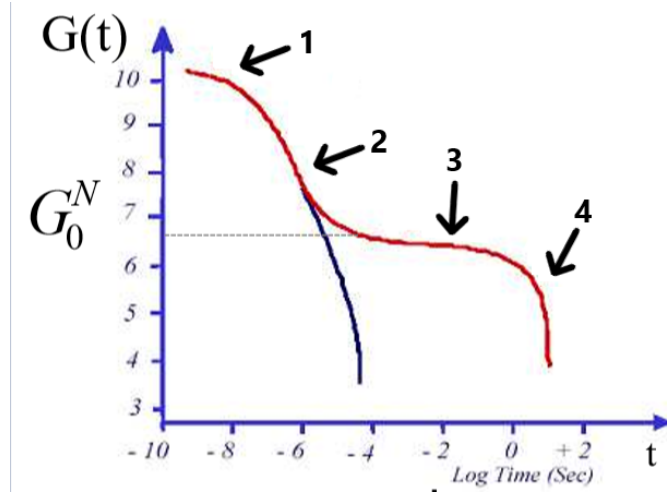


Figure 2.8: Relaxation modulus $G(t)$ for a polymer melt [12]. The blue curve corresponds to an unentangled polymer and the red curve to an entangled polymer. The different steps of the relaxation are indicated by an arrow: (1) Glassy region (2) Rouse process (3) Rubbery plateau (4) Terminal relaxation.

2.5 Reptation

The reptation is the main process behind the terminal relaxation of linear polymer chains. It consists of a one-dimensional diffusion process of the chain out of its tube. The mechanism is depicted on Figure 2.9.

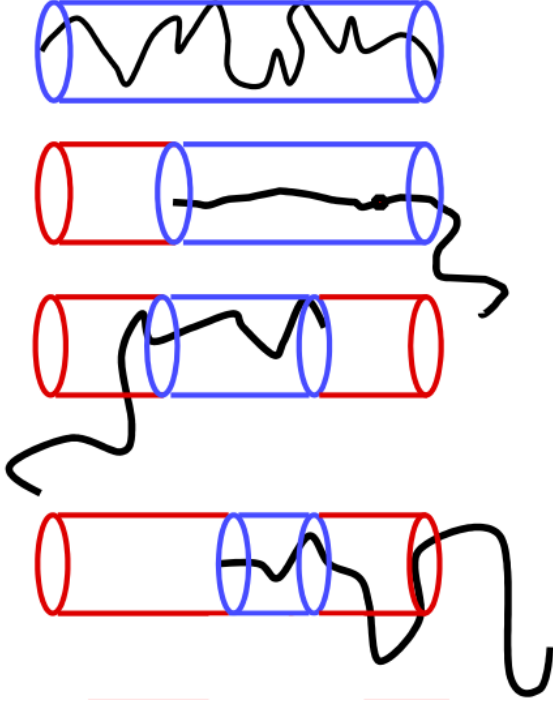


Figure 2.9: Reptation mechanism for relaxation of linear polymer chains. Example of a possible sequence of motions along the axis of the tube[12].

Initially, the chain is entirely inside the tube, and for it to be relaxed, it has to escape from the tube. The initial tube is represented in blue. At this stage, the walls of the tube are assumed to be fixed. The motions of the molecule are limited by these walls, so it has to come out of the tube through its two extremities. Hence, the only possibility for the chain to escape is by diffusing along the curvilinear axis of the tube. As it is the only one axis available to the chain, reptation is a one-dimensional process.

When a part of the chain leaves the tube, it creates a new tube while the initial tube is shortened: it becomes red on Figure 2.9. Thereby, a new tube without correlation with the initial one is gradually created. The segment that has left the tube is relaxed, but the part that is still inside the blue tube still contributes to the stress.

The diffusion coefficient for reptation is defined as follows, with ζ_{tot} the friction coefficient of the chain, ζ_0 the friction coefficient of one Kuhn segment, and n the number of Kuhn segments:

$$D_e = \frac{kT}{\zeta_{tot}} = \frac{kT}{n\zeta_0} \quad (2.32)$$

The distance over which the chain has to diffuse is equal to the length of the tube, which is also the primitive path of the chain L_{eq} . The computation of the reptation time is similar to that used for finding the Rouse relaxation time in Equation 2.14: the diffusion time is equal to the square of the distance to be covered divided by the diffusion coefficient.

$$\tau_{rept} = \frac{L_{eq}^2}{D_e} \quad (2.33)$$

According to Equation 2.23, L_{eq} is proportional to n , and according to Equation 2.32, D_e is proportional $\frac{1}{n}$. This leads to the reptation time varying with the cube of the number of segments, or in other words, with the mass of the chain cubed:

$$\tau_{rept} = \frac{L_{eq}^2}{D_e} \propto \frac{n^2}{n^{-1}} = n^3 \quad (2.34)$$

The exact value of the reptation time is given by Equation 2.35.

$$\tau_{rept} = 3\tau_e \left(\frac{n}{n_e} \right)^3 \quad (2.35)$$

On Figure 2.10, experimental data for the relaxation times of linear chains are shown as a function of the molecular weight of the chain. When $M < M_e$, the chains are short and unentangled, the relaxation time is thus the Rouse time. The slope of 2 in the experimental data confirms the dependence of τ_{rel} on the square of the mass, as predicted by Equation 2.14: $\tau_R \propto M^2$. Above M_e , the chain are entangled, so the relaxation time is the reptation time, the slope increases to 3.4. The Equation 2.35 predicts a dependence of τ_{rept} on M^3 , which is close but not equal to the relationship experimentally found $\tau_{rel} \propto M^{3.4}$. This small discrepancy can be corrected if we take into account another relaxation process: the contour length fluctuations (CLF, see section 2.6).

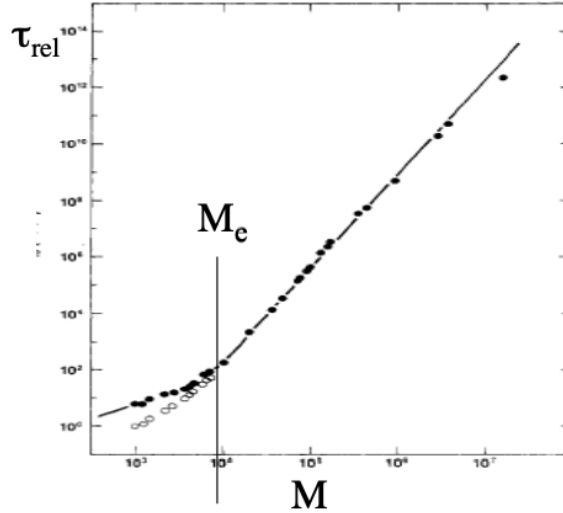


Figure 2.10: Relaxation times of linear chains as a function of their molecular weight M , experimental results [12].

The Doi and Edwards model describes mathematically the reptation and therefore allows to compute the relaxation modulus. To this end, they introduce the function $p(x, t)$, which is the survival probability by reptation at time t of a tube segment located at a distance x from the extremity of the tube (see Figure 2.11).



Figure 2.11: Representation of a linear chain within the Doi and Edwards model. The first extremity of the chain is located at the point 0, and the other extremity is at a distance L_{eq} from the point 0. A segment of the tube situated at a distance x from the extremity 0 is indicated in blue.

As reptation is a diffusion process, the diffusion equation 2.36 is used to find an expression for $p(x, t)$.

$$\frac{\partial p(x, t)}{\partial t} = D_e \frac{\partial^2 p(x, t)}{\partial x^2} \quad (2.36)$$

The two boundary conditions used are the following:

$$p(0, t) = p(L_{eq}, t) = 0 \quad (2.37)$$

$$p(x, 0) = 1, \forall x \in (0, L_{eq}) \quad (2.38)$$

The first condition stipulates that the two points at the extremities of the chain, in $x = 0$ and $x = L_{eq}$, are always completely relaxed by reptation. And the second condition says that initially, the survival probability of all the other points in the tube is 1. With these two boundary conditions, the Equation 2.36 can be solved through separation of the variables. The result is shown on the Equation 2.39.

$$p(x, t) = \sum_{k \text{ odd}} \frac{4}{i\pi} \cdot \sin\left(\frac{k\pi x}{L_{eq}}\right) \cdot \exp\left(\frac{-k^2\pi^2 Dt}{L_{eq}^2}\right) \quad (2.39)$$

Then, in order to find $p_{rept}(t)$, the proportion of the chain that is relaxed by reptation at time t , one has to integrate the Equation 2.39 over the whole length of the chain, from 0 to L_{eq} .

$$p_{rept}(t) = \int_0^{L_{eq}} p(x, t) dx \quad (2.40)$$

$$= \frac{8}{\pi^2} \sum_{k \text{ odd}} \frac{1}{k^2} \exp\left(\frac{-k^2 Dt}{L_{eq}^2}\right) \quad (2.41)$$

The quantity $p_{rept}(t)$ represents the fraction of the chain that will contribute to the stress. Hence, in the equation of the relaxation modulus, Equation 2.31, G_N^0 is now multiplied by this fraction $p_{rept}(t)$.

$$\begin{aligned} G(t) &= G_N^0 \cdot p_{rept}(t) + G_{Rouse}(t) \\ &= \frac{8}{\pi^2} G_N^0 \sum_{k \text{ odd}} \frac{1}{k^2} \exp\left(\frac{-k^2 t}{\tau_{rept}(M)}\right) \end{aligned} \quad (2.42)$$

It must be noted that the process of reptation is only valid for linear chains, not for branched and complex polymers. Indeed, a branch will act as a friction point, and it will prevent the diffusion of the chain out of its tube. Hence, additional relaxation processes are needed for the complete relaxation of complex polymers.

2.6 Contour Length Fluctuations

Contour length fluctuations (CLF) designate a relaxation process that is only valid for the chain ends. It is a secondary relaxation mechanism, so its effect is not as important as reptation or as the Rouse process. Nonetheless, it allows accelerating the relaxation of linear chains by reptation, which leads to the relaxation time being proportional to $M^{3.4}$ instead of M^3 as predicted by the Equation 2.35. It is also the main relaxation mechanism for star polymers. The CLF is based on the fact that the length of the chain is not always exactly equal to its equilibrium L_{eq} , but it varies slightly around this value.

An energy is associated with the chain conformation, and this energy varies with the chain length: this is described by a potential of energy $U(L_{chain})$, which has already been

presented on Figure 2.7. There are two contributions to this potential. Firstly the entropic force tends to bring the two extremities of the chain closer, in order to increase the number of possible conformations of the chain. And secondly the topological force, that has the opposite effect, it tends to increase the length of the chain. The equilibrium length is the length for which these two forces balance each other. L_{eq} is much smaller than the extended length of the chain, which is thus wrinkled inside its tube. Consequently, thanks to Brownian motions, the chain can stretch and retract, its length fluctuates around L_{eq} . When the chain retracts, a small portion of the tube is lost, and when it stretches, the chain end creates a new tube. This mechanism is depicted on Figure 2.12.

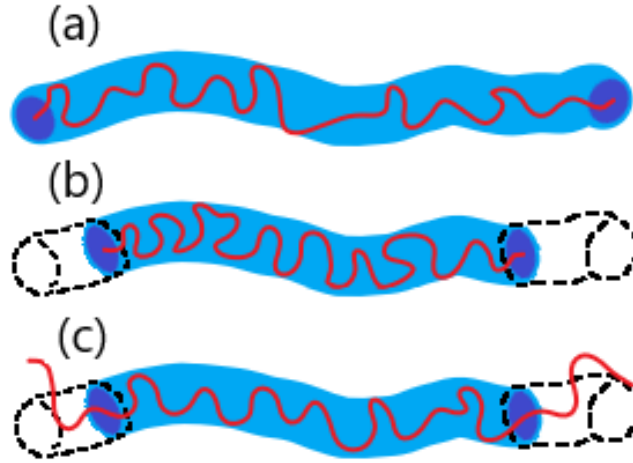


Figure 2.12: Contour length fluctuations for a linear chain. (a) The chain is initially inside the tube, and its length is equal to the equilibrium length L_{eq} . (b) Thanks to Brownian motions, the chain retracts inside the tube, its length becomes smaller than L_{eq} , and the tube segments drawn in dots are lost. The stress which was associated to the chain sections that were in these tube segments is relaxed. (c) The chain stretches ($L > L_{eq}$), and thereby creates a new tube randomly oriented.

The relaxation by CLF is fast for the tube sections that are close to the extremities, but for segments closer to the centre of the tube, it becomes very slow. These longer relaxation times are due to the fact that it is highly unfavourable for the chain to retract its ends on large distances, because its length becomes much smaller than L_{eq} , and the potential associated to this conformation is very large. Before going into the mathematical details, it is necessary to define a new coordinate system. Instead of treating a molecule as a whole, the branches are considered individually, as the same mechanism applies to each of them. Hence, a linear chain is considered as a star with two arms. The new coordinate system is shown on Figure 2.13. The variable x , used before to designate the position of a tube segment between the two extremities (s on Figure 2.13), is now defined as the ratio between s and the equilibrium length: $x = \frac{s}{L_{eq}}$. Within this system, the potential of energy changes compared to the Equation 2.25 given earlier, it is expressed as a function of x instead of L_{chain} , and its new definition is shown by the Equation 2.43.

$$U(x) = \frac{3kT}{2} Zx^2 + cste \quad (2.43)$$

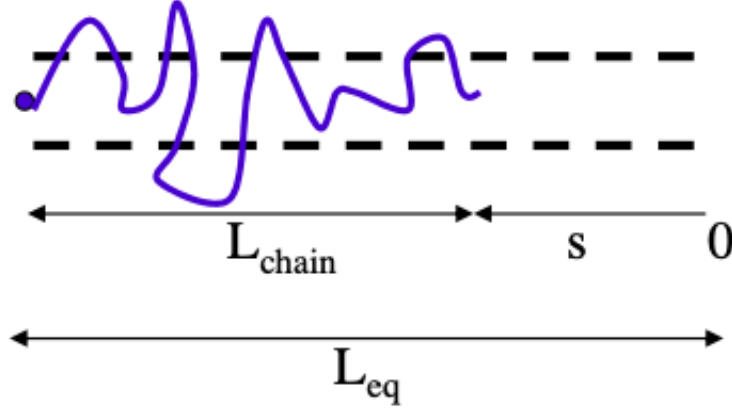


Figure 2.13: Coordinate system used to describe the contour length fluctuations. Only one arm is considered individually, and its end is situated at the point 0.

Two types of fluctuations can be distinguished, each one having a different relaxation time. The first type is called *early fluctuations*, characterised by the time τ_{early} . These fluctuations are due to the thermal energy alone. Consequently, the portions of the tube that can relax thanks to early fluctuations are the ones situated at a distance s from the extremity such as the potential associated is inferior to the thermal energy. This corresponds to x such as $U(x) < kT$. The relaxation time associated to the early fluctuations is defined as:

$$\tau_{early}(x) = \frac{9\pi^3}{16} \cdot \left(\frac{M_{arm}}{M_e}\right)^2 \cdot \tau_{R,chain} \cdot x^4 \quad (2.44)$$

The second type of fluctuations is called *activated fluctuations*. They refer to the relaxation by CLF of the segments for which the thermal energy is not sufficient to allow retraction of the arm over their entire length, that is x such as $U(x) > kT$. The arm must retract over a very long distance to allow relaxation by CLF, which is entropically unfavourable. In that case, the relaxation time, noted $\tau_{activated}$, increases exponentially: $\tau_{activated}(x) = \exp\left(\frac{U(x)}{kT}\right)$. However, $\tau_{activated}$ is more often used under another form, given by Equation 2.45.

$$\frac{\partial \ln \tau_{activated}(x)}{\partial x} = 3 \cdot \left(\frac{M_{arm}}{M_e}\right) \cdot x \quad (2.45)$$

The value of x for which the fluctuations switch from early to activated is noted x_{trans} , and $U(x_{trans}) = kT$. The global fluctuation time is then defined as follows:

$$\begin{aligned} \tau_{fluc}(x) &= \tau_{early}(x) && \text{for } x < x_{trans} \\ \tau_{fluc}(x) &= \tau_{early}(x) \exp\left(\frac{U(x) - U(x_{trans})}{kT}\right) && \text{for } x > x_{trans} \end{aligned} \quad (2.46)$$

Finally, the Equation 2.47 gives the definition of the survival probability by CLF at time t of a tube segment located at position x , noted $p_{CLF}(x, t)$.

$$p_{CLF}(x, t) = \exp\left(\frac{-t}{\tau_{fluc}(x)}\right) \quad (2.47)$$

The signification of $p_{CLF}(x, t)$ is similar to the one $p_{rept}(x, t)$, which is given by the Equation 2.39. Therefore, these two functions are always combined to give the function $\Phi(t)$, which represent the polymer fraction that is not relaxed both by CLF and reptation.

$$\Phi(t) = \sum_x p_{rept}(x, t) \cdot p_{CLF}(x, t) \cdot \Delta x \quad (2.48)$$

This function $\Phi(t)$ can be introduced into the expression of the relaxation modulus of Equation 2.42, which leads to the following equation:

$$G(t) = G_N^0 \cdot \Phi(t) + G_{Rouse}(t) \quad (2.49)$$

2.7 Constraint Release process

Constraint release is a process that helps the relaxation of polymer molecules by increasing the diameter of their tube. In all preceding molecular models, it was assumed that the size of the tube was fixed. However, this assumption is not exactly true, because the size of the tube is dictated by the environment of the chain, and this environment varies over time: as the neighbouring chains are getting relaxed, they leave more space around the chain of interest, whose tube becomes larger, and the relaxation becomes easier. This effect is particularly important for polymers diluted in a theta solvent or blends composed of long and short chains.

When a polymer melt is diluted in a theta solvent, the chains are getting more distant from each other, because of the solvent that occupies some space. Each chain has less neighbours, hence its tube becomes wider. This evolution of the tube size upon transition from melt to solution is shown on Figure 2.14.

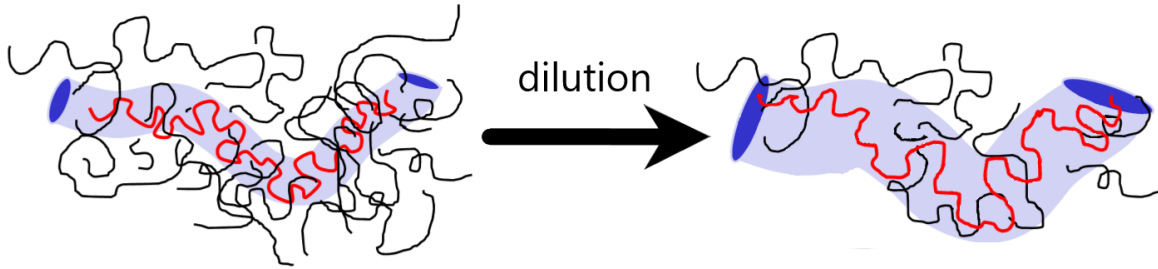


Figure 2.14: Upon dilution, the diameter of the tube occupied by the chain increases.

Consequently, some parameters must be adapted to take into account the effect of dilution. And this is done by introducing c , the weight fraction of polymer.

$$M_{e,sol} = M_{e,0}/c \quad (2.50)$$

$$G_{N,sol}^0 = \frac{(\rho \cdot c)RT}{M_{e,0}/c} = G_N^0 \cdot c^2 \quad (2.51)$$

There is the same effect for a polymer blend composed of two distinct types of chains, one being much longer than the other. The long and the short chains have a different reptation time, and $\tau_{rept,short} < \tau_{rept,long}$, which means that the short chains will relax much faster than the long chains.

- At $t < \tau_{rept,short}$, the polymer behaves as a standard melt, the tube is fixed. The molecular weight between two entanglements is noted $M_{e,0}$.
- At $\tau_{rept,short} < t < \tau_{rept,long}$, the short chains are now relaxed, they do not constraint the long chains anymore. In fact, the short chains now act as a solvent for the long chains. Hence, the diameter of the tube of the long chains is increased.

This effect of the relaxed polymer fraction that acts as a solvent is called "*Dynamic Tube Dilution*" (DTD). The entanglements created by the shorter chains are no more active, hence, the effective molecular weight between two entanglements, M_e , is now smaller than the actual weight between two entanglements $M_{e,0}$.

$$M_e = \frac{M_{e,0}}{\Phi(t)^\alpha} \quad (2.52)$$

In the Equation 2.52, $\Phi(t)$ is the fraction of polymer that is not relaxed, as defined in the Equation 2.48. And the exponent α is equal to 1. This equation of M_e with the DTD effect is very similar to the Equation 2.50 because it is a constraint release process in both cases. Other parameters than M_e must be adapted because of constraint release:

- $L_{eq}(t) = L_{eq,0} \cdot \Phi(t)^{\alpha/2}$
- $a(t) = \frac{a_0}{\Phi(t)^{\alpha/2}}$
- As the length of the tube decrease, it takes less time for the chain to diffuse out of the tube by reptation.

$$\tau_{rept}(t) = \frac{L_{eq}(t)^2}{D_e} = \tau_{rept}(0) \cdot \Phi(t)^\alpha$$

- For the activated fluctuations, the DTD has a large effect on the relaxation. Indeed, when getting closer to the branching point, the relaxation time increases largely along the axis of the tube. The time interval between the relaxation of one point and the following point is larger and larger. Hence, the extremity of the chain has already had a long time to move, and it can be considered as solvent.

$$\frac{\partial \ln \tau_{fluc}(x)}{\partial x} = 3 \cdot \left(\frac{M}{M_{e,0}} \right) \cdot x \cdot \Phi(t)^\alpha \quad (2.53)$$

In conclusion, upon a constraint release process, the relaxation modulus of Equation 2.49 becomes

$$G(t) = G_{Rouse}(t) + \frac{\rho RT}{M_{e,0}} \cdot \Phi(t)^{\alpha+1} \quad (2.54)$$

2.8 Cates' model

The relaxation of a supramolecular polymer is more complex than for a standard polymer. The complexity comes from the reversible bonds: as they are not permanent, these bonds constantly dissociate and recombine within a certain time scale, and this has an influence on the relaxation. Hence, the models used for standard polymers cannot be used as such

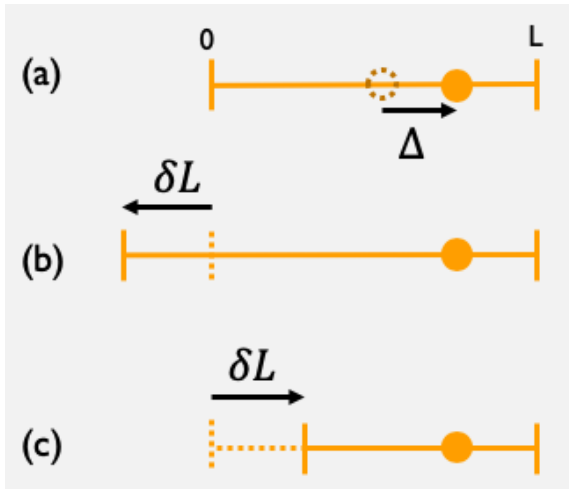
for supramolecular polymers, they have to be modified. One example is the Cates' model that allows describing the relaxation of entangled supramolecular polymers [15].

This model uses the processes that dictate the relaxation of standard polymers (namely the reptation, the Rouse process, and the contour length fluctuations), and in addition, it takes into account the kinetics related to the breakage and recombination of the chains. A chain of length L larger than the length between two entanglements l_e is considered. Firstly, several hypotheses are made:

1. A chain will break with a fixed probability per unit time and per unit length anywhere along its length L .
2. Recombination occurs at a rate proportional to the product of the concentrations of the two reacting subchains and independent of the molar mass of these subchains. It follows that, at high concentration, the rate-limiting step is not the diffusion of the chains, but a local kinetic process.
3. Successive dissociation and recombination are not correlated. Hence, the probability to recombine with the chain end from which it has just been dissociated is the same as the probability to recombine with another surrounding chain end.

According to the tube model, in order for a linear chain to be relaxed, it must diffuse out of its tube by reptation. The Doi and Edwards equation allows to compute $\Phi(t)$, that the probability for a chain fraction to be unrelaxed at time t .

$$\Phi(t) = \frac{8}{\pi^2} \sum_{p=\text{odd}} \frac{1}{p^2} \exp\left(-\frac{tp^2}{\tau_{\text{rept}}}\right) \quad (2.55)$$



$$L_{\text{left}} \rightarrow L_{\text{left}} + \Delta; L_{\text{right}} \rightarrow L_{\text{right}} - \Delta$$

$$L_{\text{left}} \rightarrow L_{\text{left}} - \Delta; L_{\text{right}} \rightarrow L_{\text{right}} + \Delta$$

$$L_{\text{left}} \rightarrow L_{\text{left}} + L' \pm \delta L$$

$$L_{\text{right}} \rightarrow L_{\text{right}} + L' \pm \delta L$$

$$L_{\text{left}} \rightarrow L'_{\text{left}} \pm \delta L (L'_{\text{left}} < L_{\text{left}})$$

$$L_{\text{right}} \rightarrow L'_{\text{right}} \pm \delta L (L'_{\text{right}} < L_{\text{right}})$$

Figure 2.15: Tube model and reptation within the Cates' model. (a) Representation of the reptation process. The particle is moving of a distance Δ along the chain of length L . (b) Recombination. (c) Breakage.

In the Cates' model $\Phi(t)$ is described from another perspective that allows to introduce the breakage and recombination processes. Instead of having a chain moving into a tube,

the chain is fixed and the tube is moving. The function $\Phi(t)$ is now defined as the survival probability of a particle diffusing along a segment of length L with a certain diffusion coefficient D_c and with absorbing boundary conditions at both ends. It means that when the particle goes beyond the boundaries, it is relaxed. This is represented at Figure 2.15 (a). In addition, the boundaries are able to move, they can make discrete jumps. If the jump increases the length of the chain by δL , it is a recombination (Figure 2.15 (b)). And if the jump creates a chain with a length decreased by δL , it is a breakage (Figure 2.15 (c)). The part of the chain on the left of the particle is noted L_{left} , and the one on the right is noted L_{right} . If either of these two lengths becomes negative, the particle dies, hence the corresponding chain segment is relaxed.

For each one of the three processes described on Figure 2.15, there is a certain probability of having a transition within a time interval δt . One can now define τ_{break} , which is the survival time of a chain before breakage.

$$\tau_{break} = (c_1 \bar{L})^{-1} \quad (2.56)$$

The parameter c_1 is the rate constant for breakage, and it can also be described as the breakage probability per unit length and time. And $\bar{L}$ is the mean length of a chain before breakage. The aim is to find an expression to describe the relaxation time of the supramolecular chains. In order to do that, two cases must be taken into account: either τ_{break} is smaller or greater than the reptation time τ_{rept} .

1. $\tau_{break} > \tau_{rept}$

The chain has enough time to relax by reptation before the reversible bonds dissociate. Hence, the relaxation time will be equal to τ_{rept} .

$$\tau \cong \tau_{rept} \quad (2.57)$$

The reptation is dominant in this case, the supramolecular polymer behaves as a classic polymer.

2. $\tau_{break} \leq \tau_{rept}$

Here, the time before breakage is smaller than the reptation time, so new relaxation regimes appear. Several dissociations and recombinations occur before the chain leaves the tube by reptation.

- (a) If one consider only **reptation** as relaxation process, what happens is shown on Figure 2.16. The hatched part constitutes the segment of interest, which is located at the position x . If there is a breakage close enough to x , the segment will have enough time to diffuse out of the tube by reptation before a recombination occurs, hence the segment will be able to relax. The largest distance from the point x at which the chain can dissociate while allowing the relaxation of the segment in x is noted λ and is given by Equation 2.58. The rate-limiting step is the step during which one waits for such a dissociation to occur. Thus, the relaxation time depends on the probability of a break to occur per unit length and time, multiplied by the distance λ (see Equation 2.59).

$$\lambda^2 \cong \bar{L} \cdot \xi \quad \text{with} \quad \xi = \tau_{break} / \tau_{rept} \quad (2.58)$$

$$\tau \cong (c_1 \lambda)^{-1} = \tau_{rept} \cdot \xi^{1/2} \quad (2.59)$$

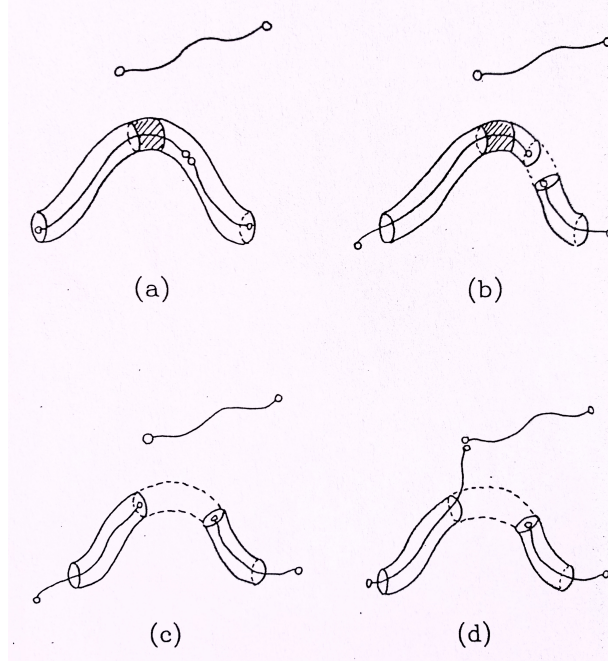


Figure 2.16: Different steps of the relaxation mechanism of the supramolecular polymer by reptation, when the time before chain dissociation is smaller than the reptation time. Retrieved from [15].

- (b) So far, the only relaxation process taken into account is the reptation. However, other processes can also have some significance by helping the relaxation: the first one is the **contour length fluctuations (CLF)**. Indeed, if the distance λ at which the breakage occurs is smaller than a length $\Delta L = \bar{L}\alpha^{1/2}$, the chain will relax faster by CLF than by reptation. A new constant is introduced here $\alpha = l_e/\bar{L}$. The maximum distance for which the relaxation by CLF is dominant is noted λ' and is defined by Equation 2.60. The relaxation time is defined in a similar way as Equation 2.59, as the rate-limiting step is again the step during which one waits for a dissociation to occur within a distance λ' .

$$\lambda' \cong \bar{L} \cdot \alpha^{1/4} \xi^{1/4} \quad (2.60)$$

$$\tau \cong (c_1 \lambda')^{-1} = \tau_{rept} \cdot \xi^{3/4} \alpha^{-1/4} \quad (2.61)$$

- (c) Finally, if the dissociation occurs at a distance λ' smaller than the length between two entanglement l_e , the relaxation by a **Rouse process** will be faster, and thus becomes dominant. The relaxation time now depends on λ'' , which is the maximum distance for which the relaxation is faster by a Rouse process after dissociation.

$$\lambda'' \cong \left(\frac{D_0}{l_e} \right)^{1/2} \tau_{break}^{1/2} \quad (2.62)$$

$$\tau \cong (c_1 \lambda'')^{-1} = \tau_{rept} \cdot \xi^{1/2} \alpha^{1/2} \quad (2.63)$$

It is also important to mention that, according to the Cates' model, the probability of survival $\Phi(t)$, which is defined by the Doi and Edwards equation for standard polymers, tends more and more towards a pure exponential when the value of ξ decreases.

Part II

Materials and methods

Chapter 3

Materials

The samples investigated for this work are supramolecular polymers based on metal-ligand interactions similar to the ones studied by Zhuge et al. [10], they are thus called metallo-supramolecular polymers (MSP). The building blocks are linear telechelic chains of poly(n-butyl acrylate) terminated by tridentate terpyridine ligands (PnBA-tpy₂). The chemical structure of this building block is represented on Figure 3.1, and their properties are the following:

- $\overline{M}_w = 113200\text{g/mol}$
- $\mathcal{D} = 1.13$
- $M_e = 17000\text{g/mol}$
- $G_N^0 = 160\text{kPa}$

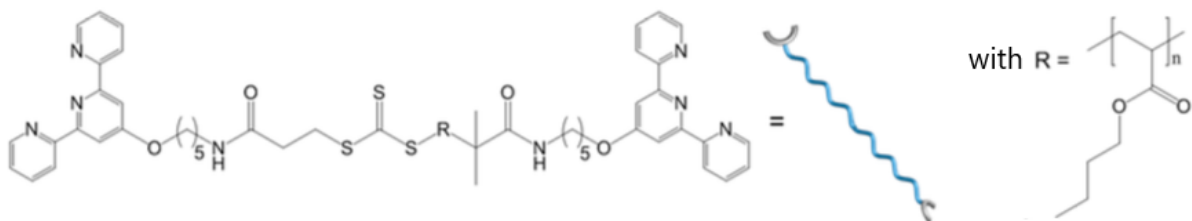


Figure 3.1: Chemical structure of a telechelic linear chain of poly(n-butyl acrylate) terminated at both ends by a terpyridine functional group. [10]

When adding divalent metal ions with the building blocks, two terpyridine ligands create a complex with one metal ion through metal-ligand coordination. Metal-ligand coordination is a type of non-covalent interaction, it is thus reversible. It is also very directional. The mechanism behind this type of interaction involves on one hand the donor atoms of the ligand and on the other hand a metal ion [16]. The terpyridine is a tridentate ligand, which means that a transition metal ion can bond with three donor atoms on each terpyridine group. These donor atoms are the nitrogen atoms present on each of the three pyridine rings of terpyridine. A pyridine is a heterocyclic compound resembling benzene, but with one CH₂ group replaced by a N atom. This nitrogen atom is very electronegative, it has a lone pair of electrons directed outwards. Besides, the metal cation has an incomplete

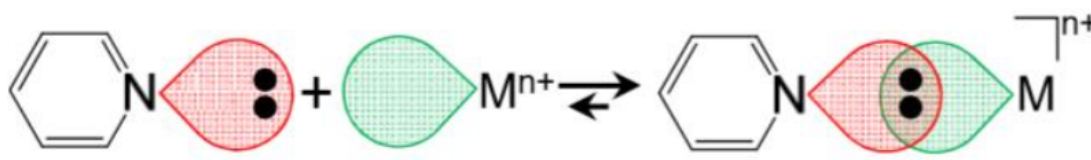


Figure 3.2: Transfer of the lone pair of electrons from the nitrogen atom of the pyridine to the valence shell of the metal cation [18].

valence layer. This causes a charge transfer from the lone pair orbital of pyridine to the metal cation orbital [17]. The transfer of the lone electron pair is depicted on Figure 3.2. The binding energy of a metal-ligand coordination is around 100 – 300kJ/mol [18] and depends on the compounds involved, namely the nature and valence of the metal ion, and the number of donor atoms [4]. The complexes formed between two ligands and one metal ion are chelate complexes, but in this work, the terpyridine ligands are referred to as "stickers" and the chelate complexes are thus called "associated stickers" or "active stickers".

When metal ions are added to the linear telechelic chains of PnBA-tpy₂, junctions are formed in between the chains, leading to the creation of a longer, self-assembled, chain, as shown on Figure 3.3. Two different metal ions were used here to create metallo-supramolecular polymers: Zn²⁺ and Cu²⁺.

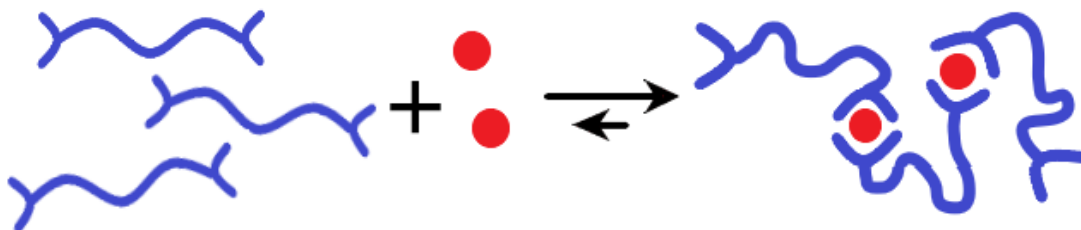


Figure 3.3: Association of the linear telechelic chains (in blue) upon addition of metal ions (in red) by self-assembly. As the bonds are reversible, the stickers can dissociate.

