

Dynamics and Structure of Metallo-supramolecular Polymers Based on Short Telechelic Precursors

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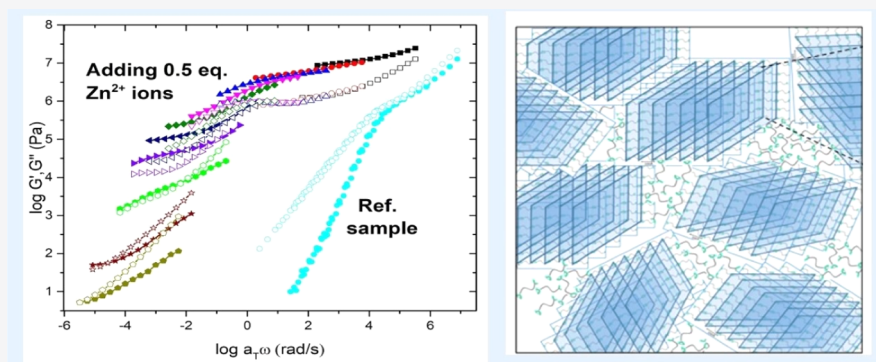
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ABSTRACT: We study the viscoelastic properties and the structure of a short hydrogenated polybutadiene (HPB) building block end-capped by terpyridine ligands. Adding metal ions in the sample leads to the formation of metallo-supramolecular junctions between the blocks, while the difference in polarity between the HPB chains and the metal complexes leads to the phase separation of the complexes into well-organized structures. By varying the nature and amount of metal ions added to the system, with the temperature, as well as with the sample thermal history, we show that it is possible to modulate these associations and obtain a very rich range of properties. In particular, while increasing the amount of metal ions leads to the sample reinforcement, it also causes a decrease of its melting temperature. This result is linked to the structure of the sample, which is characterized, in specific conditions, by the co-existence of two lamellar structures that we attribute to the existence of mono-complexes. The stability of these two lamellar structures is discussed based on the structural evolution during several heating and cooling ramps. We also show that the usually observed lamellar structure can be changed into a hexagonal structure if excess of metal ions are added to the sample.

1. INTRODUCTION

Thanks to their large tunability and capability to show reversible properties from rubber to liquid-like behavior in function of external stimuli, supramolecular polymers have demonstrated their important potential for developing new smart materials.^{1–14} Such transient assemblies are built from small or polymeric building blocks, linked together through reversible junctions such as π – π stacking,¹⁵ van der Waals or electrostatic interactions,^{16,17} hydrogen bonds,^{18–21} or metal–ligand coordination.^{22–30} Their dynamics depends thus directly on the strength and lifetime of these reversible junctions,^{22,30–32} on their density,^{20,21} as well as on their localization.⁹ Since the lifetime of the transient bonds can be further modified by temperature,^{29,30,33} pH,³⁴ or even light,³⁵ the properties of these supramolecular materials can easily be modulated to be suitable for specific applications such as self-healing materials,^{12,14,36} dampers, sensors, or drug delivery.^{12,37–39}

There are several ways to categorize the different supramolecular polymers. An important characteristic is related to the number of chain segments involved in an association.⁹ While some supramolecular junctions are directional and involve the association of a limited but controlled number of building blocks,⁸ others are not, for example, when specific moieties associate into, sometimes ill-defined, clusters.⁹ Common examples of the latter case are ionomers^{16,17,40,41} and self-assembled block copolymers in bulk or solutions.^{14,42,43} Ionomers create a transient network through electrostatic interactions between the ionic groups attached along the polymer chains. Furthermore, if the clusters formed

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by the association of several ions are large enough, they can form a new, hard, phase which eventually reinforces the sample and therefore has an important influence on the mechanical properties.^{14,24,44} Thus, the possible interaction between the clusters formed by the associated functional groups potentially leads to a new level of tunability, showing a large influence on the properties of the corresponding networks.

The well-defined reversible junctions of supramolecular polymers can also further aggregate to form clusters. Indeed, these recent past years, it was proven that in many of these systems, phase separation takes place due to the difference in polarity between the supramolecular junctions and the polymer backbone.^{9,14,24,28,45–56} This aggregation, which occurs if it is thermodynamically favored, leads to the formation of a hard phase containing the supramolecular motifs, which physically crosslinks the softer domains made of polymer chains. For example, several works have reported that short linear building blocks end-functionalized with stickers able to associate via H bonding lead to the formation of a network despite their linear architecture.^{46,47,53,54} This was clearly attributed to the association of the supramolecular junctions into larger structures. If the latter are small, their main role is to act as physical crosslinking points. However, if larger domains are formed by the association of the supramolecular junctions, they can significantly contribute to the mechanical properties of the material, increasing its elastic modulus. In specific cases, mainly with flexible chains bearing terminal groups leading to strong interactions, well-ordered structures can even be obtained.^{14,57} For example, Zha et al. have shown that polydimethylsiloxane chains end-functionalized with hydrogen-bonding ureidopyrimidinone units form lamellar to cylinder to body-centered cubic structures depending on the molar mass of the chains.⁵⁷ Similar results were obtained with linear building blocks associating through metal–ligand coordination.⁵⁸ In particular, as further detailed below, Rowan, Weder, and coworkers^{24,35,50,59} have shown that well-ordered structures are observed in supramolecular polymers made by assembling telechelic poly(ethylene-co-butylene) (PEB) macromonomers end-capped with 2,6-bis(1'-methylbenzimidazolyl) pyridine (Mebip) ligand through their complexation with transition metal ions or lanthanoid ions. Depending on the ions, counterions, and length of the macromonomers, crystallization of the metal–ligand complexes into lamellar or hexagonal morphologies was found with notable enhancement of the sample mechanical properties.²⁴ Nevertheless, the formation of such crystalline structure with Mebip ligands and metal ions is not systematically observed and depends on the nature of the polymer chains as well as on the position of the ligands alongside their backbone. For instance, it has been shown that adding metal ions in poly(*n*-butyl acrylate) linear chains with pendant Mebip ligands leads to phase separation of the complexes into separated or percolated clusters, but ordered structures were not obtained.^{48,52}

As for telechelic linear building blocks, the supramolecular moieties resulting from the assembly of mono-functional linear chains can also phase-separate into larger objects.⁹ Since the chains only have one functionalized extremity, the secondary aggregation of the supramolecular junctions does not allow the formation of a network but rather leads to the formation of micelle-like objects, from star-like polymers to colloidal particles.^{9,60,61} If the supramolecular junctions organize into well-defined stacks, it has been shown that supramolecular

polymer brushes can be obtained, with either lamellar or hexagonal cylinder morphologies, depending on the aggregation strength as well as on the mobility of the pending chains.^{10,62}

The examples described above support that it is possible to obtain a strong reversible network based on the short linear building blocks bearing directional binding motifs at their extremities. This requires the phase separation, aggregation, glass formation, or crystallization of the supramolecular junctions,²⁴ which strongly affect the sample properties. In a sense, supramolecular polymers are able to further associate into clusters, and these clusters have properties that can be compared to the ones of block copolymers, in which the hard blocks phase-separate into ill- or well-defined structures, causing a reversible polymer network. Thanks to the simplicity of the preparation of such supramolecular polymers and to the possibility of forming (ordered) secondary structures by the association of the supramolecular junctions, such systems have received growing attention these last years.^{9,14}

In the present work, we take advantage of this specific property of supramolecular polymers to propose a system which combines very high modulus and stability at room temperature (RT), which is still able to flow at high temperature. Metal–ligand complexes are used as supramolecular junctions. They are particularly interesting since their strength and lifetime can easily be modulated in a very broad range by changing the nature of the ligand or of the metal ions, leading to a large variety of behaviors.^{22–30} In order to favor the organization of the metal–ligand complexes into well-defined secondary structures at RT, the molar mass of the building blocks must be relatively short, the polarity of the chain backbone must be different from that of the complexes and the ligands must be located at the chain extremities.^{24,46,50,51,55}

As already mentioned, the association of metallo-supramolecular polymers based on short building blocks has been recently studied by Neumann et al. using PEB macromonomers end-capped by Mebip.²⁴ In their study, the authors show that the thermomechanical properties of these materials are largely influenced by both the ion and the counterion added to the system.^{24,56} While complexes based on lanthanoid ions phase-separate into hard domains which crystallize very poorly and lead to a glassy hard phase able to flow at 130 °C, complexes based on transition metal ions associate into a well-ordered and stable crystalline lamellar morphology. Large reinforcement of the sample was obtained, with the mechanical failure of the samples being directly linked to the melting of their semi-crystalline hard metal–ligand complex phase. However, with this sample, no order-to-disorder (ODT) transition could be observed up to very high temperatures (240 °C with Zn²⁺-based complexes) due to the elevated melting temperature of the crystals. This means that sample degradation was observed before its melting. As mentioned by the authors, semi-crystalline metallo-supramolecular polymers with similar mechanical properties but with a lower melting transition would be highly desirable to allow for self-healing and reversible melt-processing. In their work, Neumann et al. also showed that, while at RT complexes based on transition metal always form lamellar morphologies, it is possible to observe hexagonal morphologies if 1:3 metal: ligand coordination complexes are used, and in very specific conditions (depending on the nature of the metal ion, on the counterion, and on the polymer molar mass) and always below

170 a certain volume fraction of hard phase. While no clear trend
171 could be pointed out, the analogy with the behavior of block
172 copolymers did not seem to hold.

173 In the present work, we study the structure–property
174 relationships of a similar system, which is based on
175 hydrogenated polybutadiene (HPB) of 3 kg/mol end-
176 functionalized with terpyridine ligands in the presence of
177 transition metal salts. Compared to the macromonomer used
178 in ref 24, these samples have the great advantage to display a
179 lower melting temperature of the crystalline structures formed
180 from the phase separation of the transition metal complexes,
181 which allows us to approach their full relaxation as well as their
182 ODT within the experimental window ($T < 180\text{ }^{\circ}\text{C}$) and
183 potentially makes them healable, re-usable, and processable.
184 Furthermore, these samples can be properly annealed and
185 equilibrated, which allows us to study the reversibility of the
186 crystalline structures which are formed. A last benefit of the
187 system proposed here, in comparison to the PEB macro-
188 monomer end-capped by the Mebip ligand, is the fact that,
189 before adding metal salts, the telechelic building blocks are
190 flowing in a similar way as the unfunctionalized precursor
191 macromonomers. This ensures that, at RT, the terpyridine
192 ligands which are not involved in complexes do not phase-
193 separate and therefore do not participate in the phase-
194 separated network. Thus, a clear signature of the uncomplexed
195 chain-ends can be achieved.

196 Our objective is to investigate and understand how the
197 structure and thermomechanical properties of these function-
198 alized building blocks are affected by various parameters
199 including temperature, the nature of the metal ions, and the
200 metal/ligand ratio in the system. Based on previous research
201 studies,^{30,33} it is expected that the latter parameter has a large
202 impact on the sample dynamics. When ions are added in a
203 lower amount than the stoichiometric 1:2 (metal/ligand) ratio,
204 it is anticipated that the presence of many dangling ends (free
205 ligands) causes a lower volume fraction of the crystalline hard
206 phase. Adding ions above the stoichiometric ratio should affect
207 the way the complexes associate and therefore the lifetime of
208 these crystalline structures. In order to estimate the length and
209 corresponding relaxation time of the dangling ends, a statistical
210 approach combined with a tube-based model was developed to
211 predict the relaxation of entangled polymer melts.^{63–66} We
212 show that by playing with the three abovementioned
213 parameters, a very rich behavior is obtained. In particular,
214 lamellar or hexagonal morphologies can be obtained for the
215 same sample, depending on its thermal equilibration, with
216 important consequences on the viscoelastic properties.

2. EXPERIMENTAL SECTION

217 **2.1. Materials.** Hydroxyl-terminated HPB with a number-average
218 molar mass of 3.1 kg/mol and a molar mass dispersity of 1.3 (Krasol
219 HLBH-P3000) is used as building block. It is a kind donation of Cray
220 Valley and was used as received. Bis(trifluoromethanesulfonyl)imide
221 (96% purity) and zinc(II) bis(trifluoromethanesulfonyl)imide (98%
222 purity) were used as received from commercial sources. The synthesis
223 of the telechelic terpyridine-terminated HPB (HPB-(tpy)₂) is
224 described in the Supporting Information.

225 **2.1.1. Preparation of Metallo-supramolecular Polymers.** Samples
226 were prepared by dissolving a given amount of HPB-(tpy)₂ (100 mg)
227 in THF (800 μL). The desired amount of metal salt was dissolved in a
228 mixture of methanol (100 μL) and THF (100 μL), and the clear
229 metal solution was added dropwise to the polymer solution and
230 stirred at RT for 1 h. The solvent was evaporated under vacuum to
231 obtain the metallo-supramolecular polymers. To this end, the solvent

was first removed in a rotary evaporator for 20 min at 40 $^{\circ}\text{C}$. Then,
we used a vacuum pump for removing the possible remaining trace of
solvent for 24 h.

Table 1 presents the detailed information of all the metallo-
supramolecular samples. Two different metal ions, Zn^{2+} and Cu^{2+} ,

Table 1. Description of the Different Samples

name	summary name	ion content (equivalent with respect to the tpy ligand)	T_g [$^{\circ}\text{C}$]
ref. sample	PB		−53.3
terpyridine-terminated HPB	Tpy-PB		−47.2
	Zn-0.125 equiv	0.125	−48.9
	Zn-0.25 equiv	0.25	−50.4
	Zn-0.5 equiv	0.5 (stoichiometric)	−51.2
	Zn-1 equiv	1	−52.2
	Cu-0.125 equiv	0.125	−48.8
	Cu-0.25 equiv	0.25	−50.7
	Cu-0.5 equiv	0.5 (stoichiometric)	−51.8
	Cu-1 equiv	1	−50.5

were used to create the complexes. The stoichiometric amount of ions
corresponds to 0.5 equiv with respect to the terpyridine ligand, that is,
to a 1:2 metal/ligand ratio.

2.2. Instrumentation. **2.2.1. Rheological Characterization.** The
viscoelastic properties of all samples were investigated by oscillatory
shear measurement using an MCR 301 (Anton Paar, Germany)
rheometer with a parallel plate geometry of 8 mm diameter. The
temperature was controlled using a convection oven operating under
nitrogen. Data were measured between −20 and 140 $^{\circ}\text{C}$. No-slip
problem was observed due to the good adhesion of the HPB-based
polymers to the surface of the steel geometry. At each temperature, an
amplitude sweep test was performed in order to determine the linear
viscoelastic regime. A deformation amplitude of 1% was chosen for all
the frequency sweep measurements. In order to obtain reproducible
results, the samples were loaded at 150 $^{\circ}\text{C}$ and a time sweep was
performed at 140 $^{\circ}\text{C}$ over 2 h, ensuring a stable viscoelastic response.
Then, frequency sweeps tests were performed every 20 $^{\circ}\text{C}$ down to
−20 $^{\circ}\text{C}$. At each of these temperatures, a time sweep was performed
until the storage and loss moduli were constant. For checking the
reproducibility of measurements, all measurements were repeated
from −20 to 140 $^{\circ}\text{C}$. A good overlap was found (see the Supporting
Information, Figure S3).

2.2.2. DSC Characterization. DSC thermograms were recorded on
a Mettler Toledo DSC821e from (Switzerland) equipped with STARe
software. Calibration was performed using three standards, covering
the wide temperature range required for measuring the HPBs (−85 to
180 $^{\circ}\text{C}$). The polymer samples were dried overnight in a vacuum
oven at 60 $^{\circ}\text{C}$ and subsequently measured at 10 $^{\circ}\text{C min}^{-1}$ both for
cooling and heating. DSC data are shown in the Supporting
Information (Figure S2). Only the first heating curve of the samples
with 0.5 or 1 equiv Zn shows melting peaks. This is in line with the
results from SAXS, which show that structures need time to develop.
The data were used to confirm the melting temperature found by
SAXS measurements.

2.2.3. X-ray Scattering. X-ray scattering was performed using the
GANESHA-SAXS/WAXS instrument from SAXSLAB/Xenocs (Den-
mark/France) installed at the Niels Bohr Institute. The instrument is
equipped with a GeniX 3D Cu microfocus-sealed X-ray tube with
FOX3D multilayer optics (Xenocs, France) and a two-dimensional
300k Pilatus detector from Dectris (Switzerland). Measurements were
performed with a 2 “pinhole” collimated beam using scatterless slits.
The two-dimensional isotropic scattering spectra were azimuthally
averaged, giving the scattering function versus the scattering vector q

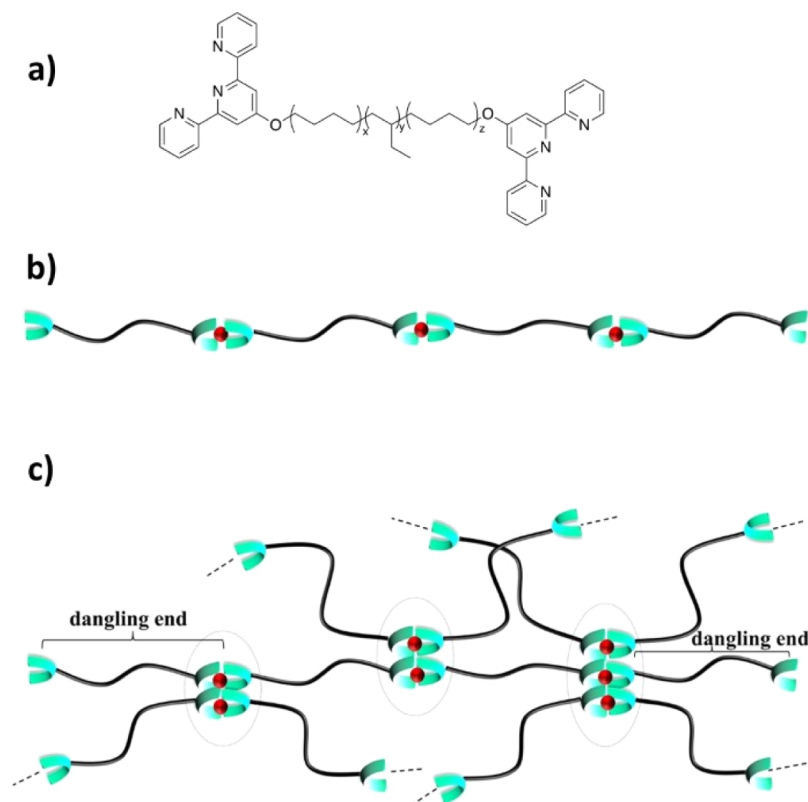


Figure 1. (a) Chemical structure of the terpyridine-functionalized telechelic polymer. Schematic representation of a linear assembly (represented by the thick curves) created from the association of the chains via the formation of metal–ligand complexes. (b) If the latter do not phase-separate, the linear assembly can relax by reptation or by scission. (c) Otherwise, only the dangling ends (uncomplexed terpyridines) are able to relax.

defined by $q = 4\pi/\lambda \sin(\theta)$, where $\lambda = 1.54 \text{ \AA}$ is the X-ray wavelength and θ half of the scattering angle.

With the given SAXS/WAXS setup applied in this study, we obtained a q -range from 0.007 to $0.25 \text{ \AA}^{-1}$ within a single measurement. The SAXS/WAXS instrument is designed such that the X-ray beam and sample are under vacuum. The samples were all loaded in vacuum-tight sample holders with a 1 mm flight path and equipped with two $57 \text{ }\mu\text{m}$ -thick mica windows transparent to the X-ray. The sample holders were mounted on a temperature-controlled sample stage (Linkam Scientific Instrument, LNP95), and diffraction measurements were performed within the temperature range from -35 to $180 \text{ }^\circ\text{C}$ in steps of 5° . Each step required 10 min of equilibration and 10 min of acquisition time.

3. MODELING

In Section 4, the viscoelastic data are analyzed with our tube-based model or with a Rouse model.^{63–66} While such models cannot be used to predict the viscoelastic properties of polymer chains associating into large, well-ordered, structures, they are suitable for describing the rheological behavior of non-associating chains or the behavior of supramolecular chains associating into small, uncorrelated clusters. Since the precursor is very short and unentangled, it is expected that its viscoelastic behavior is well captured by a Rouse model. The corresponding relaxation modulus, $G(t)$, is described as

$$G_R(t) = \frac{\rho RT}{M_w} \sum_{p=1}^n \exp\left(-\frac{2p^2 t}{\tau_R(M_w)}\right) \quad (1)$$

where τ_R is the Rouse time of the chains, n is its number of Kuhn segments, R is the gas constant, and ρ is the density, which is equal to 0.9 g/cm^3 at $20 \text{ }^\circ\text{C}$.⁶³ The prefactor in front

of the sum is also equal to $5M_e/4MG_N^0$, where G_N^0 represents the entangled plateau modulus and is fixed, here, as equal to 1.2 MPa .⁶⁴

When metal ions are added into the system, larger supramolecular assemblies are formed through the formation of metal/ligand bis-complexes. If there is no phase separation (see Figure 1b), the functionalized reference sample self-assembles into linear supramolecular assemblies, which relax as a long linear chain made of several building blocks, that is, by reptation if the complexes have a long lifetime, or by a combination of reptation and chain scission if the lifetime of the complexes is short, as it has been described by Cates.⁶⁷ On the other hand, if the complexes can phase-separate and form stable (i.e., with very long lifetime) hard domains, only the unentangled free chains will be able to relax at a short time, as well as the dangling ends (uncomplexed terpyridines). The latter relaxes in a similar way as the branches of a star molecule, that is, by retraction (see Figure 1c).