The amount of ions added to the melt is quantified in "equivalents", and is derived from the ratio of the number of metal ions to the number of terpyridine ligands. The stoichiometric amount refers to the case where all terpyridine ligands are bonded to an ion. As two terpyridines are linked to one ion, this correspond to 0.5 equivalent, as shown by Equation 3.1.

$$\frac{1 \text{ ion}}{2 \text{ tpy}} = 0.5\text{eq} \quad (3.1)$$

The different quantities of ions that were added in the samples are the following:

- 0.25eq, 0.5eq, 1eq and 2.5eq of copper
- 0.5eq, 1eq and 2.5eq of zinc
- 0.5eq and 1eq of a blend of 50% copper and 50% zinc

In addition to the linear telechelic chains, the data for two star metallo-supramolecular polymers with 0.5eq and 1eq of copper were also used in this work. These two samples

were also made of poly(n-butyl acrylate), but the building blocks are stars with four arms, each one being terminated by a terpyridine ligand (PnBA-tpy₄). Their total molar mass is 250kg/mol. However, it must be noted that the data for these stars come from a source external to this work [11].

To summarise, all the samples used, as well as their characteristics and the name by which they will be designated hereafter, are listed in the Table 3.1 below.

Name	Building block	Ions	Ion density
Reference sample	PnBA-tpy ₂	–	–
PnBA-tpy ₂ 0.25eq Cu ²⁺	PnBA-tpy ₂	Cu ²⁺	0.25eq
PnBA-tpy ₂ 0.5eq Cu ²⁺	PnBA-tpy ₂	Cu ²⁺	0.5eq
PnBA-tpy ₂ 1eq Cu ²⁺	PnBA-tpy ₂	Cu ²⁺	1eq
PnBA-tpy ₂ 2.5eq Cu ²⁺	PnBA-tpy ₂	Cu ²⁺	2.5eq
PnBA-tpy ₂ 0.5eq Zn ²⁺	PnBA-tpy ₂	Zn ²⁺	0.5eq
PnBA-tpy ₂ 1eq Zn ²⁺	PnBA-tpy ₂	Zn ²⁺	1eq
PnBA-tpy ₂ 2.5eq Zn ²⁺	PnBA-tpy ₂	Zn ²⁺	2.5eq
PnBA-tpy ₂ 0.5eq blend	PnBA-tpy ₂	50% Cu ²⁺ /50% Zn ²⁺	0.5eq
PnBA-tpy ₂ 1eq blend	PnBA-tpy ₂	50% Cu ²⁺ /50% Zn ²⁺	1eq
Star 0.5eq Cu ²⁺	PnBA-tpy ₄	Cu ²⁺	0.5eq
Star 1eq Cu ²⁺	PnBA-tpy ₄	Cu ²⁺	1eq

Table 3.1: Summary of all the samples used with their names and characteristics.

Chapter 4

Sample preparation

All the samples were prepared from the same reference polymer, that is a linear poly(*n*-butyl acrylate) end-functionalised with tridentate terpyridine ligands. These PnBA-tpy₂ building blocks were synthesised through reversible addition-fragmentation chain transfer (RAFT) polymerisation [10].

The mixing of the ions with the polymer was subsequently done in solution. For each sample, between 40 and 50mg of PnBA-tpy₂ was firstly taken and weighted. From the mass of the polymer, noted $m_{polymer}$, and its molecular weight $\overline{M}_w = 113200\text{g/mol}$, one can find the number of moles of polymer $n_{polymer}$, and the number of moles of terpyridine ligands n_{tpy} in the sample collected.

$$n_{polymer} = \frac{m}{\overline{M}_w} \quad (4.1)$$

$$n_{tpy} = 2n_{polymer} \quad (4.2)$$

In order to compute the right amount of ions to be added, the ratio of the number of moles of ions over the number of moles of ligands must be equal to the number of equivalents wanted. This equation allows to find the number of moles of ions needed.

$$\frac{n_{ion}}{n_{tpy}} = x \text{ eq.} \Leftrightarrow n_{ion} = x \cdot n_{tpy} \quad (4.3)$$

The ions were initially under the form of a powder, either copper(II) chloride CuCl₂ or zinc chloride ZnCl₂. Their molar mass is respectively $M_{CuCl_2} = 134.45\text{g/mol}$ and $M_{ZnCl_2} = 136.29\text{g/mol}$. The mass of ion powder was then computed as follows:

$$m_{ion} = n_{ion} \cdot M_{CuCl_2/ZnCl_2} \quad (4.4)$$

This mass of copper(II) chloride or zinc chloride was dissolved into methanol at a concentration of 5g/L. However, the value of m_{ion} found in Equation 4.4 was always very small, of the order of 0.1mg to 0.01mg, which is not possible to weight accurately. Hence, a much larger amount of powder was dissolved in methanol (8.2mg of CuCl₂ and 12.3mg of ZnCl₂), and the same solution was used for all the samples containing the same ions. The volume of copper chloride or zinc chloride solution necessary for each sample was computed as:

$$V_{ion} = \frac{m_{ion}}{5\text{g/L}} \quad (4.5)$$

At the end, the concentration of polymer wanted is $C = 400\text{g/L}$, which leads to the following equation for the total volume of the sample V_{total} :

$$V_{total} = \frac{m_{polymer}}{C} \quad (4.6)$$

This total volume includes the pure polymer dissolved in acetone $V_{polymer}$, and the ion solution V_{ion} , which is already known from Equation 4.5. Hence, one can finally find the volume of acetone required to dissolve the polymer:

$$V_{polymer} = V_{total} - V_{ion} \quad (4.7)$$

The two solutions were agitated to ensure a good dissolution of the compounds, and only then the right amount of the ion solution was added to the polymer. The polymeric solution obtained was stirred for 30 minutes so that good mixing is achieved. Then, the solvents were removed thanks to a rotary evaporator. Finally, the samples were put in a vacuum oven at 60°C for 24h to remove any remaining traces of solvent.

The method just described was used to prepare samples containing only one type of ion. The preparation of the blends is slightly different, as they were obtained from already existing samples, the latter being produced as explained above.

- PnBA-tpy₂ 0.5eq blend was made from PnBA-tpy₂ 0.5eq Cu²⁺ and PnBA-tpy₂ 0.5eq Zn²⁺
- PnBA-tpy₂ 1eq blend was made from PnBA-tpy₂ 1eq Cu²⁺ and PnBA-tpy₂ 1eq Zn²⁺

The same mass of each of the two polymers used as base materials was weighed very accurately and placed in a flask. Acetone was added in the flask to obtain a solution at a concentration of $C = 400\text{g/L}$. The samples were then agitated for 30 minutes to achieve a uniform blend. The solvent was finally removed with a rotary evaporator and by placing the sample in a vacuum-over at 60°C for 24h, as it was done for the other samples.

Chapter 5

Experimental method

The supramolecular polymers were studied from a rheological point of view thanks to dynamic oscillatory shear measurements. But in order to be able to understand the results obtained, it is necessary to review some basics about rheometry.

5.1 Rheometry

Rheometry refers to all the experimental methods used to measure the rheological properties of a material. For this work, the experiments carried out were oscillatory shear measurements in the linear viscoelastic regime. They aim at accurately measuring the relaxation modulus in the linear regime of deformation, as well as the storage and the loss moduli, which are described below.

5.1.1 Linear viscoelasticity

The linear viscoelastic regime is the range of deformation rate which is characterised by the fact that the viscosity is only a function of the time, not of the deformation rate. This regime, as well as the non-linear regime, is shown on Figure 5.1. Linear viscoelasticity thus corresponds to the regime of small shear rates, where the viscosity is constant and tends to the zero-shear viscosity η_0 , which is defined as follows:

$$\eta \rightarrow \eta_0 \text{ when } \dot{\gamma} \rightarrow 0 \quad (5.1)$$

When measuring rheological properties of a polymer melt under a linear deformation, the polymer coils are oriented but the entanglements density stays constant, hence the structure of the polymer remains intact, it is still at equilibrium. In contrast, with a non-linear deformation, the polymer coils are stretched, and the entanglements density decreases. Consequently, the polymeric structure is damaged. The polymer melt is not at equilibrium anymore. Since the relaxation function is measured when the polymer is at equilibrium, this must be done in the linear regime.

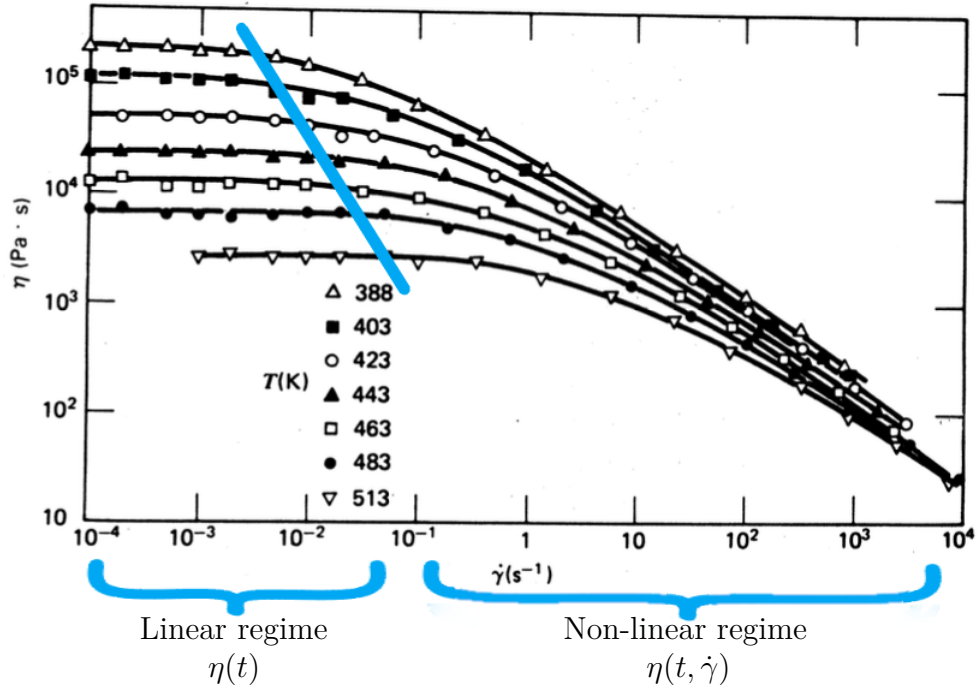


Figure 5.1: Non-Newtonian viscosity as a function of the shear rate for a sample of LDPE at different temperatures[12]. The blue line indicates the transition from the linear to the non-linear regime. On the left of this line, the linear regime is characterised by a viscosity that is only dependent on the time. While in the non-linear regime on right of the line, the viscosity depends both on the time and the shear rate.

5.1.2 Boltzmann superposition principle

The Boltzmann superposition principle is key to understand what the relaxation modulus is, and it is used to describe stress relaxation phenomena in viscoelastic materials. When a deformation is suddenly applied to a viscoelastic material, the stress to apply in order to keep the deformation constant does not remain the same indefinitely, it decreases over time: this is the stress relaxation, which is depicted on Figure 5.2. And the relaxation modulus is defined by the ratio between the stress and the strain:

$$G(t) = \frac{\tau(t)}{\gamma_0} \text{ [Pa]} \quad (5.2)$$

This relaxation modulus allows to get rid of the influence of the amplitude of the deformation γ_0 . Hence, the relaxation modulus measured for one sample will always be the same as long as the measurements are carried out in the linear regime, which is very useful.

Then, if a viscoelastic specimen is subjected to several successive step-deformations, the stress might not be yet fully released when a new deformation is applied. Therefore, the previous states of the material must be taken into account to compute the total stress at a time t , as it will depend on its history. The Boltzmann superposition principle states that all the deformations applied in the past have an additive effect on the stress at time

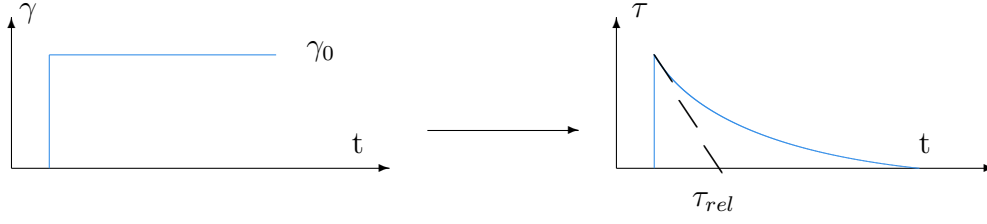


Figure 5.2: Stress relaxation in a viscoelastic material when applying a constant deformation of amplitude γ_0 .

t . This stress can be computed as given by Equation 5.3.

$$\tau(t) = \lim_{d\gamma \rightarrow 0} \sum_i G(t - t_i) d\gamma(t_i) \quad (5.3)$$

An example of several small deformations applied at different times and their effect on the stress is shown on Figure 5.3. Finally, the Boltzmann superposition principle given in Equation 5.3 can also be expressed under a continuous form, where the sum is replaced by an integral.

$$\tau(t) = \int_{-\infty}^t G(t - t') \frac{d\gamma}{dt'} dt' \quad (5.4)$$

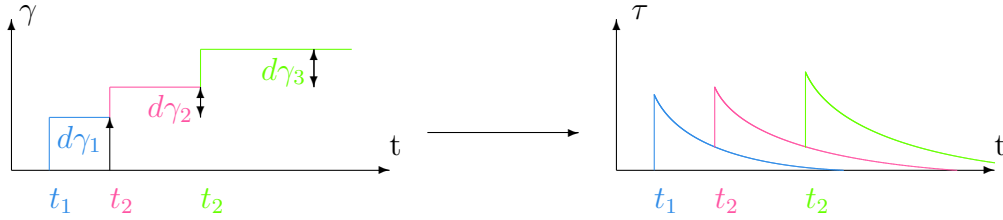


Figure 5.3: Relaxation of the stress after application of three small deformations $d\gamma_1$, $d\gamma_2$ and $d\gamma_3$.

5.1.3 Oscillatory shear measurements

The oscillatory shear measurements performed in the linear regime allow precise measurement of the relaxation of polymers in the molten state. A sinusoidal deformation, as defined by Equation 5.5, is applied to the sample and the stress response is measured as a function of the frequency ω . The amplitude of the deformation γ_0 is constant and small enough to stay in the linear regime.

$$\gamma(t) = \gamma_0 \sin(\omega t) \quad (5.5)$$

If this kind of sinusoidal deformation was applied to an elastic solid, the response of the material would be a stress in phase with the deformation, hence they would be proportional, with the elastic modulus $G \equiv \frac{\tau}{\gamma}$ as the proportionality constant. While if it was applied to a Newtonian liquid, the stress would be out of phase by $\pi/2$ with the deformation, and thus in phase with the shear rate

$$\begin{aligned} \dot{\gamma} &= \omega \gamma_0 \sin(\omega t + \pi/2) \\ &= \omega \gamma_0 \cos(\omega t) \end{aligned} \quad (5.6)$$

The proportionality constant between the stress and the shear rate is the viscosity $\eta \equiv \frac{\tau}{\dot{\gamma}}$. The relations between $\tau(t)$ and $\gamma(t)$ for these two extreme cases, the elastic solid and the Newtonian liquid, are represented on Figure 5.4, and the equation corresponding are given by Equation 5.7 and 5.8.

$$\text{Elastic solid: } \tau(t) = \tau_0 \sin(\omega t) \quad (5.7)$$

$$\text{Viscous liquid: } \tau(t) = \tau_0 \sin(\omega t + \pi/2) \quad (5.8)$$

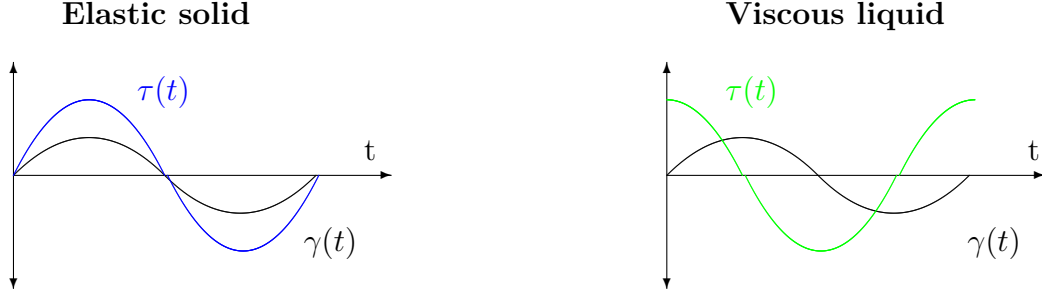


Figure 5.4: Stress measured in response to an oscillatory deformation $\gamma(t)$ for an elastic solid on the left and for a viscous liquid on the right. For the elastic solid, $\tau(t)$ and $\gamma(t)$ are in phase and proportional. For the viscous liquid, there is a phase difference of $\pi/2$ between $\tau(t)$ and $\gamma(t)$, which means that $\tau(t)$ is proportional to the shear rate $\dot{\gamma}$.

A polymer being viscoelastic, its response to a sinusoidal deformation is in between the elastic solid and the viscous liquid. The stress is also sinusoidal, but with a phase shift δ , which is called the loss or phase angle. The expression of $\tau(t)$ for a viscoelastic material is given by Equation 5.9.

$$\tau(t) = \tau_0 \sin(\omega t + \delta) \quad (5.9)$$

It is possible to decompose the stress in Equation 5.9 into two terms, which leads to Equation 5.10. The first term in blue is in phase and proportional to the deformation, as for an elastic solid. Hence, it is the elastic term. And the second part in green is out of phase and proportional to the shear rate as a viscous liquid, it is the viscous term. The relationship between the stress and the deformation in a viscoelastic material, and the decomposition of the stress are depicted on Figure 5.5.

$$\tau(t) = \underbrace{\tau_0 \cos \delta \cdot \sin(\omega t)}_{\tau' \propto \gamma} + \underbrace{\tau_0 \sin \delta \cdot \cos(\omega t)}_{\tau'' \propto \dot{\gamma}} \quad (5.10)$$

One can then define two new variables, the storage and the loss moduli, noted G' and G'' respectively, whose units are Pascal. Their expressions are given by Equation 5.12 and Equation 5.12.

$$G'(\omega) = \frac{\tau_0}{\gamma_0} \cos \delta \quad (5.11)$$

$$G''(\omega) = \frac{\tau_0}{\gamma_0} \sin \delta \quad (5.12)$$

When introducing these expressions in Equation 5.10, it leads to:

$$\tau(t) = \gamma_0 [G'(\omega) \cdot \sin(\omega t) + G''(\omega) \cdot \cos(\omega t)] \quad (5.13)$$

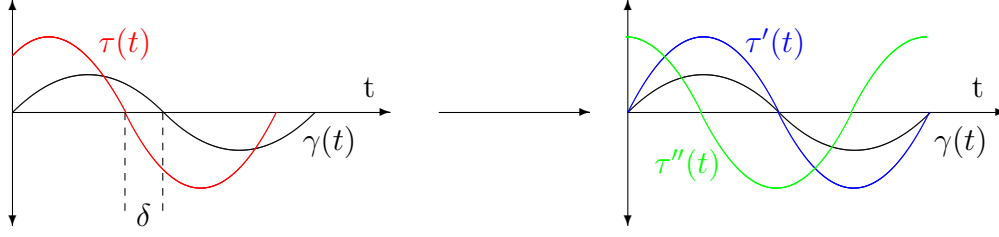


Figure 5.5: Stress measured for a viscoelastic material in response to an oscillatory deformation $\gamma(t)$. On the right, one can see the phase shift δ between the stress $\tau(t)$ and the deformation $\gamma(t)$. On the left, the stress is decomposed into two parts: in blue the elastic term and in green the viscous term.

The storage and loss moduli can be seen as the real and imaginary components of the complex modulus, noted $G^*(\omega)$.

$$G^*(\omega) = G'(\omega) + iG''(\omega) \quad (5.14)$$

From the storage and loss moduli, it is possible to recover the phase angle, through the damping factor $\tan \delta$:

$$\tan \delta = \frac{G''}{G'} \quad (5.15)$$

The relationships between the storage modulus, loss modulus, the complex modulus and the damping factor can be easily represented on a vector diagram, as shown on Figure 5.6. The storage and loss moduli can also be linked to the relaxation modulus as they are the Fourier transforms of $G(t)$.

$$G'(\omega) = \omega \int G(t) \cdot \sin(\omega t) dt \quad (5.16)$$

$$G''(\omega) = \omega \int G(t) \cdot \cos(\omega t) dt \quad (5.17)$$

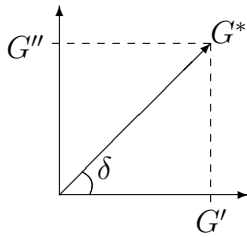


Figure 5.6: Vector diagram representing the complex modulus G^* , the storage modulus G' , the loss modulus G'' and the damping factor $\tan \delta$

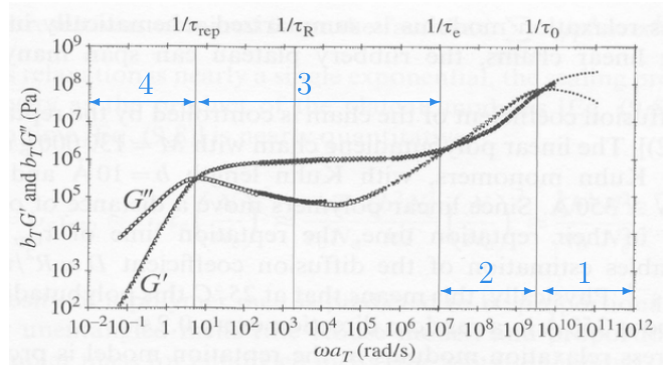


Figure 5.7: $G'(\omega)$ and $G''(\omega)$ for a sample of PBD 130kg/mol [12]. The main relaxation times and relaxation steps seen in chapter 2 are indicated on the graph.

The shape of G' and G'' is shown on Figure 5.7. Firstly, one can easily locate the four steps of relaxation on this graph, because it is similar to what can be seen on the graph of $G(t)$ as shown on Figure 2.8. At very high frequency, G' forms a plateau, this is the glassy

region (1). Then, still at high frequency, the slope of G' and G'' is equal to 1/2. That is characteristic of the Rouse process (2). When the frequency continues to decrease, the storage modulus reaches a plateau, which is the rubbery plateau (3). And finally, at very low frequencies, both moduli decrease rapidly, with a slope of 1 for G'' and a slope of 2 for G' : this is the terminal relaxation (4).

The storage modulus represents the elastic part of the sample. As a viscoelastic material is more elastic at high frequency, the value of G' is the largest at high frequency and it always decreases at lower frequencies. On the other hand, the loss modulus represents the energy dissipations in the sample when it is getting relaxed. Thus, at low frequency, it is higher than G' . And in the plateau region, there is a minimum for G'' : as nothing happens, there is no energy that can be lost.

5.1.4 Time-Temperature Superposition (TTS) principle

In order to get the master curve of the storage and loss moduli, the range of frequencies to cover is very large. It can be seen in Figure 5.7, where the master curve span over 14 decades. Unfortunately, in practice, it is not feasible to achieve the oscillatory shear measurements over such a wide range of frequencies. On one hand, a rheometer cannot reach very high frequency while still being able to make accurate measurements. And on the other hand, when going to low frequencies, the duration of the experiment increases exponentially, so one has to wait a very long time to get some results. The range of the reachable frequencies is thus quite narrow.

However, the Time-Temperature Superposition principle is a tool that allows to overcome this difficulty. It is based on the fact that the viscoelastic behaviour of a polymer depends on the temperature and the time, and there is an equivalence between the two. Hence, to measure the properties of a polymer at high frequency, one can decrease the temperature instead of increasing the frequency. And to measure the properties at low frequency, one can increase the temperature instead of decreasing the frequency.

Thanks to this method, several curves for G' and G'' are obtained, each one being measured at a different temperature but always over the same frequency range. It is therefore necessary to shift all these curves horizontally in order to recreate the master curve of the material. The shift factors $a(T)$ can be derived from the Williams–Landel–Ferry equation, where T_0 is the reference temperature, that is the temperature of the curve with respect to which all the others will be moved:

$$\log a(T) = -\frac{c_1 \cdot (T - T_0)}{c_2 + (T - T_0)} \quad (5.18)$$

It is an empirical equation, and the parameters c_1 and c_2 depend on the nature of the polymer. Consequently, for one type of polymer, the shift factors are always the same, regardless of its molecular weight or chain architecture.

At high temperatures, the Arrhenius equation can also be used to determine the shift factors. This Arrhenius equation is usually found to be more appropriate to describe the shift factors of supramolecular polymers. In this equation, an energy of activation E_a

appears:

$$\log a(T) = \frac{E_a}{RT} \left(\frac{1}{T} - \frac{1}{T_0} \right) \quad (5.19)$$

5.2 Experimental determination of the storage and loss moduli

The rotational rheometer used was an ARES from TA Instruments, which is a strain-controlled rheometer with a 8mm plate-plate geometry. It means that for each measurement, the strain applied to the sample was fixed, and the stress was measured.

All the experiments were conducted under a nitrogen atmosphere, that is under an inert atmosphere. A few exceptions were made for measurements at 25°C and 40°C where the oven was filled with air, because at these temperatures the sample was not at risk of being damaged by oxygen.

The plates were firstly cleaned with acetone and heated at 130°C for 15 minutes before doing the zero fixture in order to reset the zero gap. Then, the gap was increased to 5mm and the oven was opened in order to load the sample in the middle of the plates. Once loaded, the sample was heated at 130°C under a nitrogen atmosphere, and the gap was adjusted around 400µm in order for the sample to completely fill the gap. Afterwards, the temperature was lowered to that of the first measurement. These were always done from high temperatures to low temperatures, that is in the following order: 100°C, 80°C, 60°C, 40°C, 25°C, 0°C, -20°C. However, the measurements were not carried out at all of these temperatures for each of the samples. Most often, G' and G'' were evaluated between 80°C and 0°C.

Three types of measurements were carried on each sample: Dynamic Time Sweep, Dynamic Strain Sweep, and Dynamic Frequency Sweep tests.

5.2.1 Dynamic Time Sweep

The Dynamic Time Sweep test was the first to be conducted at each temperature. For this measurement, the temperature, the frequency, and the strain are fixed, and the moduli G' and G'' are measured over time. It serves to determine when the sample reaches equilibrium, which corresponds to the moment when the values of G' and G'' reach a stable value. Each time when changing the temperature of the sample, the gap had to be readjusted because of the shrinkage of both the plates and the sample. Hence, there are always residual stresses in the sample, which is no longer in equilibrium. However, the sample must be equilibrated before making further measurements if one wants to get accurate values for G' and G'' . Therefore, the Time Sweep test is necessary.

5.2.2 Dynamic Strain Sweep

The Dynamic Strain Sweep test was done only once for each sample, at the highest temperature (that is usually at 100°C or 80°C), right after the Dynamic Time Sweep test. The Strain Sweep allows to determine the range of deformation over which the linear

viscoelastic regime extends. To perform this test, the temperature and the frequency are fixed. Then the storage and loss moduli are measured as a function of the strain, which varies from 0.01% to 50%. This test must be stopped as soon as the moduli start to decrease, because if the sample enters the non-linear regime, it is at risk to be damaged.

5.2.3 Dynamic Frequency Sweep

While the two previous tests are performed in order to prepare the sample and to ensure that the experimental conditions are appropriate, the Dynamic Frequency Sweep test is the one that provides the data that conveys meaningful information about the rheological properties of the sample. These are the Frequency Sweep data that are thus used in the rest of this work.

A Dynamic Frequency Sweep test was performed at each temperature, once the sample had been equilibrated with the Time Sweep test. The temperature was fixed, as well as the strain, which was chosen on the basis of the Dynamic Strain Sweep test (usually its value was around 10% at high temperatures, and around 1% at low temperatures). The storage and loss moduli were measured as a function of the frequency, which was varying from 100rad/s to approximately 10^{-2} rad/s.

Once all the Frequency Sweep measurements had been performed at all temperatures, the Time-Temperature Superposition principle was used to create the master curve of each sample, with 25°C chosen as the reference temperature. The same shift factors were used for all the samples. In addition to the horizontal shift, the curves were also shifted vertically to take into account the effect of the pressure on the density of the material upon a change of temperature [13]. All the shift factors were already pre-determined, and their values are listed in Table 5.1.

	100°C	80°C	60°C	40°C	25°C	0°C	−20°C
$a(T)$	0.0055	0.0148	0.0502	0.2461	1	30.6836	1739.2
$b(T)$	0.84021	0.87575	0.91589	0.96153	1	1.07399	1.14414

Table 5.1: Horizontal shift factor $a(T)$ and vertical shift factors $a_v(T)$ for poly(n-butyl acrylate)

Part III

Experimental results

Chapter 6

Viscoelastic properties of metallo-supramolecular linear polymers: Relaxation times and Failure of the TTS principle.

Before looking at the data obtained for the supramolecular polymers, it is interesting to take a look at the results for the reference sample. As there are no metal ions in this polymer, its behaviour is the one of a standard entangled polymer. All the differences between this sample and the supramolecular ones must necessarily arise from the presence of ions. The master curve of this reference sample is shown on Figure 6.1.

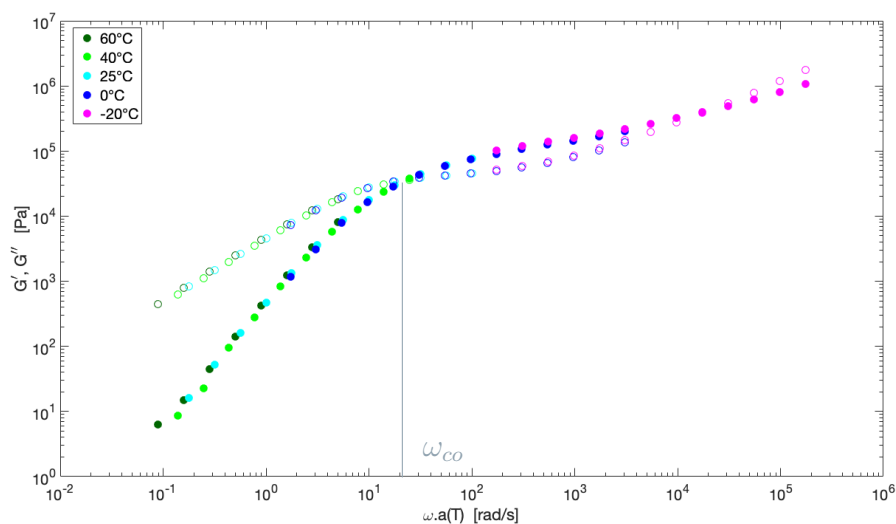


Figure 6.1: Master curve of the reference sample at 25°C.

The Time-Temperature Superposition principle is working very well for this sample, the curves of the different temperatures overlap properly. The crossover frequency, noted ω_{co} , is indicated on the graph by a grey line, and it is located at approximately 20 rad/s.

6.1 Failure of the Time-Temperature Superposition

The reference sample is compared to the MSPs on Figures 6.2 to 6.10, in which its moduli are always represented by continuous black lines. The master curves of these samples were built with the shift factors of the reference sample in order to suppress the temperature dependence of the segmental dynamics. The first thing that can be seen is that the TTS does not work when metal ions are added. The curves overlap at high frequency, that is down to the rubbery plateau, but not at lower frequencies. The disagreement also increases as the ion density increases. This failure of the TTS principle is due to the fact that for these supramolecular polymers, the temperature has not only an impact on the viscoelastic properties of the material but also on the dynamics of the stickers. The latter are not taken into account in the Time-Temperature Superposition Principle, which is why it cannot be used for the MSP's. However, it is still interesting to apply the TTS on these samples, as it allows to get rid of the effect of the temperature on the viscoelastic properties. That way, it is possible to highlight the impact of stickers on polymer properties. It is also easier to compare the MSP's with the reference sample when the TTS is used for all of them.

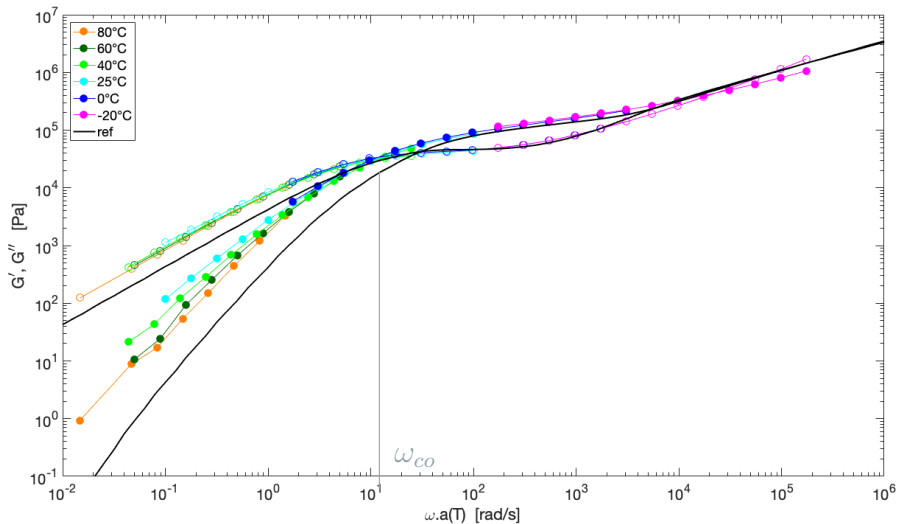


Figure 6.2: Master curve of PnBA-tpy₂ 0.25eq Cu²⁺ at 25°C.

6.2 Second plateau and aggregates

Secondly, it appears that some samples show a second plateau. This is particularly obvious at low temperature and for MSPs with a high ion density, namely PnBA-tpy₂ 2.5eq Cu²⁺ and PnBA-tpy₂ 2.5eq Zn²⁺, that are represented on Figure 6.5 and Figure 6.8 respectively. However, all the samples are made from telechelic linear chains, where the stickers are formed through complexation of two chain ends with one metal ion. Consequently, the supramolecular polymers created should always be linear chains, made of one or several building blocks of PnBA-tpy₂. Linear polymer chains are always able to relax by reptation, and thus cannot give rise to a second plateau. Nevertheless, a second plateau can clearly be seen for some MSPs. This could be explained by the presence of aggregates in the material: a phase segregation would occur between the polymer backbone and the stickers

that would tend to draw closer to each other. In that case, the polymer can relax normally until it is blocked by the aggregates, which form the second plateau. And it will only be able to flow once the aggregates have dissociated.

6.3 Variations of the crossover frequency

Then, the comparison of the crossover frequency ω_{co} also brings some information. It is expected that it will be shifted towards lower frequency when metal ions are added. Indeed, when stickers are formed, linear assemblies are created, that are longer than the precursor, PnBA-tpy₂. Because of their length, the relaxation of these assemblies takes more time than the reference sample. For the PnBA-tpy₂ 0.25eq Cu²⁺ (see Figure 6.2), ω_{co} is still a unique value, although it is shifted towards lower frequencies, which indicates that the relaxation is indeed slightly more difficult compared to the reference sample. But for all the other samples, the crossover frequency is not a single value anymore. As the Frequency Sweep curves at different temperatures do not overlap, the crossover frequencies do not overlap either. On Figures 6.3 to 6.10, the position of the crossover is marked by a vertical line, whose colour is that of the temperature of the measurement.

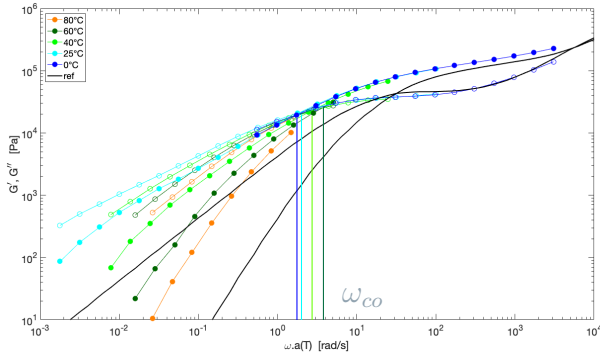


Figure 6.3: Master curve of PnBA-tpy₂ 0.5eq Cu²⁺ at 25°C.

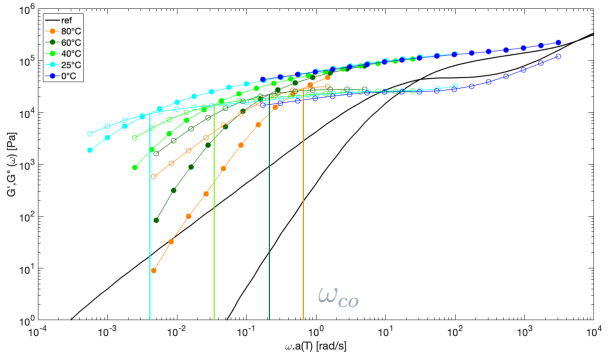


Figure 6.4: Master curve of PnBA-tpy₂ 1eq Cu²⁺ at 25°C.

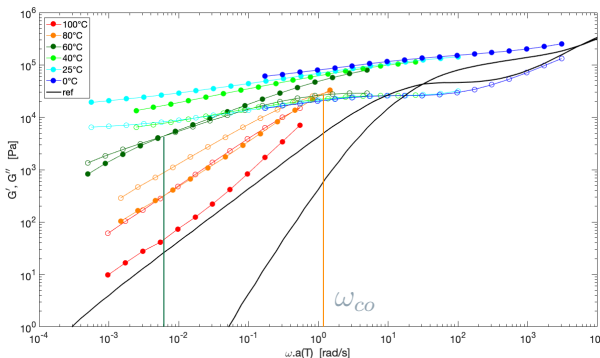


Figure 6.5: Master curve of PnBA-tpy₂ 2.5eq Cu²⁺ at 25°C.

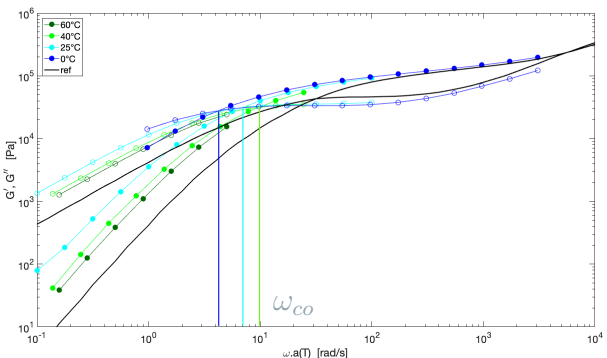


Figure 6.6: Master curve of PnBA-tpy₂ 0.5eq Zn²⁺ at 25°C.

From a qualitative point of view, one can already see that the crossover cannot be observed at all temperatures within the experimental frequency window. At high temperature, only the terminal region is visible, which is already below the crossover. And at low

temperature, the end of the plateau is not observable, so neither is the crossover. When changing the ion concentration, the temperature of the curves at which the crossover can be seen is changing. For example, with 0.5eq Cu^{2+} at Figure 6.3, the crossover is visible at all temperatures, except at 80°C where the polymer flows, that is from 60°C to 0°C. When increasing the ion content to 1eq (Figure 6.4), the crossover of 80°C becomes visible, but the one at 0°C disappear. And by increasing the ion content further to 2.5eq (Figure 6.5), ω_{co} is hidden at 25°C and 40°C, it remains only at 60°C and 80°C. The same observations can be made for the samples containing zinc and the blends. It can be concluded that the temperature range at which the crossover is present shifts towards higher temperatures when the ion density increases. This shows that the more ions are added, the longer is the plateau before relaxation, hence the relaxation takes more and more time.

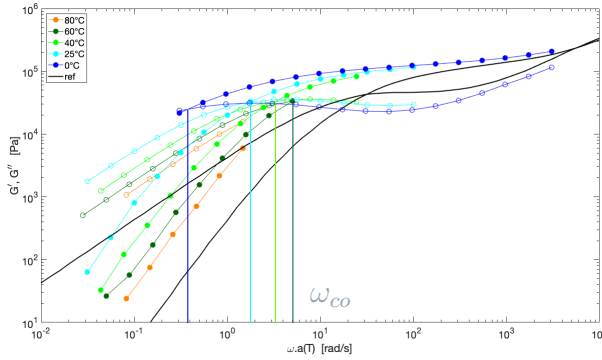


Figure 6.7: Master curve of PnBA-tpy₂ 1eq Zn^{2+} at 25°C.

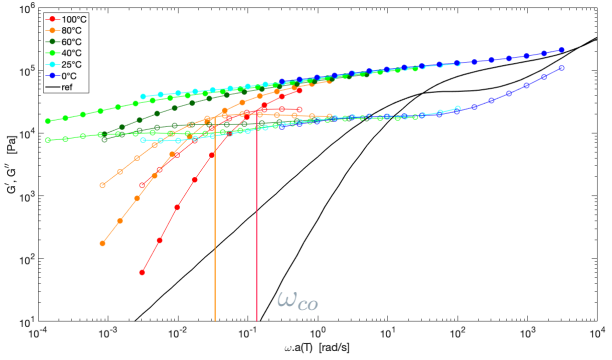


Figure 6.8: Master curve of PnBA-tpy₂ 2.5eq Zn^{2+} at 25°C.

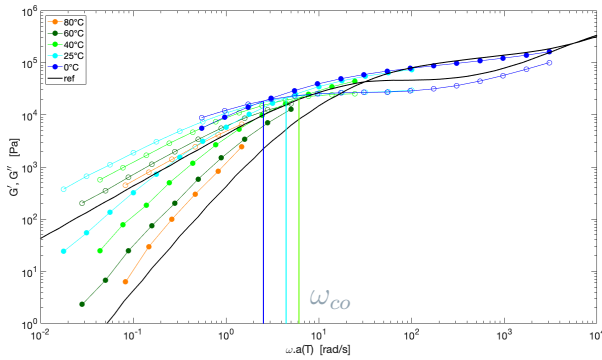


Figure 6.9: Master curve of PnBA-tpy₂ 0.5eq blend at 25°C.

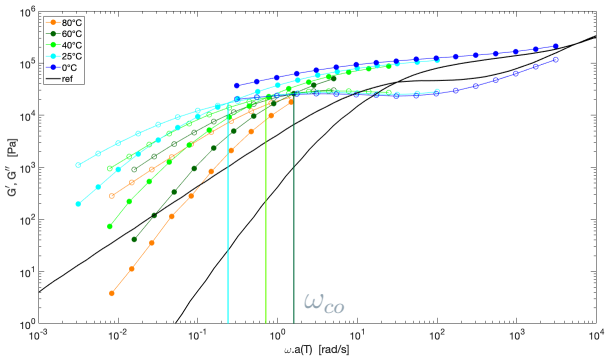


Figure 6.10: Master curve of PnBA-tpy₂ 1eq blend at 25°C.

In order to better visualise how the crossover frequency changes with temperature and in between the different samples, and thereby to understand the impact of the metal ions on the behaviour of the polymer, the value of $1/\omega_{co}$ is reproduced in Figures 6.11 to 6.14, as a function of the temperature and the ion density.

6.3.1 Influence of the ion density

Figure 6.11 shows the impact of the ion density on the crossover frequency. It appears that $1/\omega_{co}$ increases with the ion content, hence, the more ions, the more difficult is the

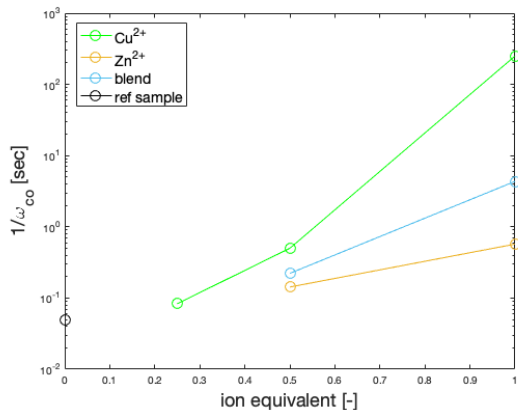


Figure 6.11: Inverse of the crossover frequency $1/\omega_{co}$ as a function of the ion density at 25°C.

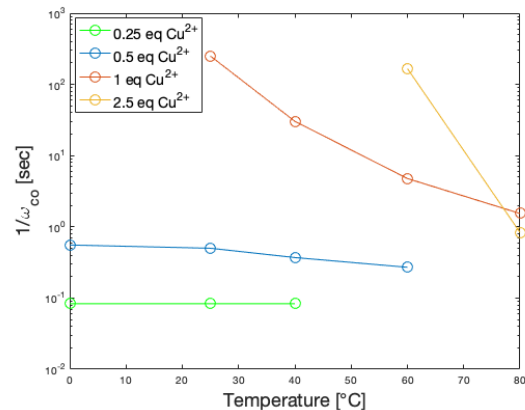


Figure 6.12: Inverse of the crossover frequency $1/\omega_{co}$ as a function of the temperature for the samples with copper.

relaxation. It makes sense, as with more ions, more stickers are formed, and thus the chains composing the MSPs are longer, leading to longer relaxation times. This result also suggests that, with the ions used, the formation of bis-complexes is favoured over the formation of mono-complexes, as the latter would lead to the creation of shorter chains in the presence of an excess of ions. Figure 6.11 only shows the crossover at 25°C, and the samples containing 2.5eq of ions are not shown as they have a too long plateau at 25°C, which doesn't allow to see the crossover. Nonetheless, this observation is valid for all samples and at all temperatures. Besides, the increase of $1/\omega_{co}$ with ion density can be seen on Figure 6.12 to 6.14, as the data corresponding to higher ion content are always above the ones of lower content.

6.3.2 Influence of the metal ion nature

It is also possible to compare the impact of the different ions on the relaxation. $1/\omega_{co}$ is larger with copper, smaller with zinc, and the blend is in between the two. It indicates that zinc is more labile than copper, hence the stickers formed with zinc are less stable than those formed with copper. Consequently, one can suppose that the supramolecular chains formed with zinc ions are shorter, and that the stickers dissociate more easily than with copper. As the blends are composed of 50% of copper ions and 50% of zinc ions, it seems logical that their length, and therefore their relaxation time, is located between the two first ones.

There is however one exception to this trend. Unfortunately, it cannot be seen on Figure 6.11, as the samples with 2.5eq do not appear on it. But if one compares the crossovers of the PnBA-tpy₂ 2.5eq Cu²⁺ with the ones of the PnBA-tpy₂ 2.5eq Zn²⁺, that are on Figure 6.12 and Figure 6.13 respectively, one can observe that $1/\omega_{co}$ is larger with zinc than with copper. The crossover also becomes visible at 100°C with zinc while it doesn't appear at the same temperature with copper. So at high ion density, there is an inversion of the tendency, the self-assembled chains containing zinc relax less easily than the ones containing copper.

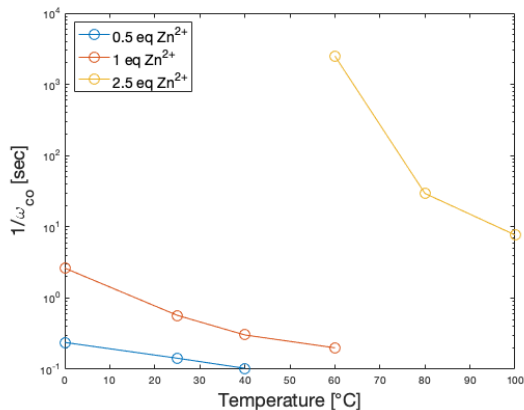


Figure 6.13: Inverse of the crossover frequency $1/\omega_{co}$ as a function of the temperature for the samples with zinc.

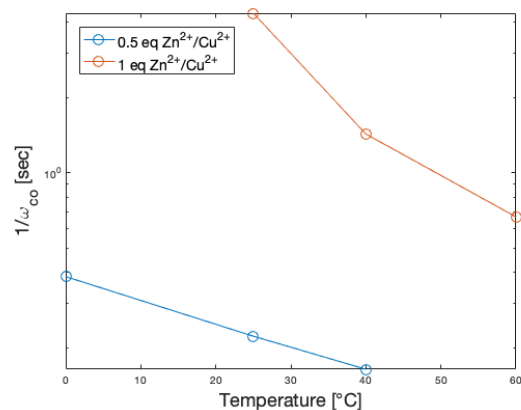


Figure 6.14: Inverse of the crossover frequency $1/\omega_{co}$ as a function of the temperature for the blends.

6.3.3 Influence of the temperature

In addition, the effect of the temperature is presented in Figures 6.12 to 6.14. On these graphs, it can be seen that $1/\omega_{co}$ increases when the temperature drops for all types of ions and for all ion contents, except for the PnBA-tpy₂ 0.25eq Cu²⁺, where there is only one crossover frequency. But as the ion content is very low for this one, the building blocks might not be associated enough to see clearly the effect of the metal ions.

For all the other MSPs, the increase of $1/\omega_{co}$ with decreasing temperature shows the large influence of the temperature on the stability of the supramolecular assemblies. The crossover frequency is shifted towards higher frequencies when the temperature rises, which means that the relaxation is speeded up. It is due to the fact that the stickers become less and less stable when the temperature increases, which leads to shorter assemblies, that can relax more easily as a whole object.

It can also be noted that the slope of the curves grows with ion density. In other words, it indicates that the range over which the crossover frequencies extend becomes larger and larger as the ion density increases. It means that the effect of the temperature is more pronounced when there are more ions.

Chapter 7

Viscoelastic properties of metallo-supramolecular linear polymers: Influence of the reversible bonds on the sample elasticity

A larger sample elasticity is observed when metal ions are introduced, that is when metallo-supramolecular polymers are created. This enhanced elasticity does not designate an increase of the plateau modulus here, but an increase of the elasticity at lower frequencies when the samples start relaxing. The relaxation time spectrum can become very large, and a second rubbery plateau can also appear in some samples. This phenomenon is investigated here through the storage modulus, its value, and how it evolves with temperature and ion density.

7.1 Qualitative observations

Figures 7.1 to 7.6 allow to compare the different samples qualitatively. Figures 7.1 and 7.2 show the storage modulus at high and low temperatures for samples with different quantities of Cu^{2+} ions, namely 0.25eq, 0.5eq, 1eq and 2.5eq. Without surprise, the behaviour of the sample with the lowest amount of ion, PnBA-tpy₂ 0.25eq Cu^{2+} , is the closest to the reference sample. When adding more copper ions, the relaxation time spectrum enlarges in a constant way.

The storage modulus at high and low temperatures are shown on Figure 7.3 and Figure 7.4 for the MSPs containing zinc ions. The broadening of the viscoelastic curves is also observed upon increasing the ion density. But this broadening is not as constant as with copper. For low ion densities, namely at 0.5eq and 1eq, the two curves are quite close to each other and also close to the reference sample. Then when going from 1eq to 2.5eq, the relaxation time spectrum suddenly increases in a significant way.

On Figure 7.5 and Figure 7.6, the two blends are compared to the samples containing the same quantity of only one type of metal ion. One can see that at all temperatures, the curve of the blend is in between the two pure ions. At 0.5eq, the blend seems to be slightly closer to the curves of Zn^{2+} than Cu^{2+} (Figure 7.5, while at 1eq, the blend seems right in

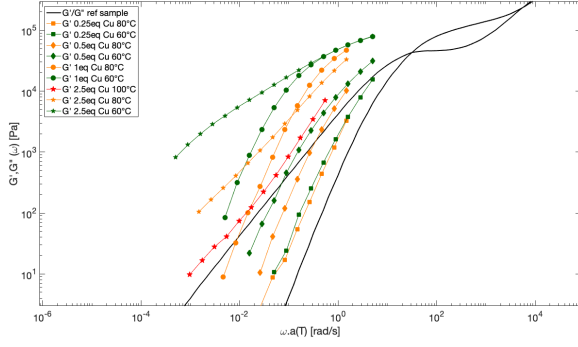


Figure 7.1: Storage modulus of PnBA-tpy₂ containing Cu²⁺ ions in different quantities at high temperatures (100°C in red, 80°C in orange and 60°C in dark green).

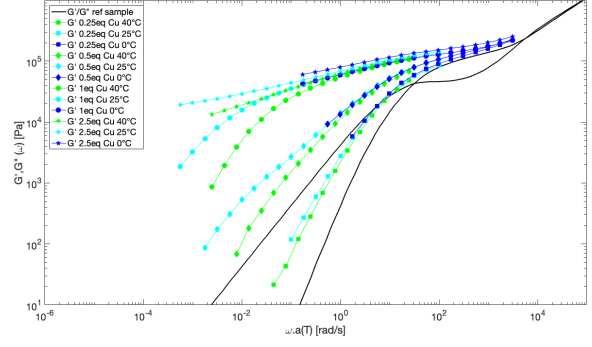


Figure 7.2: Storage modulus of PnBA-tpy₂ containing Cu²⁺ ions in different quantities at low temperatures (40°C in light green, 25°C in light blue and 0°C in dark blue).

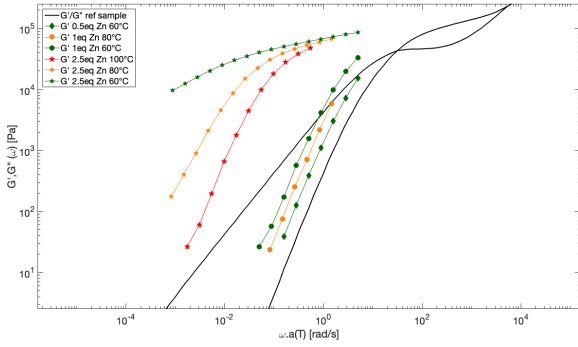


Figure 7.3: Storage modulus of PnBA-tpy₂ containing Zn²⁺ ions in different quantities at high temperatures (100°C in red, 80°C in orange and 60°C in dark green).

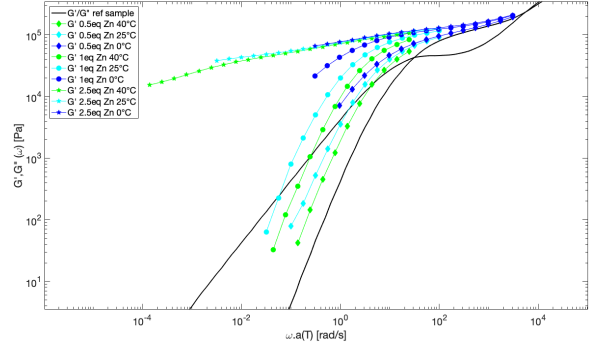


Figure 7.4: Storage modulus of PnBA-tpy₂ containing Zn²⁺ ions in different quantities at high temperatures (40°C in light green, 25°C in light blue and 0°C in dark blue).

the middle between the pure ions. However, it must be noted that the data for the sample PnBA-tpy₂ 0.5eq blend are too low by a factor 1.5 approximately. This inaccuracy must be due to an error during the rheological measurements. Consequently, no conclusion can be drawn from the absolute values of the data provided for this sample. But considering the results for the PnBA-tpy₂ 1eq blend and the fact that the data of PnBA-tpy₂ 0.5eq blend should be shifted upwards, one can deduce that the influence of each type of ion is similar: it does not seem that one specific kind of ions has a greater impact on the properties of the resulting MSP than the other.

7.2 Second plateau and aggregates

Moreover, a second plateau in G' can be observed for some of the samples in these figures. It was already mentioned when discussing the crossover frequency, but it is more clearly visible here. With copper, the second plateau is visible at high temperature only for a high ion content (2.5eq on Figure 7.1), but at low temperature it can already be seen with a lower ion density. For instance at 25°C for 0.5eq, a short second plateau appears around a frequency of 0.1rad/s (see Figure 7.2). With zinc ions, a second plateau is only

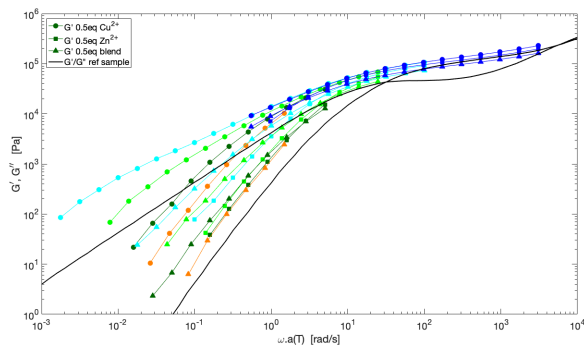


Figure 7.5: Storage modulus of PnBA-tpy₂ containing 0.5eq of Cu²⁺ ions (circles), Zn²⁺ ions (squares), and a blend of Cu²⁺ and Zn²⁺ ions (triangle). The colors of the curve are related to the temperature of the experiment: 80°C in orange, 60°C in dark green, 40°C in light green, 25°C in light blue and 0°C in dark blue.

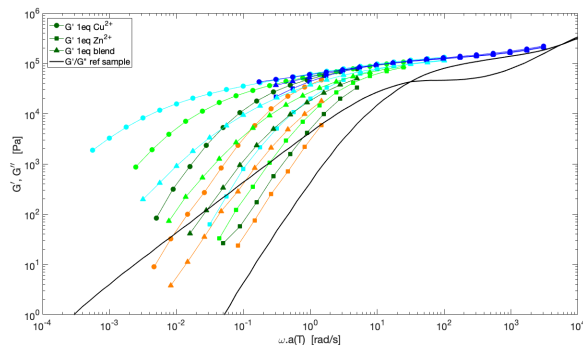


Figure 7.6: Storage modulus of PnBA-tpy₂ containing 1eq of Cu²⁺ ions (circles), Zn²⁺ ions (squares), and a blend of Cu²⁺ and Zn²⁺ ions (triangle). The colors of the curve are related to the temperature of the experiment: 80°C in orange, 60°C in dark green, 40°C in light green, 25°C in light blue and 0°C in dark blue.

present at high ion density, that is for the sample PnBA-tpy₂ 2.5eq Cu²⁺. It is more easily visible at low temperature on Figure 7.4, although it is also present at higher temperatures, notably at 40°C on Figure 7.3. Recently, SAXS data on metallo-supramolecular polymers obtained from the association of telechelic star PnBA have shown the possible aggregation of the complexes. Therefore, we believe that the second plateau observed here is also due to aggregates. As the second plateau is more easily visible with copper, one can deduce that the aggregates are more easily formed with copper ions than with zinc ions. A larger amount of ions is needed to start forming aggregates with zinc. It is however interesting to notice that while zinc has a smaller tendency of forming aggregates, at 2.5eq, the proportion of these seems more important than with 2.5eq of copper ions.

7.3 Quantitative analysis of the storage modulus

On another hand, Figures 7.7 to 7.10 provide a more quantitative analysis of the enhancement of the elasticity occurring in the MSPs at low frequency by looking at the value of the storage modulus at a frequency of 0.1rad/s.

7.3.1 Influence of the ion density

Figure 7.7 shows the impact of the ion density on G' . Whatever the nature of the ions used, there is always a broadening of the viscoelastic curves that appears when increasing the ion content. When stickers are associating, the linear assemblies become longer. As their reptation time is known to scale with the cube of their molar mass (see Equation 2.35), τ_{rept} becomes larger. Thus, the terminal relaxation is delayed and the plateau is becoming longer. Moreover, with a larger quantity of ions, more complexes can be formed, which leads to an even longer plateau. The presence of aggregates can also affect the length of the plateau, since it can lead to the appearance of a second plateau. Both these phenomenons

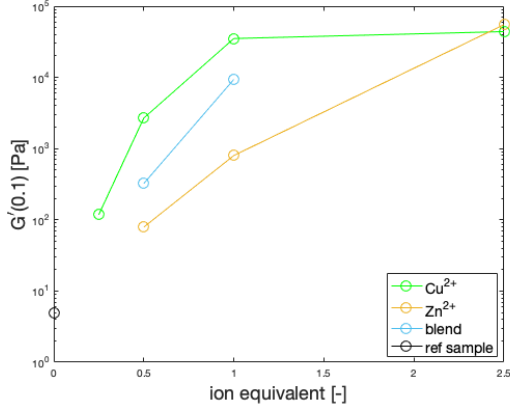


Figure 7.7: Value of the storage modulus at $\omega = 0.1\text{rad/s}$ and at 25°C as a function of the ion density.

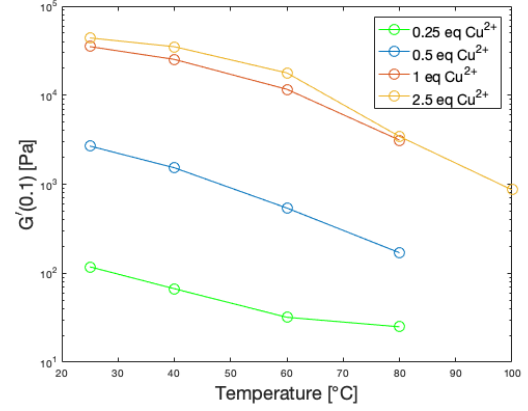


Figure 7.8: Value of the storage modulus at $\omega = 0.1\text{rad/s}$ as a function of the temperature for the samples of PnBA-tpy₂ containing Cu^{2+} metal ions.

are reinforced when the number of associated stickers, and thus the number of ions, is increased, which leads to an increase of G' with ion density.

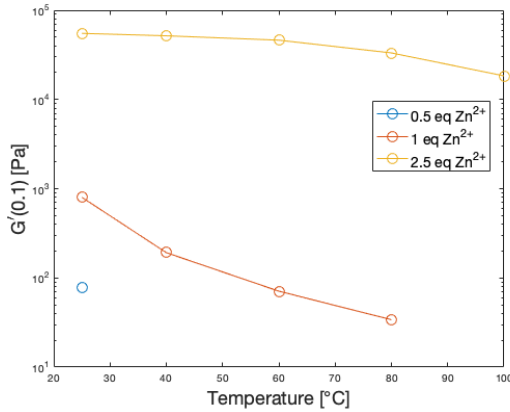


Figure 7.9: Value of the storage modulus at $\omega = 0.1\text{rad/s}$ as a function of the temperature for the samples of PnBA-tpy₂ containing Zn^{2+} metal ions.

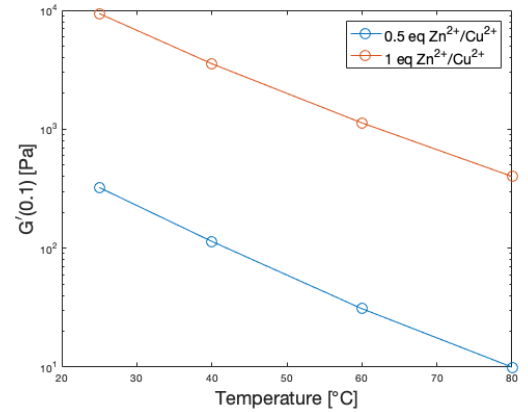


Figure 7.10: Value of the storage modulus at $\omega = 0.1\text{rad/s}$ as a function of the temperature for the two blends (PnBA-tpy₂ 0.5eq blend and PnBA-tpy₂ 1eq blend).

7.3.2 Influence of the ion nature

At 2.5eq, the behaviour differs when using copper or zinc. With copper, the increase of G' between 1eq and 2.5eq is very small, which could indicate that the polymer has reached a certain level of saturation. From 1eq, the addition of more metal ions does not change the properties significantly anymore. This can be seen by comparing the different curves in Figure 7.8. Between 0.25eq, 0.5eq and 1eq, the value of the storage modulus increases each time by approximately a decade. But between 1eq and 2.5eq, the two curves are nearly at the same level for all temperatures.

In comparison, at low ion density, G' is smaller with zinc than with copper, showing that the samples containing zinc are softer. But as already mentioned, at 2.5eq, an inversion of this tendency is observed: PnBA-tpy₂ 2.5eq Zn²⁺ becomes harder than PnBA-tpy₂ 2.5eq Cu²⁺ (see Figure 7.7 on the upper right corner of the graph). The very sharp transition from 1eq to 2.5eq with zinc indicates that this sample does not reach saturation as quickly as with copper. And as already mentioned, we attribute this large and sudden increase of G' to the formation aggregates that only appears at high ion density with zinc.

7.3.3 Influence of the temperature

Figures 7.8 to 7.10 show the impact of the temperature on the stickers. It has already been discussed in the previous chapter when looking at the crossover frequency, but it is also visible here. For all samples, an increase of the temperature leads to a softening of the material. It proves again that a rise of the temperature leads to stickers associations that are less stable, and thus to self-assembled chains that are shorter, and that can dissociate more easily. This reasoning applies also to the aggregates, which are therefore diminished at high temperature.

Chapter 8

Comparison with star samples

In this chapter, the linear assemblies are compared to four-arm star polymers at 0.5eq Cu^{2+} and 1eq Cu^{2+} . The aim is to look if the formation of the metal-ligand complexes has the same effect on these two polymers having different architectures. The master curves of the star samples are represented on Figures 8.1 and 8.5. While on Figures 8.2 to 8.4, and 8.6 to 8.8, the Frequency Sweep data measured at different temperatures are compared to the ones of the linear chains with the same amount of ions.

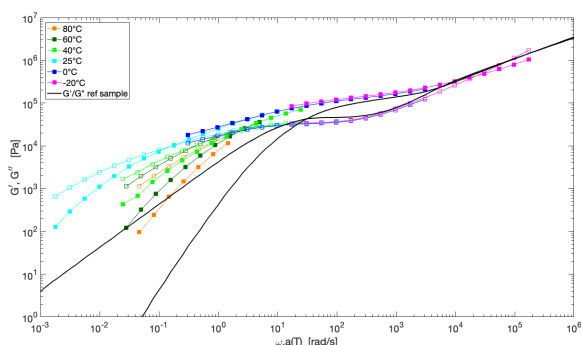


Figure 8.1: Master curve of the Star 0.5eq Cu^{2+} using 25°C as reference temperature.

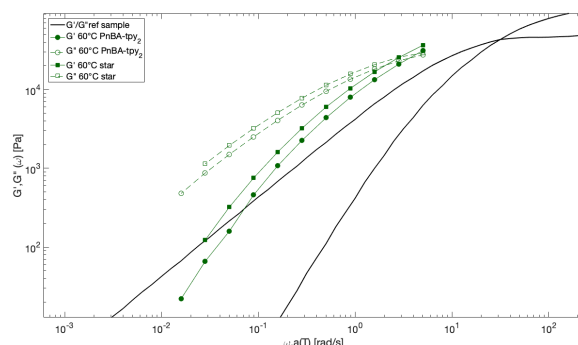


Figure 8.2: Comparison of the storage and loss moduli between the Star 0.5eq Cu^{2+} and the PnBA-tpy₂ 0.5eq Cu^{2+} at 60°C.

On these images, it can be noted that the curves of the stars have a similar shape as the ones of the linear chains. The difference between the two samples is that the data for the stars are slightly shifted upwards. This observation is valid for both samples, Star 0.5eq Cu^{2+} and Star 1eq Cu^{2+} . And it is particularly true at high temperature, that is from 80°C to 40°C. However, at low temperature, that is at 25°C and 0°C, the shape of the curves become less and less similar, they are not parallel anymore. For the Star 0.5eq Cu^{2+} , a second plateau appears at low temperature between 1 and 0.1rad/s, which is much more pronounced than for the linear chains (see Figure 8.4). The presence of this second plateau suggests that aggregates are also formed with the stars.

The moduli of the Star 1eq Cu^{2+} also starts to differ from those of the linear chains at low temperature, despite the fact that there is no second plateau (see Figure 8.8). Instead, it is the rubbery plateau, where the storage modulus is equal to G_N^0 , which becomes much longer than the one of the linear assemblies.

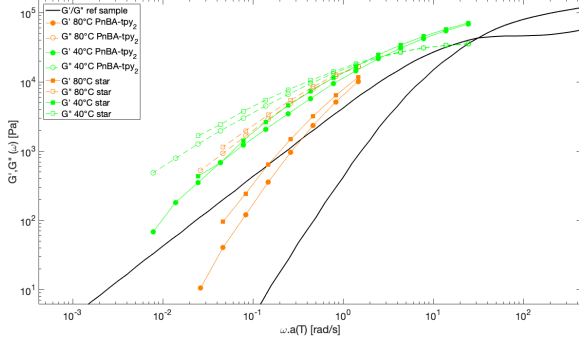


Figure 8.3: Comparison of the storage and loss moduli between the Star 0.5eq Cu²⁺ and the PnBA-tpy₂ 0.5eq Cu²⁺ at 80°C and 40°C.

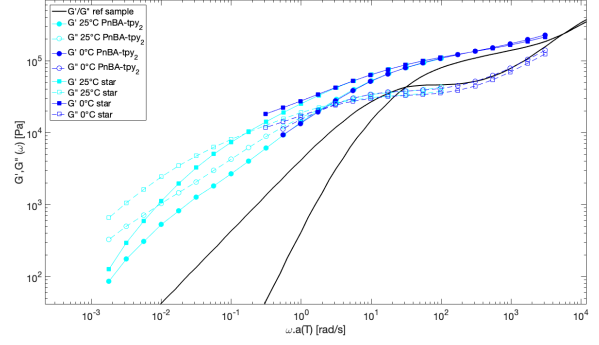


Figure 8.4: Comparison of the storage and loss moduli between the Star 0.5eq Cu²⁺ and the PnBA-tpy₂ 0.5eq Cu²⁺ at 25°C and 0°C.

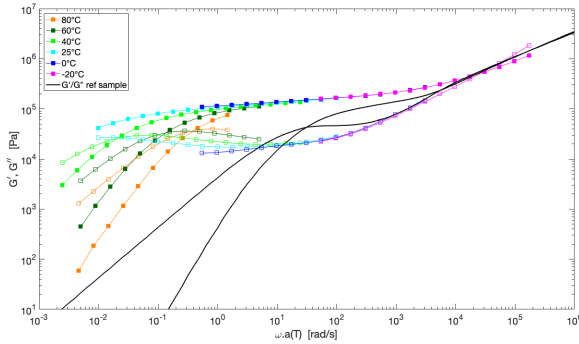


Figure 8.5: Master curve of the Star 1eq Cu²⁺ using 25°C as reference temperature.

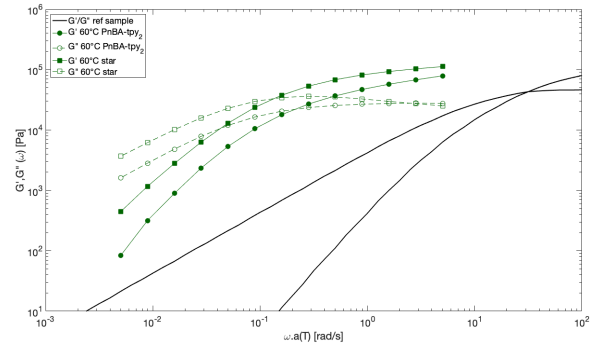


Figure 8.6: Comparison of the storage and loss moduli between the Star 1eq Cu²⁺ and the PnBA-tpy₂ 1eq Cu²⁺ at 60°C.1

The values of the crossover frequency and the storage modulus at $\omega = 0.1\text{rad/s}$ are compared in Figure 8.10 and Figure 8.9 respectively.

The graph of the storage modulus on Figure 8.9 allows to visualise better the gap between the curves of the star and the linear chains. This figure shows that the gap is about the same at all temperatures, and for all samples. Only one point, at 40°C for the Star 0.5eq Cu²⁺, doesn't follow this trend.

And when looking at the crossover frequencies in Figure 8.10, it can be observed that $1/\omega_{co}$ is delayed for the stars compared to the linear chains. The gap between the crossover frequencies remains also the same at high temperatures, that is between 80°C and 40°C. Thus, it corresponds to the range where the shape of the curves is similar for both chain architectures. Then, at 25°C for 0.5eq Cu²⁺ the gap between the two crossover frequencies increases largely. Unfortunately, the crossover is not visible for the two star samples at lower temperatures, which is because the plateau becomes much longer.

Star polymers are different from linear chains because they cannot relax by reptation, their main relaxation process is the CLF. Hence, the relaxation of a star polymer will

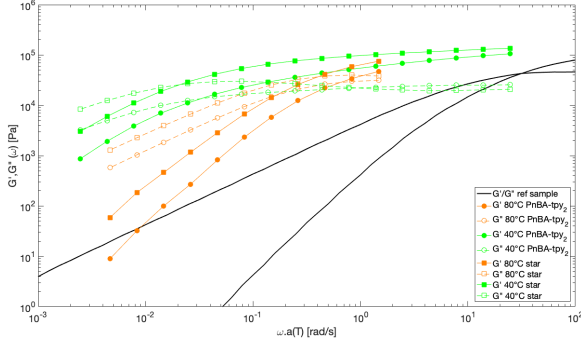


Figure 8.7: Comparison of the storage and loss moduli between the Star 1eq Cu²⁺ and the PnBA-tpy₂ 1eq Cu²⁺ at 80°C and 40°C.

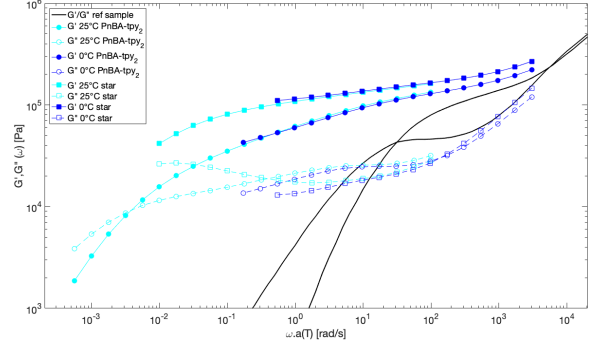


Figure 8.8: Comparison of the storage and loss moduli between the Star 1eq Cu²⁺ and the PnBA-tpy₂ 1eq Cu²⁺ at 25°C and 0°C.

always be delayed compared to the linear chain of the same size¹. This explains easily the increases of $1/\omega_{co}$ and G' that occurs at high temperature.