The viscoelastic properties corresponding to both situations can be modeled with our tube-based TMA model.^{63–65} To this end, we first build a large ensemble of supramolecular linear assemblies formed through the formation of metal–ligand complexes (see Figure 1a). The molar mass distribution of these linear assemblies can be determined statistically based on the probability p_{ass} of a building block to link to another building block via metal–ligand associations. Using Flory assumptions, we have^{33,68,69}

$$w_{N,k} = p_{\text{ass}}^{k-1} (1 - p_{\text{ass}}) \quad (2)$$

$$w_{w,k} = \frac{k w_N}{\sum k w_N} \quad (3)$$

where $w_{N,k}$ and $w_{w,k}$ are the number and weight fractions of linear assemblies containing k building blocks, respectively. The probability p_{ass} that a selected building block associates with another one directly depends on the metal/ligand ratio in the system and is fixed to 0.25 and 0.5 equiv of ions for 1 equiv of ligand for samples **Zn-0.125 equiv** and **Zn-0.25 equiv**, respectively. Figure 2 shows the molar mass distributions

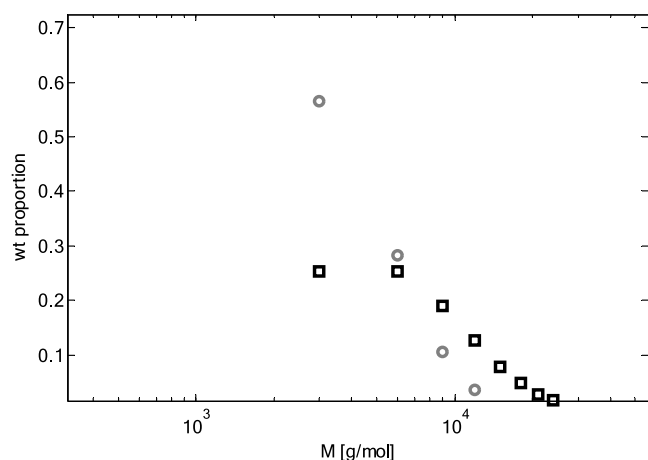


Figure 2. Molar mass distribution of the linear assemblies created from **Zn-0.125 equiv** (in gray) and **Zn-0.25 equiv** (in black) Zn(II) ions.

determined based on eqs 3 and 4 for these two samples. With 0.125 equiv of Zn(II), it is seen that around 85 wt % of the assemblies only contain 1 or 2 building blocks, while there is nearly no linear assembly which contains four building blocks or more. In the case of 0.25 equiv of Zn(II), the assemblies are longer; however, 50 wt % of the assemblies also contain only one or two building blocks. Since the free terpyridines do not associate (see Section 4.1), it is therefore expected that a large fraction of the sample, that is, all the unassociated building blocks and the dangling ends (uncomplexed terpyridines), relaxes at a short time and does not contribute to the elastic plateau.

These molecular weight distributions (MWDs) are then used to model the viscoelastic data based on two different scenarios:

First, we consider that the complexes in the linear assemblies do not phase-separate, and consequently, the linear assemblies relax by reptation, similar to long linear chains (see Figure 1a). In such case, the relaxation modulus, $G(t)$, can be approximated as⁶³

$$G(t) = G_{\text{Rouse}}(t) + G_N^0 \left(\sum_k w_{w,k} \varphi(M_{w,k}, t) \right)^2 \quad (4)$$

$$\varphi(M_{w,k}, t) = \sum_{x=1/100}^{x=100/100} p_{\text{rept}}(M_{w,k}, x, t) p_{\text{fluc}}(M_{w,k}, x, t) \Delta x \quad (5)$$

where $G_{\text{Rouse}}(t)$ accounts for the high-frequency Rouse relaxation, $\varphi(M_{w,k}, t)$ represents the fraction of initial tube segments around a chain of mass $M_{w,k}$, which are still existing at time t , x is the normalized position of a chain segment from 0 at one extremity of the linear assembly to 1 in its middle, $p_{\text{rept}}(M_{w,k}, x, t)$ is the probability that a chain segment localized at a position x is not relaxed by reptation at time t , and $p_{\text{fluc}}(M_{w,k}, x, t)$ is the probability that a chain segment localized at a position x is not relaxed by fluctuations or chain retraction at time t . More details about this model can be found in refs.^{63,65} It must be noted that there is no free parameter since the three material parameters of the model, namely, G_N^0 , M_e , and τ_e , have been fixed in previous works and the association probability, p_{ass} , is fixed based on the metal/ligand ratio of the sample.

As the second scenario, we consider that all the bis-complexes in the linear assemblies phase-separate and act as crosslinking points, that is, prevent the chain segments localized between two complexes to relax and disentangle. While in the real case, it is not expected that all complexes phase-separate, considering that this scenario gives us an indication about the maximum elastic modulus that can be reached if the phase-separated complexes play the role of physical crosslinking points. In such case, the relaxation modulus $G(t)$ mainly depends on two parameters: the fraction of chain segments trapped within the network built from the

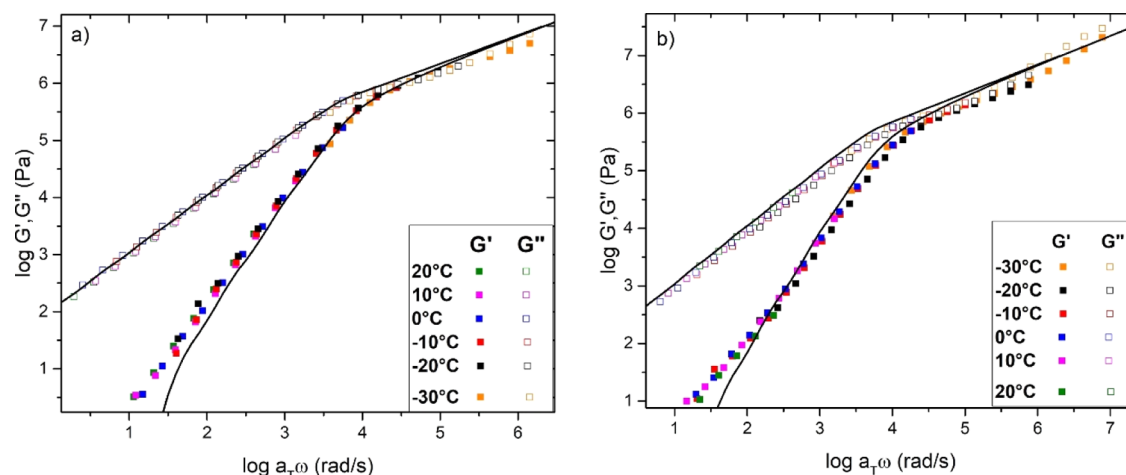


Figure 3. Storage and loss moduli of the reference sample (HPB) before (a) and after (b) its functionalization with terpyridine end groups at iso- T_g conditions with $(T_{\text{ref}} - T_g) = 73.3$ °C. The continuous curves correspond to the predictions obtained with the Rouse model.

physical crosslinking that arises upon phase separation, v_{trapped} , and the fraction of chain segments able to relax, $v_{\text{free}} = 1 - v_{\text{trapped}}$, which includes the dangling ends (uncomplexed terpyridines, see Figure 1c) as well as the free building blocks. Their values are directly determined from the statistical MWD of the samples. Indeed, since all the bis-complexes are assumed to participate in the phase-separated domains, only the two outer building blocks of the linear assemblies contribute to v_{free} , while the middle blocks are counted in the fraction of trapped segments, v_{trapped} . In the model, we consider that the chain segments trapped between two hard domains cannot relax. Furthermore, the level of the rubbery plateau must be determined by accounting for both the crosslinking points (or nano-domains) and the trapped entanglements. Since the molar mass of the polymer segment which bridges these phase-separated domains is considered to be equal to the molar mass of one building block, M_{ref} , we have

$$G(t) = G_{\text{Rouse}}(t) + G_{\text{N}}^0(v_{\text{trapped}} + v_{\text{free}}\varphi_{\text{free}}(t))^2 + \frac{\rho RT}{M_{\text{ref}}}v_{\text{trapped}} \quad (6)$$

where $\varphi_{\text{free}}(t)$ accounts for the relaxation of the dangling segments. In eq 6, the lifetime of complexes' association has been considered as infinite.

4. RESULTS AND DISCUSSION

4.1. Reference Sample—Influence of the Terpyridine Ligand. We first study the structure and the viscoelastic behavior of the reference linear HPB end-functionalized with terpyridine ligands and compare its properties with the ones of the pure, unfunctionalized macromonomer. No structure or phase-separated domains are observed from the SAXS data of the reference sample. In order to determine their viscoelastic behavior, a series of frequency sweeps have been measured for the two samples in the temperature range from 20 to -40 °C in the linear viscoelastic regime. Figure 3a shows the master curve of the unfunctionalized sample, which has been built based on the WLF equation⁷⁰

$$\log a_T = \frac{-c_1(T - T_{\text{ref}})}{c_2 + (T - T_{\text{ref}})} \quad (7)$$

with $c_1 = 20.33$ and $c_2 = 174.3$ °C at a reference temperature T_{ref} of 20 °C.

It is seen that the storage modulus does not show any plateau and reaches the terminal regime at rather high frequency. This is consistent with the fact that the building blocks are very short (with an average molar mass in weight, M_{w} , of 4 kg/mol) and are mostly unentangled if we consider that the average molar mass between two entanglements, M_{e} , is equal to 1650 g/mol.⁶⁴

These data are well modeled with the Rouse model (see eq 1), if we consider that the Rouse time of the chains, τ_{R} , is equal to 2.25×10^{-4} s (or equivalently, the Rouse time of an entanglement segment, τ_{e} , is equal to 3.5×10^{-5} s) at 20 °C.

The viscoelastic data of the sample end-functionalized with terpyridine groups are shown in Figure 3b. A master curve has also been built based on the same c_1 and c_2 values as for the unfunctionalized sample, but at another reference temperature, $T_{\text{ref}} = 26.1$ °C (see eq 1). Indeed, the functionalized sample is characterized by a slightly higher glass-transition temperature (see Table 1), which must be taken into account in the

construction of the master curve, to ensure iso- T_{g} conditions, that is, that $(T_{\text{ref}} - T_{\text{g}})$ is constant.⁷¹ As it can be observed, very similar curves are found, which indicates that apart from a difference in T_{g} , the terpyridine ligand does not affect the relaxation modes of the chains. This result differs from the metallo-supramolecular polymers based on Mebip ligands,²⁴ which phase-separate and crystallize even if no ions are added to the sample. As mentioned in the Introduction section, the fact that the uncomplexed terpyridine groups do not phase-separate ensures that the formation of a non-relaxing sample can only be due to the phase separation of the metal–ligand complexes, the dangling ends (uncomplexed ligand) of the supramolecular assemblies, and the free precursor chains being always able to move and relax.⁶³

In the following sub-section, we investigate the structure and dynamics of systems containing different metal/ligand ratios from 0.125 to 1 equiv of Zn^{2+} per equiv of terpyridine ligand, that is, from a sub-stoichiometric ratio to excess of Zn^{2+} .

4.2. Structure and Viscoelastic Properties in the Presence of Different Zn^{2+} /Ligand Ratios. 4.2.1. Structure and Viscoelastic Properties of Sample Zn-0.125 equiv.

In order to determine the structure of samples Zn-0.125 equiv, SAXS and WAXS measurements were performed. Figure 4a shows the data obtained for sample Zn-0.125 equiv during the first heating ramp, from -35 °C to high temperature (180 °C). The representative data obtained during the cooling cycle can be seen in Figure 4b.

It is observed that this sample shows major changes during the initial heating. The data at low temperatures show some scattering at the smallest angles and a broad peak centered around $0.028 \text{ \AA}^{-1}$, reflecting some correlated domain structure, but otherwise a rather smooth scattering function. At temperatures close to 90 °C, the q -value of the peak position decreases markedly and gets below the beam-stop near 140 °C. Additional small-angle scattering observed at q -values below roughly $q = 0.025 \text{ \AA}^{-1}$ is observed in the 90–110 °C temperature range, indicating some kind of clustering/inhomogeneity. At temperatures of the order of 130–140 °C, the dominating scattering develops into equidistant correlation peaks, indicating the formation of a lamellar order characterized by a first order peak value of $q = 0.06 \text{ \AA}^{-1}$, corresponding to a lamellar periodicity of 103 Å. While it is still present at 180 °C, its intensity decreases, suggesting that the sample is approaching its disordered phase. Upon cooling the sample back to ambient temperature, this well-defined lamellar structure remains unchanged, within experimental accuracy (see Figure 4b). The original $0.028 \text{ \AA}^{-1}$ peak does not reappear within hours.

These results can be understood as follows. Since the sample has been prepared in solution, it is expected that before any heat treatment, the supramolecular metal–ligand junctions are formed; however, the secondary structure which arises from the phase separation (or crystallization) of the metal–ligand complexes is not yet present. Indeed, this secondary structure only appears in the bulk state and takes time to develop. Since the removal of solvent is a rather fast process, the sample before heating is most probably quenched in a disordered state, which does not correspond to its equilibrium state. Therefore, the first heating curve is strongly dependent on the sample preparation and cannot be reproduced once the sample has been annealed at high temperature. It also suggests that there are some long-time dynamic processes that stabilize the sample into a final stable state, which take several weeks to occur at

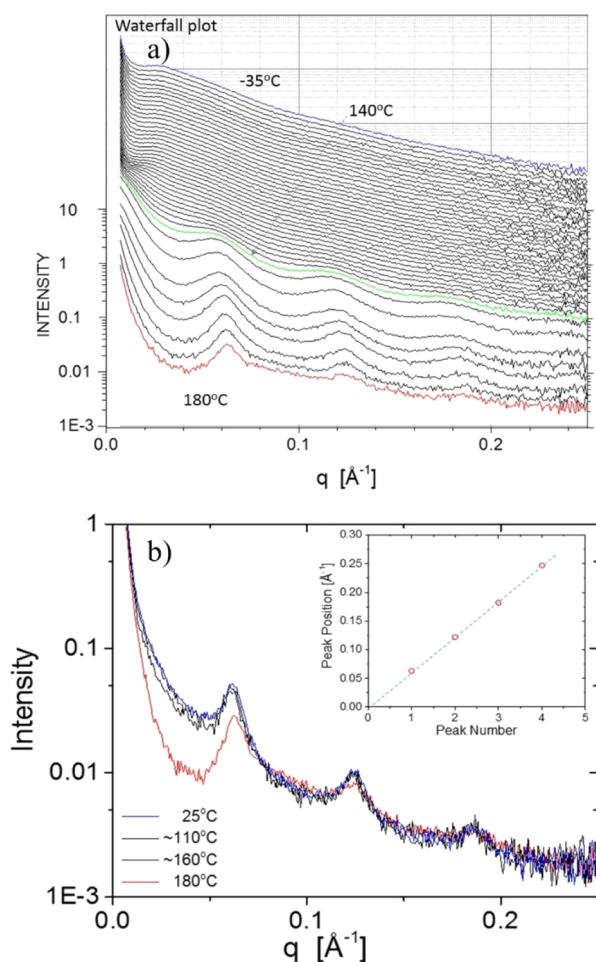


Figure 4. SAXS data of sample **Zn-0.125 equiv**: (a) first heating ramp from $-35\text{ }^{\circ}\text{C}$ to high temperature ($180\text{ }^{\circ}\text{C}$). To better visualize the data, they are shown in a “waterfall” plot, that is, separated proportionally to temperature. (b) SAXS data as obtained during the cooling back to RT. The inset shows the peak position vs the peak number, proving a lamellar structure.

RT. As further discussed below, indications of such long-time processes have been observed in the X-ray studies performed over months on the **Zn-0.5 equiv** sample. Below $90\text{ }^{\circ}\text{C}$, the association dynamics of the aggregates is too slow to allow them to break and reorganize into a more stable structure unless the studies are performed over months.

As already mentioned, the long period of the lamellar structure is of the order of $100\text{ }\text{\AA}$, which should be compared to the two characteristic lengths of the 3 kDa HPB polymer: the maximum end-to-end distance of the linear chain is $260\text{ }\text{\AA}$, while its radius of gyration assuming a random coil conformation is $21\text{ }\text{\AA}$. This shows that the conformation of the polymer chains is far from a random coil configuration. It must be noted here that we cannot fully exclude the possibility to have metal–ligand bis-complexes which are not involved in the lamellae and which would lead to two or more associated building blocks between two lamellae. However, this situation does not seem probable since the metal ions are in sub-stoichiometric amount (more specifically, its amount is 4 times smaller than the stoichiometric amount). Therefore, the probability that a building block has its two extremities involved in bis-complexes, one belonging to a lamella and the other one belonging to the unassociated bis-complex, is very low. In parallel, the rheological properties of the sample have been measured after its annealing at high temperature. The results are shown in Figure 5a. Master curves have been built based on the same shift factors used for the reference samples and under iso- T_g conditions. In such a way, the temperature dependence of the segmental dynamics of the chains is considered, while the influence of temperature on the association and phase separation dynamics is not.

A first relaxation takes place at high frequency (at around 10^4 rad/s), right after the Rouse regime. This relaxation process is only slightly slower than the relaxation of the reference HPB (Figure 3) and does not lead to any thermorheological complexity. This suggests that the dissociation/association dynamics of the complexes is not governing this first decrease of elasticity, which rather corresponds to the relaxation of dangling ends and of linear chains, which are largely present in this sample (see Section 3). Then, a long

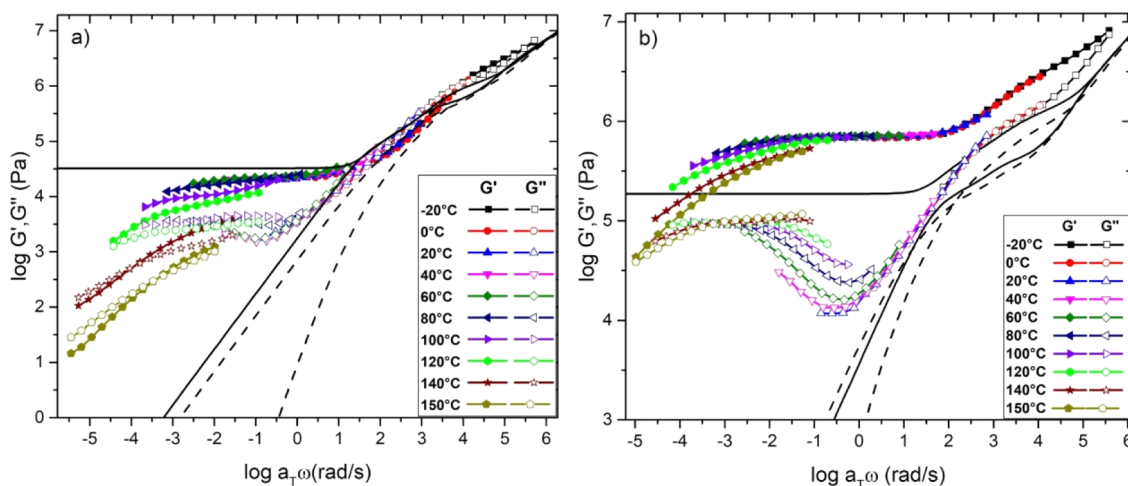


Figure 5. Storage and loss moduli of the samples **Zn-0.125 equiv** (a) and **Zn-0.25 equiv** (b) of ions per equiv of ligands. The master curves are shown at the iso- T_g condition with $(T_{\text{ref}} - T_g) = 73.3\text{ }^{\circ}\text{C}$. Data have been measured between -20 and $150\text{ }^{\circ}\text{C}$. The curves correspond to the predictions obtained by considering the relaxation of linear assemblies, assuming (dashed curves) or not (continuous curves) that all the complexes are acting as crosslinking points.

elastic plateau is observed, indicating that the sample can only partially relax at short time. This plateau is too long to be attributed to the delayed reptation time of the linear assemblies and is rather due to the phase separation of the metal–ligand complexes into ordered nanoscale structures, which act as physical crosslinking points for the building blocks. This is also confirmed by the thermo–rheological complex behavior observed at low frequency for temperatures higher than 100 °C. While below this temperature, the lifetime of the complex association is rather long and can be considered as infinite within the experimental frequency window, it becomes shorter at high temperature and the sample starts to relax.^{29,30} This result is consistent with the X-ray data, which show that below 90 °C, the association dynamics of the aggregates is very slow. The terminal crossover between the storage and loss moduli is observed above 130 °C, a temperature at which the sample displays a liquid-like behavior. However, the terminal flow regime, characterized by a $G' \propto \omega^2$ and $G'' \propto \omega$, is not fully reached at 150 °C, in agreement with X-ray studies showing indications of lamellar structure even at the highest temperature measured (~180 °C), temperature at which the sample is approaching its disordered phase.