In addition, when junctions are formed between the stars, a network is created. Hence, the star chains cannot relax, not even by CLF, as long as the stickers remain attached. It is not the case for the linear assemblies, that can always relax by reptation, as long as there are no aggregates. When decreasing the temperature, the complexes become more stable, so the relaxation of the stars is further hindered. This is less pronounced for linear chains, as they can still relax at least partially. This could explain why the plateau is longer with the stars, while it decreases faster for the linear chains at low temperature.

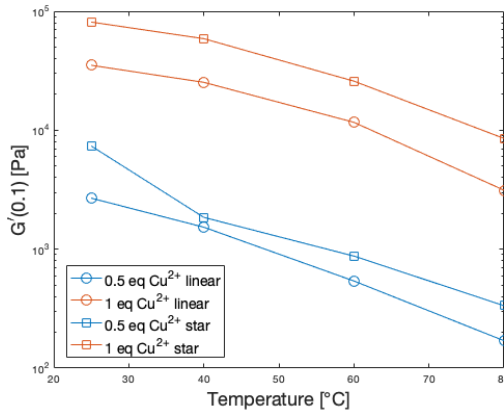


Figure 8.9: Value of the storage modulus at $\omega = 0.1 \text{ rad/s}$ as a function of the temperature: comparison between the stars and the linear assemblies.

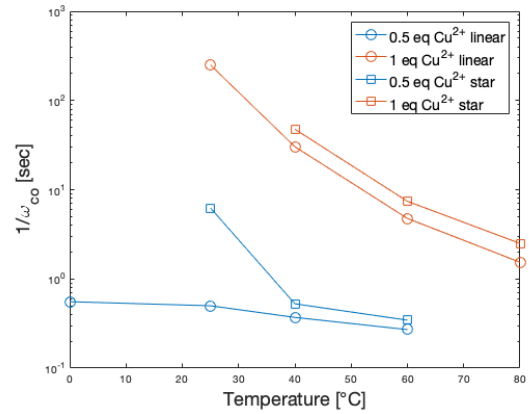


Figure 8.10: Inverse of the crossover frequency $1/\omega_{co}$ as a function of the temperature: comparison between the stars and the linear assemblies.

¹ A linear chain can be considered as a two-arm star that can relax by reptation. Hence, a star and a linear chain are considered to be the same size when one arm of the star has the same molecular weight as half the molecular weight of the linear chain. For the samples here, the molar mass of the star is 250kg/mol, which gives 62.5kg/mol for one arm. And half the molecular weight of the linear chains is equal to $113.2/2 = 56.6 \text{ kg/mol}$. These two values are not exactly equal, but they are still very close. Hence, the two polymers here can be considered as having the same size.

Part IV

Modeling

Chapter 9

Model based on the Time Marching Algorithm

The model used for the simulation of the Frequency Sweep data relies on the Time Marching Algorithm (TMA), and it is also based on the equations associated with the molecular rheological models. As their names suggest, these models describe the polymer dynamics at the level of the molecule, that is at the level of the polymer chain. Hence, it is of great importance to know as precisely as possible the composition of the sample studied, because even a small change in the sample composition can have an impact on the results.

In practice, for each sample, a matrix called LI is built, as shown by Equation 9.1. The samples used were very pure, composed only of linear chains, so the shape of LI is quite simple here: M_i represents the molecular weight of the different chains present in the sample, and ν_i the weight fraction of each of these chain of mass M_i in the sample, with $\sum_{i=1}^n \nu_i = 1$.

$$LI = \begin{pmatrix} M_1 & \nu_1 \\ M_2 & \nu_2 \\ \dots & \dots \\ M_n & \nu_n \end{pmatrix} \quad (9.1)$$

However, this matrix LI is unknown, it must be constructed from the available data about the samples, like its weight-average molecular weight and dispersity. In order to make the transition from the global polymer properties to the matrix LI , several statistical tools are used, each one allowing to describe a certain type of sample. The global model used for the simulation is thus always the same, but the differences between the several versions of the model always reside in this LI matrix, which is constructed in a different way thanks to these statistical tools. For example, as described later, this LI matrix can be composed of the supramolecular assemblies, rather than the building blocks.

9.1 Description of the TMA Model

Once the matrix LI has been constructed, the Time Marching Algorithm is used to compute the relaxation modulus of the polymer described by this matrix. This model integrates all the relaxation processes described in the chapter 2, namely the Rouse relaxation, reptation, contour length fluctuations, and constraint release. At each step of time, the value of $G(t)$ is computed thanks to the Equation 9.2. This approach is

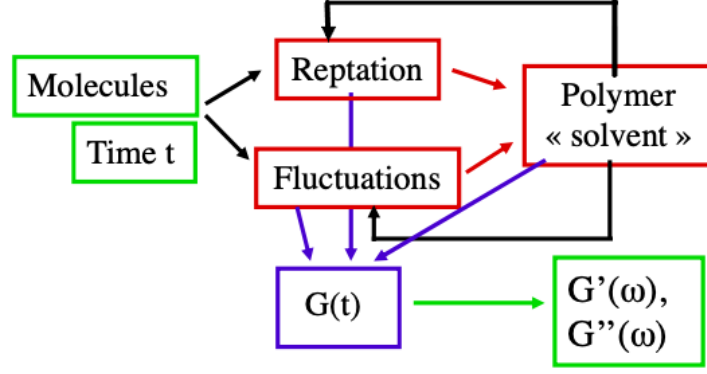


Figure 9.1: Illustration of the intricate relationships between the variables and the relaxation processes needed for the computation of $G(t)$, $G'(\omega)$ and $G''(\omega)$ [12].

used because so far, no analytical function exists for complex polymers [19]. Indeed, the different relaxation processes are interconnected. The relaxed fraction of polymer acts as a solvent for the unrelaxed fraction, following to the Dynamic Tube Dilution effect. The DTD has an influence on the tube diameter, which in turn has an impact on the relaxation times for reptation and fluctuation. This interconnectivity, illustrated on Figure 9.1, makes it impossible to find an analytical function for the relaxation modulus. Hence, with the TMA, the fraction of polymer that is relaxed is computed at each step of time, and then introduced in the Equation 9.2 to find the relaxation modulus. Moreover, as the melt is not monodisperse, each parameter (reptation time, Rouse relaxation time, fluctuation time,...) is different for each type of chain, which makes the computation much more complicated than what is described in chapter 2, where all the computations are given for one chain of given molecular weight. In all the following equations, the subscript i is thus used to refer to each type of chain present in the matrix LI .

$$G(t_k) = G_N^0 \cdot \varphi(t_k) \cdot \Phi_{tube}(t_k) + G_{Rouse}(t_k) \quad (9.2)$$

In addition to the matrix LI , only three parameters have to be known to be able to use the Equation 9.2:

- The plateau modulus $G_N^0 = 160\text{kPa}$
- The molecular weight between two entanglements $M_e = 17\text{kg/mol}$
- The Rouse relaxation time for the segment of mass M_e between two entanglements $\tau_e \approx 5 \cdot 10^{-4}\text{s}$

In Equation 9.2, $G(t)$ is decomposed into two terms. The left one corresponds to the contribution of the disentanglement processes to the modulus, and the term $G_{Rouse}(t_k)$ designates the relaxation of the stress at high-frequency thanks to the Rouse process. In this equation, the plateau modulus is defined as

$$G_N^0 = \frac{4}{5} \frac{\rho RT}{M_e} \quad (9.3)$$

In the first part of $G(t)$, the function $\varphi(t_k)$ describes the fraction of polymer that is not relaxed by reptation or by CLF. This function thus depends on the survival probabilities

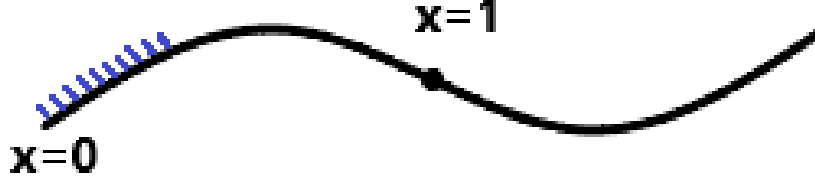


Figure 9.2: Representation of a linear chain as a two-arm star polymer that can relax by reptation. The position of each segment is only defined on one half of the chain, which is divided into 100 segments x , whose value is 0 at the extremity and 1 in the middle of the chain.

of a tube segment x by reptation and by CLF, $p_{rept}(x, t)$ and $p_{fluc}(x, t)$. It must be noted that here, a linear chain is treated as a two-arm star polymer that can relax by reptation. Therefore, x is defined for only half the chain, which is divided into 100 segments. And its value is 0 at the extremity and is 1 at the middle of the chain, so the survival probability is computed for only half the chain. This approach is used because both ends of the chain relax in the same way, hence it makes more sense to look at the relaxation of only half the chain, and then use it for the two parts of the chain. The survival probabilities $p_{rept}(x, t)$ and $p_{fluc}(x, t)$ take the form of a matrix where the 100 columns correspond to the 100 segments x and the lines correspond to each molar mass M_i from the matrix LI .

The value of $p_{rept}(x, t)$ is derived from the Doi and Edwards equation seen in chapter 2.

$$p(x, t) = \sum_{k \text{ odd}} \frac{4}{k\pi} \cdot \sin\left(\frac{k\pi x}{2}\right) \cdot \exp\left(\frac{-k^2 t_k}{\tau_{rept}(M_i)}\right) \quad (9.4)$$

with

$$\tau_{rept} = 3\tau_e \left(\frac{M_i}{M_e}\right)^3 \quad (9.5)$$

However, the Doi and Edwards equation is originally defined for an entire linear chain, from one extremity to the other, and not only for a half chain as should be the case here. To overcome this problem, a change of variable is used in Equation 9.4:

$$x = \frac{1}{2} + (1 - x')\frac{1}{2} \quad (9.6)$$

In this equation x' denotes the position of the segments when the linear chain is considered as a two-arm star, thus $x' = 0$ at one end and $x' = 1$ in the middle.

On another hand, the survival probability by contour length fluctuations is computed as follows, which is similar to Equation 2.47 in chapter 2, the only difference being that $\tau_{fluc}(x_i)$ is different for each type of chain present in the matrix LI .

$$p_{fluc}(x, t) = \exp\left(\frac{-t}{\tau_{fluc}(x_i)}\right) \quad (9.7)$$

Where

$$\begin{aligned} \tau_{fluc}(x_i) &= \tau_{early}(x_i) && \text{for } x_i < x_{trans,i} \\ \tau_{fluc}(x_i) &= \tau_{early}(x_i) \exp\left(\frac{U(x_i) - U(x_{trans,i})}{kT}\right) && \text{for } x_i > x_{trans,i} \end{aligned} \quad (9.8)$$

With

$$\tau_{early}(x_i) = \frac{9\pi^3}{16} \cdot \left(\frac{M_i/2}{M_e} \right)^2 \cdot \tau_{R,chaini} \cdot x_i^4 \quad (9.9)$$

$$\frac{\partial \ln \tau_{activated}(x)}{\partial x} = \frac{dU/kT}{dx_i} = 3 \cdot \left(\frac{M_i/2}{M_e} \right) \cdot x_i \cdot \Phi(x_i) \cdot \Delta x_i \quad (9.10)$$

In Equation 9.10, the function $\Phi(x_i)$ represents the fraction of unrelaxed tube segments in the polymer when the segment x_i is relaxing. For a monodisperse sample, it is simply equal to $(1 - x_i)$. However, in the general case of a polydisperse sample, all molar masses must be taken into account. Two segments x_i and x_j belonging to two chains of different lengths and that are relaxing at the same time are not located at the same position: $x_i \neq x_j$. However, they are related through their potential energy.

$$U(x_i, M_i) = U(x_j, M_j) \Leftrightarrow \sqrt{M_i}x_i = \sqrt{M_j}x_j \quad (9.11)$$

It leads to the following equation for the unrelaxed fraction of polymer:

$$\Phi(x_i) = \sum_j \nu_j \cdot (1 - x_i \sqrt{\frac{M_i}{M_j}}) \quad (9.12)$$

Finally, $p_{rept}(x, t)$ and $p_{fluc}(x, t)$ are used to compute the function $\varphi(t_k)$

$$\varphi(t_k) = \sum_i \nu_i \varphi_i(t) \quad (9.13)$$

with

$$\varphi_i(t) = \sum_{x=0.01}^1 p_{rept}(x, t) p_{fluc}(x, t) \Delta x \quad (9.14)$$

Coming back to Equation 9.2, the variable $\Phi_{tube}(t_k)$ is the dilation factor, which takes into account the constraint release process. It is equal to the unrelaxed fraction of polymer $\varphi(t_k)$. However, a lower bound must be added, because it can happen that the tube widening occurs too fast, so that the chain is not able to explore it [19]. This lower bound, noted Φ_{max} , is defined by Equation 9.15.

$$\Phi_{max} = \Phi_{tube}(t_{k-1}) \cdot \left(\frac{t_{k-1}}{t_k} \right)^{1/2} \quad (9.15)$$

And the dilation factor is thus the maximum value between $\varphi(t_k)$ and the lower bound Φ_{max} :

$$\Phi_{tube} = \max(\varphi(t_k), \Phi_{max}) \quad (9.16)$$

Then, the last term of the relaxation modulus, $G_{Rouse}(t_k)$, that represents the Rouse process, is given by Equation 9.17.

$$G_{Rouse}(t_k) = \sum_i \nu_i G_{Rouse,i}(t_k) \quad (9.17)$$

with

$$G_{Rouse,i}(t_k) = \frac{\rho RT}{M_i} \sum_{p=Z+1}^N \exp\left(\frac{-2p^2 t_k}{\tau_R(M_i)}\right) + \frac{\rho RT}{5M_i} \sum_{p=1}^Z \exp\left(\frac{-p^2 t_k}{\tau_R(M_i)}\right) \quad (9.18)$$

This last equation is similar to the Equation 2.29 seen in chapter 2, except that two terms are present instead of one. In fact the first term represent the contribution of the transverse Rouse modes to the stress, and the second term represent the contribution of the longitudinal Rouse modes. The longitudinal motions, through which monomers rearrange themselves along the tube, are still possible even in the presence of entanglements [20], therefore they are treated separately.

Finally, the Schwarzl relations are used to find the storage and loss moduli $G'(\omega)$ and $G''(\omega)$ from the relaxation modulus $G(t)$ [21]. These approximate formulas are used instead of the Fourier transform.

9.2 TMA model applied to the reference sample

9.2.1 Log-normal distribution

In order to describe the sample of reference, that is the PnBA-tpy₂ chains without addition of metal ions, the hypothesis is made that the molecular weight of this sample follows a log-normal distribution. It will be used here to create the molecular weight distribution of the sample, on the basis of two of its properties:

- Its weight-average molecular weight $\overline{M}_w = 113.2\text{kg/mol}$.
- Its dispersity $\mathbb{D} = 1.13$.

A variable x follows a log-normal distribution, characterised by a mean μ and standard deviation σ , if $y = \ln(x)$ is normally distributed. A log-normal distribution describes well variables that are the result of the multiplication of many independent events. The probability density function associated is given by Equation 9.19 [22].

$$f_Y(x; \mu, \sigma) = \frac{1}{x\sigma\sqrt{2\pi}} \exp\left(-\frac{(\ln x - \mu)^2}{2\sigma^2}\right) \quad (9.19)$$

Within the framework of the molecular weight distribution, the variable x is replaced by the molecular weight M , and the probability density function $f_Y(x; \mu, \sigma)$ becomes the molecular weight distribution in number $N(M; \mu, \sigma)$.

$$N(M; \mu, \sigma) = \frac{1}{M\sigma\sqrt{2\pi}} \exp\left(-\frac{(\ln M - \mu)^2}{2\sigma^2}\right) \quad (9.20)$$

However, one still needs to find a value for the mean μ and the standard deviation σ as a function of the known parameters $\overline{M}_w$ and $\mathbb{D}$ in order to compute the distribution. To that end, it is necessary to come back to some definitions [23].

A polydisperse polymer is composed of N_i moles of chains of mass M_i , with $i = 1, 2, \dots, n$. The molecular weight distribution in number $N(M)$ is the function giving the number of moles N_i versus the molar mass M_i . Another distribution also exists: the molecular weight distribution in weight $W(M)$, and it gives the weight fraction W_i for each polymer chain of mass M_i . The weight fraction is defined as $W_i = N_i M_i$. At the end, we are more interested into this distribution in weight than by the distribution in number, because

the variable ν_i in the matrix LI represents the weight fraction, it is thus equal to W_i . Fortunately, is quite easy to switch between the two distributions thanks to Equation 9.21.

$$W(M) = \frac{N(M)M}{\overline{M}_n} \quad (9.21)$$

Although the molecular weight distributions are very useful, they contain a lot of information. Hence, average molecular weights are most often used to characterise polymers. The number-average molecular weight $\overline{M}_n$ and the weight-average molecular weight $\overline{M}_w$ are defined as follows:

$$\overline{M}_n = \frac{\sum_i N_i M_i}{\sum_i N_i} \quad (9.22)$$

$$\overline{M}_w = \frac{\sum_i W_i M_i}{\sum_i W_i} = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} \quad (9.23)$$

The dispersity $\mathbb{D}$ is defined as the ratio of these two averages. When the dispersity is exactly equal to 1, the polymer is said to be monodisperse, and it is composed at 100% by chains of mass $M = \overline{M}_w = \overline{M}_n$. However, it is nearly impossible to achieve such a perfect polymer, and most polymers are polydisperse, with $\mathbb{D} > 1$.

$$\mathbb{D} \triangleq \frac{\overline{M}_w}{\overline{M}_n} \quad (9.24)$$

The average molar masses $\overline{M}_w$ and $\overline{M}_n$ are given under a discrete form in Equation 9.22 and 9.23, but it is also possible to rewrite it in a continuous form, with integrals instead. The discrete variable M_i is replaced by the continuous variable M , and N_i is replaced by $N(M)dM$, which is the value of the molecular weight distribution in number for a molar mass between M and $M + dM$. Similarly to N_i , W_i is replaced by $W(M)dM$.

$$\overline{M}_n = \frac{\int M N(M) dM}{\int N(M) dM} \quad (9.25)$$

$$\overline{M}_w = \frac{\int M^2 N(M) dM}{\int M N(M) dM} = \frac{\int M W(M) dM}{\int W(M) dM} \quad (9.26)$$

Knowing that $\int_0^\infty N(M) dM = 1$ and $\int_0^\infty W(M) dM = 1$ (as the integral of a probability density function over the entire space is always equal to 1), it is possible to integrate these equations 9.25 and 9.26 by replacing $N(M)$ with its expression given by Equation 9.20. The following results are obtained [24].

$$\overline{M}_n = \int_0^\infty M N(M) dM = \exp(\mu + \sigma^2/2) \quad (9.27)$$

$$\overline{M}_w = \int_0^\infty M W(M) dM = \exp(\mu + 3\sigma^2/2) \quad (9.28)$$

Combining Equation 9.27 and 9.28 into the Equation 9.24 leads to:

$$\begin{aligned} \mathbb{D} &= \frac{\exp(\mu + 3\sigma^2/2)}{\exp(\mu + \sigma^2/2)} \\ &= \exp(\sigma^2) \end{aligned} \quad (9.29)$$

$$\Leftrightarrow \sigma^2 = \ln(\mathbb{D}) \quad (9.30)$$

The Equation 9.30 is the first result needed to compute the distribution, and it is injected into Equation 9.28, in order to also find an equation for μ as a function of $\overline{M}_w$ and $\mathfrak{D}$.

$$\overline{M}_w = \exp\left(\mu + \frac{3}{2} \ln(\mathfrak{D})\right) \quad (9.31)$$

$$\Leftrightarrow \mu = \ln\left(\frac{\overline{M}_w}{\mathfrak{D}^{3/2}}\right) \quad (9.32)$$

With these Equation 9.30 and 9.32, it is possible to compute the molecular weight distribution in number with a log-normal distribution on the basis of known polymer properties. Then the Equation 9.21 allows to transform the distribution in number to a distribution in weight, as needed to compute LI .

However, the distribution obtained is a continuous distribution, it contains a lot of points. Such a large number of data points is not necessary for the matrix LI . Hence, a threshold was set in order to remove all the points for which the weight fraction is below 0.001, as these chains are in a too low amount to have a significant impact on the relaxation modulus. Then, 20 points are extracted at a regular interval on the curve. At this stage, one already has a matrix LI composed of 20 different chains. This matrix is finally normalised in order to fulfil the equation $\sum_{i=1}^n \nu_i = 1$.

9.2.2 Results

The molecular weight distribution in weight obtained thanks to the log-normal distribution for the reference sample is shown on Figure 9.3.

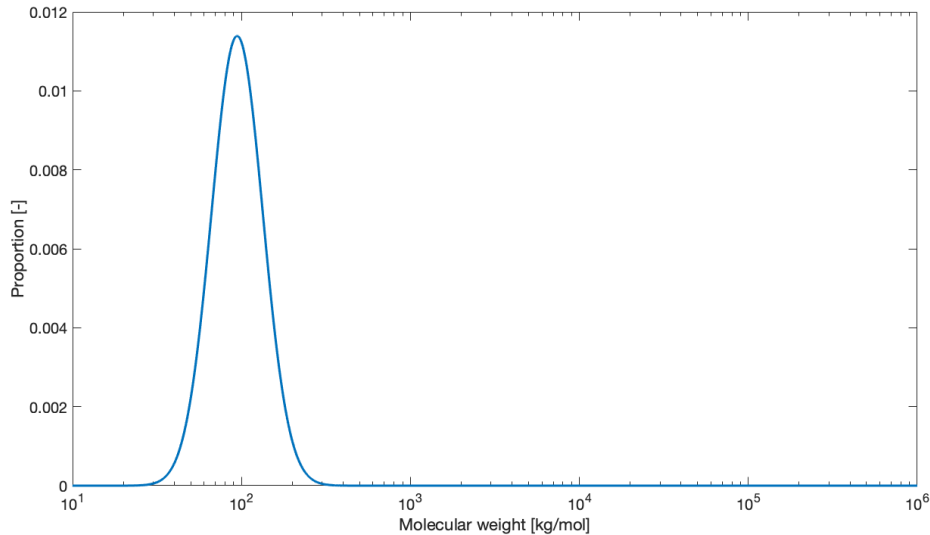


Figure 9.3: Molecular weight distribution in weight obtained from a log-normal distribution for the reference sample.

The matrix LI based on this distribution allowed the application of the TMA model to the reference sample. The result is represented on Figure 9.4. It appears that the modelling of the experimental data is very good, except for the crossover which is located

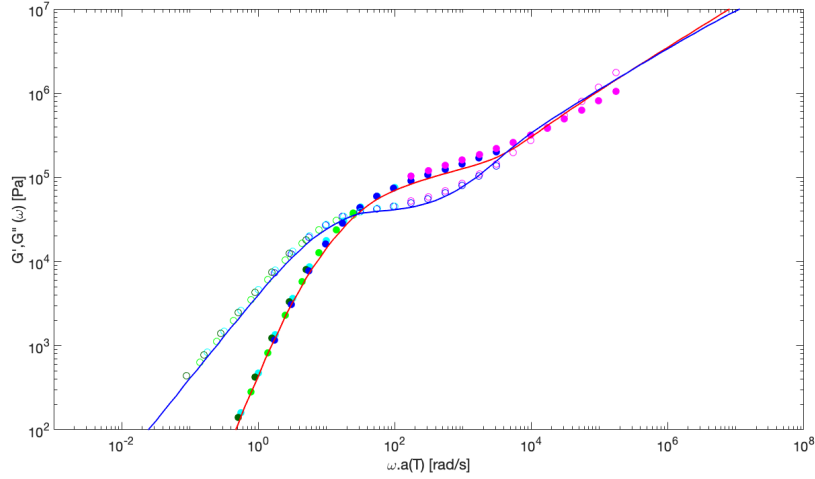


Figure 9.4: Storage and loss modulus of the reference sample obtained from the TMA model (continuous lines) and from experimental measurements (dots). The parameters used to construct the matrix LI in the TMA model are $\overline{M}_w = 113.2\text{kg/mol}$ and $\mathfrak{D} = 1.13$.

at a slightly too high frequency. There is also a small difference between the model and the experimental data for $G''(\omega)$ in the terminal regime.

This discrepancy between the simulation and the experimental data shows that the value of weight-average molecular weight of the reference sample, as provided by the SEC data, is slightly under-evaluated. Hence, the value of $\overline{M}_w$ was corrected to 118kg/mol . This variation of molar mass represents about 4% of the initial molecular weight, which is quite small. This corrected value was also used for all the metallo-supramolecular polymers. The curves of $G'(\omega)$ and $G''(\omega)$ obtained with this value are shown on Figure 9.5. In that case, the model works fine at high and low frequencies.

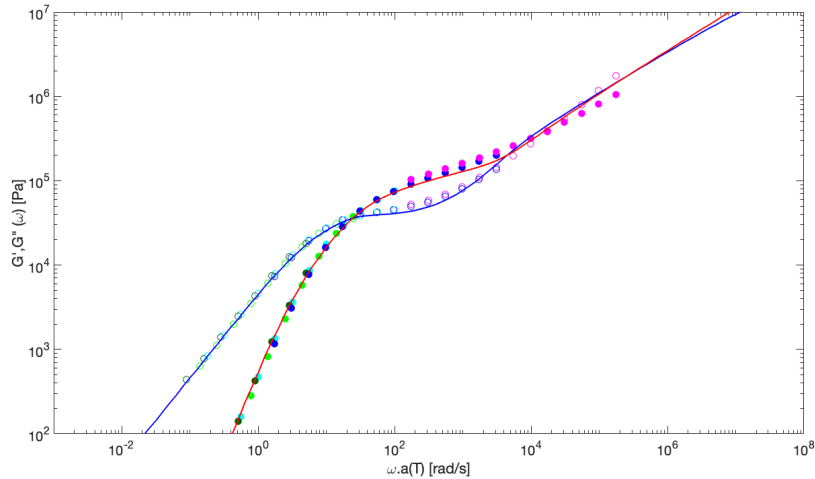


Figure 9.5: Storage and loss modulus of the reference sample obtained from the TMA model (continuous lines) and from experimental measurements (dots). The parameters used to construct the matrix LI in the TMA model are $\overline{M}_w = 118\text{kg/mol}$ (corrected value) and $\mathfrak{D} = 1.13$.

Chapter 10

TMA model applied to the metallo-supramolecular polymers

10.1 Flory distribution

In order to compute the molecular weight distribution of the supramolecular samples, and thus the matrix LI , the log-normal distribution is not used anymore, it is replaced by a Flory distribution.

When the metal ions are added, complexes are formed in between the terpyridine ligands and the ions, hence the stickers become active, and long linear assemblies are created. The effect of the dispersity is thus ignored here, because when several building blocks are linked together, the fact that one building block is slightly smaller or larger than the weight-average molecular weight is attenuated by the other building blocks of the assembly. This hypothesis is true as long as the proportion of active stickers is high enough, that is if the proportion of non-associated building blocks is not too large.

If the dispersity is not taken into account, the molecular weight of one building block, noted M_0 , is fixed to the weight-average molecular weight.

$$M_0 = \overline{M_w} = 118\text{kg/mol} \quad (10.1)$$

Consequently, it is known that the molecular weight of the linear assemblies will only take discrete values, each of them being a multiple of M_0 .

In order to compute the proportion of chains of molecular weight $x \cdot M_0$, and thus the molecular weight distribution of the sample, the Flory distribution is used. This distribution is based on the Flory equal reactivity principle [25, 26]. It says that the probability that two building blocks react together is a fixed, constant value, regardless of the size of the chain already assembled. This probability is called the probability of association and is noted p_{ass} . Then, the total probability that a linear assembly is composed of x building blocks is defined by the Equation 10.2.

$$P(x) = p_{ass}^{x-1}(1 - p_{ass}) \quad (10.2)$$

In this equation, one can find p_{ass} to the power $x - 1$, which corresponds to the $x - 1$ building blocks that have reacted each time with a probability p_{ass} . And the last part,

$(1 - p_{ass})$, corresponds to the last building block that has not reacted further. $(1 - p_{ass})$ is thus the probability that the end-group has not reacted.

This probability $P(x)$ is also equal to the mole fraction of linear assemblies composed of x building blocks in the mixture. Hence, $P(x)$ provides directly the proportion in number of chains of weight $x \cdot M_0$. In order to have the molecular weight distribution in number $N(x)$, $P(x)$ simply has to be normalised, thanks to the following equation:

$$N(x) = \frac{P(x)}{\sum P(x)} \quad (10.3)$$

However, the matrix LI is constructed on the basis of the distribution in weight, not with the distribution in number. The computation of the molecular weight distribution in weight, $W(x)$, is thus given by

$$W(x) = \frac{N(x) \cdot x}{\sum N(x) \cdot x} \quad (10.4)$$

In Equation 10.4, the denominator serves to normalise the distribution. Finally, to derive the matrix LI , all the points for which $W(x)$ is larger than 0.001 are kept, and the others are removed. Hence, the size of the LI is not always the same, it depends on p_{ass} . Examples of molecular weight distribution in weight that can be obtained thanks to a Flory distribution with different values of p_{ass} are represented on Figure 10.1. On this graph, even though they are linked by a continuous line, the only values that the molecular weight can take are represented by the circles.

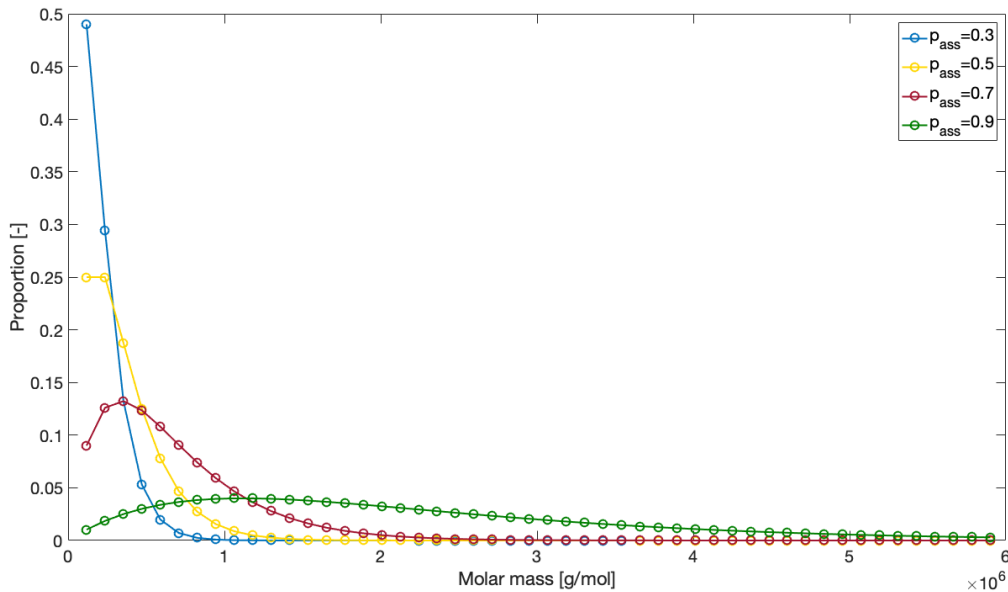


Figure 10.1: Molecular weight distribution in weight obtained from a Flory distribution for different values of p_{ass} . The discrete values of the molecular weight are indicated by the circles.

10.2 Aggregates

It was seen in the experimental results in the Part III that a second plateau is present in some samples, which indicates the presence of aggregates. These must be taken into account in the model, as they change substantially the curves of $G'(\omega)$ and $G''(\omega)$.

An aggregate is formed through a phase separation between the complexes and the polymer backbone. The small domains where metal-ligand complexes are concentrated are called aggregates, and their presence prevents the relaxation of the polymer, because the aggregate acts as a cross-linking point. Indeed, an aggregate creates a junction between complexes belonging to different chains, and the lifetime of this junction is considered to be much larger than the lifetime of a simple complex. In the presence of aggregates, the polymer melt can thus be separated into four different categories of chain segments [27], that are represented on Figure 10.2:

- Free linear chains that do not contain aggregates. They are able to relax by reptation.
- The chains that only contain one aggregate cannot relax by reptation anymore, hence they can be considered as two-arm stars, that relax by CLF.
- If the chain contains more than one aggregate, the two chain ends become dangling ends, that can relax by CLF like the star arms.
- The subchain which is in between two aggregates is a trapped segment. More precisely, the trapped segment refers to the part of the chain in between the first and last aggregate of the chain. But additional aggregates may be present within the trapped segment. To take that into account, the trapped segments can be subdivided into strands, which are the subchains in between two consecutive aggregates. The strands cannot relax as long as the aggregates are intact. Alternatively, if there are active stickers in between the two aggregates, the segment can relax by CLF after dissociation of the complex. In that case, the strand is separated into two dangling ends after some delay.

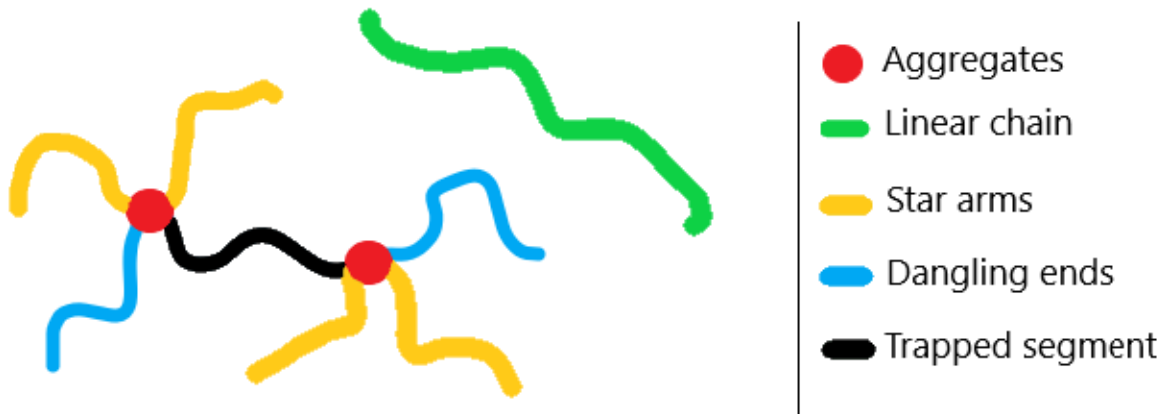


Figure 10.2: Schematic representation of the different types of chains which compose a polymer melt in the presence of aggregates.

The molecular weight of these different categories of chains are respectively noted $W_{lin}(M)$, $W_{star}(M)$, $W_{dang}(M)$, $W_{trap}(m)$ and $W_{strand}(M)$. Three hypotheses are made in order to describe the aggregates and to compute the distributions:

1. The aggregates can only be formed at the location of a bis-complex.
2. The chain ends are not considered as active sticker's sites. Hence, the formation of aggregates cannot involve chain ends, which are always free. This hypothesis is equivalent to assuming that the chain ends are always terpyridine ligands alone, or that they form mono-complexes unable to aggregate.
3. The lifetime of an aggregate is considered to be infinite.

The Flory distribution is always used in the first place to provide a matrix with linear chains only, and the aggregates are then added to the chains of this matrix. The main parameter that is needed to add the aggregates is noted p_{aggr} , and it represents the probability of having a sticker that is part of an aggregate. Then, the method used is the following:

1. For each chain length present in the Flory distribution, a matrix R of size $(10000 \times x - 1)$ is created, which represents the complexes for a sample composed of 10000 chains having a molecular weight $x \cdot M_0$. A random number in the range $[0; 1]$ is attributed to each element of the matrix R . The chains composed of only one building block are however an exception: according to the assumptions described above, they do not contain active stickers that could participate in an aggregate. Hence, all these chains are directly accounted for in the molecular distribution of the free linear chains.
2. Then the elements of the matrix are evaluated: if their value is larger than the probability p_{aggr} , the complex takes part in an aggregate, and its value is changed to 1. Otherwise, the complex does not form an aggregate, and its value is changed to 0. The resulting matrix is only composed of 0 and 1, the 1 representing the aggregates.
3. Afterwards, the matrix R is sorted, in order to separate the chains according to the number of aggregates that they contain.
 - The chains without aggregates are linear chains.
 - The chains containing 1 aggregate are considered as star molecules with two arms.
 - And if the chain has two or more aggregates, it must be separated into dangling ends, strands and trapped segments.

Finally, the length and the proportion of each type of chain is computed and introduced into the corresponding molecular weight distribution.