On these viscoelastic curves, it is also observed that the level of the rubbery plateau remains lower than the entanglement plateau of the entangled HPB polymer chains, which has been fixed to 1.2 MPa.⁶³ Therefore, while it is clear from both SAXS and rheological data that the complexes phase-separate and organize into lamellar structures acting as physical crosslinking points along the linear assemblies, it does not seem that these ordered structures are able to reinforce the samples and contribute to the sample elasticity. In order to quantitatively address this question, the data are analyzed with the help of our tube-based TMA model (see Section 3).^{63–65} The viscoelastic curves predicted by assuming no phase separation of the bis-complexes are presented in Figure 5 as dashed curves, while the curves predicted by assuming that all the bis-complexes phase-separate into domains which act as crosslinking points are represented by the continuous curves. While the first scenario does not allow capturing the long terminal relaxation time found experimentally, the second assumption leads to a good description of the data (see Figure 5a). Only the final relaxation is not reproduced since the lifetime of the complex domains has been considered as infinite in the model, which is not the real case. This good agreement between theoretical and experimental data confirms that the complexes phase-separate into nano-domains; however, the proportion of the latter appears to be too low to observe a significant reinforcement of the sample, which would have led to a large increase of the level of the rubbery plateau. If the temperature is increased above 100 °C, the rubbery plateau decreases, which indicates that some complexes dissociate from the aggregates, allowing a larger fraction of the sample to relax.

4.2.2. Structure and Viscoelastic Properties of Sample Zn-0.25 equiv. The X-ray data of sample Zn-0.25 equiv are shown in Figure 6.

Before annealing, rather broad peaks are observed, indicating a lack of long-range order. Still, the periodic peaks indicate a lamellar order with a 100 Å period. During the initial heating, the peaks sharpen above approximately 120 °C, and the lamellar structure becomes even more pronounced as observed by the sharpening of the Bragg peaks. During the heating cycle, an additional Bragg peak appears, emerging at low- q and shifting toward a higher q -value with increasing temperature.

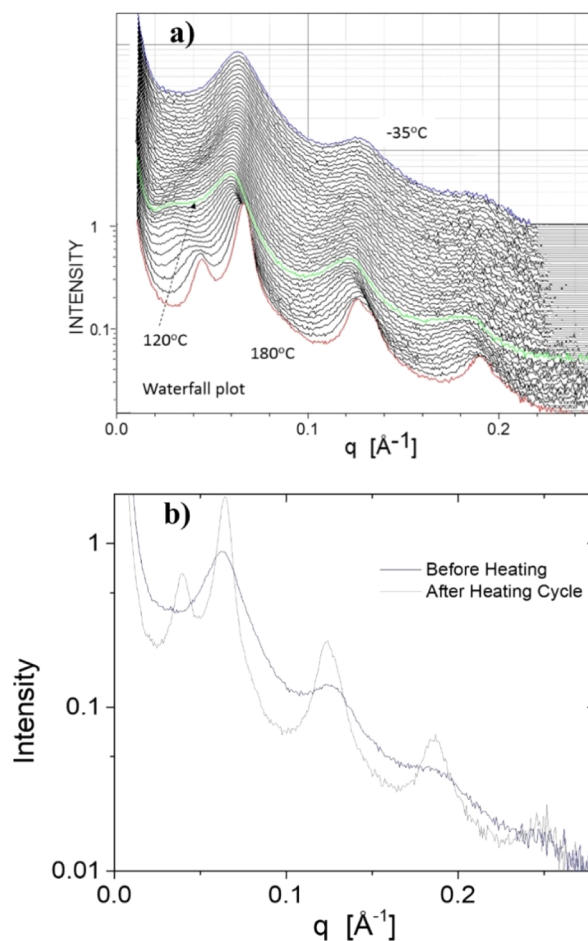


Figure 6. SAXS data of sample Zn-0.25 equiv: (a) first heating ramp from −35 °C to high temperature (180 °C) (to better visualize the data, they are shown in the “waterfall” plot, that is, separated proportionally to temperature). (b) Comparison between the data measured at RT before and after the heating cycle and a cooling cycle back to RT.

At high temperature, this additional 0.038 Å^{−1} peak corresponds to a length scale of 162 Å. It could reflect the presence of another kind of domain structure, which does not participate in the lamellar structure. As discussed in Sections 4.2.3 and 4.2.4, related additional structural features are observed in the Zn-0.5 equiv and Zn-1.0 equiv samples, indicating that this is not due to non-homogenous samples, but it is rather a true characteristic for these systems.

The Bragg peak characteristics remain to the highest temperatures, indicating that the order–disorder transition is not yet reached. On cooling back to RT, the peaks regain their sharp characteristics, attributed to the regained long-range crystalline order (Figure 6b). Both the lamellar peaks and the additional peak remain at ambient temperature. This history dependence is thus equivalent to that of the Zn-0.125 equiv sample discussed in Section 4.2.1, as well as those of the Zn-0.5 equiv and Zn-1.00 equiv samples discussed below. It is observed that the lamellar structure after annealing is much better defined than that before annealing, as seen with the significantly narrower peaks, but the lamellar length scale is unchanged (100 Å).

Compared to sample Zn-0.125 equiv, sample Zn-0.25 equiv shows similar properties; however, the intensity of its Bragg peaks is more pronounced, which may indicate a larger degree

of crystallinity or changes in the crystalline texture. As proposed in Figure 7, the lamellar domains seem quite similar

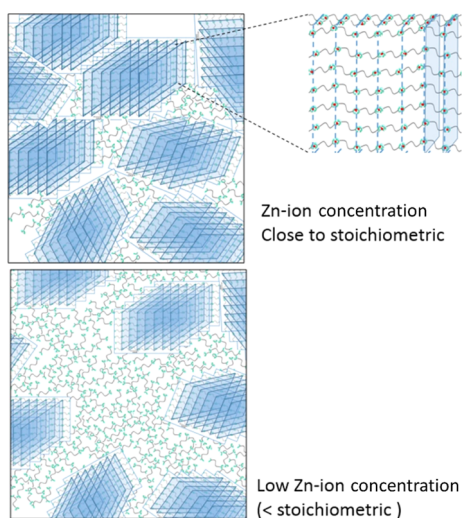


Figure 7. Cartoon representing the structure of samples containing Zn^{2+} ions in different metal/ligand ratios, either close to the stoichiometric amount or lower. Note that the lamellar periodicity is approximately the same, and it is the fraction of the amorphous domains between the ordered domains and consequently their coherence, which differs.

in both samples and represent the bulk of the sample. However, these domains are likely isolated, being separated by the amorphous phase composed of the dangling ends (due to uncomplexed ligands), which do not participate in the lamellae. Since the fraction of dangling ends decreases with the increasing amount of ions from 0.125 to 0.25 equiv of ion per ligand, the coherence of the lamellar domains is expected to increase, as it is observed. This picture is also in agreement with the higher elasticity observed in the viscoelastic data of sample **Zn-0.25 equiv** (see Figure 5b). Indeed, for sample **Zn-0.25 equiv**, the modulus predicted by considering that all the complexes are trapped into hard domains and act as crosslinking points is much lower than the one measured experimentally. Despite the model considers the extreme case of 100% phase-separated bis-complexes, the experimental data cannot be captured. Even at high frequency, in the Rouse domain, a discrepancy is already visible. From this result, we can conclude that the origin of the second plateau cannot be explained by only counting the sub-chains elastically active between the phase-separated domains; the complexes are associated into larger structures, which also play a role in the sample elasticity. The volume fraction of the hard phase created from the association of the complexes seems to be important enough, compared to sample **Zn-0.125 equiv**, to reinforce the sample.^{9,14} The lamellar structures start to melt at 150 °C (at which the crossover of G' and G'' is observed), giving some room for re-using or re-processing the samples.^{9,24}

To conclude this section, the X-ray study has demonstrated that the **Zn-0.25 equiv** sample organizes into domains of ordered lamellar structure, which restricts chain dynamics, in agreement with the viscoelastic data. The coherence of the lamellar domains increases with increasing amount of ions, which eventually leads to the reinforcement of the sample, characterized by an enhanced elasticity.

4.2.3. Structure and Viscoelastic Properties of Sample Zn-0.5 equiv. Then, the structure of sample **Zn-0.5 equiv** and its evolution with temperature is analyzed. This sample, which contains a stoichiometric amount of Zn^{2+} ions, was measured in some more detail to learn about the influence of thermal history. The most important results are shown in Figure 8. The

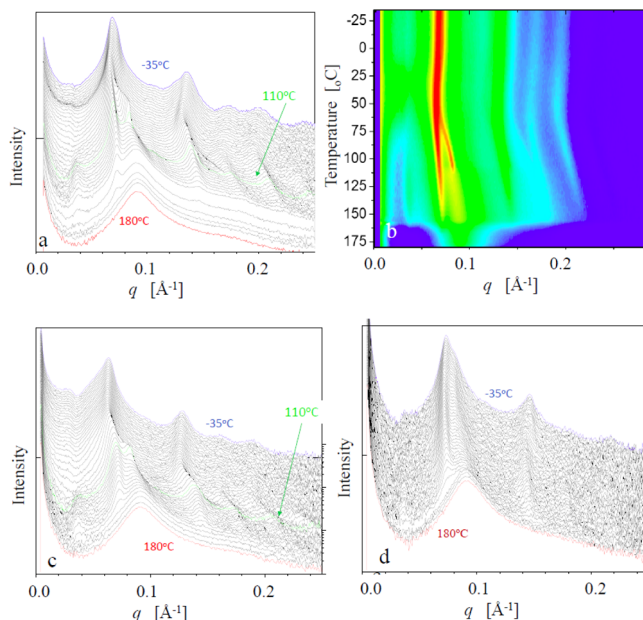


Figure 8. X-ray scattering data of sample **Zn-0.5 equiv** and its evolution with temperature. (a,b) SAXS data obtained during the heating cycle after initial short annealing at 160 °C (a) in a waterfall plot and (b) in a contour diagram. (c) Second heating cycle after 4 months of storage at ambient temperature. (d) Data as obtained during controlled cooling (the same results obtained during fast cooling after the first heating cycle).

sample was initially annealed for a short time (about 20 min) at 160 °C (see the Supporting Information, Figure S4), then cooled to −35 °C, and successively heated slowly (in steps of 5 °C per 10 min) to 180 °C (see Figure 8a,b). After heating, the sample was cooled quickly to ambient temperature (see the Supporting Information, Figure S5). After about 4 months of storage at RT, the sample was cooled to −35 °C, heated slowly with the same rate as before (see Figure 8c), and successively cooled slowly with the same stepwise change in temperature (see Figure 8d). It is observed that the structural properties during this second heating show results very similar to those originally observed, proving reproducibility but with very extended relaxation times (months). The slow cooling cycle showed similar results as the initial fast cooling. Finally, the **Zn-0.5 equiv** sample was re-heated and re-cooled once more, according to the same procedure (see the Supporting Information, Figure S6). This last heating–cooling cycle showed results similar to the ones obtained previously. It is interesting to note that the initial short-time heating to 160 °C did not make many changes beyond yielding more coherent structures as indicated by the sharper Bragg peaks. The structural developments of the **Zn-0.5 equiv** sample are discussed in more detail below.