An example of molecular weight distributions in weight for the five types of chain segments is shown on Figure 10.3. The assumption that dispersity can be neglected also applies here, since the formation of the aggregates is based on a Flory distribution. Hence, the molecular weight can only take discrete values, that are indicated by the circles on the

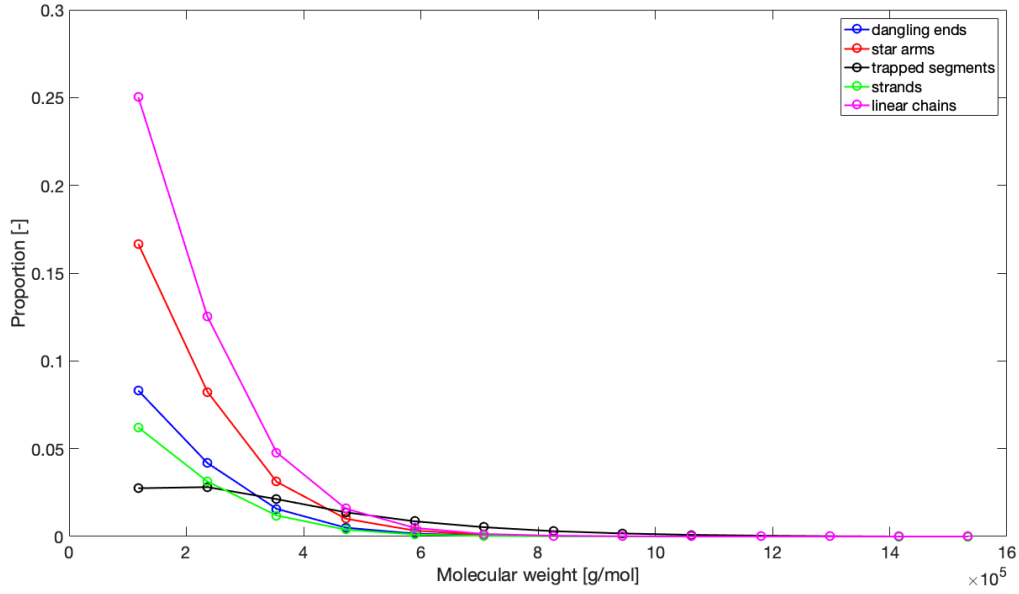


Figure 10.3: Molecular weight distributions in weight of the different types of chains in presence of aggregates. The parameters used are $p_{ass} = 0.5$ and $p_{aggr} = 1/2$. The discrete values of the molecular weight are indicated by the circles.

graph.

It must be noted that the integral of each distribution over the whole range of molecular weight is not equal to 1, because the normalisation is made over the whole sample, which is composed of different types of chain segments, and not on each category of segment individually. The integration of the distribution over M provides instead the total weight fraction of each type of segment.

$$\int_0^\infty W_{lin}(M)dM = \nu_{lin} \quad (10.5)$$

$$\int_0^\infty W_{dang}(M)dM = \nu_{dang} \quad (10.6)$$

$$\int_0^\infty W_{star}(M)dM = \nu_{star} \quad (10.7)$$

$$\int_0^\infty W_{trap}(M)dM = \nu_{trap} \quad (10.8)$$

$$\int_0^\infty W_{strand}(M)dM = \nu_{strand} \quad (10.9)$$

Moreover, the molecular weight distributions for the trapped segments and for the strands represent the same fraction of the polymer melt that is in between aggregates. These are just two different ways of counting them. Hence,

$$\nu_{trap} = \nu_{strand} \quad (10.10)$$

And the normalisation over the whole polymer sample is verified if

$$\nu_{lin} + \nu_{dang} + \nu_{star} + \nu_{trap} = 1 \quad (10.11)$$

Or, if one consider the strands instead of the trapped segments:

$$\nu_{lin} + \nu_{dang} + \nu_{star} + \nu_{strand} = 1 \quad (10.12)$$

10.3 First version of the model: the associated chains are stable

In the first version of the model, the hypothesis was made that the linear assemblies formed by complexation of the ligands with the ions are stable. In regard to the Cates' model (see section 2.8), it corresponds to the case where τ_{ass} ¹, the time of association of a sticker before breakage, is larger than the reptation time τ_{rept} : $\tau_{ass} > \tau_{rept}$. It means that the linear assemblies will have enough time to relax by the reptation before dissociation of the stickers occurs.

10.3.1 Construction of the matrix LI

For the chains without aggregates, the Flory distribution is used alone to provide the matrix LI , which is then composed of linear chains only. If aggregates are present, the different molecular weight distributions described in the preceding section are used to create LI , which will have the following shape:

$$LI = \begin{bmatrix} LI_{lin} \\ LI_{dang} \\ LI_{trap} \end{bmatrix} \quad (10.13)$$

- LI_{lin} contains the molecular weights of the linear chains (without aggregates) and their weight fraction as provided by $W_{lin}(M)$. They are able to relax by reptation, and thus their reptation time is given by the Equation 9.5 previously seen:

$$\tau_{rept} = 3\tau_e \left(\frac{M_i}{M_e} \right)^3 \quad (9.5)$$

- LI_{dang} represents the distribution of the star arms and the dangling ends. Indeed, the mechanism of relaxation is the contour length fluctuations for both of them. They cannot relax by reptation, thus their τ_{rept} is fixed to 10^{30} s, which is an arbitrary very high value. To apply the TMA model to these chains, their molecular weight is multiplied by 2. Indeed, in the code, $\varphi(t_k)$, the survival probability by CLF and reptation, is calculated for only one half of a chain, which is divided into 100 segments x . This is done because both halves of the chain relax in the same way, and the point in the middle of the chain is the one that needs the longest time before being reoriented. However, for the dangling ends and the arms of the stars, one extremity of the subchain is free and the other is fixed, so both halves do not relax similarly. To overcome this problem, the molecular weight of these chains are doubled, such as the fixed end of the chain becomes the middle of the chain, which will be the last segment to relax.

¹The association time τ_{ass} corresponds to τ_{break} , the survival time of a chain before breakage, in section 2.8. These two notations are equivalent.

- LI_{trap} is based on the molecular weight distribution of the trapped segments. As the linear assemblies are assumed to be stable, the stickers do not dissociate. Consequently, the trapped segments are never able to relax, neither by reptation nor by CLF. LI_{trap} is thus only made of one type of chain of molecular weight 10^{30} g/mol, in order to suppress the contour length fluctuations. The weight fraction of these chains is ν_{trap} , the total weight fraction of the trapped segments. As reptation is not allowed, τ_{rept} is also fixed to 10^{30} s for these chains.

10.3.2 Results

This TMA model was then used to simulate the experimental data presented in Part III. As the Time-Temperature Superposition does not work for the metallo-supramolecular polymers, the curves measured at different temperatures were modelled individually. The values of p_{ass} and p_{aggr} were manually modified to find the best possible fitting of the data.

Considering the experimental results found in Part III, it is expected that the parameters p_{ass} and p_{aggr} will increase when the temperature decreases, as the stickers and the aggregates are more and more stable at low temperatures. They are also supposed to increase with ion density. Moreover, it is expected that, for the same ion density, the association probabilities will be classified as such:

$$(p_{ass})_{Cu} > (p_{ass})_{blend} > (p_{ass})_{Zn} \quad (10.14)$$

Except at 2.5eq, where

$$(p_{ass})_{Zn} > (p_{ass})_{Cu} \quad (10.15)$$

PnBA-tpy₂ 0.25eq. Cu²⁺

The fitting of the PnBA-tpy₂ 0.25eq. Cu²⁺ is shown on Figures 10.4 to 10.9 for each temperature. This sample containing only few ions does not show a second plateau, so only the Flory distribution was used. The model fits correctly the experimental data, especially at high temperatures. Hence, the relation $\tau_{ass} > \tau_{rept}$ must be true for this sample.

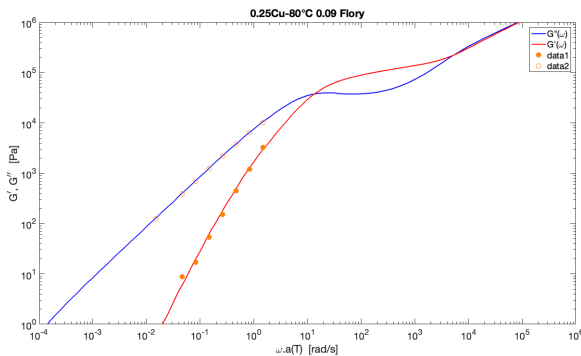


Figure 10.4: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 0.25eq. Cu²⁺ at 80°C with the TMA model considering stable linear assemblies and $p_{ass} = 0.09$.

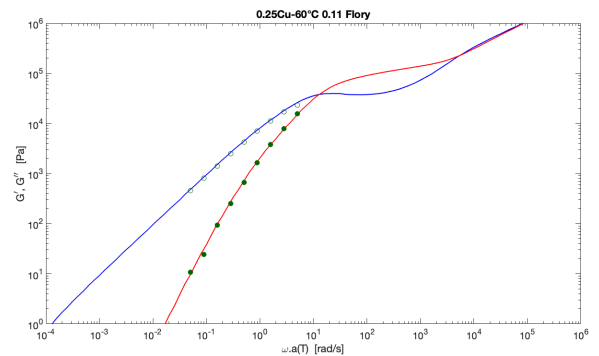


Figure 10.5: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 0.25eq. Cu²⁺ at 60°C with the TMA model considering stable linear assemblies and $p_{ass} = 0.11$.

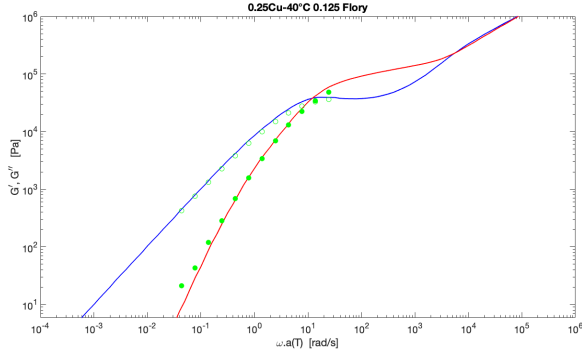


Figure 10.6: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 0.25eq. Cu²⁺ at 40°C with the TMA model considering stable linear assemblies and $p_{ass} = 0.125$.

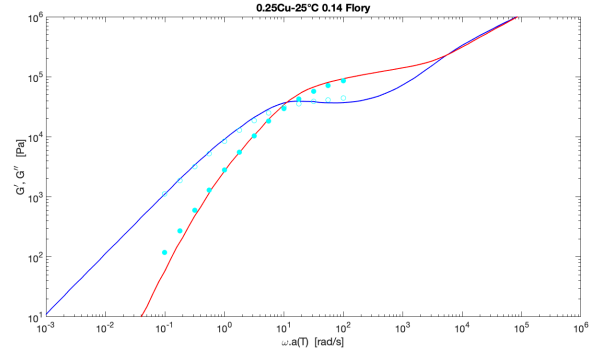


Figure 10.7: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 0.25eq. Cu²⁺ at 25°C with the TMA model considering stable linear assemblies and $p_{ass} = 0.14$.

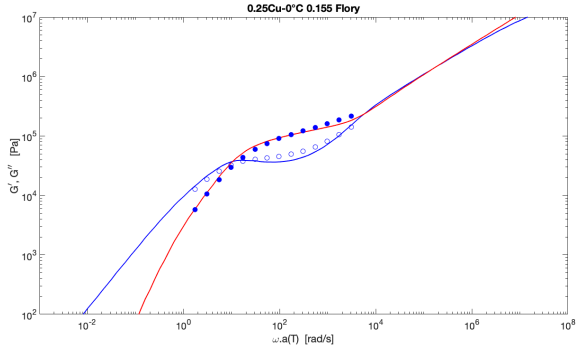


Figure 10.8: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 0.25eq. Cu²⁺ at 0°C with the TMA model considering stable linear assemblies and $p_{ass} = 0.155$.

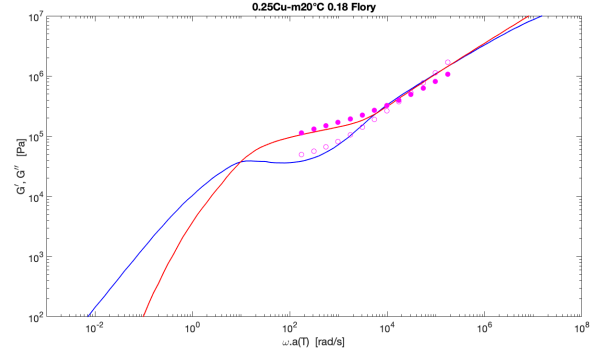


Figure 10.9: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 0.25eq. Cu²⁺ at -20°C with the TMA model considering stable linear assemblies and $p_{ass} = 0.18$.

Nonetheless, the model deviates slightly from the experimental data at 40°C and 25°C (Figures 10.6 and 10.7), where the relaxation of the model is too sharp compared to the data. This shows that the hypothesis that the dispersity can be ignored might not be valid here. Indeed, the probability of association p_{ass} is always low for this sample (between 0.09 and 0.18), hence the proportion of single building blocks is quite high, as can be seen on Figure 10.10. And the dispersity cannot be neglected for these single chains, because they do not have the same molecular weight. If that was taken into account, the relaxation of the model would happen more gradually as the chains of different lengths do not relax at the same time.

Finally, the probabilities of association are listed in the Table 10.1, and plotted as a function of the temperature on Figure 10.11. This graph shows that $\log(p_{ass})$ follows approximately a linear relationship with respect to the temperature.

	80°C	60°C	40°C	25°C	0°C	−20°C
p_{ass}	0.09	0.11	0.125	0.14	0.155	0.18

Table 10.1: Association probabilities of PnBA-tpy₂ 0.25eq. Cu²⁺

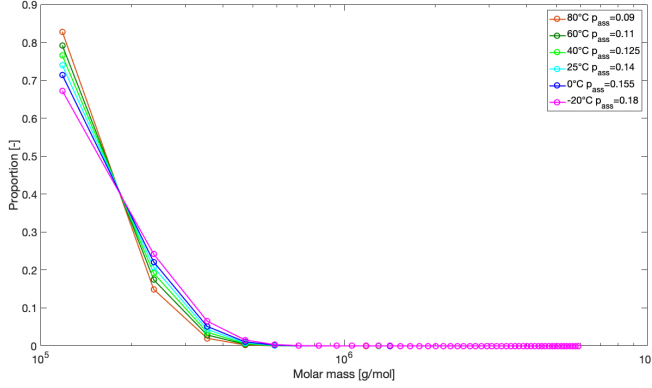


Figure 10.10: Molecular weight distributions as provided by the Flory distribution for the PnBA-tpy₂ 0.25eq. Cu²⁺ at each temperature.

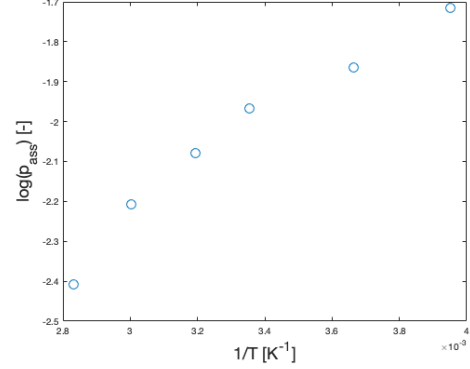


Figure 10.11: Association probability of PnBA-tpy₂ 0.25eq. Cu²⁺ versus the temperature.

PnBA-tpy₂ 0.5eq. Cu²⁺

The fittings for the PnBA-tpy₂ 0.5eq. Cu²⁺ are represented on Figures 10.12 to 10.15. At high temperatures, namely 80°C and 60°C, the modelling works with the Flory distribution alone. However, at 80°C, the relaxation depicted by the experimental data is a little too fast compared to the model. It could show that the hypothesis $\tau_{ass} > \tau_{rept}$ is not verified at this temperature. Indeed, if some stickers dissociate, the relaxation is accelerated.

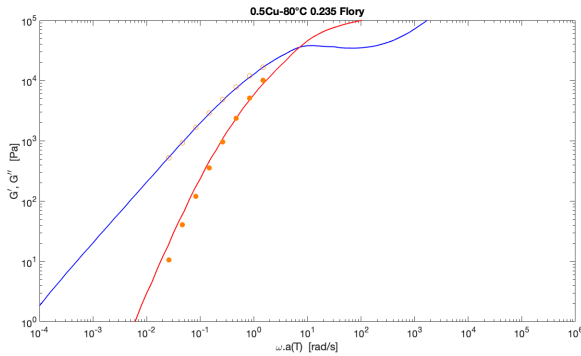


Figure 10.12: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 0.5eq. Cu²⁺ at 80°C with the TMA model considering stable linear assemblies and $p_{ass} = 0.235$.

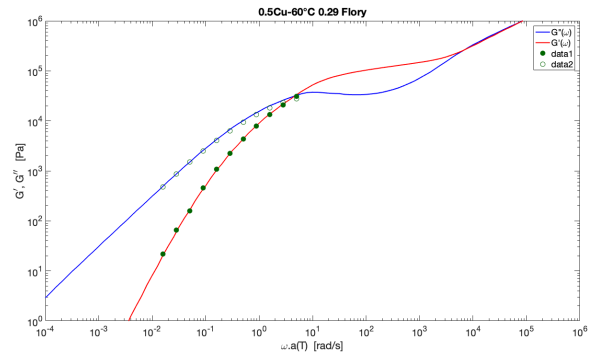


Figure 10.13: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 0.5eq. Cu²⁺ at 60°C with the TMA model considering stable linear assemblies and $p_{ass} = 0.29$.

At lower temperatures, 40°C and 25°C on Figures 10.14 and 10.15, the aggregates have to be taken into account to fit the data correctly, but even so, the result is not perfect. The fitting at 0°C is not shown, as this curve is similar to the one at 25°C. The second plateau is not strongly defined for the PnBA-tpy₂ 0.5eq. Cu²⁺, so the presence of aggregates is not obvious at first sight. However, the model confirms that they are already present at a

rather low ion content with Cu(II) as metal ion.

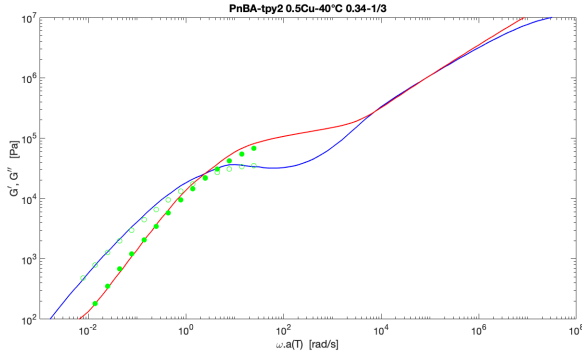


Figure 10.14: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 0.5eq. Cu²⁺ at 40°C with the TMA model considering stable linear assemblies, $p_{ass} = 0.34$ and $p_{aggr} = 1/3$.

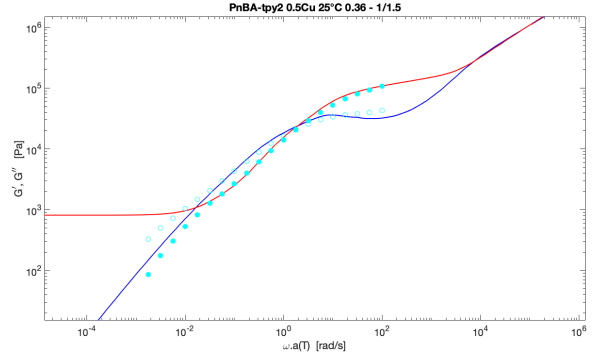


Figure 10.15: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 0.5eq. Cu²⁺ at 25°C with the TMA model considering stable linear assemblies, $p_{ass} = 0.36$ and $p_{aggr} = 1/1.5$.

The relaxation of the second plateau is also missing in the presence of aggregates. Hence, the hypothesis that the time of association of the aggregates is infinite is somewhat too strong. The values of p_{ass} and p_{aggr} are listed in the Table 10.2 for each temperature.

It can be concluded that this version of the model gives a fairly good idea about the sample behavior, but it still fails to fit the data very accurately, except at 60°C.

	80°C	60°C	40°C	25°C	0°C
p_{ass}	0.235	0.29	0.34	0.36	0.36
p_{aggr}	—	—	1/3	1/1.5	1/1.5

Table 10.2: Parameters of the TMA model for PnBA-tpy₂ 0.5eq. Cu²⁺

PnBA-tpy₂ 1eq. Cu²⁺

The conclusions drawn for the PnBA-tpy₂ 0.5eq. Cu²⁺ can also be applied and are amplified for the PnBA-tpy₂ 1eq. Cu²⁺. Therefore, the application of the TMA model on the experimental data is not reproduced here for all temperatures.

On Figures 10.16 and 10.17 representing the curves at 80°C and 60°C, the model is used without aggregates. It allows to fit the data at high frequency, but the terminal relaxation of the model is too slow compared to the experimental data. In fact, it is possible to fit the data at low frequency with a lower value of p_{ass} , but it is not possible to fit the data at high and low frequencies with the same p_{ass} . For instance, the last points at 80°C fall on the curves provided by the model with $p_{ass} = 0.37$, hence p_{ass} decreases with the frequency. It proves that the hypothesis $\tau_{ass} > \tau_{rept}$ is not valid, the chains also relax by dissociation of the stickers.

Then, at lower temperatures, from 40°C to 0°C, aggregates must be added to fit the data correctly in the intermediate regime of frequencies. The results at 25°C and 0°C

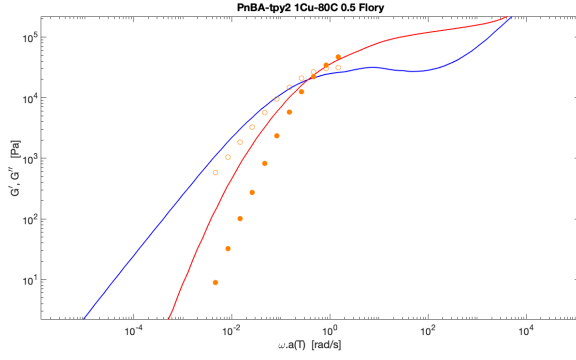


Figure 10.16: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 1eq. Cu²⁺ at 80°C with the TMA model considering stable linear assemblies and $p_{ass} = 0.5$.

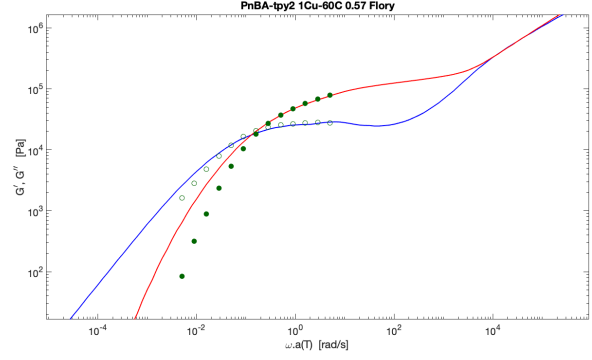


Figure 10.17: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 1eq. Cu²⁺ at 60°C with the TMA model considering stable linear assemblies and $p_{ass} = 0.57$.

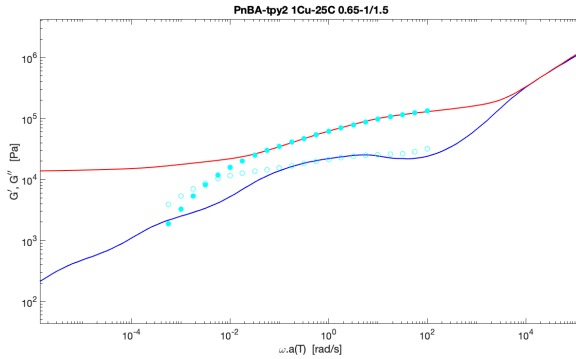


Figure 10.18: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 1eq. Cu²⁺ at 25°C with the TMA model considering stable linear assemblies, $p_{ass} = 0.65$ and $p_{aggr} = 1/1.4$.

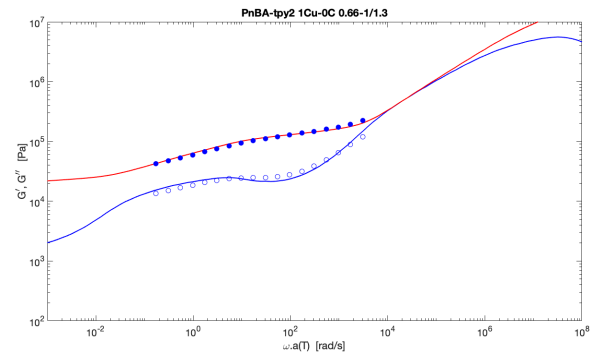


Figure 10.19: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 1eq. Cu²⁺ at 0°C with the TMA model considering stable linear assemblies, $p_{ass} = 0.66$ and $p_{aggr} = 1/1.3$.

are shown on Figures 10.18 and 10.19. At 25°C and 40°C, the model works well at high frequency, but the relaxation of the second plateau is missing. And at 0°C, the relaxation of the second plateau is not visible, hence the model is efficient at all frequencies.

The parameters of the model are summarised for all temperatures in the Table 10.3.

	80°C	60°C	40°C	25°C	0°C
p_{ass}	0.5-0.37	0.57-0.48	0.62	0.65	0.66
p_{aggr}	—	—	1/2.3	1/1.5	1/1.3

Table 10.3: Parameters of the TMA model for PnBA-tpy₂ 1eq. Cu²⁺

PnBA-tpy₂ 2.5eq. Cu²⁺

For the PnBA-tpy₂ 2.5eq. Cu²⁺, aggregates are present at all temperatures. The corresponding curves are not all represented here, but their parameters p_{ass} and p_{aggr} are listed

in the Table 10.4.

At high temperature, that is 100°C and 80°C (see Figure 10.20), the fitting of the data is not perfect at high frequency, the probability of association is under-estimated. It indicates again that the chains dissociate more quickly than assumed, thus helping the relaxation. This effect is no longer visible at higher temperatures. This might be due to the aggregates that block the relaxation processes.

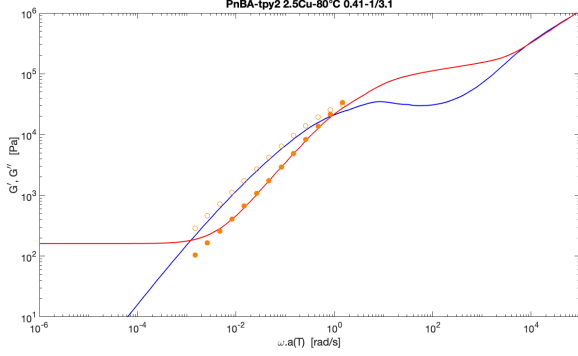


Figure 10.20: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 2.5eq. Cu²⁺ at 80°C with the TMA model considering stable linear assemblies, $p_{ass} = 0.41$ and $p_{aggr} = 1/3.1$.

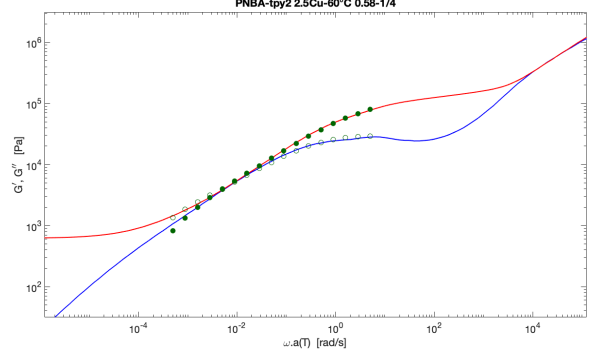


Figure 10.21: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 2.5eq. Cu²⁺ at 60°C with the TMA model considering stable linear assemblies, $p_{ass} = 0.58$ and $p_{aggr} = 1/4$.

It can be noted that at 60°C, whose curve is shown on Figure 10.21, p_{aggr} suddenly increase before decreasing again for lower temperature. However, it is expected that both p_{ass} and p_{aggr} increase with decreasing temperature. Nevertheless, since this version of the model, where the linear assemblies are assumed to be stable, is not exactly successful at fitting the experimental data, this surprising result must certainly be due to the flaws in the model, and should therefore be considered with caution.

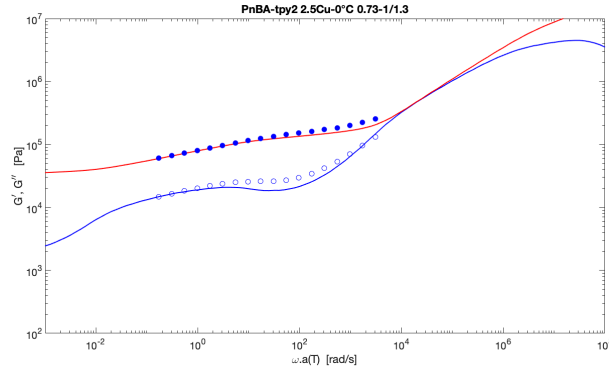


Figure 10.22: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 2.5eq. Cu²⁺ at 0°C with the TMA model considering stable linear assemblies, $p_{ass} = 0.73$ and $p_{aggr} = 1/1.3$.

Finally, at all temperatures except 0°C, whose data are represented on Figure 10.22, the relaxation of the second plateau is missing, which confirms that the lifetime of the aggregates should not be considered as infinite.

	100°C	80°C	60°C	40°C	25°C	0°C
p_{ass}	0.31	0.41	0.58	0.66	0.69	0.73
p_{aggr}	1/3.7	1/3.1	1/4	1/2	1/1.5	1/1.3

Table 10.4: Parameters of the TMA model for PnBA-tpy₂ 2.5eq. Cu²⁺

PnBA-tpy₂ 0.5eq. Zn²⁺

The sample PnBA-tpy₂ 0.5eq. Zn²⁺ was modelled without aggregates, only using the Flory distribution. This is already different from the sample with the same content of copper ions, the later already containing aggregates at low temperatures, while it isn't the case here with zinc ions.

For this sample, at all temperatures except 0°C, the model fails to correctly describe the data over the entire frequency range with the same value of p_{ass} . Hence, the hypothesis $\tau_{ass} > \tau_{rept}$ is not verified. This is illustrated at 40°C on Figure 10.23.

And for the experimental data measured at 0°C, the simulation works fine at all frequencies, as shown on Figure 10.24. The value of the probability of association is given for all temperatures in the Table 10.5.

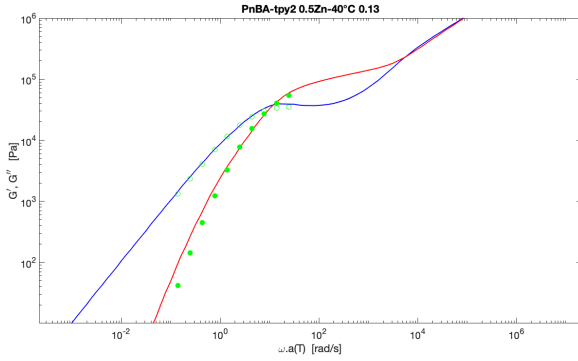


Figure 10.23: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 0.5eq. Zn²⁺ at 40°C with the TMA model considering stable linear assemblies and $p_{ass} = 0.13$.

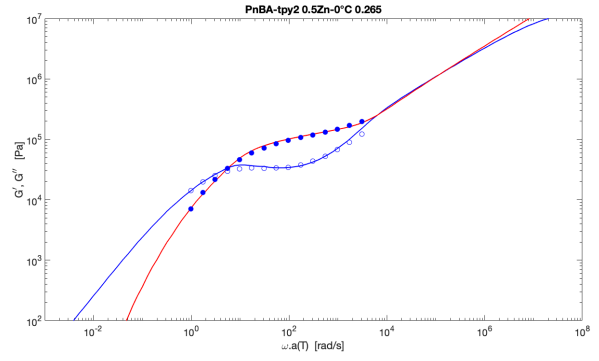


Figure 10.24: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 0.5eq. Zn²⁺ at 0°C with the TMA model considering stable linear assemblies and $p_{ass} = 0.265$.

	60°C	40°C	25°C	0°C
p_{ass}	0.09	0.13	0.2	0.265

Table 10.5: Association probabilities of PnBA-tpy₂ 0.5eq. Zn²⁺

PnBA-tpy₂ 1eq. Zn²⁺

The results for the PnBA-tpy₂ 1eq. Zn²⁺ are the same than for the PnBA-tpy₂ 0.5eq. Zn²⁺. On one hand, there are no aggregates in this sample, while they are present with 1eq of copper ions. And on the other hand, the relaxation of the chains by dissociation of the stickers should be taken into account, the linear assemblies should not be considered as

stable. Consequently, this version of the model is not working for this sample. Examples are given at 60°C and 25°C for this sample on Figures 10.25 and 10.26.

However, in contrast to the PnBA-tpy₂ 0.5eq. Zn²⁺, the dissociation of the chains is missing at all temperatures, even at low temperature, hence the model never works properly. The parameters used to fit the data at high frequency are listed in the Table 10.6.

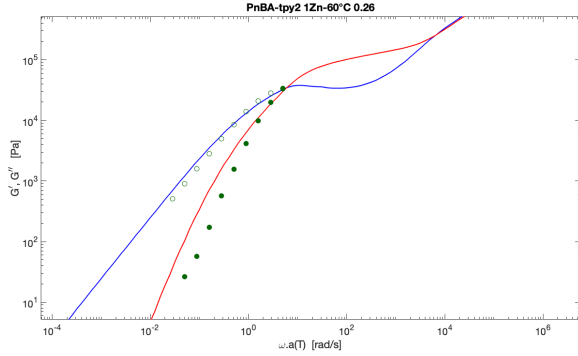


Figure 10.25: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 1eq. Zn²⁺ at 60°C with the TMA model considering stable linear assemblies and $p_{ass} = 0.26$.

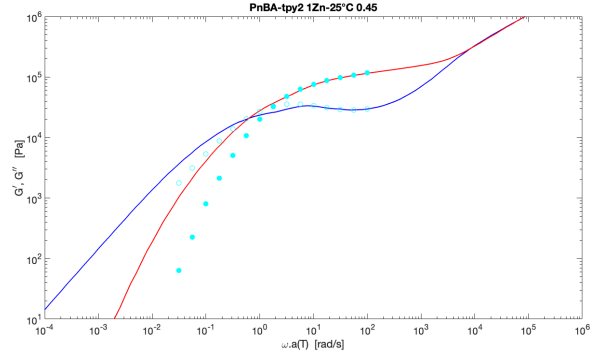


Figure 10.26: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 1eq. Zn²⁺ at 25°C with the TMA model considering stable linear assemblies and $p_{ass} = 0.45$.

	80°C	60°C	40°C	25°C	0°C
p_{ass}	0.155	0.26	0.35	0.45	0.57

Table 10.6: Association probabilities of PnBA-tpy₂ 1eq. Zn²⁺

PnBA-tpy₂ 2.5eq. Zn²⁺

With 2.5 equivalents of zinc ions, only the highest temperature, that is 100°C which is represented on Figure 10.27, does not contain aggregates, it can be modelled with the Flory distribution alone. However, the fitting is not very good, the value of p_{ass} needed to model the data decreases with the frequency. Hence, the hypothesis $\tau_{ass} > \tau_{rept}$ is again not valid here.

	100°C	80°C	60°C	40°C	25°C	0°C
p_{ass}	0.61	0.66	0.7	0.72	0.73	0.73
p_{aggr}	—	1/3	1/1.5	1/1.3	1/1.2	1/1.1

Table 10.7: Parameters of the TMA model for PnBA-tpy₂ 2.5eq. Zn²⁺

For all the other, lower temperatures, aggregates are needed to fit the data correctly. The relaxation of the second plateau is missing between 80°C and 40°C, as shown on Figures 10.28 and 10.29. And at the two lowest temperatures, 25°C and 0°C (see Figure 10.30), the relaxation of the second plateau is not visible, the model works for all frequencies.

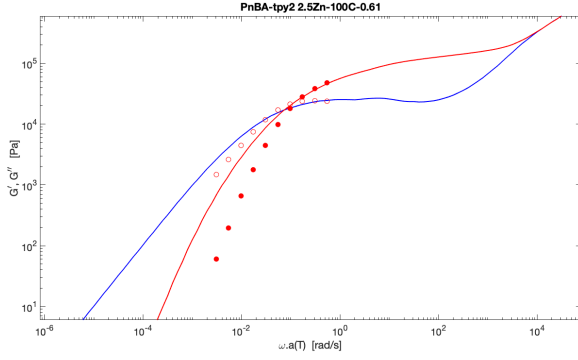


Figure 10.27: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 2.5eq. Zn²⁺ at 100°C with the TMA model considering stable linear assemblies and $p_{ass} = 0.61$.