4.2.3.1. Sample Annealing. Before any heat treatment, the sample shows broad Bragg peaks with a ratio of 1:2:3 and with the first order peak at 0.068 Å^{−1}, indicating relatively small domains of lamellar ordered mesophase with a lattice spacing

of 92 Å. During the initial short annealing (see Figure S4), the q -value of the Bragg peaks increases and that of the higher-order peaks decreases, showing a dominating amorphous structure with $q = 0.09 \text{ Å}^{-1}$ at 160 °C, but with new small, but sharp, Bragg peaks developing at 0.075 and 0.15 Å⁻¹ proving mesoscale ordering, likely 84 Å lamellar. After quenching back to RT, the original dominating 0.068 Å⁻¹ lamellar structure is regained, but now with sharper Bragg peaks, and an additional weaker peak at 0.034 Å⁻¹ corresponding to the lattice spacing equal to 184 Å (see the low-temperature data at Figure 8a). The dominating 92 Å lattice spacing (at ambient temperature) is equivalent to the characteristic lattice spacing of the samples discussed above, and likely a primary length scale, indicating that the weaker 184 Å structure reflects a dimerization of the lamellar structure.

4.2.3.2. Controlled Heating Ramps (Figure 8a–c). In the first controlled heating from –40 to 180 °C, the SAXS data show complex structural development, similar to those that were observed for the samples discussed above. In the temperature range from –35 to 100 °C, the Zn-0.5 equiv sample shows a lamellar structure. The periodicity increases slightly by increasing temperature. The temperature-dependent lamellar structure shows strong peaks corresponding to a 97 Å periodicity (at –35 °C), but also $q = 0.032 \text{ Å}^{-1}$ peaks corresponding to the double periodicity, 194 Å, which is attributed to the dimerization of the lamellar structure. The weak first-order and third-order peaks may be a matter of the form factor.

Interestingly, close to 60 °C, an additional structure develops. The peak near $q = 0.7 \text{ Å}^{-1}$ splits into two peaks related to the presence of two lamellar structures. As discussed below, we attribute it to the presence of mono-complexes in the sample. Both peaks change continuously to higher q -values upon raising the temperature, and the splitting becomes more pronounced. Close to 110 °C, the structure characterized by the highest q -value of the two structures melts, leaving a broad peak typical of a liquid-like structure. The other ordered structure remains and melts between 165 and 170 °C.

To test the reproducibility of these data, the sample was rapidly cooled back to ambient temperatures. Under these conditions, the two sets of peaks observed during the heating ramp appeared again, indicating the reformation of the two lamellar structures (see the Supporting Information, Figure S5). Thus, the original lamellar structure was not regained during this fast cooling. However, after leaving the sample at an ambient temperature for 4–5 months, the dimerized lamellar structure observed after the initial annealing was regained, ensuring that upon subsequent heating, the exact same complex structural development is observed (see Figure 8c).

4.2.3.3. Controlled Cooling Ramp (Figure 8d). Upon controlled cooling, measuring the structure every 5 °C, the two-lamellar structures observed originally in the controlled heating study (see Figure 8b,c), and which have also been observed in the fast cooling study (see the Supporting Information, Figure S5), are recovered. The sample shows exactly the same properties, with one ordered structure developing at 165 °C and the other one developing at about 110 °C. Successive heating and cooling give similar results. To recover the structure observed initially (i.e., the dimerized lamellar structure), a 4–5 months of waiting time is again required.

4.2.3.4. Crystalline Metal–Ligand Structure. As shown in Figure 9, the samples show further Bragg peaks in the wide-

angle regime, likely reflecting the crystalline order in the domains of metal–ligand complexes.

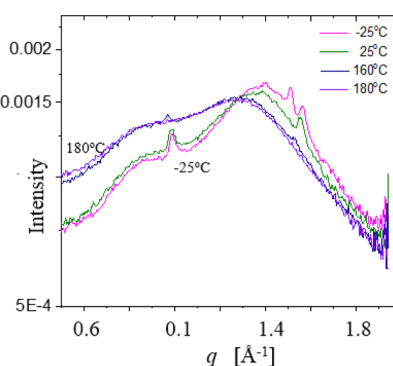


Figure 9. Representative WAXS data of Zn-0.5 equiv sample obtained during controlled heating.

The initial measurements of the Zn-0.5 equiv sample at ambient temperature before any annealing and the ambient temperature measurement after the temperature cycles are the same: Bragg peaks at 0.99 and 1.55 Å⁻¹ are observed, indicating that the ionic domains are not responsible for the significant influence of thermal history. This structure melts at 165 °C (the same melting temperature as the mesoscale structure). An additional crystalline structure appears at the lowest temperatures, giving additional Bragg peaks at 1.4 and 1.5 Å⁻¹. This structure melts close to –10 °C, proving complex behavior not only in the complexation of the polymers and the metal ions but also within the domains of metallic ions.

4.2.3.5. Rheological Data. The viscoelastic curves of samples Zn-0.5 equiv after its equilibration at 150 °C are shown in Figure 10a. As it can be seen, its behavior remarkably differs from the dynamics of the samples with a metal/ligand ratio lower than the stoichiometric ratio. The first difference lies in the very high level of its rubbery plateau, of around 10 MPa. Another important difference is the shorter relaxation time of a large fraction of the samples. In particular, at high temperature and low frequency, the storage modulus of sample Zn-0.5 equiv quickly decreases and becomes lower than the storage modulus observed for sample Zn-0.25 equiv (see Figure 10c). This decrease of relaxation time goes together with a larger thermorheological complexity, indicating the large temperature sensitivity of the supramolecular moieties, even at low temperatures.

The structure and viscoelastic data can be understood as follows. From the X-ray results, one can conclude that the two lamellar structures observed at ambient temperature when cooling the sample from the liquid state, and successive heating and cooling cycle, are apparently at a metastable phase, but “stable” for days or more. Only after leaving the sample at ambient temperature for months, does a stable phase (dimerized lamellar structure) emerge, which is reproducible and gives rise to the complex structural development on the first heating (see Figure 8a,c). It must also be noted that the effect of the initial heating (annealing) to 160 °C is apparently primarily to make the lamellar domains larger and the dimerization clearer.

We attribute the two lamellar structures, which appear at around 60 °C, to the co-existence of bis-complexes and mono-complexes within the sample. Mono-complexes are usually favorably formed when the samples contain excess of zinc ions,

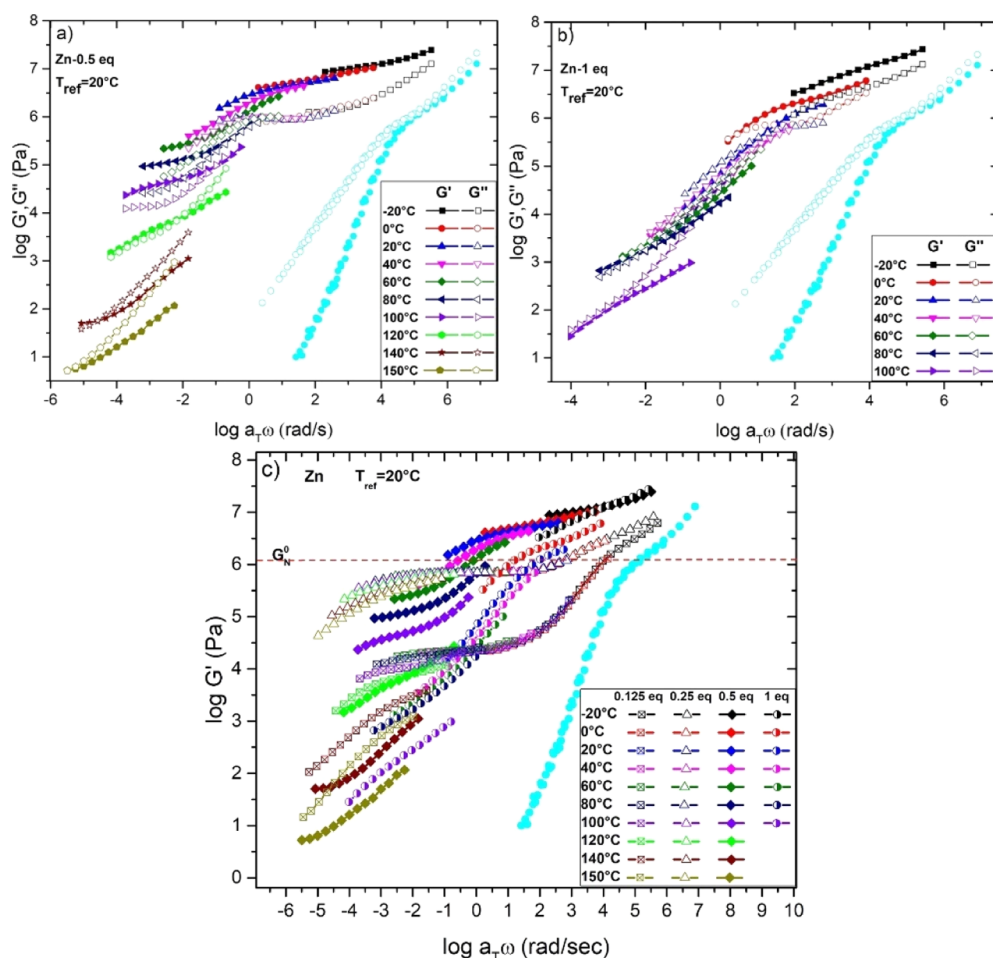


Figure 10. Storage and loss moduli of samples **Zn-0.5 equiv** (a) and **Zn-1 equiv** (b) compared to the viscoelastic response of the building block (cyan curves). The master curves are shown at the iso- T_g condition with $(T_{ref} - T_g) = 73.3^\circ\text{C}$ and based on the shift factors as the reference sample. (c) Comparison between the storage moduli of the different samples containing Zn^{2+} ions, presented separately in Figure 5a,b (a and b). Data have been measured between -20 and 150°C .