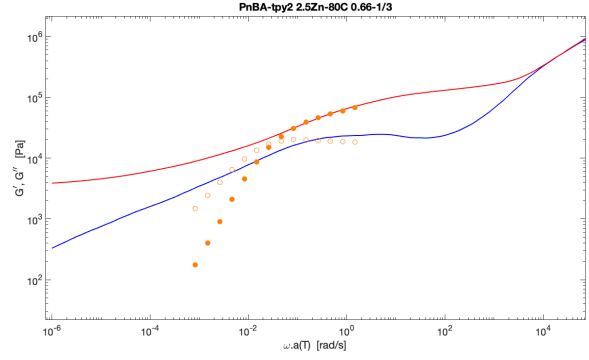


Figure 10.28: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 2.5eq. Zn²⁺ at 80°C with the TMA model considering stable linear assemblies, $p_{ass} = 0.66$ and $p_{aggr} = 1/3$.

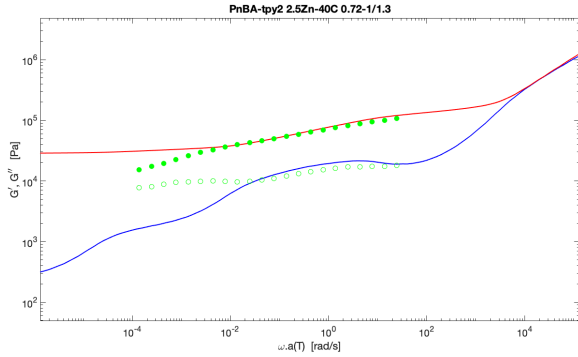


Figure 10.29: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 2.5eq. Zn²⁺ at 40°C with the TMA model considering stable linear assemblies, $p_{ass} = 0.72$ and $p_{aggr} = 1/1.3$.

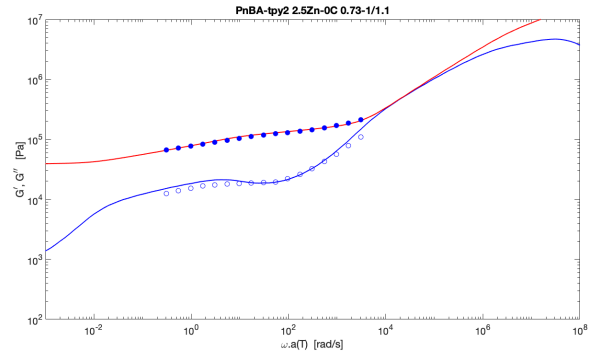


Figure 10.30: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 2.5eq. Zn²⁺ at 0°C with the TMA model considering stable linear assemblies, $p_{ass} = 0.73$ and $p_{aggr} = 1/1.1$.

Finally, all the parameters of the model are listed in the Table 10.7. Comparing them with those of the PnBA-tpy₂ 2.5eq. Cu²⁺ in Table 10.4, it appears that they are all larger with zinc than with copper, as it was expected.

PnBA-tpy₂ 0.5eq. blend

It was already stated in the experimental results that the moduli of the PnBA-tpy₂ 0.5eq. blend are too low, compared to the expected value of the rubbery plateau. This is confirmed by the simulation: it is not possible to fit the data at any temperature with the model, the values of $G'(\omega)$ and $G''(\omega)$ are always overestimated. There is no reason that could explain these lower experimental data for this sample, other than an error when performing the measurements.

Nevertheless, the shape of the curves still seems to be correct, this is just the absolute values of the curves that are not consistent. Hence, to be able to extract some information, the curves of $G'(\omega)$ and $G''(\omega)$ provided by the model were shifted downwards by a factor of 1.5 in order to fit the data. Figure 10.31 shows the result of the simulation at 0°C without moving the curves, and Figure 10.32 shows the same data,

but with the curves of the model shifted. The result obtained is pretty satisfying, the model works quite well. It is also the case at 25°C, even if this curve is not represented here.

It can also be noted that this sample does not seem to contain aggregates even at low temperatures, as it is the case with copper. It is not surprising since the behaviour of this MSP is expected to be an intermediate between the pure copper and the pure zinc samples, and pure zinc does not exhibit aggregates below 2.5 equivalents.

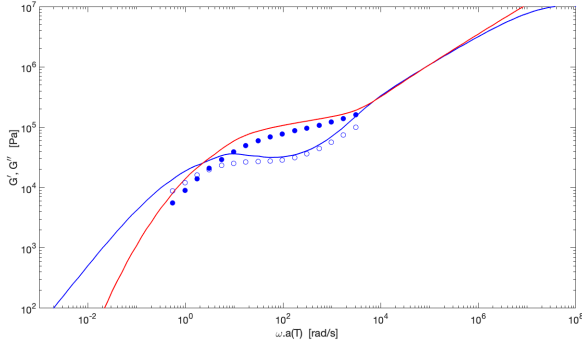


Figure 10.31: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 0.5eq. blend at 0°C with the TMA model considering stable linear assemblies and $p_{ass} = 0.345$.

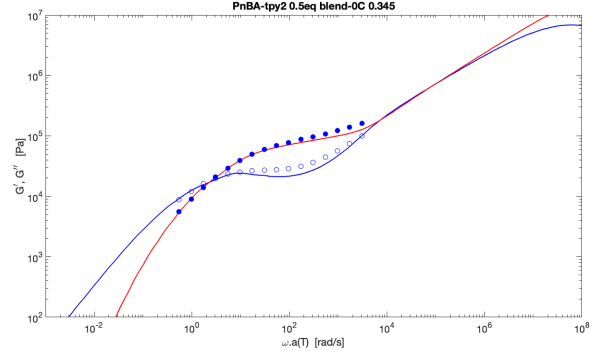


Figure 10.32: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 0.5eq. blend at 0°C with the TMA model considering stable linear assemblies and $p_{ass} = 0.345$. G' and G'' are shifted downwards by a factor 1.5.

However, at all the other higher temperatures, the model is unable to fit the data at both high and low frequencies with a fixed p_{ass} , the later decreases towards lower frequencies. Again, that indicates that the chains also relax by dissociation of the stickers. It is depicted on Figure 10.33 for the curve at 60°C.

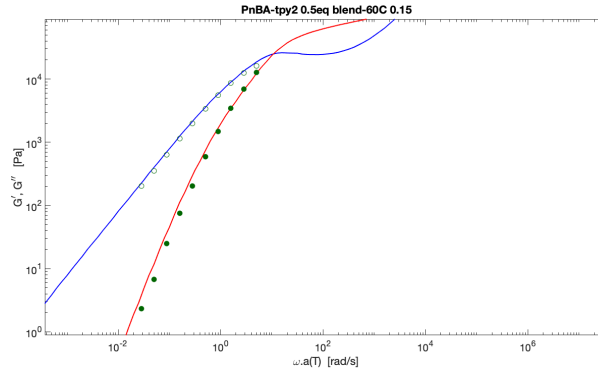


Figure 10.33: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 0.5eq. blend at 60°C with the TMA model considering stable linear assemblies and $p_{ass} = 0.15$. G' and G'' are shifted downwards by a factor 1.5.

The probabilities of association are summarised in the Table 10.8. These values are indeed in between the ones of PnBA-tpy₂ 0.5eq. Cu²⁺ and PnBA-tpy₂ 0.5eq. Zn²⁺, and they increase with decreasing temperature.

	80°C	60°C	40°C	25°C	0°C
p_{ass}	0.1	0.15	0.23	0.29	0.345

Table 10.8: Association probabilities of PnBA-tpy₂ 0.5eq. blend

PnBA-tpy₂ 1eq. blend

Concerning the PnBA-tpy₂ 1eq. blend, the data at high temperature, from 80°C (see Figure 10.34) to 40°C do not contain aggregates. But they present the same problem as the other samples: the hypothesis $\tau_{ass} > \tau_{rept}$ is not verified.

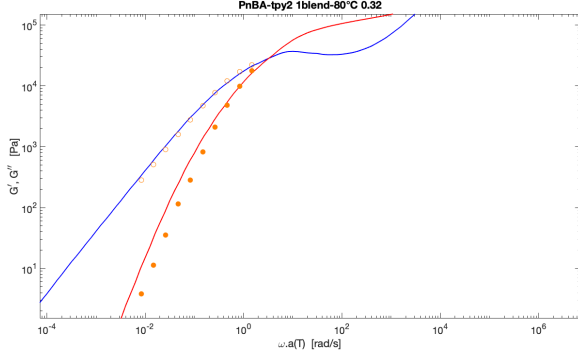


Figure 10.34: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 1eq. blend at 80°C with the TMA model considering stable linear assemblies and $p_{ass} = 0.32$.

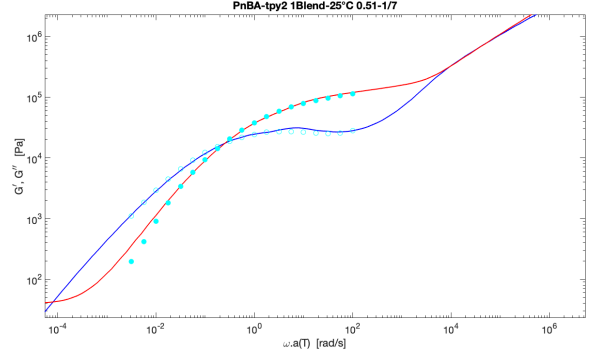


Figure 10.35: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 1eq. blend at 25°C with the TMA model considering stable linear assemblies, $p_{ass} = 0.51$ and $p_{aggr} = 1/7$.

Then, at 25°C and 0°C, a better fitting of the data is obtained when considering the presence of few aggregates. These two temperatures are represented on Figures 10.35 and 10.36 respectively. At 25°C, the relaxation of the second plateau is missing. When looking at the experimental data, the presence of aggregates is not obvious, as the second plateau is not much marked. Nonetheless, it is not surprising to find aggregates in this sample, as there are already some in the PnBA-tpy₂ 1eq. Cu²⁺, and the behaviour of the blend should be in between this sample and PnBA-tpy₂ 1eq. Zn²⁺.

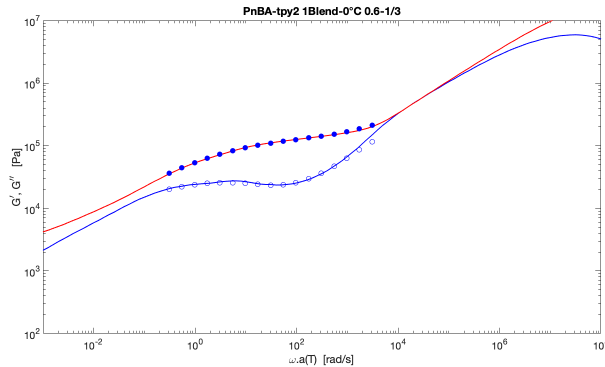


Figure 10.36: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 1eq. blend at 0°C with the TMA model considering stable linear assemblies and, $p_{ass} = 0.6$ and $p_{aggr} = 1/3$.

The values of p_{ass} and p_{aggr} are contained in the Table 10.9. The probabilities of association for this blend are again higher than the ones for the pure zinc sample, and lower than

the ones for the pure copper sample. The probabilities of forming an aggregate are also smaller than for the PnBA-tpy₂ 1eq. Cu²⁺.

	80°C	60°C	40°C	25°C	0°C
p_{ass}	0.32	0.395	0.445	0.51	0.6
p_{aggr}	—	—	—	1/7	1/3

Table 10.9: Parameters of the TMA model for PnBA-tpy₂ 1eq. blend

10.3.3 Conclusion

The results obtained with the first version of the TMA model are not fully convincing. The model presents several shortcomings, which makes it unfit to produce sufficiently accurate simulations of the experimental data. Therefore, the values of the probabilities p_{ass} and p_{aggr} should be considered with caution. No conclusion can be drawn from their absolute values. Nonetheless, their variations, with respect to the temperature and the ion content for instance, can still provide some information. Figures 10.37 and 10.38 show how p_{ass} and p_{aggr} vary with temperature for all the MSPs.

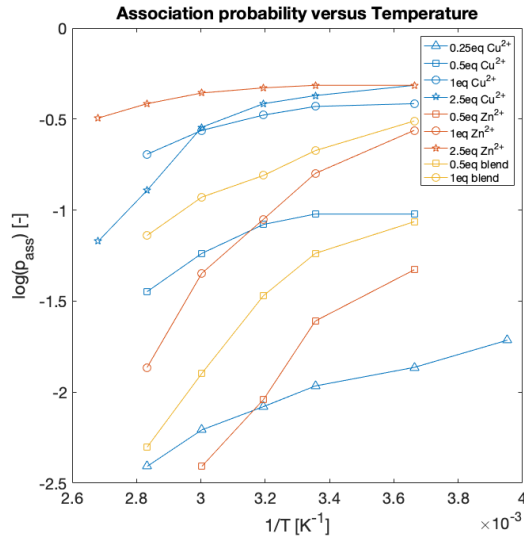


Figure 10.37: Natural logarithm of the probability of association plotted against the temperature for all the MSPs based on the linear PnBA-tpy₂. When the sample contains Cu(II) ions, the colour blue is used. Red is used for the Zn(II) ions and yellow is used for the blend 50%Cu(II)/50%Zn(II). The different symbols correspond to the different ion densities.

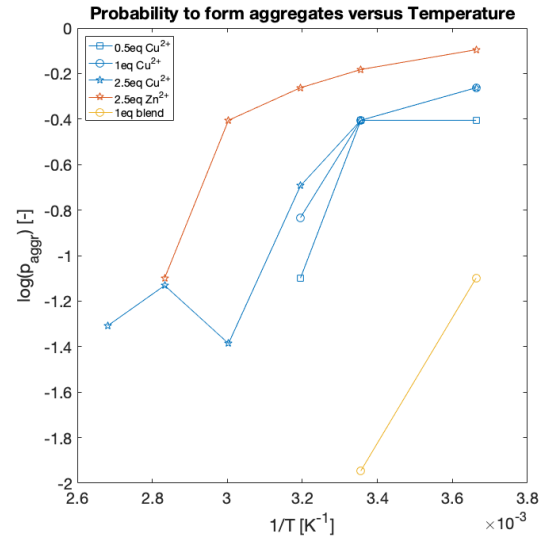


Figure 10.38: Natural logarithm of the probability to form aggregates plotted against the temperature for all the MSPs based on the linear PnBA-tpy₂. When the sample contains Cu(II) ions, the colour blue is used. Red is used for the Zn(II) ions and yellow is used for the blend 50%Cu(II)/50%Zn(II). The different symbols correspond to the different ion densities.

Variation of p_{ass} and p_{aggr} with the ion density: The analysis of the experimental data in Part III showed that with more ions, more complexes and aggregates are formed,

the relaxation is thus delayed. This should translate here into an increase of p_{ass} and p_{aggr} with the ion density. It is indeed true for p_{ass} with all types of ions, it can be seen on Figure 10.37. The only exception concerns the samples with copper: at high temperature, the probability of association of the sample with 2.5 ions equivalents is below the one with 1 equivalent, but it then exceeds it when the temperature decreases. And for p_{aggr} , there are some exceptions at 25°C and 0°C with different quantities of copper ions, where p_{aggr} keeps the same value (see Figure 10.38). However, the probability of having an aggregate is computed as the fraction of complexes that participate in an aggregate. Hence, since p_{ass} increases between 1eq and 2.5eq Cu^{2+} , more complexes are formed, which means that if p_{aggr} remains constant, the total number of aggregates still increases.

Variation of p_{ass} with the ion nature: It was found previously that the zinc ions were more labile than the copper ions, leading to less stable associated stickers. And as the blend is composed of 50% of copper ions and 50% of zinc ions, it lies in between them. This is valid for all temperatures and ion density, except at 2.5 equivalents, for which the assemblies created with zinc become more stable than those containing zinc. As shown by Figure 10.37, it is verified with the model that at 0.5eq and 1eq

$$(p_{ass})_{Cu} > (p_{ass})_{blend} > (p_{ass})_{Zn} \quad (10.16)$$

And at 2.5eq

$$(p_{ass})_{Zn} > (p_{ass})_{Cu} \quad (10.17)$$

Variation of p_{aggr} with the ion nature: It was expected that aggregates are more easily created with copper than with zinc. And the model shows indeed that they are present as from 0.5eq with copper, whereas they appear only at 2.5eq of zinc. The use of the model is very interesting here, because the second plateau due to the aggregates is not always very pronounced, it can therefore be difficult to detect the presence of aggregates with certainty at first sight. And again, the behaviour of the blend is in between the pure copper and the pure zinc samples, with aggregates appearing for 1 equivalent (see Figure 10.38).

Variation of p_{ass} and p_{aggr} with the temperature: The experimental results indicated that the stability of both the complexes and the aggregates decreases when the temperature is increased. This should lead to values of p_{ass} and p_{aggr} that decrease when the temperature rises. This trend is indeed confirmed for all samples, and it can be observed in Figures 10.37 and 10.38. There is only one exception for the PnBA-tpy₂ 2.5eq. Cu^{2+} , where p_{aggr} is smaller at 60°C than at 40°C. However, this unique anomaly is most likely due to the flaws in the model.

Finally, it is important to address the shortcomings of the model, because, on the one hand, it also provides information about the behaviour of the metallo-supramolecular polymers, and on the other hand, it will allow to correct the model effectively. The two major flaws of the model are the following:

1. In the presence of aggregates, the relaxation of the second plateau is not taken into account by the model. This is not a problem at the lowest temperatures where

this relaxation is not visible, but it is missing in all other cases. It means that the hypothesis that the aggregates have an infinite lifetime is most often too strong. Their lifetime is indeed larger than the one of the complexes, and it increases when the temperature drops, but it is not infinite.

2. When using the model without aggregates, a problem occurs for almost all samples, at least at the highest temperatures: the curves cannot be fitted at all frequencies with the same p_{ass} . It appears in fact that the value of p_{ass} needed to fit the data decreases with the frequency. This invalidates the assumption that $\tau_{ass} > \tau_{rept}$, hence that the chains are stable. In reality, the assemblies relax not only by CLF and reptation, but also by breakage of the complexes. This failure of the model is particularly important for the samples containing zinc. This makes sense because these ions are more labile, so the stickers are more likely to dissociate than with copper. It is also visible more often at high temperatures, that is when the stickers are less stable.

10.4 Second version of the model: the associated chains can break before being relaxed

The TMA model was then modified to overcome the shortcomings of the first version. The major difference between the two versions is that the association time τ_{ass} is not anymore considered to be always larger than the reptation time τ_{rept} in this second version. All the changes that have been made to the TMA model are based on the Cates' model, which is described in section 2.8.

10.4.1 Modification of the model

In this second version of the TMA model, the hypothesis is made that the linear assemblies are able to relax by dissociation of the complexes, which corresponds to the case where $\tau_{ass} \leq \tau_{rept}$ in the Cates' model. The computation of the Flory distribution remains unchanged in this model, as well as the calculation of the molecular weight distributions of the different kinds of segments that compose the MSPs in the presence of aggregates. It is mainly the construction of the matrix LI and the relaxation times that are modified.

Without aggregates, the matrix LI describing the different chains present in the sample is provided by the Flory distribution. As these chains are not stable, it is assumed that they can relax by reptation after breakage of the associated stickers. Since there are only linear chains without aggregates, their main relaxation process is supposed to always be the reptation, even after dissociation of the metal-ligand complexes. The reptation time τ_{rept} is replaced by an effective reptation time $\tau_{rept,eff}$ to account for the possible rupture of the chains, which occurs after a time τ_{ass} , which is the mean time during which two stickers stay associated.

$$\tau_{rept,eff} = \tau_{rept} \cdot \xi^{1/2} \text{ with } \xi = \frac{\tau_{ass}}{\tau_{rept}} \quad (10.18)$$

$$\Leftrightarrow \tau_{rept,eff} = \sqrt{\tau_{rept} \cdot \tau_{ass}} \quad (10.19)$$

The Equation 10.18 is equivalent to the Equation 2.58 in the Cates' model of section 2.8. There is however on difference with the Cates' model for the non-associated chains, that have a molecular weight $\overline{M}_w = M_0$. These chains do not contain associated stickers, hence they will not be affected by the association time of the complexes, they will always be able to relax through a normal reptation process. Therefore, their relaxation time is not affected by τ_{ass} :

$$\tau_{rept,eff}(M_0) = \tau_{rept}(M_0) \quad (10.20)$$

When aggregates are added in the model, the molecular weight distributions of the linear chains, dangling ends, star arms, strands and trapped segments are firstly computed as described in the section 10.2. Then, the matrix LI is constructed in the following way:

$$LI = \begin{bmatrix} LI_{lin} \\ LI_{dang} \\ LI_{trapdang} \\ LI_{trap} \end{bmatrix} \quad (10.21)$$

- LI_{lin} represents the molecular weight distribution of the linear assemblies that do not contain any aggregates. They relax by reptation, helped by the dissociation of the complexes, hence their reptation time is the effective reptation time from the Cates' model, as defined by the Equations 10.18 to 10.20.
- LI_{dang} contains the molecular weights and weight fractions of the dangling ends and the star arms. As already explained in the first version of the model, their molecular weights are multiplied by two in order to be able to use the same representation of the chain when computing their survival probabilities. As these segments are fixed on one hand, they cannot relax by reptation, and their reptation time is set at 10^{30} s, which is a very high value. Hence, these segments can only relax by CLF. The relaxation by dissociation of the stickers is not considered for these segments.
- $LI_{trapdang}$ refers to the segments trapped between two aggregates, but that can still relax by CLF after breakage of the complexes present between the aggregates. Hence, this kind of relaxation is only possible if there is at least one complex between two successive aggregates. This part of the matrix LI is based on the molecular weight distribution of the strands, and it includes all segments having a molecular weight greater than M_0 , so that at least one complex is present along these segments. The reptation is suppressed for these chains, so $\tau_{rept} = 10^{30}$ s. They relax by CLF after some delay brought by τ_{ass} . The relaxation time of these chains is given by the Equation 2.61 of the Cates' model, which is reproduced here:

$$\tau_{CLF_{cates}} \cong \tau_{rept} \cdot \xi^{3/4} \alpha^{-1/4} \text{ with } \alpha = \frac{M_e}{M_i} \quad (10.22)$$

$$\Leftrightarrow \tau_{CLF_{cates}} = (\tau_{ass})^{3/4} \cdot \left(\frac{\tau_{rept} \cdot M_i}{M_e} \right)^{1/4} \quad (10.23)$$

It must be noted that $\tau_{CLF_{cates}}$ is the relaxation time for the whole subchain of length M_i , it does not depend on the position of the segment x like τ_{fluc} . Hence, it cannot be used in the same equations as τ_{fluc} . However, the Cates' model also mentions that when the value of ξ decreases, the survival probability of a chain

fraction, $\Phi(t)$, tends more and more towards a pure exponential. For these trapped segments, we have

$$\xi = \frac{\tau_{ass}}{\tau_{rept}} = \frac{\tau_{ass}}{10^{30}} \ll 1 \quad (10.24)$$

As ξ is indeed very small, the probability of survival by reptation and CLF for each chain, noted $\varphi_i(t)$ in the equations of the TMA model and which is normally defined by the Equation 9.14, is replaced by the Equation 10.25:

$$\varphi_i(t) = \sum_{x=0.01}^1 p_{rept}(x, t) p_{fluc}(x, t) \Delta x \quad (9.14)$$

$$\varphi_i(t) = \exp\left(\frac{-t}{\tau_{CLF_{cates}}}\right) \quad (10.25)$$

- LI_{trap} represents the trapped segments composed of one building block only. As there is no stickers between the two successive aggregates, these segments cannot relax by reptation nor by CLF. Their reptation time is thus fixed to 10^{30} s, and their molecular weight is set to 10^{30} g/mol to suppress the contour length fluctuations. These are the segments that will truly participate in the formation of the second plateau.

It must be noted that the lifetime of the aggregates is still assumed to be infinite, they cannot be broken.

10.4.2 Results

For this second version of the model, a third parameter is added to p_{ass} and p_{aggr} : the association time τ_{ass} . The objective is again to find the values of these parameters that provide the best modelling of the experimental data.

In order to reduce the uncertainty over these parameters, it was assumed that the association time follows an Arrhenius law with respect to the temperature, with E_a the energy of activation:

$$\tau_{ass} = \tau_{ass,0} \exp\left(\frac{-E_a}{RT}\right) \quad (10.26)$$

Moreover, the parameter p_{ass} , which was defined so far as a probability of association, can also be described in another way. This value quantify the equilibrium between the mean time during which a sticker remains associated, τ_{ass} , and the mean time during which it is dissociated. The later is noted τ_{free} . According to this definition, p_{ass} is given by the following equation:

$$p_{ass} = \frac{\tau_{ass}}{\tau_{ass} + \tau_{free}} \quad (10.27)$$

In the same way as τ_{ass} , the mean time that a sticker stays free, τ_{free} is expected to follow an Arrhenius law, with $E_{a,f}$ the activation energy:

$$\tau_{free} = \tau_{free,0} \exp\left(\frac{-E_{a,f}}{RT}\right) \quad (10.28)$$

Consequently, as both τ_{ass} and τ_{free} follow an Arrhenius law, it is expected that $\log(p_{ass})$ will also follow a linear relationship with respect to the temperature.

The values of the three modelling parameters p_{ass} , p_{aggr} and τ_{ass} are given below for each samples, as well as the corresponding curves.

PnBA-tpy₂ 0.25eq. Cu²⁺

The application of the second version of the TMA model did not provide better results than with the previous version. For this reason, the curves for each temperature are not reproduced here, as there is little to no difference with the ones shown in section 10.3. The aggregates have again not been used for this sample. The parameters p_{ass} and τ_{ass} are contained in the Table 10.10 and they are plotted against $1/T$ in Figures 10.40 and 10.39. It can be seen on these graphs that they both follow a linear relationship with respect to the temperature. The energy of activation for τ_{ass} is equal to 54.3kJ/mol.

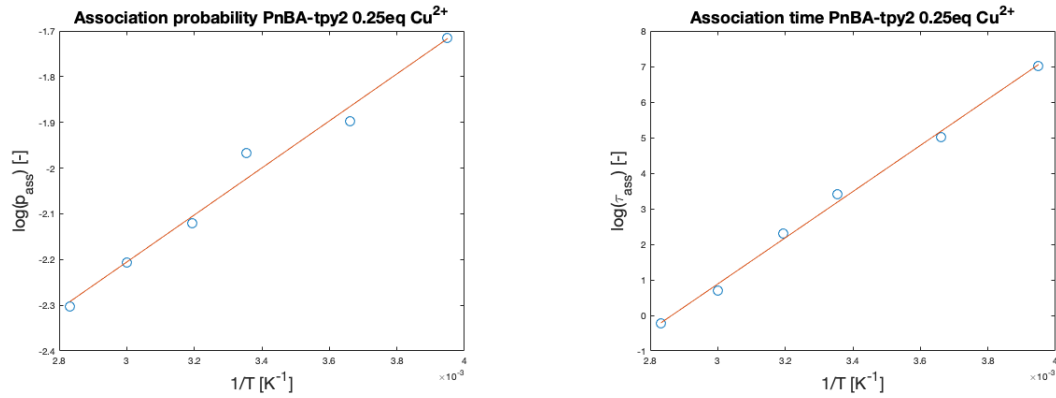


Figure 10.39: Association probability of Figure 10.40: Association time of PnBA-PnBA-tpy₂ 0.25eq. Cu²⁺ versus the temperature. The values of the parameter used in the model are represented by the blue circles, and the linear fitting of these points is represented in yellow. The activation energy corresponding is 54.3kJ/mol.

	80°C	60°C	40°C	25°C	0°C	−20°C
p_{ass}	0.1	0.11	0.12	0.14	0.15	0.18
τ_{ass}	0.7	2	10	30	150	1100

Table 10.10: Parameters of the TMA model for PnBA-tpy₂ 0.25eq. Cu²⁺

The values of p_{ass} change only slightly or not at all compared to those of the Table 10.1 in the previous model. The fact that the results are very similar for the two models is linked to the amount of non-associated chains that is always important for this sample. As there are only few active stickers, incorporating their disassociation into the code has only a minor effect. Consequently, the observations made in the previous section remain valid here.

PnBA-tpy₂ 0.5eq. Cu²⁺

The Table 10.11 summarises the values of the three parameters for the PnBA-tpy₂ 0.5eq. Cu²⁺ at each temperature. The use of the Cates' model did not produce a better description of the results, except at 80°C (see Figure 10.41). For this high temperature, dissociation of the complexes is required to account for the acceleration of the relaxation in the terminal region.

	80°C	60°C	40°C	25°C	0°C
p_{ass}	0.25	0.3	0.33	0.35	0.35
p_{aggr}	—	—	1/2	1/1.3	1/1.2
τ_{ass}	1	6	50	200	3000

Table 10.11: Parameters of the TMA model for PnBA-tpy₂ 0.5eq. Cu²⁺

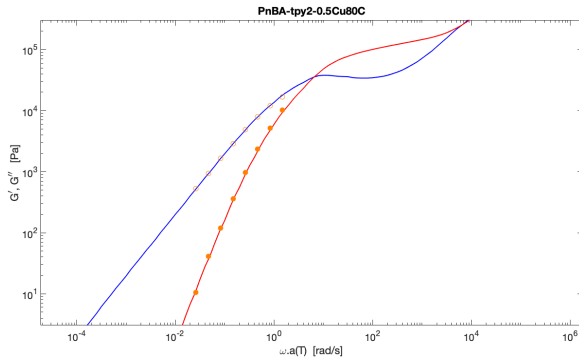


Figure 10.41: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 0.5eq. Cu²⁺ at 80°C with the TMA model based on the Cates' model, with $p_{ass} = 0.25$ and $\tau_{ass} = 1$ s.

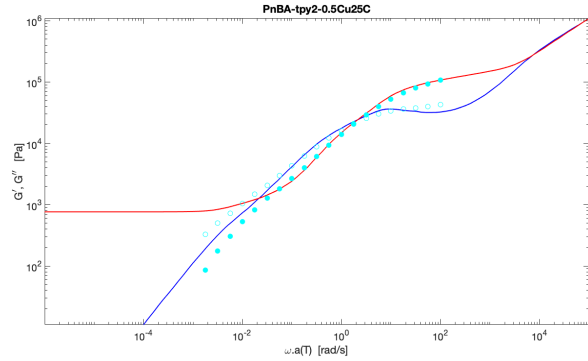


Figure 10.42: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 0.5eq. Cu²⁺ at 25°C with the TMA model based on the Cates' model, with $p_{ass} = 0.35$, $p_{aggr} = 1/1.3$ and $\tau_{ass} = 200$ s.

For all the other temperatures, this second model is no better than the previous one. At 60°C, a good fitting is again obtained at all frequencies. And below 60°C, aggregates have to be added in the code, but it does not seem to improve the fitting. The relaxation of the second plateau through breakage of the aggregates should provide a better modelling, but it was not taken into account in the TMA model. For instance, the curve at 25°C is shown on Figure 10.42. It is nearly the same as the one in section 10.3 (Figure 10.15).

The values p_{ass} and τ_{ass} are also shown as a function of the temperature on the Figures 10.43 and 10.44. The association time follows an Arrhenius relationship, and its energy of activation amounts to 80kJ/mol. The probability of association does not follow a linear relationship as for PnBA-tpy₂ 0.25eq. Cu²⁺, the slope seems to decrease as the temperature drops.

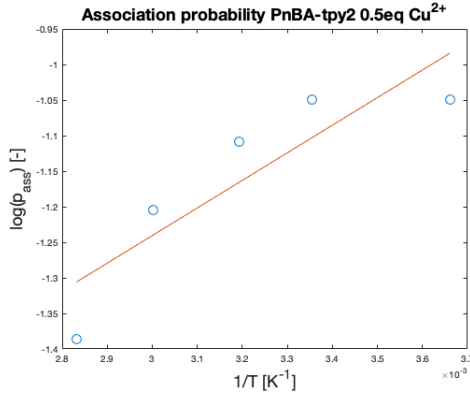


Figure 10.43: Association probability of PnBA-tpy₂ 0.5eq. Cu²⁺ versus the temperature. The values of the parameter used in the model are represented by the blue circles, and the linear fitting of these points is represented in yellow.

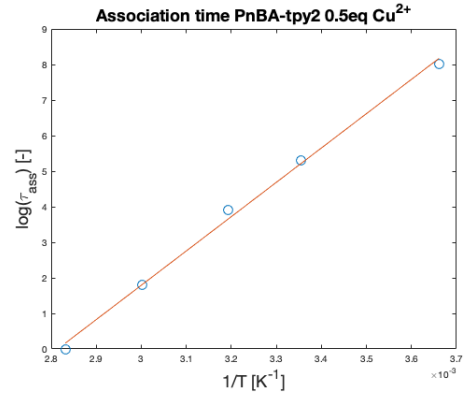


Figure 10.44: Association time of PnBA-tpy₂ 0.5eq. Cu²⁺ versus the temperature. The values of the parameter used in the model are represented by the blue circles, and the linear fitting of these points is represented in yellow. The activation energy corresponding is 80kJ/mol.

PnBA-tpy₂ 1eq. Cu²⁺

The PnBA-tpy₂ 1eq. Cu²⁺ is the first sample containing copper ions for which a real improvement is observed for all temperatures with the Cates' model. At the two highest temperatures, 80°C and 60°C on Figures 10.45 and 10.46, the relaxation is modelled correctly at all frequencies with the same probability of association, which wasn't the case previously. This is now possible by considering the breakage of the stickers.

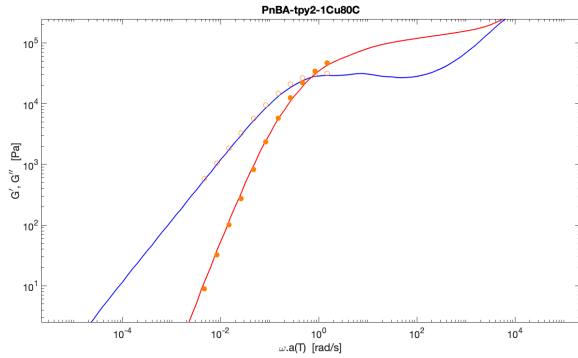


Figure 10.45: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 1eq. Cu²⁺ at 80°C with the TMA model based on the Cates' model, with $p_{ass} = 0.5$ and $\tau_{ass} = 1.3s$.

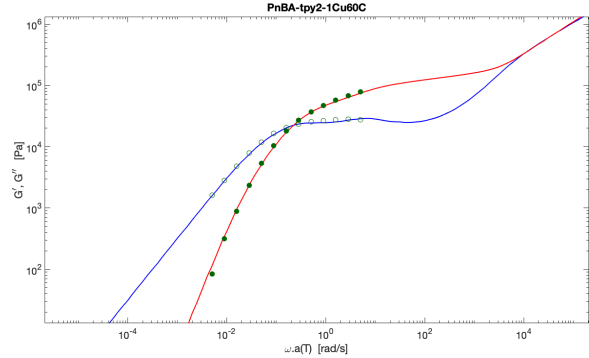


Figure 10.46: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 1eq. Cu²⁺ at 60°C with the TMA model based on the Cates' model, with $p_{ass} = 0.57$ and $\tau_{ass} = 8s$.

Then, at 40°C and 25°C (see Figures 10.47 and 10.48), aggregates must be taken into account. The second version of the model provides a good fitting of the experimental data on a larger frequency range than the first version. However, the final relaxation is still missing, which should be due to the disintegration of the aggregates.

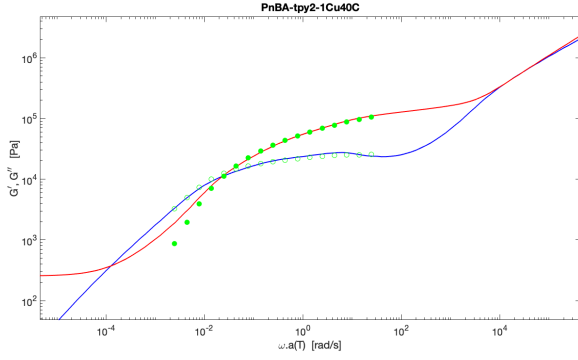


Figure 10.47: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 1eq. Cu²⁺ at 40°C with the TMA model based on the Cates' model, with $p_{ass} = 0.65$, $p_{aggr} = 1/1.4$ and $\tau_{ass} = 80$ s.

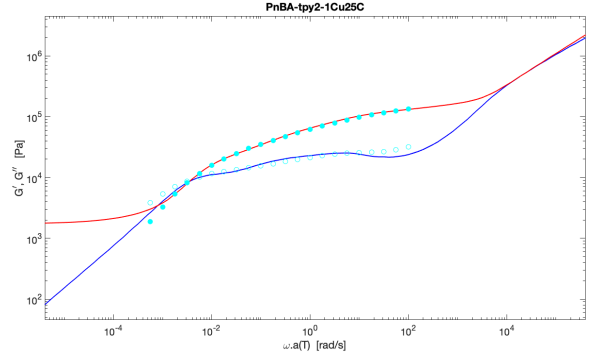


Figure 10.48: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 1eq. Cu²⁺ at 25°C with the TMA model based on the Cates' model, with $p_{ass} = 0.66$, $p_{aggr} = 1/1.3$ and $\tau_{ass} = 300$ s.

Finally, the modelling parameters are listed in the Table 10.12. The variations of p_{ass} and τ_{ass} with temperature, represented on Figures 10.49 and 10.50 show that τ_{ass} always follow an Arrhenius law with an energy of activation equal to 87kJ/mol, but $\log(p_{ass})$ is not linear.

	80°C	60°C	40°C	25°C	0°C
p_{ass}	0.5	0.56	0.61	0.66	0.66
p_{aggr}	—	—	1/3	1/2	1/1.3
τ_{ass}	1.3	8	80	300	8000

Table 10.12: Parameters of the TMA model for PnBA-tpy₂ 1eq. Cu²⁺

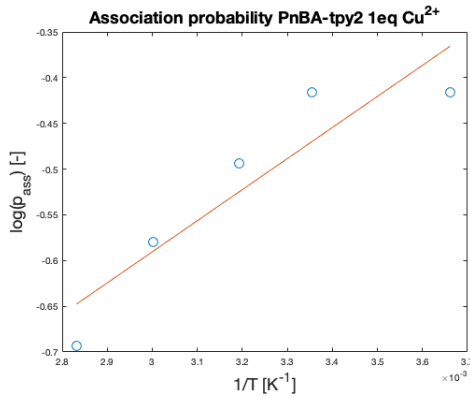


Figure 10.49: Association probability of PnBA-tpy₂ 1eq. Cu²⁺ versus temperature. The values of the parameter used in the model are represented by the blue circles, and the linear fitting of these points is represented in yellow.

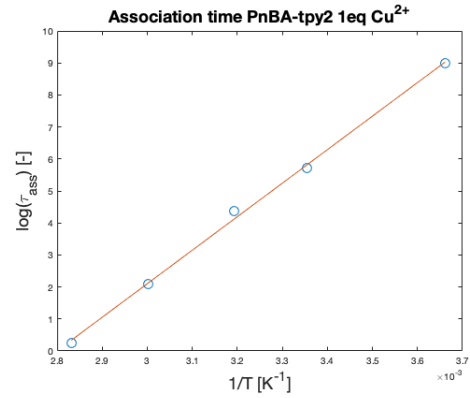


Figure 10.50: Association time of PnBA-tpy₂ 1eq. Cu²⁺ versus temperature. The values of the parameter used in the model are represented by the blue circles, and the linear fitting is represented in yellow. The activation energy corresponding is 87kJ/mol.

PnBA-tpy₂ 2.5eq. Cu²⁺

For this sample, the model was used with aggregates at all temperatures. At 60°C and above, there is no change between the curves provided by the two different models, the relaxation of the second plateau is missing again. The curve at 80°C is represented on Figure 10.51 to illustrate that. At 0°C (Figure 10.54), the modelling is not improved with the Cates' model either.

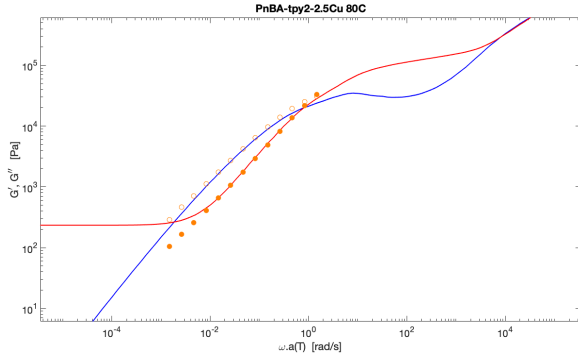


Figure 10.51: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 2.5eq. Cu²⁺ at 80°C with the TMA model based on the Cates' model, with $p_{ass} = 0.42$, $p_{aggr} = 1/2.1$ and $\tau_{ass} = 7s$.

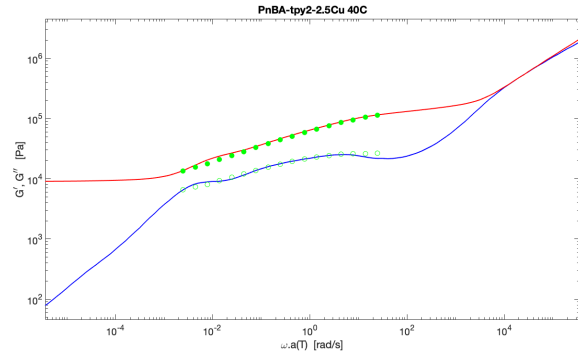


Figure 10.52: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 2.5eq. Cu²⁺ at 40°C with the TMA model based on the Cates' model, with $p_{ass} = 0.66$, $p_{aggr} = 1/1.32$ and $\tau_{ass} = 300s$.

However, at 40°C and 25°C, whose curves are shown on Figures 10.52 and 10.53), the Cates' model allows to obtain a simulation of the data that works on the whole frequency window, which was not the case before.

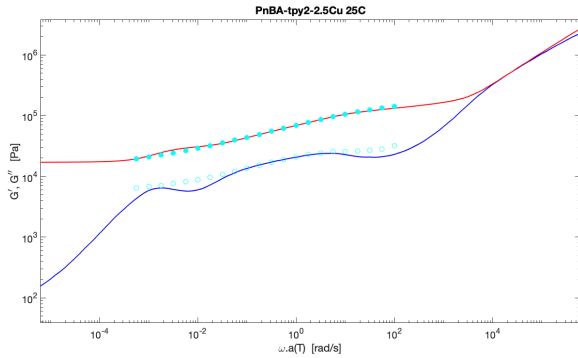


Figure 10.53: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 2.5eq. Cu²⁺ at 25°C with the TMA model based on the Cates' model, with $p_{ass} = 0.685$, $p_{aggr} = 1/1.17$ and $\tau_{ass} = 1500s$.

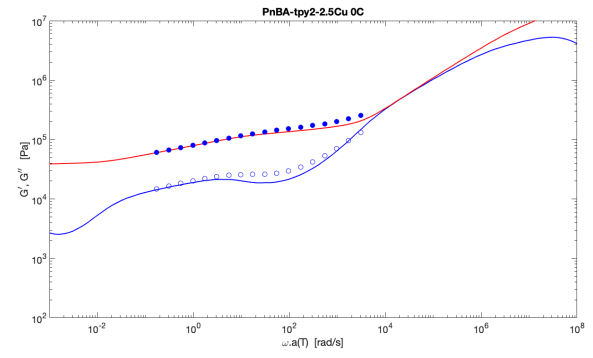


Figure 10.54: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 2.5eq. Cu²⁺ at 25°C with the TMA model based on the Cates' model, with $p_{ass} = 0.73$, $p_{aggr} = 1/1.12$ and $\tau_{ass} = 50000s$.

The fact that the Cates' model does not improve the fittings at high temperature, but only from 40°C and below might be surprising, because the dissociation of the stickers occurs more easily at high temperature, hence the Cates' model should be more appropriate for the simulations at high temperature. Nonetheless, the molecular weight distribution of the

different types of chains can help to understand what happens. At 60°C (see Figure 10.55), the linear chains compose the largest fraction of the sample. This is also the case at higher temperatures, where the proportion of linear chains even increases. These chains can relax by dissociation, but as the complexes formed with copper ions are rather stable, they usually relax by reptation before dissociating. It is confirmed by the previous samples for which the Cates' model did not provide much better fittings than the first TMA model.

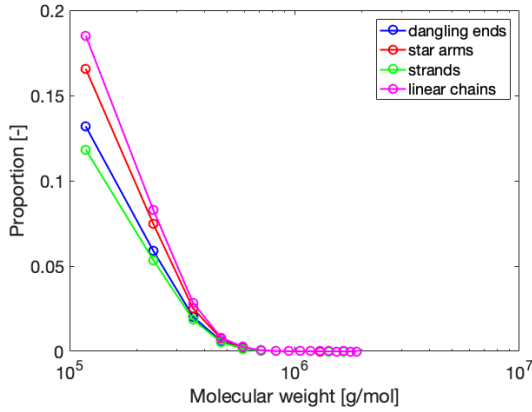


Figure 10.55: Molecular weight distributions of the different types of segments that compose the PnBA-tpy₂ 2.5eq. Cu²⁺ at 60°C.

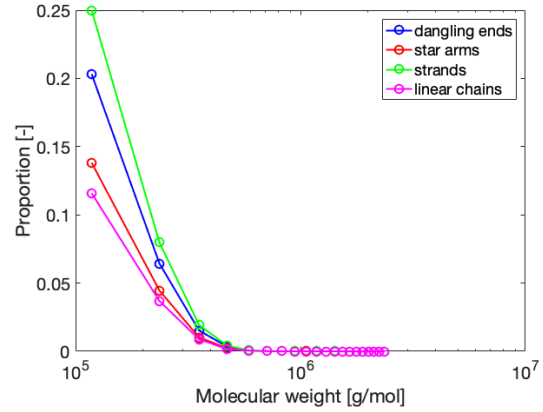


Figure 10.56: Molecular weight distributions of the different types of segments that compose the PnBA-tpy₂ 2.5eq. Cu²⁺ at 40°C.

However, when decreasing the temperature to 40°C, there are more aggregates, and the trapped strands now compose the largest fraction of the sample, as shown on Figure 10.56. The only possibility for these segments to get relaxed is through the dissociation of the stickers between two aggregates. The Cates' model is thus more appropriate to describe the behaviour of this sample at lower temperatures.

All the modelling parameters are contained in the Table 10.13. The natural logarithms of p_{ass} and τ_{ass} are plotted against the temperature on Figures 10.57 and 10.58. It indicates again that τ_{ass} follows an Arrhenius relationship, while it is not the case for p_{ass} . The activation energy of τ_{ass} is $E_a = 89.8\text{kJ/mol}$.

	100°C	80°C	60°C	40°C	25°C	0°C
p_{ass}	0.335	0.42	0.57	0.66	0.685	0.73
p_{aggr}	1/3.2	1/2.1	1/1.65	1/1.32	1/1.17	1/1.12
τ_{ass}	1	7	50	300	1500	50000

Table 10.13: Parameters of the TMA model for PnBA-tpy₂ 2.5eq. Cu²⁺

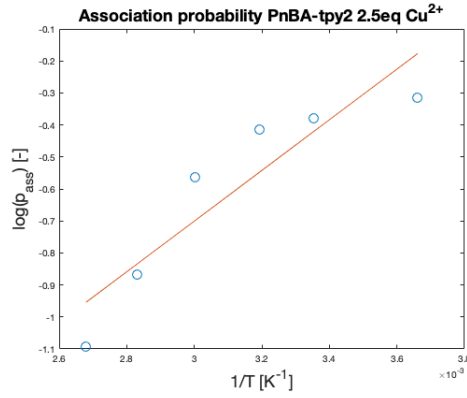


Figure 10.57: Association probability of PnBA-tpy₂ 2.5eq. Cu²⁺ versus the temperature. The values of the parameter used in the model are represented by the blue circles, and the linear fitting of these points is represented in yellow.

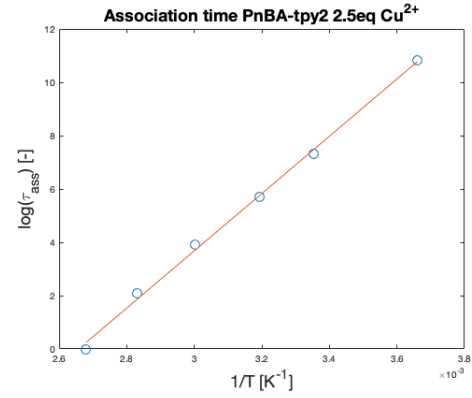


Figure 10.58: Association time of PnBA-tpy₂ 2.5eq. Cu²⁺ versus the temperature. The values of the parameter used in the model are represented by the blue circles, and the linear fitting of these points is represented in yellow. The activation energy corresponding is 89.8kJ/mol.

PnBA-tpy₂ 0.5eq. Zn²⁺

The results for the PnBA-tpy₂ 0.5eq. Zn²⁺ are shown on Figures 10.59 to 10.62, and they were obtained without considering aggregates in the model. The modelling parameters used are listed in the Table 10.14.

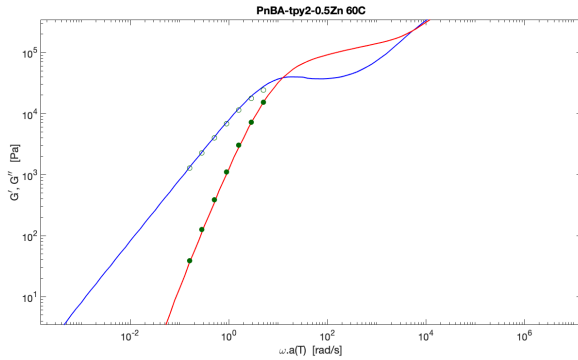


Figure 10.59: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 0.5eq. Zn²⁺ at 60°C with the TMA model based on the Cates' model, with $p_{ass} = 0.12$ and $\tau_{ass} = 0.07s$.

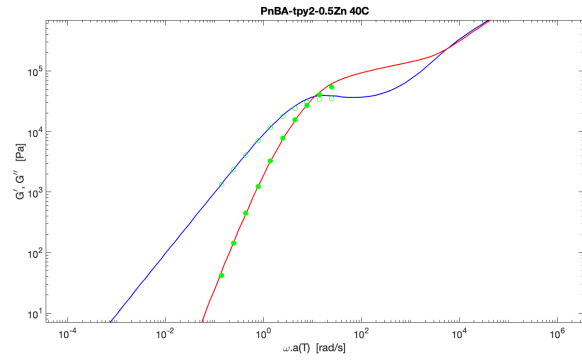


Figure 10.60: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 0.5eq. Zn²⁺ at 40°C with the TMA model based on the Cates' model, with $p_{ass} = 0.142$ and $\tau_{ass} = 0.18s$.

For this sample, the Cates' model allowed to achieve a great fitting of the curves at all temperatures. Indeed, the problem for all four temperatures of this sample with the previous version was that the breakage of the assemblies was not taken into account.

The modelling parameters also represented on Figures 10.63 and 10.64 as a function of the temperature. For this sample, both p_{ass} and τ_{ass} follow a Arrhenius law. The activation energy of the association time is equal to 42.5kJ/mol.

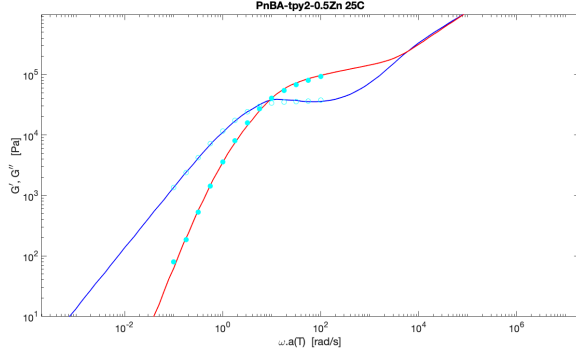


Figure 10.61: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 0.5eq. Zn²⁺ at 25°C with the TMA model based on the Cates' model, with $p_{ass} = 0.195$ and $\tau_{ass} = 2$ s.

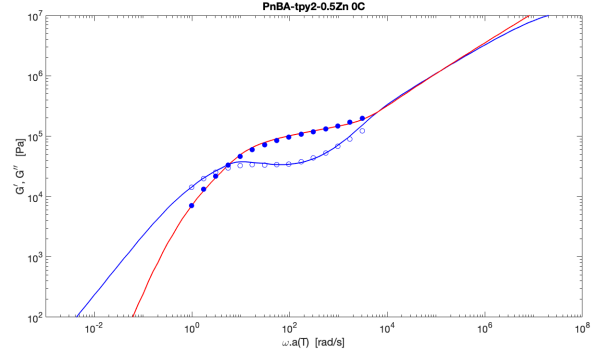


Figure 10.62: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 0.5eq. Zn²⁺ at 0°C with the TMA model based on the Cates' model, with $p_{ass} = 0.265$ and $\tau_{ass} = 2$ s.

	60°C	40°C	25°C	0°C
p_{ass}	0.12	0.142	0.195	0.265
τ_{ass}	0.07	0.18	0.45	2

Table 10.14: Parameters of the TMA model for PnBA-tpy₂ 0.5eq. Zn²⁺

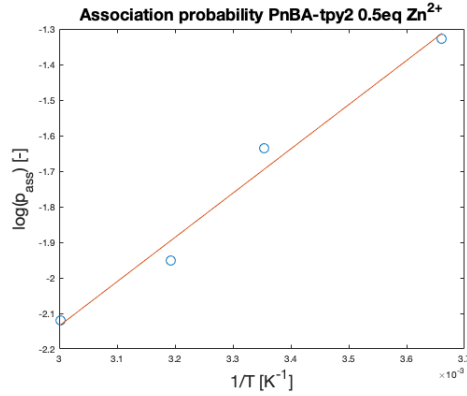


Figure 10.63: Association probability of PnBA-tpy₂ 0.5eq. Zn²⁺ versus temperature. The values of the parameter used in the model are represented by the blue circles, and the linear fitting of these points is represented in yellow.

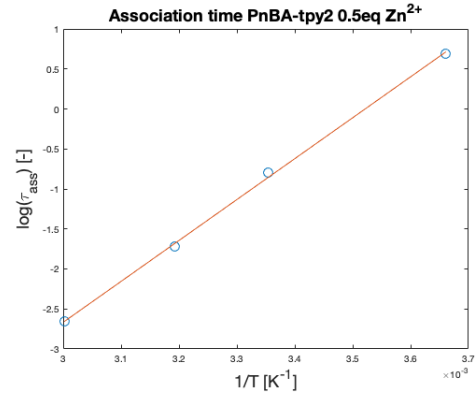


Figure 10.64: Association time of PnBA-tpy₂ 0.5eq. Zn²⁺ versus temperature. The values of the parameter used in the model are represented by the blue circles, and the linear fitting of these points is represented in yellow. The activation energy corresponding is 42.5kJ/mol.

PnBA-tpy₂ 1eq. Zn²⁺

The results of the modelling for the PnBA-tpy₂ 1eq. Zn²⁺ are similar to those for the PnBA-tpy₂ 0.5eq. Zn²⁺. It means that the Cates' model works well at all temperatures, and that no aggregates were needed in the code. Not all temperatures are shown, only two examples at 60°C and 25°C are represented on Figures 10.65 and 10.66.

The values of p_{ass} and τ_{ass} are summarised in Table 10.15, and Figures 10.67 and 10.68

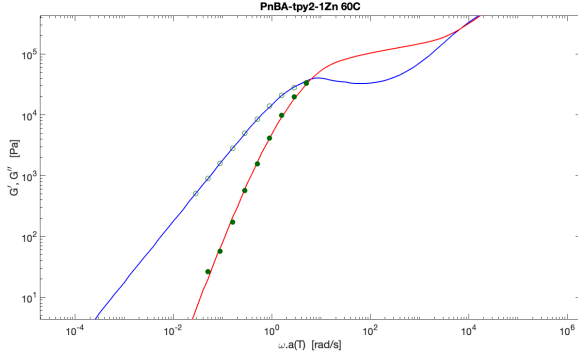


Figure 10.65: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 1eq. Zn²⁺ at 60°C with the TMA model based on the Cates' model, with $p_{ass} = 0.29$ and $\tau_{ass} = 0.09$ s.

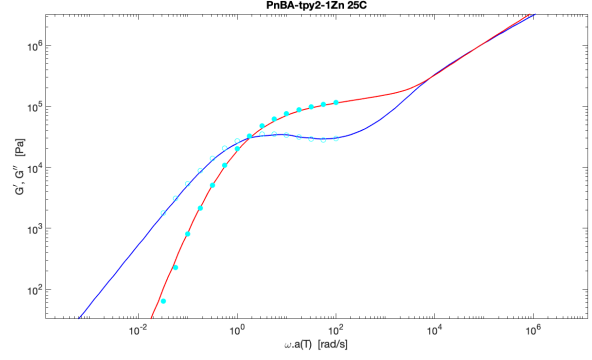


Figure 10.66: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 1eq. Zn²⁺ at 25°C with the TMA model based on the Cates' model, with $p_{ass} = 0.42$ and $\tau_{ass} = 2.7$ s.

indicate that both of them follow a linear relationship with respect to the temperature. The value of the activation energy is $E_a = 45.3$ kJ/mol. It is interesting to notice that the values of τ_{ass} and E_a do not increase much between this sample and the PnBA-tpy₂ 0.5eq. Zn²⁺. It is mainly the value of p_{ass} that increases with the ion density.

	80°C	60°C	40°C	25°C	0°C
p_{ass}	0.26	0.29	0.355	0.42	0.545
τ_{ass}	0.03	0.09	0.18	0.5	3

Table 10.15: Parameters of the TMA model for PnBA-tpy₂ 1eq. Zn²⁺

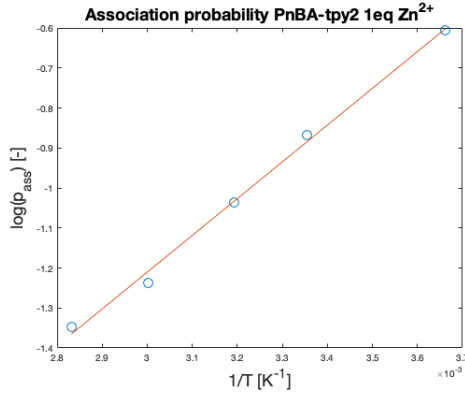


Figure 10.67: Association probability of PnBA-tpy₂ 1eq. Zn²⁺ versus temperature. The values of the parameter used in the model are represented by the blue circles, and the linear fitting of these points is represented in yellow.

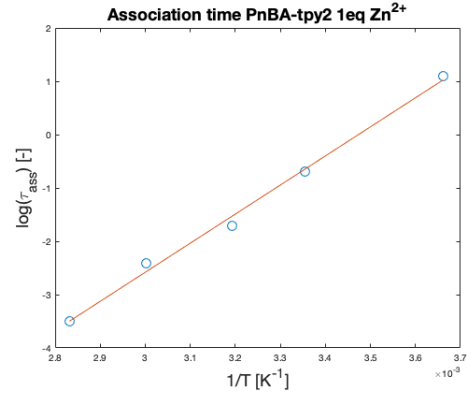


Figure 10.68: Association time of PnBA-tpy₂ 1eq. Zn²⁺ versus temperature. The values of the parameter used in the model are represented by the blue circles, and the linear fitting of these points is represented in yellow. The activation energy corresponding is 45.3kJ/mol.

PnBA-tpy₂ 2.5eq. Zn²⁺

The fittings of the PnBA-tpy₂ 2.5eq. Zn²⁺ were improved at high temperature compared to the ones obtained from the previous version of the model, namely from 40°C and up to 100°C. The Cates' model allowed to obtain a fitting of the moduli on the entire frequency range for these high temperatures, which was not the case before. These curves can be seen on Figures 10.69 to 10.72.

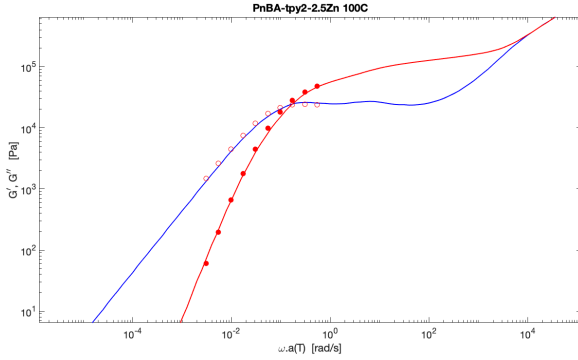


Figure 10.69: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 2.5eq. Zn²⁺ at 100°C with the TMA model based on the Cates' model, with $p_{ass} = 0.6$ and $\tau_{ass} = 7s$.

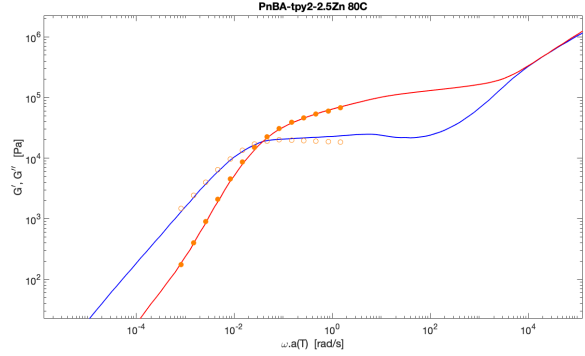


Figure 10.70: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 2.5eq. Zn²⁺ at 80°C with the TMA model based on the Cates' model, with $p_{ass} = 0.65$, $p_{aggr} = 1/80$ and $\tau_{ass} = 75s$.

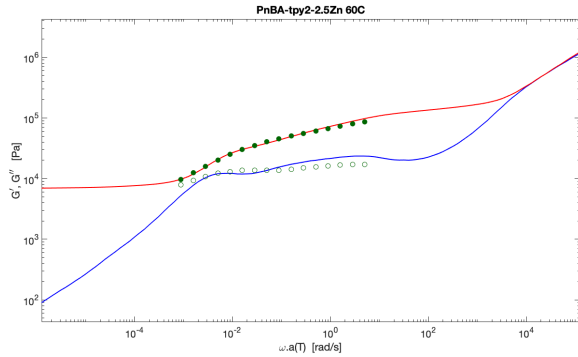


Figure 10.71: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 2.5eq. Zn²⁺ at 60°C with the TMA model based on the Cates' model, with $p_{ass} = 0.7$, $p_{aggr} = 1/1.5$ and $\tau_{ass} = 350s$.

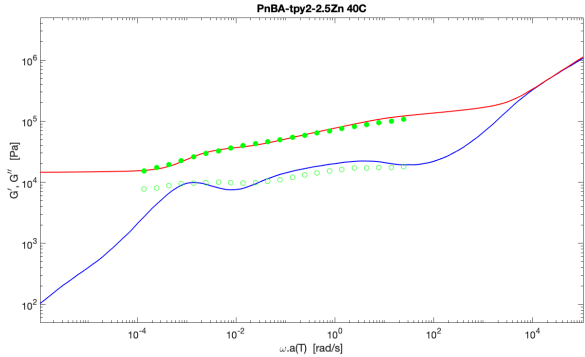


Figure 10.72: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 2.5eq. Zn²⁺ at 40°C with the TMA model based on the Cates' model, with $p_{ass} = 0.72$, $p_{aggr} = 1/1.28$ and $\tau_{ass} = 2000s$.

At low temperature, 25°C and 0°C, this model also provided a good modelling at all frequencies, but it showed no difference compared to the version considering the stable chains. For this reason, the curves corresponding to these two temperatures are not shown here.

It can be noted that the version of the TMA model based on the Cates' model was particularly successful at modelling the relaxation of the MSPs containing zinc ions, while

it did not improve much the results for the MSPs containing copper ions. It confirms the fact that the complexes formed with copper are more stable than those with zinc, and therefore, they are less likely to relax by dissociation.

Finally, the values of the parameters used for the modelling are given in the Table 10.16, and $\log(p_{ass})$ and $\log(\tau_{ass})$ are plotted as a function of the temperature on Figure 10.73 and 10.74. It can be observed that only the association time follow an Arrhenius law, with an energy of activation equal to 83kJ/mol.

	100°C	80°C	60°C	40°C	25°C	0°C
p_{ass}	0.6	0.65	0.7	0.72	0.73	0.73
p_{aggr}	—	1/80	1/1.5	1/1.28	1/1.15	1/1.1
τ_{ass}	7	75	350	2000	7000	2E+5

Table 10.16: Parameters of the TMA model for PnBA-tpy₂ 2.5eq. Zn²⁺

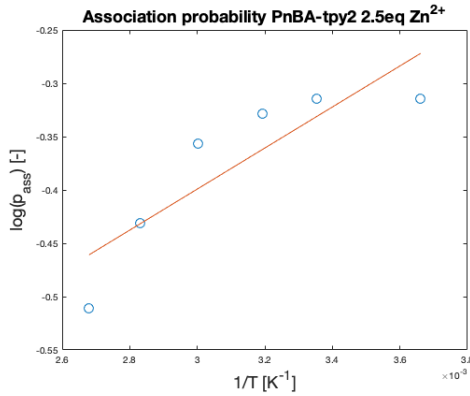


Figure 10.73: Association probability of PnBA-tpy₂ 2,5eq. Zn²⁺ versus temperature. The values of the parameter used in the model are represented by the blue circles, and the linear fitting of these points is represented in yellow.

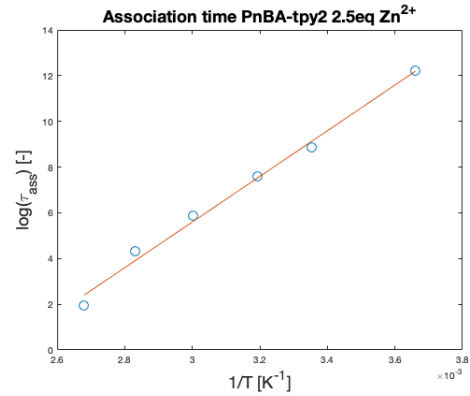


Figure 10.74: Association time of PnBA-tpy₂ 2.5eq. Zn²⁺ versus temperature. The values of the parameter used in the model are represented by the blue circles, and the linear fitting of these points is represented in yellow. The activation energy corresponding is 83kJ/mol.

PnBA-tpy₂ 0.5eq. blend

Given the moduli of the PnBA-tpy₂ 0.5eq. blend that are too low, the curves provided by the TMA model were again shifted downwards by a factor 1.5. When looking at the results for this sample, except the curve at 0°C which was already modelled correctly with the model with the stable auto-associated chains, on can see that all the fittings were improved with the Cates' model. Examples are shown on Figures 10.75 and 10.76 for 60°C and 25°C.

However, while for the first version of the model, all the temperatures could be fitted without taking the aggregates into account, with this second version based on the Cates'

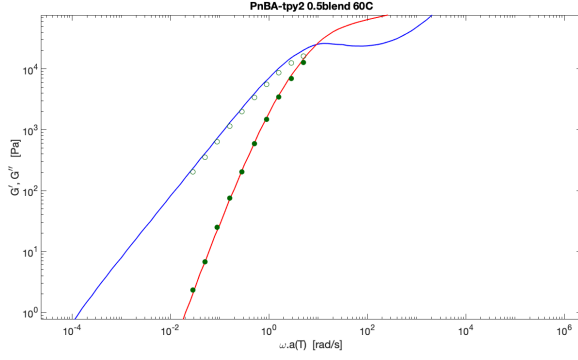


Figure 10.75: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 0.5eq. blend at 60°C with the TMA model based on the Cates' model, with $p_{ass} = 0.19$ and $\tau_{ass} = 0.05$ s.

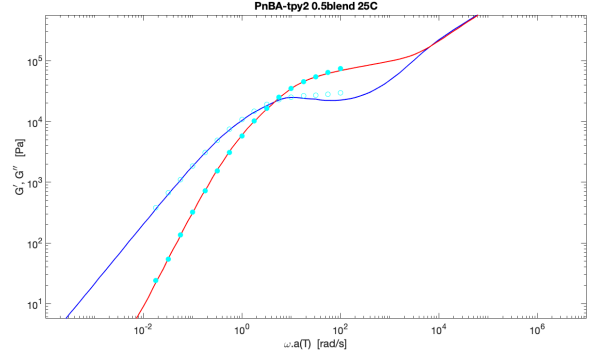


Figure 10.76: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 0.5eq. blend at 25°C with the TMA model based on the Cates' model, with $p_{ass} = 0.29$, $p_{aggr} = 1/9$ and $\tau_{ass} = 3$ s.

model, considering aggregates allows obtaining better fittings at low temperature, from 40°C and below. All the values of the modelling parameters are listed in the Table 10.17. The variations of p_{ass} and τ_{ass} with the temperature are shown on Figures 10.77 and 10.78. The energy of activation of τ_{ass} is $E_a = 60.7$ kJ/mol.

	80°C	60°C	40°C	25°C	0°C
p_{ass}	0.17	0.19	0.23	0.29	0.34
p_{aggr}	—	—	1/25	1/9	1/5
τ_{ass}	0.05	0.18	1	3	20

Table 10.17: Parameters of the TMA model for PnBA-tpy₂ 0.5eq. blend

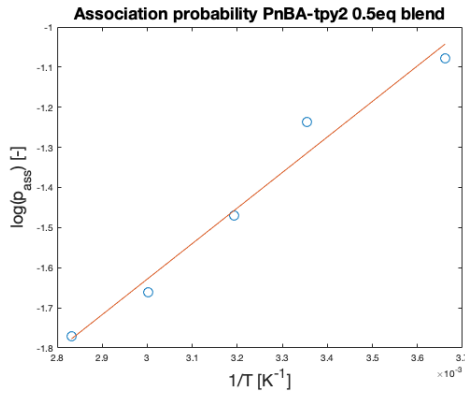


Figure 10.77: Association probability of PnBA-tpy₂ 0.5eq. blend versus temperature. The values of the parameter used in the model are represented by the blue circles, and the linear fitting of these points is represented in yellow.

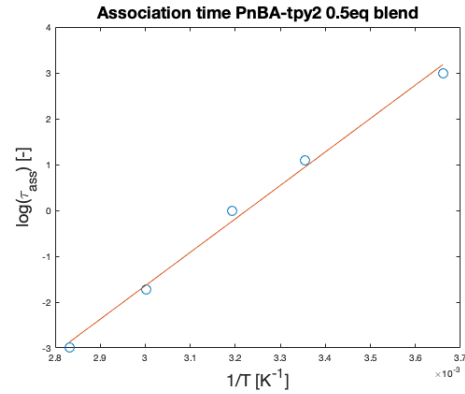


Figure 10.78: Association time of PnBA-tpy₂ 0.5eq. blend versus temperature. The values of the parameter used in the model are represented by the blue circles, and the linear fitting of these points is represented in yellow. The activation energy corresponding is 60.7kJ/mol.

PnBA-tpy₂ 1eq. blend

The last sample, PnBA-tpy₂ 1eq. blend, also showed better results with the Cates' model, except at 0°C for which the modelling was already correct with the first version of the model. The curves given by Figures 10.79 and 10.80 illustrates the successful application of this TMA model at 60°C and 25°C.

In order to obtain these results, aggregates have been added to the code at low temperatures, that is between 0°C and 40°C. The values of p_{ass} , p_{aggr} and τ_{ass} for each temperature are shown in the Table 10.18.

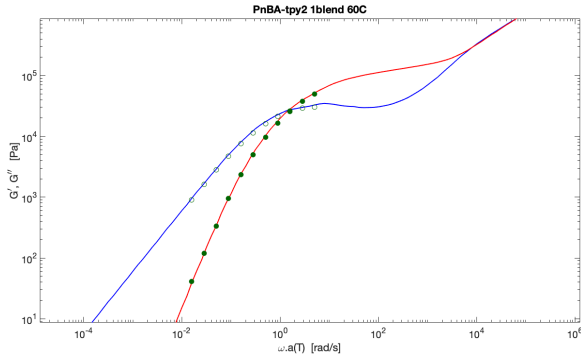


Figure 10.79: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 1eq. blend at 60°C with the TMA model based on the Cates' model, with $p_{ass} = 0.41$ and $\tau_{ass} = 1.1$ s.

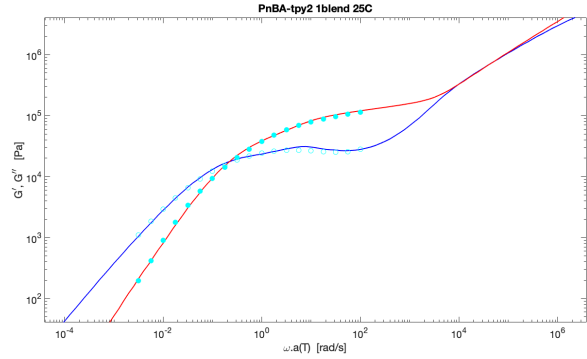


Figure 10.80: Modelling of $G'(\omega)$ and $G''(\omega)$ of PnBA-tpy₂ 1eq. blend at 25°C with the TMA model based on the Cates' model, with $p_{ass} = 0.515$, $p_{aggr} = 1/9$ and $\tau_{ass} = 25$ s.