813 as it has been shown in ref 72. In sample **Zn-0.5 equiv**, zinc
 814 ions are not in excess, but the high temperature promotes the
 815 dissociation of the bis-complexes into free terpyridines and
 816 mono-complexes since it is known that zinc-terpyridine bis-
 817 complexes are rather labile, even at RT. In other words, the
 818 lifetime of the bis-complexes decreases with increasing
 819 temperature, and the formed “transient” mono-complexes
 820 aggregate, preventing the reformation of the bis-complexes.
 821 Only when the material is left for a long time at RT can the bis-
 822 complexes be reformed, together with the initial lamellar
 823 structure. This hypothesis is further confirmed in Section 4.2.4,
 824 with sample **Zn-1 equiv**, which surely contains a large fraction
 825 of mono-complexes since excess of zinc ions have been added.
 826 Since the mono-complexes do not involve specific, directional,
 827 associations between the ligands anymore, one can expect that
 828 they will phase-separate differently compared to the bis-
 829 complex. The mono-complexes are indeed characterized by a
 830 larger freedom within the ionic phase, from which they can
 831 escape more easily. Consequently, the ionic phase built from
 832 the association of mono-complexes should lead to a shorter
 833 relaxation time of the molecular segments, in agreement with
 834 the two different melting temperatures observed for the two
 835 different lamellar structures, the first one melting at around
 836 110°C and the second one melting at around 165°C . This is
 837 also in good agreement with the viscoelastic data, which shows

the presence of two different lifetimes (and two elastic 838
 plateaus), with a fraction of the sample relaxing at low 839
 temperature (and high frequency) and the other one relaxing 840
 at a higher temperature. 841

The high elasticity of sample **Zn-0.5 equiv** is similar to the 842
 one we can find with phase-separated block copolymers^{57,73} 843
 and can only be due to the phase separation of the complexes 844
 into a nanoscale structure able to reinforce the sample. This is 845
 consistent with the fact that these samples contain a low 846
 fraction of free ligands, which leads to a large coherence 847
 between the ordered structures. The sparsity of free ligands is 848
 also confirmed by the absence of relaxation peak in the 849
 frequency range where the relaxation of the free chains takes 850
 place. In addition to the large volume fraction of the ionic 851
 domains, the reinforcement of the sample can also partially 852
 come from the orientation of the HPB chains. Indeed, as 853
 mentioned in Section 4.2.1, a lamellar periodicity of around 854
 $100\text{ \AA}$ implies that the HPB chains located between two 855
 lamellae are oriented, especially in the vicinity of the lamellae 856
 where the segments are strongly stretched and impenetrable. 857
 As discussed in refs 10 and 62, this also contributes to the 858
 sample rigidity. 859

4.2.4. Structure and Viscoelastic Properties of Sample Zn-1 equiv. The main scattering properties of sample **Zn-1 equiv** 860
 are shown in Figure 11. 861
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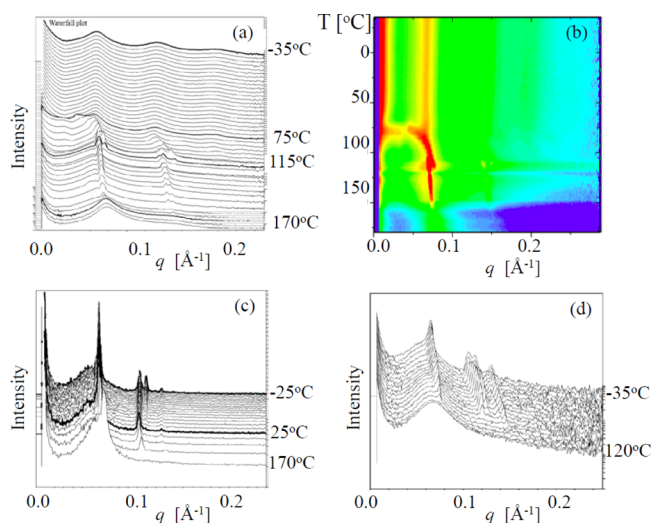


Figure 11. SAXS data of sample **Zn-1 equiv**: first heating ramp from $-35\text{ }^{\circ}\text{C}$ to high temperature ($180\text{ }^{\circ}\text{C}$) (a) waterfall plot and (b) contour plot. (c) Cooling ramp from high temperature back to RT. (d) Second heating ramp from -35 to $180\text{ }^{\circ}\text{C}$ (only shown to $120\text{ }^{\circ}\text{C}$).

peaks but still with an underlying broad liquid-like structure factor peak around $q = 0.057\text{ }\text{\AA}^{-1}$ (see Figure 11c). Interestingly, the **Zn-1 equiv** structure is no longer lamellar. As shown in Figure 11c, at around $25\text{ }^{\circ}\text{C}$, narrow peaks appear, which can now be divided into two sets of peaks, each of them with high-order peaks at ratio $1:\sqrt{3}:\sqrt{4}$, that is, indicating the co-existence of two hexagonal phases, both with lattice characteristics close to $90\text{ }\text{\AA}$.

4.2.4.3. Second Heating Ramp. As shown in Figures 11d and 12, upon heating, the HEX structures melt at around 65

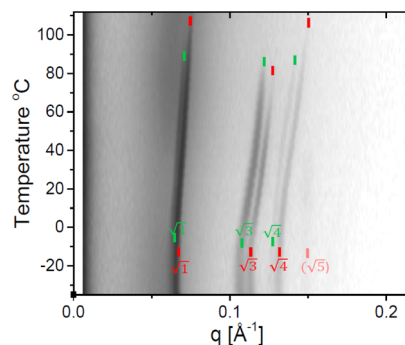


Figure 12. SAXS data of sample **Zn-1 equiv**: Contour plot corresponding to the second heating ramp from -35 to $180\text{ }^{\circ}\text{C}$ (only shown to $120\text{ }^{\circ}\text{C}$).

and $70\text{ }^{\circ}\text{C}$, respectively, and undergo a transition to lamellar structures, as indicated by the second-order Bragg reflection. The two HEX structures reform after the second cooling (see the Supporting Information, Figure S7).

To the best of our knowledge, the fact that adding excess of ions into a ligand-functionalized telechelic polymer leads to a change of structure, from lamellar to hexagonal, has never been reported. This structural change has obviously large consequences on the viscoelastic response of the sample. Therefore, understanding this mechanism could provide a new way to control and alter the dynamics of such metallo-supramolecular polymers.

4.2.4.4. Rheological Data. As shown in Figure 10b,c, the viscoelastic curves of sample **Zn-1 equiv** show a similar trend as sample **Zn-0.5 equiv**, but its first relaxation process is faster and more pronounced. This suggests that the fraction of fast relaxing components, that we attribute to the presence of the mono-complexes, is larger than in sample **Zn-0.5 equiv**.

The properties of sample **Zn-1 equiv** can be understood as follows. As for sample **Zn-0.5 equiv**, its evolution from one to two lamellar structures can be explained by the formation of mono-complexes, triggered by the excess of zinc salt. While prior heating the metallo-supramolecular polymer is mainly formed by bis-complexes and the sample contains many free ions, mono-complexes are formed upon heating. The presence of the latter is largely justified since the Zn^{2+} :metal ratio is twice more than the stoichiometric ratio.⁷² Moreover, as already discussed, we expect that they affect the organization of the complexes within the lamellae. The similar length scale found for the two lamellar structures as well as the similar temperature-dependence of their periodicity (see Figure 12) suggest that their difference could be related to a different number of complexes in the “2D ionic-phase”: while a monolayer of complexes would be mainly formed by bis-complexes, mono-complexes would rather form a bilayer of complexes, which appears upon heating the sample.

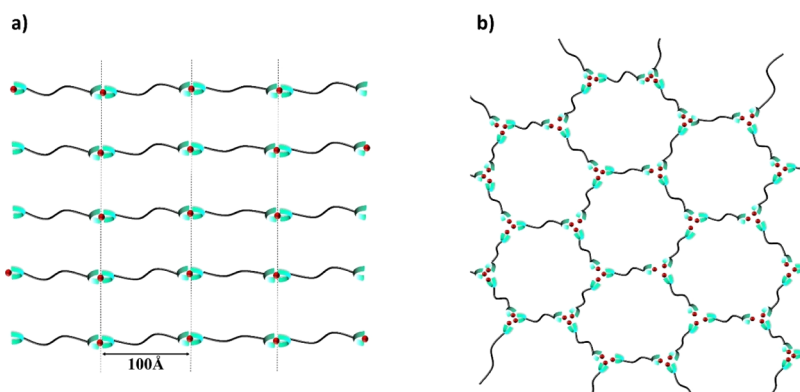


Figure 13. Cartoon representing the phase separation of bis-complexes into lamellar structures (a) and of mono-complexes into hexagonal structures (b).