	80°C	60°C	40°C	25°C	0°C
p_{ass}	0.38	0.41	0.45	0.515	0.6
p_{aggr}	—	—	1/25	1/9	1/5
τ_{ass}	0.3	1.1	6	25	250

Table 10.18: Parameters of the TMA model for PnBA-tpy₂ 1eq. blend

Figures 10.81 and 10.82 represent the relationships of the association probability and the association time with the temperature. Both are linear relationships. The energy of activation of τ_{ass} is equal to 68.3kJ/mol.

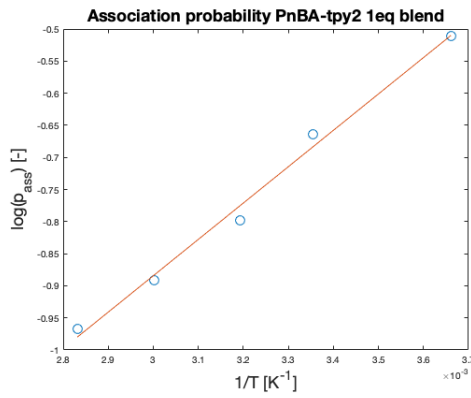


Figure 10.81: Association probability of PnBA-tpy₂ 1eq. blend versus temperature. The values of the parameter used in the model are represented by the blue circles, and the linear fitting of these points is represented in red.

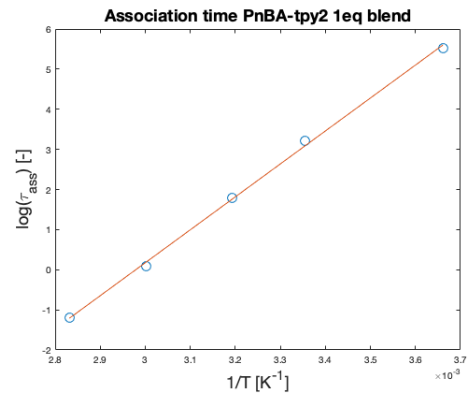


Figure 10.82: Association time of PnBA-tpy₂ 1eq. blend versus temperature. The values of the parameter used in the model are represented by the blue circles, and the linear fitting of these points is represented in red. The activation energy corresponding is 68.3kJ/mol.

Chapter 11

Discussion

In view of all the results presented above, several conclusions can be drawn that shed light on the rheological behaviour of these metallo-supramolecular polymers. Since the second version of the TMA model, which relies on the Cates' model, provided a better description of the experimental data, the following analysis is based on the parameters provided by this model only.

11.1 Probability of association p_{ass}

11.1.1 Deviation from the association probability expected from the sample preparation

The probability of association was first introduced in the Flory distribution, where it represents the probability that two building blocks react together through the association of two terpyridine end-groups with one metal ion. Hence, it is also equal to the proportion of terpyridine ligands that are associated.

When adding 0.25 ions equivalents to the PnBA-tpy₂ building blocks, there is theoretically enough ions so that 50% of the terpyridine form a complex. And for 0.5 ions equivalents, 100% of the ligands should be associated through the complexes. Hence, the expected maximum association probability, noted $p_{ass,max}$, is equal to 0.5 and 1 respectively for these two quantities of ions. However, it must be noted that the computations of the amounts of ions added during the sample preparation were based on building blocks having a weight-average molecular weight of 113.2kg/mol, while the modelling of the reference sample showed that their true weight-average molecular weight is 118kg/mol. If the molecular weight was under-evaluated, it means that the number of moles present in the same mass of material was over-evaluated. Consequently, the quantity of ions added to the samples was too large by about 4.4%. This is not a high value, so these corrections will be neglected.

The PnBA-tpy₂ 0.25eq. Cu²⁺ was the only sample with 0.25 eq. of ions. The association probabilities for this sample were determined as being between 0.1 at 80°C and 0.18 at 0°C (see Table 10.10). Both these values are much lower than the maximum value expected $p_{ass,max} = 0.5$. At 80°C, this corresponds to the situation where 80% of the ions do not

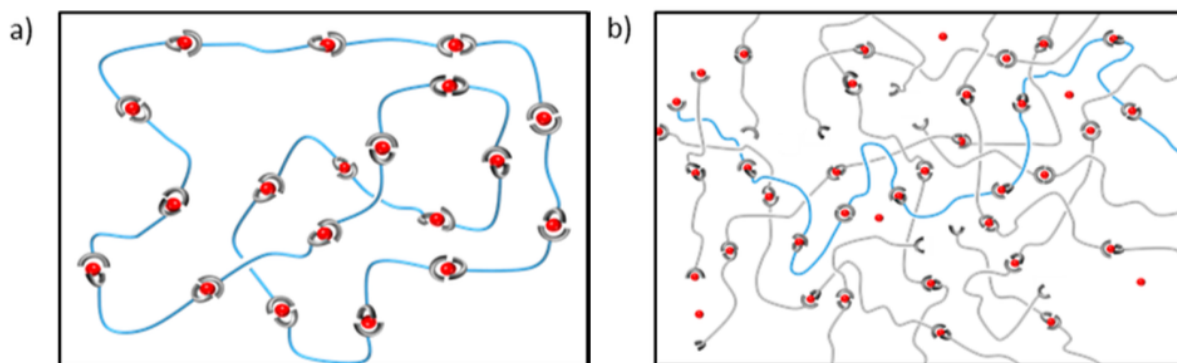


Figure 11.1: (a) Schematic drawing representing the ideal conformation of the associated PnBA-tpy₂ building blocks for 0.5 ions equivalents. All the terpyridines are linked together, there is not any ion nor any ligand left alone. (b) Schematic drawing representing an example of configurations as it is in reality. All the terpyridine ligands are not part of an active stickers. In addition to the metal-ligand complexes formed, there are free chain ends, free ions and mono-complexes. Images retrieved from [10].

give rise to active stickers, and 64% at 0°C¹. This shows that the linear assemblies created are far from perfect. Several ions must be left alone, or they may form mono-complexes with only one ligand, which does not allow long linear assemblies to be created.

The same effect can be observed for the three samples containing 0.5 ions equivalents. For these samples, the maximum expected value of the association probability is $p_{ass,max} = 1$, reflecting a situation where all terpyridines and ions participate in the formation of active stickers.

- PnBA-tpy₂ 0.5eq. Cu²⁺ has an association probability between 0.25 and 0.35 (Table 10.11). It is the sample which has the highest values of p_{ass} , as copper ions are more stable than zinc ions. Nonetheless, there are still between 75% and 65% of the ions and ligands that are not associated.
- PnBA-tpy₂ 0.5eq. Zn²⁺ has an association probability between 0.12 and 0.265 at high and low temperatures (Table 10.14). These are the lowest values of p_{ass} , which correspond to 88% and 73, 5% of non-associated ligands.
- PnBA-tpy₂ 0.5eq. blend has a probability of association of 0.17 at low temperature and 0.34 at high temperature (Table 10.17). These values are thus in between those of the PnBA-tpy₂ 0.5eq. Cu²⁺ and the PnBA-tpy₂ 0.5eq. Zn²⁺.

This difference between the ideal case at 0.5eq, where all the terpyridine ends-groups should be associated two by two, and the reality is shown on Figure 11.1.

¹These percentages were computed with the following formula:

$$p_{non-associated} = \frac{p_{ass,max} - p_{ass}}{p_{ass,max}} \cdot 100\%$$

11.1.2 Variation of p_{ass} with the temperature

The probabilities of association for each sample are plotted as a function of the temperature on Figure 11.2. This figure contains a lot of information, and it allows to summarise all the observations concerning p_{ass} . In the first step, only the influence of temperature will be examined.

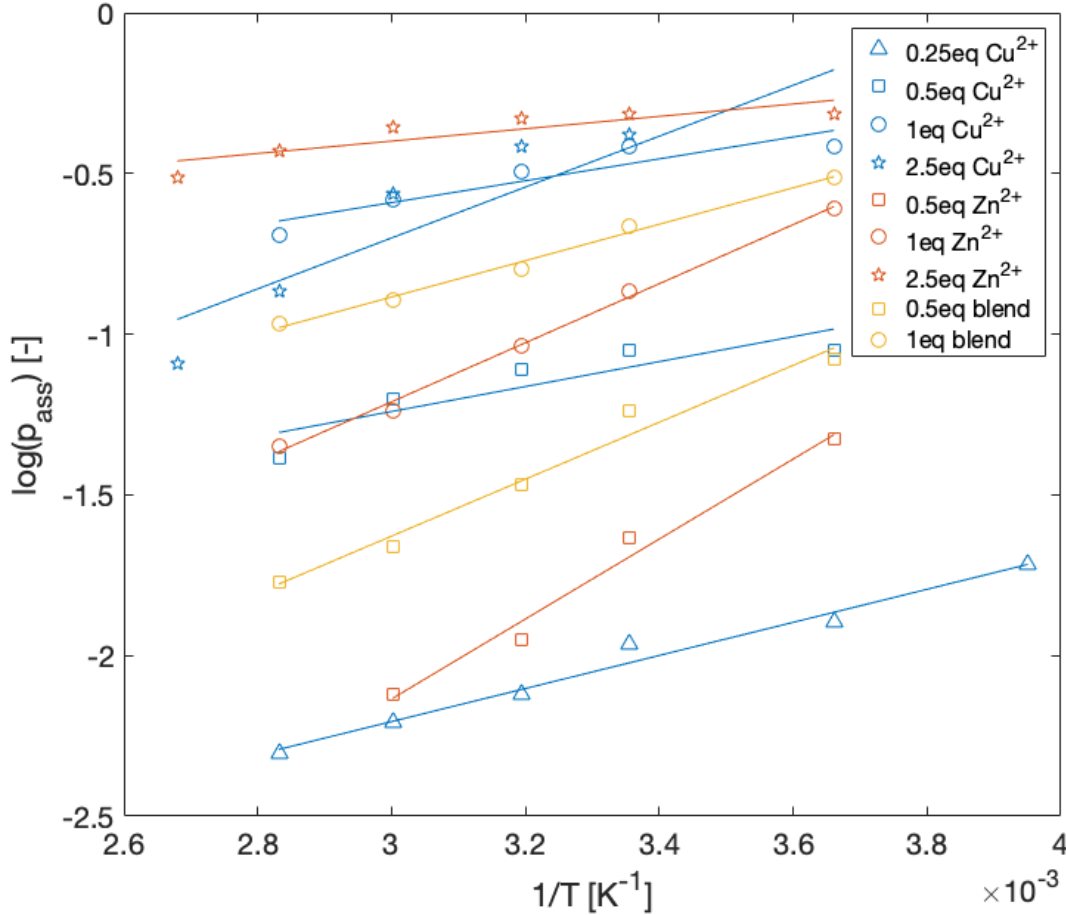


Figure 11.2: Natural logarithm of the probability of association plotted against the temperature for all the MSPs based on the linear PnBA-tpy₂. The symbols correspond to the values of p_{ass} used in the model in order to fit the experimental data, and the lines correspond to the linear fittings of these points for each sample. When the sample contains Cu(II) ions, the colour blue is used. Red is used for the Zn(II) ions and yellow is used for the blend 50%Cu(II)/50%Zn(II). The different symbols correspond to the different ion densities.

On this graph, the slopes of the linear fitting are always positive, which means that the general tendency for p_{ass} is to increase when the temperature decreases. It confirms that the stability of the stickers is strongly linked to the temperature: their formation is favoured at low temperature and they are less and less stable when the temperature rises.

However, for some samples, the linear fittings do not pass by all the points. Hence, $\log(p_{ass})$ is not always linear with respect to the temperature. This deviation is observed for samples

containing a significant amount of aggregates, namely PnBA-tpy₂ 2.5eq. Cu²⁺, PnBA-tpy₂ 1eq. Cu²⁺, PnBA-tpy₂ 0.5eq. Cu²⁺ and PnBA-tpy₂ 2.5eq. Zn²⁺. For these MSPs, two slopes are visible for $\log(p_{ass})(T)$: one larger slope at high temperature, similar to the samples without aggregates, and a smaller slope at low temperature, which often becomes flat between 25°C and 0°C. This is obviously linked to the presence of aggregates: when aggregates are formed, at least two metal-ligand complexes are bonded together, creating a phase separation between the associated stickers and the polymer matrix. And it is very likely that additional free ions join the aggregates. When this happens, the ions participating in the aggregates are no longer available for creating new complexes. As a result, p_{ass} does not increase in the same way as for samples with few or no aggregates. It must be noted here that the aggregates are not accounted for in p_{ass} , and are discussed in section 11.4.

11.1.3 Variation of p_{ass} with the ion density

Secondly, the position of the curves in Figure 11.2 allows to understand the influence of the ion density on the probability of association. On this graph:

- the triangles correspond to 0.25 ions equivalent.
- the squares correspond to 0.5 ions equivalent.
- the circles correspond to 1 ions equivalent.
- the stars correspond to 2.5 ions equivalents.

For each colour, that is for each type of ions used, the data are shifted upwards when the ion content increases. It indicates that p_{ass} increases with the quantity of ions.

$$(p_{ass})_{0.25eq} < (p_{ass})_{0.5eq} < (p_{ass})_{1eq} < (p_{ass})_{2.5eq} \quad (11.1)$$

This trend was already predicted by the experimental results. It is logical since it becomes easier for the terpyridine ligands to find an ion in their vicinity with which they can bind when there are more ions.

There is however an exception for the PnBA-tpy₂ 2.5eq. Cu²⁺. At high temperature, its probability of association is smaller than the one of the PnBA-tpy₂ 1eq. Cu²⁺, then it exceeds it starting at 60°C. It can again be explained by the presence of aggregates, that are always present at 2.5 equivalents, but that only appear from 40°C and below at 1 equivalent. The ions participating to the aggregates are no longer available to create new junctions between the different building blocks, leading to a smaller probability of association for 2.5 equivalents than for 1 equivalent where there are no aggregates at high temperature.

Another, more plausible, explanation is related to the formation of mono-complexes. Above 0.5 ions equivalent, there are more ions than the stoichiometric amount with respect to the terpyridines, which means that there are more ions than needed to create complexes with all the ligands. Both the PnBA-tpy₂ 2.5eq. Cu²⁺ and the PnBA-tpy₂ 1eq. Cu²⁺ corresponds to this case. With an excess of ions, it may be possible that the formation of mono-complexes is favoured compared to the bis-complexes. Mono-complexes are not

included in the association probability of the Flory distribution as they do not allow the formation of long linear assemblies, so they are counted among the unreacted chain ends. Hence, if many mono-complexes are formed instead of bis-complexes, it will look like p_{ass} is very small, even though complexes (i.e. bis- and mono-complexes) are formed. Considering that this excess of ions is larger for 2.5eq. than for 1eq, this effect would be more important for the PnBA-tpy₂ 2.5eq Cu²⁺, and would lead to a smaller p_{ass} . However, this hypothesis could not be verified, and one could also expect p_{ass} to be smaller at all temperatures with this effect, not only above 60°C. Nevertheless, the presence of mono-complexes can explain why the probability of association never reaches very high values, the maximum found being 0.73 at 0°C for the samples containing 2.5 ions equivalents.

11.1.4 Variation of p_{ass} with the ion nature

Figure 11.2 can provide a last information about the influence of the nature of the ions. It can be seen that for 0.5eq and 1eq, the following relationship is verified at all temperatures:

$$(p_{ass})_{Cu} > (p_{ass})_{blend} > (p_{ass})_{Zn} \text{ below 2.5eq} \quad (11.2)$$

While there is an inversion at 2.5eq:

$$(p_{ass})_{Zn} > (p_{ass})_{Cu} \text{ at 2.5eq} \quad (11.3)$$

It must be noted that although the linear fitting of the PnBA-tpy₂ 2.5eq Cu²⁺ may suggest that the association probability of this sample exceeds the one of PnBA-tpy₂ 2.5eq Zn²⁺ at 0°C, the two association probabilities are actually equal to 0.73 for this temperature, hence the two points are superimposed.

These two relationships described by the Equations 11.2 and 11.3 were already discussed, based on the experimental results. The inversion of the probabilities of association with respect to the ions nature that occurs at 2.5eq is a very interesting effect, which is related to the tendency of the various ions to form aggregates. Hence, it will not be addressed here, but in the section 11.4 covering the aggregates.

11.2 Association time τ_{ass}

11.2.1 Variation of τ_{ass} with the temperature

Figure 11.3 summarises all the information concerning the association time τ_{ass} . At first sight, it can be seen that this variable well follows an Arrhenius relationship for all the samples. The values of the activation energies are listed in the Table 11.1. As a result, the association time always increases when the temperature decreases. It is again a confirmation that the stickers are more stable at low temperatures. As they are more stable, they will need more time before dissociating.

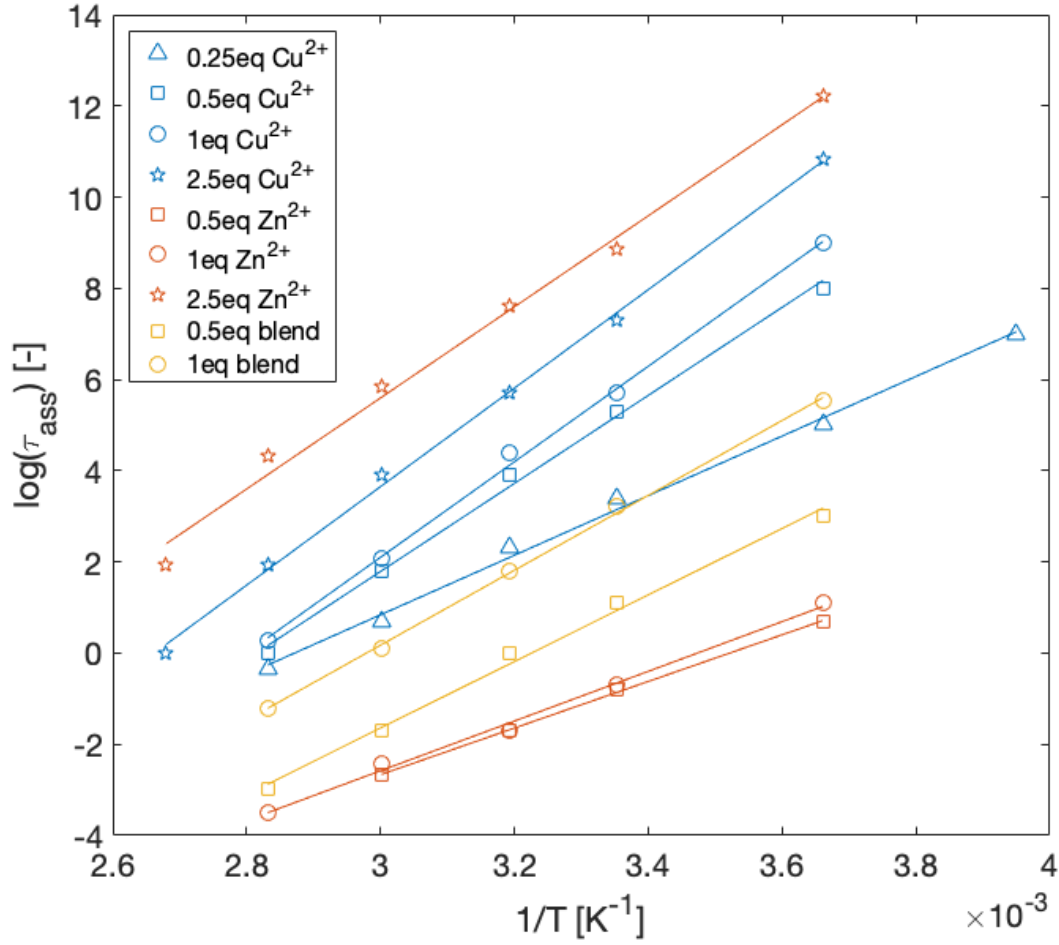


Figure 11.3: Natural logarithm of the association time plotted against the temperature for all the MSPs based on the linear PnBA-tpy₂. The symbol corresponds to the values of τ_{ass} used in the model in order to fit the experimental data, and the lines correspond to the linear fittings of these points for each sample. When the sample contains Cu(II) ions, the colour blue is used. Red is used for the Zn(II) ions and yellow is used for the blend 50%Cu(II)/50%Zn(II). The different symbols correspond to the different ion densities.

11.2.2 Variation of τ_{ass} with the ion density

Figure 11.3 shows that for all samples, the association time increases with the ion density. For each type of ion, the following relation is verified:

$$(\tau_{ass})_{0.25eq} < (\tau_{ass})_{0.5eq} < (\tau_{ass})_{1eq} < (\tau_{ass})_{2.5eq} \quad (11.4)$$

This last equation is similar to the Equation 11.1 for the association probability. It means that increasing the ion content leads to a larger probability to form a complex and a longer time before its dissociation. However, the increase of τ_{ass} is not as obvious as the increase of p_{ass} . Indeed, at first glance, one could logically believe that the association time would remain the same at a given temperature and for a given ion, regardless of the quantity of ion. However, it is observed that when there are more ions, the value of τ_{ass} rises. This result can be explained if we consider that the dissociation of the active stickers occurs by

	Zn ²⁺	blend	Cu ²⁺
0.25eq	–	–	54.3kJ/mol
0.5 eq	42.5kJ/mol	60.7kJ/mol	80.3kJ/mol
1eq	45.3kJ/mol	68.3kJ/mol	87.1kJ/mol
2.5eq	83kJ/mol	–	89.8kJ/mol

Table 11.1: Energies of activation of the association time

a mechanism of ion exchange rather than by a simple dissociation without re-association of the ion with another ligand, as it is the process that necessitates the lower energy [11]. It means that the ligand that leaves the bis-complex is immediately replaced by another ligand. The chain ended by the ligand released from the complex is then able to move and relax, until it is involved in a new complex. However, this exchange mechanism is only possible if there are free ligands in the vicinity of the stickers. Since the proportion of free chain ends decreases when the ion content increases, more time is needed before the dissociation can occur and τ_{ass} increases.

This effect is also reflected in the values of the activation energy. If the dissociation process is made more difficult, it is logical that E_a grows. And it is indeed the case for all types of ions: the slope of τ_{ass} in Figure 11.3 increases with the ion density, and so is E_a (see Table 11.1). However, this increase is not always constant. With copper, there is a very small difference between the activation energies at 1eq and 2.5eq, which could indicate a saturation of the sample around 1eq, as already mentioned in the Part III. Adding ions above 1 equivalent does not significantly modify the properties of the material.

And for zinc, both τ_{ass} and E_a does not seem to increase much between 0.5eq and 1eq, while there is a very large increase between 1eq and 2.5eq. As the zinc ion is more labile, it indicates that a much larger ion quantity is needed to obtain a real change of the material properties, unlike copper. Then at 2.5eq of zinc ions, it is probable that the bis-complexes are associated into aggregates, which explains the very high values of τ_{ass} .

11.2.3 Variation of τ_{ass} with the ion nature

The influence of the ion nature is much more evident on Figure 11.3 than on Figure 11.2 above representing the association probability (the later was more sensible on the ion density). On the graph 11.3 of the association time, it is clear that the red curves of the zinc are at the bottom, except the one of the PnBA-tpy₂ 2.5eq Zn²⁺ which is at the top. Then, the blends are above 0.5eq and 1eq zinc, and finally, the curves of copper are in between the blends and the PnBA-tpy₂ 2.5eq Zn²⁺.

$$(\tau_{ass})_{Cu} > (\tau_{ass})_{blend} > (\tau_{ass})_{Zn} \quad \text{below 2.5eq} \quad (11.5)$$

$$(\tau_{ass})_{Zn} > (\tau_{ass})_{Cu} \quad \text{at 2.5eq} \quad (11.6)$$

This is a very good indicator of the stability of the different complexes with respect to one another, and it is again in agreement with all the previous result.

11.3 Dissociation time τ_{free}

The dissociation time represents the mean time during which a ligand stays dissociated. It is linked to the values of p_{ass} and τ_{ass} by the Equation 10.27:

$$p_{ass} = \frac{\tau_{ass}}{\tau_{ass} + \tau_{free}} \quad (10.27)$$

And it is plotted as a function of the temperature on the Figure 11.4.

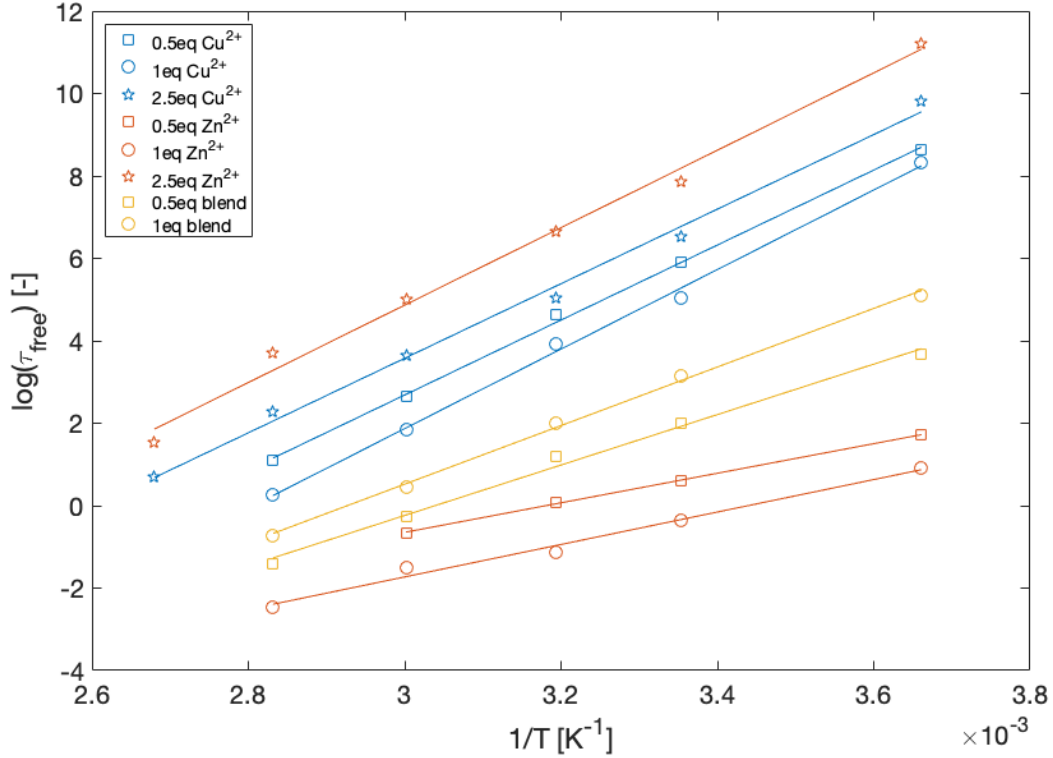


Figure 11.4: Natural logarithm of the dissociation time plotted against the temperature for all the MSPs based on the linear PnBA-tpy₂. The symbol corresponds to the values of τ_{free} used in the model in order to fit the experimental data, and the lines correspond to the linear fittings of these points for each sample. When the sample contains Cu(II) ions, the colour blue is used. Red is used for the Zn(II) ions and yellow is used for the blend 50%Cu(II)/50%Zn(II). The different symbols correspond to the different ion densities.

The dissociation time seems to follow an Arrhenius law, just as τ_{ass} . And it is also very sensible to the ion nature, hence, at first sight, τ_{free} seems to be more similar to τ_{ass} than to p_{ass} . However, its dependence on the ion density is not the same as the one of the association time. The trend seems to be the following for copper and zinc (but not for the blend)

$$(\tau_{free})_{1eq} < (\tau_{free})_{0.5eq} < (\tau_{free})_{2.5eq} \quad (11.7)$$

This relationship is very surprising because it does not follow the ascending or descending order of ion density. It might be linked to the formation of mono-complexes, which is larger when the ion density increases, especially for copper. However, as the presence of mono-complexes was not taken into account in this work, it could not be further investigated.

11.4 Formation of aggregates

The presence of aggregates is revealed by the second plateau in the Frequency Sweeps of the different samples, particularly for the PnBA-tpy₂ 2.5eq Cu²⁺ and PnBA-tpy₂ 2.5eq Zn²⁺. Nonetheless, the addition of aggregates was necessary to allow the modelling of some samples at lower ion density, for which the second plateau was not strongly marked. Thus, the modelling made it possible to detect the presence of aggregates in samples where it was not particularly noticeable. This is the case for the PnBA-tpy₂ 1eq Cu²⁺, PnBA-tpy₂ 0.5eq Cu²⁺, PnBA-tpy₂ 1eq blend, and PnBA-tpy₂ 0.5eq blend.

Unfortunately, the values of p_{aggr} cannot be compared in between the different samples. It is due to the fact that this variable represents the proportion of bis-complexes that participate in an aggregate. Consequently, it is strongly linked to the proportion of associated stickers p_{ass} , it cannot be used alone. Moreover, the formation of mono-complexes was not taken into account in the TMA model, hence it was assumed that the chain ends could not participate in the aggregates, which is most probably untrue. Hence, the absolute values of p_{aggr} are not truly representative of the quantities of aggregates in the sample, and cannot be used to form conclusions about the samples.

The fact that the chain ends forming mono-complexes were not taken into account for the aggregates explains the very high values of p_{aggr} found for some samples: up to 1/1.1 for the PnBA-tpy₂ 2.5eq Zn²⁺ at 0°C, which is equal to nearly 91% of the bis-complexes taking part in an aggregate. If mono-complexes could form aggregates, on one hand, it would increase the number of possible available sites for the aggregates. Consequently, for the same total number of aggregates, p_{aggr} would decrease. And on another hand, assuming that all chain ends are free means that they are considered as dangling ends, which can always be relaxed by CLF. If they can form aggregates, the amount of dangling ends would be reduced, and the modulus would not decrease as quickly.

11.4.1 Influence of the ion nature

It is however still possible to extract some information from the presence of aggregates in the samples and from p_{aggr} . Indeed, the two ions, copper and zinc, behave completely differently when it comes to aggregates.

With copper ions, aggregates appear very quickly: the TMA model reveals their presence from 1eq of Cu²⁺. In addition, the values of p_{aggr} are directly quite high, between 1/2 and 1/1.2 for 0.5eq, between 1/3 and 1/1.3 with 1eq, and between 1/3.2 and 1/1.12 for 2.5eq. It indicates that the metal-ligand complexes based on copper have a high tendency to phase separate, hence they are very efficient at creating aggregates.

While with zinc ions, no aggregates are present at low ion density, namely at 0.5eq and 1eq. They only appear at 2.5 ions equivalents. And in order to fully understand the difference between the two ions, the Tables 10.13 and 10.16 containing the modelling parameters of the PnBA-tpy₂ 2.5eq Cu²⁺ and the PnBA-tpy₂ 2.5eq Zn²⁺ are reproduced below.

	100°C	80°C	60°C	40°C	25°C	0°C
p_{ass}	0.335	0.42	0.57	0.66	0.685	0.73
p_{aggr}	1/3.2	1/2.1	1/1.65	1/1.32	1/1.17	1/1.12
τ_{ass}	1	7	50	300	1500	50000

Table 11.2: Parameters of the TMA model for PnBA-tpy₂ 2.5eq. Cu²⁺

	100°C	80°C	60°C	40°C	25°C	0°C
p_{ass}	0.6	0.65	0.7	0.72	0.73	0.73
p_{aggr}	–	1/80	1/1.5	1/1.28	1/1.15	1/1.1
τ_{ass}	7	75	350	2000	7000	2E+5

Table 11.3: Parameters of the TMA model for PnBA-tpy₂ 2.5eq. Zn²⁺

One can notice that the aggregates are present at all temperatures with copper. And the probability of association is quite low at 80°C, then it increases a lot when the temperature drops. While with zinc, the aggregates are not present at 100°C. They appear at 80°C, but in a very low quantity, as indicated by the value of $p_{aggr} = 1/80$. And at the same time, the value of p_{ass} is already much higher than that of copper at 100°C, although the zinc is more labile than copper. Then, the association probability reaches the same value as copper at 0°C $p_{ass} = 0.73$.

This shows that the phase segregation of the bis-complexes does not occur in the same way for zinc and for copper ions. The difference between the two ions could be explained by the fact that all the bis-complexes take part in an aggregate at 2.5eq of zinc ions. Consequently, the values of p_{ass} and τ_{ass} become linked to the aggregates, which is not the case for all the other samples for which p_{ass} and τ_{ass} only describe the complexes. This leads to high values of p_{ass} and τ_{ass} , because the bis-complexes become much more stable when they form aggregates. In contrast, there are still complexes outside the aggregates with copper.

Regarding the blends, it appears that they have again an intermediate behaviour concerning the aggregates. Aggregates are present at low temperature for the two blends, but the values of p_{aggr} are not as high as those found with copper: between 1/25 and 1/5, as shown in the Tables 10.17 and 10.18.

11.4.2 Influence of the temperature

Finally, the aggregates are also impacted by temperature. For most samples, their presence is not detected at high temperatures, above 40°C usually. This is due to the fact that aggregates are formed through phase separation of the stickers and the polymer backbones. And since the stickers are less stable when the temperature increases, it is logical that the formation of aggregates will also be compromised at high temperature.

Conclusion

The rheological behaviour of the metallo-supramolecular polymers based on metal-ligands interactions was investigated in this work through Dynamic Frequency Sweep measurements. Firstly, the experimental results were analysed in order to identify the main impacts of the creation bis-complexes on the properties of the supramolecular polymers. Then, a modified TMA model was used in order to model the data. Two versions of the model were developed: the first version assumed that the linear assemblies were stable, which led to unsatisfactory results. A second version based on the Cates' model was thus created, which allowed to integrate dissociation of the chains in the relaxation processes. A more thorough analysis of the polymer dynamics was therefore made possible by examining the three modelling parameters p_{ass} , τ_{ass} and p_{aggr} (respectively the association probability, the association time and the probability for a sticker to be part of an aggregate).

The first observation made is the failure of the Time-Temperature Superposition principle after the addition of the ions. This is due to the effect of the temperature on the stickers, which is not taken into account in the TTS.

Secondly, we discussed the presence of aggregates, often leading to a second rubbery plateau, particularly if a high amount of ions is added. The model confirmed that aggregates are needed to obtain a good description of the experimental data. It also pointed out that aggregates are already present at low ion densities with copper and for the blend, even if the presence of a second plateau is not obvious for these samples.

Then, we discussed the fact that an increase in temperature leads to a decrease in the stability of the associated stickers. Hence, p_{ass} and τ_{ass} become smaller at high temperature. The aggregates are also impacted by the temperature, because they are formed through the phase separation between the bis-complexes and the polymer backbones. If their association is less stable, the formation of aggregates also becomes more difficult. Consequently, there are fewer aggregates at high temperature.

The influence of the ion density was also investigated. It showed that more stickers are formed when the quantity of ions is increased, hence p_{ass} is very sensible to the ion density. However, the ideal configuration, where all the ions are linked to two terpyridine ligands, can never be reached for the samples containing 0.25 and 0.5 ions equivalents, the later corresponding to the stoichiometric amount. The association time τ_{ass} also increases with the ion content, which is due to the dissociation process that occurs by ligand exchange. This mechanism requires the presence of a free ligand in the vicinity of the sticker, which is less and less likely when p_{ass} increases. As a result, stickers remain associated for longer periods of time.

At last, the influence of the ion nature was analysed. The zinc ions are more labile than copper ions, which leads to less stable complexes with zinc. The metallo-supramolecular samples are thus softer when they contain zinc. However, if 2.5 equivalents of ions are added, the sample with zinc becomes harder and its relaxation becomes more difficult than the sample containing copper. This can be explained by the different behaviour of the two ions with respect to the aggregates. Their formation is very easy with copper ions, and they appear already at low ion density. However, with copper ions, there are always some bis-complexes that do not take part in the aggregates. With zinc ions, aggregates are more difficult to form, they are created only at very high ion density. But at such a high ion content, all the bis-complexes form aggregates, and they are therefore much more stable.

Finally, these investigations have provided a very interesting insight into the dynamics of these supramolecular polymers. However, it must be noted that a complete understanding of their behaviour has not been reached yet. This is due mainly to the different assumptions that have been made in order to simplify the problem for the modelling. For instance, the lifetime of the aggregates was supposed to be infinite, and the formation of mono-complexes was not taken into account. Moreover, coupling these results with those of other polymers based on the same metal-ligand interactions and additional measurements (other than only rheological ones) could help deepen our knowledge of these supramolecular polymers.

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