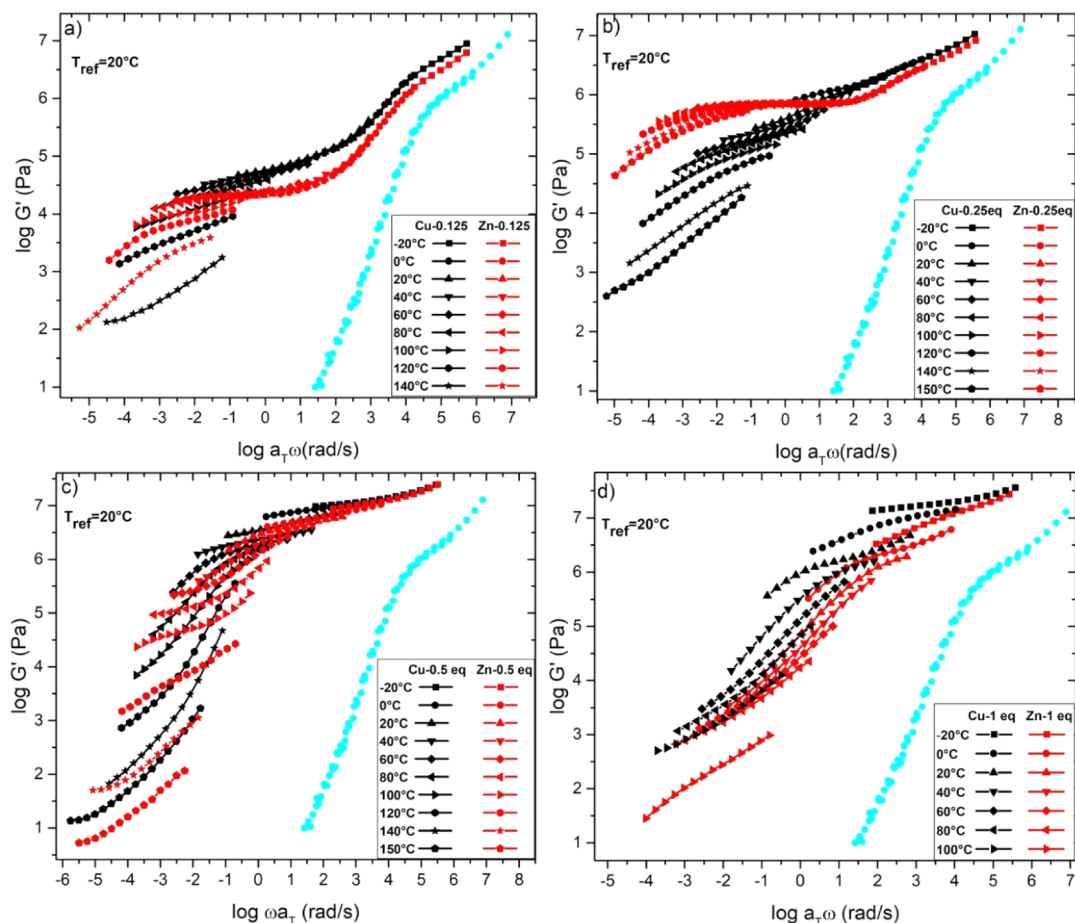


Figure 14. Storage moduli of the metallo-supramolecular polymers containing 0.125 (a), 0.25 (b), 0.5 (c), or 1 equiv (d) of Zn^{2+} or Cu^{2+} ions compared to the viscoelastic response of the building blocks (cyan curves). The master curves are shown at the iso- T_g condition with $(T_{ref} - T_g) = 73.3^\circ\text{C}$ and based on the shift factors as the reference sample. Data have been measured between -20 and 150°C .

The presence of a large number of mono-complexes within the lamellae is also consistent with the viscoelastic data (which correspond to the cooling curve of the SAXS data, see Figure 11c). While its rubbery plateau is as high as that of sample **Zn-0.5 equiv**, its first relaxation process takes place at times which are much shorter than for the latter sample. Furthermore, the level of the second rubbery plateau, which melts at temperatures similar to the melting temperature of samples **Zn-0.125 equiv** and **Zn-0.25 equiv**, and which has been attributed to the phase separation of the bis-complexes, is much lower than that

observed with sample **Zn-0.5 equiv**. This suggests that only a small fraction of the complexes is involved in these ordered structures.

In addition to this double structure, the reversible transition between lamellar and hexagonal structure, which is illustrated in Figure 13, must be discussed. Again, it is observed that two HEX structures, which have very similar q -values, co-exist, and we attribute them to the presence of mono-complexes. The $\sqrt{3}$ -peaks of these hexagonal structures seem to melt around 65 and 70°C , respectively, indicating hexagonal-to-lamellar

structural transitions for both structures (Figures 11d and 12). The fact that the melting temperatures (equal to 120 and 170 °C) of the lamellar structures that form during the heating are higher than that of the hexagonal structures which are formed during the cooling after the first heating suggests that heating the sample induces an evolution toward another equilibrium state. Since the X-ray patterns reflect the electron density variation within the sample, they are most likely dominated by the position and ordering of the metal ions within the polymer matrix. The observed change in ordering should therefore be related to a change in the aggregation of the metal–ligand complexes, taking place in addition to a change in their complexation (mono- vs bis-complexes) and favored by the large fraction of mono-complexes.⁷² Therefore, from these results, it seems that the change from lamellar to hexagonal structure upon adding excess of ions to the ligand functionalized telechelic polymer is triggered by a modification of the metal–ligand complexation, which governs the mesoscale-ordered structures.

This result differs from classical soft-matter systems based on phase-separated block copolymers, where the structure depends on the ratio between the volumes of the two blocks and on their incompatibility. Furthermore, our conclusions are in good agreement with the work of Neumann et al.,²⁴ who also concluded that there was no clear analogy between the behavior of their metallo-supramolecular polymer and the behavior of block copolymers. The authors also reported that, while lamellar morphologies were observed with most of their supramolecular systems, hexagonal morphologies could be observed in some specific cases, but only if 1:3 metal:ligand coordination complexes were used. This result also suggests that the way ligands associate affects the ordered structure of the sample.

4.3. Influence of the Metal Ions. While this study mainly focuses on the properties of metallo-supramolecular polymers based on Zn^{2+} ions, in this section, viscoelastic properties of the samples in which Cu^{2+} ions have been added. Being less labile than the Zn^{2+} ion, Cu^{2+} leads to metal–ligand association characterized by a longer lifetime.^{29,30,33} Furthermore, previous works have shown that mono-complexes form more easily with copper than with zinc.

Results are shown in Figure 14, in comparison with the previous data based on zinc ions. In general, the same trend is observed: adding excess of metal ions leads to an increase of the plateau modulus and a decrease of the relaxation time of the sample. The reinforcement obtained with copper is slightly stronger than with zinc at an intermediate frequency (at around 10^3 rad/s) in concordance with the larger stability of the bis-complexes. However, the difference is rather weak. This is consistent with the fact that the mechanism which dominates the viscoelastic response is the phase separation of the 1019 complexes. The influence of the association dynamics of the 1020 complexes themselves is therefore mostly absent. From the 1021 experiments, we also observed that adding 0.5 and 1 equiv of 1022 Cu^{2+} ions into the sample leads to a change of color, from 1023 green to blue, which suggests that free ions (blue color) are 1024 present in the system, even when they are added in 1025 stoichiometric amount. This point is not visible with zinc 1026 ions because the color of the complex and of free ions is the 1027 same (white).

Despite their overall large similarities, the difference between the viscoelastic data of samples **Cu-0.25 equiv** and **Zn-0.25 equiv** must be pointed out (see Figure 14b). While at short

time, the rubbery plateau of the metallo-supramolecular polymers containing Cu^{2+} ions is higher, which reflects a larger presence of ordered structures, its terminal relaxation time is much shorter than with Zn^{2+} ions. In fact, its behavior is rather similar to the viscoelastic properties of sample **Zn-0.5 equiv** (see Section 4.2.3), suggesting that mono-complexes are already present in sample **Cu-0.25 equiv**, despite the fact that the amount of ions is lower than the stoichiometric amount. As for sample **Zn-0.5 equiv**, this would mean that sample **Cu-0.25 equiv** contains both bis-complexes and mono-complexes, which is consistent with the viscoelastic data. Mono-complexes associate easily, leading to a large coherence of the ordered structures, but these structures are less stable than the ones formed by the association of bis-complexes and melt at a lower temperature.

In order to validate our hypothesis, we measured the viscoelastic behavior of sample **Cu-0.5 equiv** before and after its equilibration at high temperature and compared its viscoelastic curves in order to see if we can detect the evolution from bis-complexes to mono-complexes. Indeed, the metallo-supramolecular polymers contain a larger fraction of bis-complexes before annealing, and the latter are being partially transformed into mono-complexes when the sample is heated. The results obtained are presented in Figure 15. The

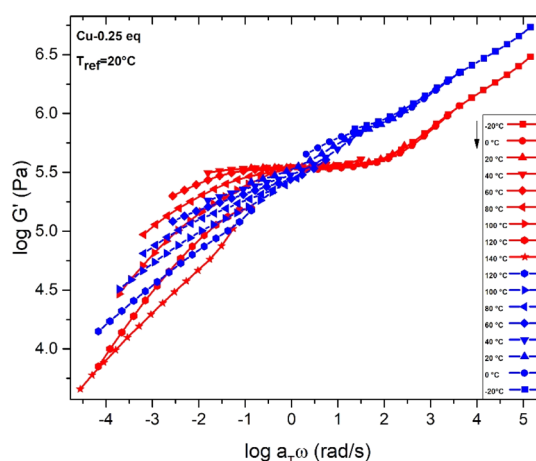


Figure 15. Storage moduli of the metallo-supramolecular polymers containing 0.25 equiv of Cu^{2+} ions, before (red symbols, measured from low to high temperature) and after (blue symbols, measured from high to low temperature) annealing of the sample. The master curves are shown at the iso- T_g condition with $(T_{\text{ref}} - T_g) = 73.3$ °C and based on the shift factors as the reference sample. Data have been measured between -20 and 140 °C.

sample is, indeed, evolving significantly, toward a larger modulus and a larger fraction of chains which relaxes at intermediate frequency (around 10 rad/s), which supports the idea that a large amount of mono-complexes are formed during sample equilibration.

5. CONCLUSIONS

In this work, we have studied the dynamics and structure of a short HPB building block end-capped by terpyridine ligands. Adding metal ions in the sample leads to the formation of metallo-supramolecular junctions between the blocks. Furthermore, due to the difference in polarity between the HPB chains and the complexes, the latter phase-separate into well-organized structures, giving rise to interesting properties. In

particular, it has been shown that the sample rheological and structural properties strongly depend on the nature and metal/ligand ratio of the system, on temperature, as well as on the sample thermal history.

Based on SAXS analysis, it was found that in most of the samples, the tpy-Zn²⁺ complexes phase-separate into a lamellar structure. If the ion content is large enough (≥ 0.25 equiv), this crystalline structure leads to the sample reinforcement, characterized by a high elastic modulus and slow relaxation process. The stability of the ionic domains is found to be largely influenced by temperature, the ODT transition being nearly observed at 180 °C.

Interestingly, if the metal/ligand ratio is increased (above 0.5 equiv), the sample elasticity further increases; however, its melting temperature significantly decreases. This evolution goes together with the appearance of a second lamellar structure, which has similar characteristics as the first one. We attributed it to the formation of mono-complexes, which organize differently in the ionic domains and probably form bilayers of metal complexes. A similar result has been found if Cu²⁺ ions are used in the place of Zn²⁺ ions.

If excess of ions are added (1 equiv), the lamellar structure transforms into a hexagonal structure after heating the sample to high temperature. This change of structure is triggered by a modification of the metal–ligand complexation, which governs the mesoscale-ordered structures. This result differs from the classical soft matter system based on phase-separated block copolymers, where the structure rather depends on the ratio between the volumes of the two molecular parts and on their incompatibility.

Finally, we have shown that the two lamellar structures induced by the presence of mono-complexes correspond to a “metastable” state, which disappears after 4–5 months at RT. Thus, by adjusting the three abovementioned parameters, a very rich behavior was obtained. In particular, lamellar or hexagonal morphologies can be obtained for the same sample, depending on its thermal equilibration, with large consequences on the viscoelastic properties.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.macromol.1c00373>.

Details on sample synthesis, NMR measurements, DSC thermograms, reproducibility of the viscoelastic data, and additional SAXS data of samples **Zn-0.5 equiv** and **Zn-1 equiv** (PDF)

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Notes

The authors declare no competing financial interest.

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