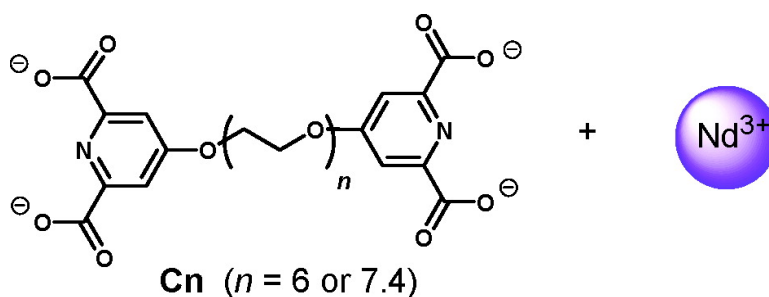


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Linear Rheology of Water-Soluble Reversible Neodymium(III) Coordination Polymers

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Abstract: The rheology of reversible coordination polymer networks in aqueous solution is studied. The polymers are formed by neodymium(III) ions and bifunctional ligands, consisting of two pyridine-2,6-dicarboxylate groups connected at the 4-positions by an ethylene oxide spacer. Neodymium(III) ions can bind three of these terdentate ligand groups. At high concentrations, the polymer networks yield viscoelastic materials, which can be described with the Maxwell model. The scaling of the elastic modulus, relaxation time, and zero-shear viscosity with concentration are in good agreement with the predictions of Cates' model that describes the dynamics of linear equilibrium polymers. This indicates that the networks have only few cross-links and can be described as linear equilibrium polymers. The gels are also thermo-reversible. At high temperatures, fast relaxation was found, resulting in liquidlike behavior. Upon cooling, the viscoelastic properties returned immediately. From the temperature dependence of the relaxation time, an activation energy of 49 kJ/mol was determined for the breaking and reptation of the polymers.

I. Introduction

(a) Reversible Coordination Polymers. Reversible or equilibrium polymers are polymers that can reversibly break and re-form by noncovalent interactions.^{1–4} These interactions can be, for example, hydrogen bonding, π – π -stacking interactions, van der Waals interactions, and coordinative bonding (metal–ligand bonding). Although reversible polymers reproduce many properties of covalent polymers, they exhibit new features due to breaking and recombination on experimental time scales. Until now, hydrogen-bonded polymers are the most studied.^{4–7}

Another promising group of reversible polymers are the coordination polymers.^{8–10,12} Linear polymers are formed by

bifunctional ligands and metal ions if ligand groups and metal ions form 2:1 complexes. This is usually the case when bifunctional terdentate ligands are used in combination with transition metal ions, like Zn^{2+} or Cd^{2+} .^{11,12} For these coordination polymers, the average chain length varies not only with concentration and temperature, but also with the molar ratio of metal ions to bifunctional ligands. When the molar ratio equals unity, the average chain length is larger than when either metal ions or ligands are in excess. However, when lanthanide ions such as La^{3+} or Nd^{3+} are used with the same ligands, polymeric networks may be obtained. This is because lanthanide ions are large and can accommodate 9-coordination, which implies that each ion can bind three terdentate ligand groups. The use of lanthanide ions will therefore yield reversible networks instead of linear polymers.¹³ Recently, the formation of coordination polymers was described with bifunctional terdentate ligands, a few percent lanthanide ions (La^{3+} or Eu^{3+}), and over 95% transition metal ions (Zn^{2+} or Co^{2+}) in an organic solvent.¹⁴ The lanthanide ions indeed act as cross-linkers and give the solutions interesting rheological properties.¹⁵

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For linear reversible polymers, some rheological properties have been reported.^{5,12,16–20,25} The dynamics of equilibrium polymers are supposed to have much in common with so-called wormlike micelles. Such micelles also have the possibility to break and recombine reversibly. The rheological properties of these micelles have been studied extensively, both experimentally and theoretically, in the last two decades.^{19,20} At very high salt concentrations, wormlike micelles from cetylpyridinium chlorate not only form linear chains but also cross-links.²¹ However, published data about the dynamics of reversible cross-linked systems or networks are scarce.^{22–26}

In this work, we investigate the rheological properties of a water-based reversible coordination network. Neodymium(III) is a suitable metal ion, because it is known to form complexes with three terdentate ligand groups (9-coordination).^{13,27} The ligand used is a bifunctional ligand, consisting of two pyridine-2,6-dicarboxylate groups connected at the 4-positions by an ethylene oxide spacer; its synthesis has been described elsewhere.¹² The measurements were performed for two ligands that differ only in spacer length. The results were fitted to the model of Cates to obtain insight into the molecular dynamics of the studied reversible networks. We first explain the existing model and then compare our results as a function of concentration and temperature with this model.

(b) Linear Rheology of Equilibrium Polymers. As mentioned in the first part of the Introduction, the rheological behavior of equilibrium polymers has a lot in common with the rheological behavior of wormlike micelles. Maxwellian behavior was predicted in theoretical studies for wormlike micelles¹⁹ and also has been found experimentally for entangled reversible hydrogen-bonded polymers and wormlike micelles.^{5,16,20} According to the Maxwell model, the storage modulus (G') and loss modulus (G'') are given by the following equations:

$$G'(\omega) = \frac{G_0(\omega\tau)^2}{1 + (\omega\tau)^2} \quad (1)$$

$$G''(\omega) = \frac{G_0\omega\tau}{1 + (\omega\tau)^2} \quad (2)$$

where ω is the angular frequency and τ is the relaxation time. The inverse relaxation time ($1/\tau$) can be found as the frequency (ω) at which G' equals G'' because $G'/G'' = \omega\tau$. G_0 is the plateau modulus and corresponds to the high-frequency plateau

of G' . At concentrations above the overlap value, the polymer chains are becoming entangled and looped around each other. For a polymer chain, one can envisage a number of entanglement sites occurring, which can be related to an average molar weight between effective cross-links, M_e , at short times. These effective cross-links may be “true” (reversible) cross-links or entanglements. The following equation gives the relation between the plateau modulus and the molar weight between effective cross-links, M_e :²⁸

$$G_0 = \frac{\rho RT}{M_e} \quad (3)$$

where ρ is the concentration of the polymer solution (g/m^3), R is the molar gas constant, and T is the absolute temperature. ρ/M_e equals the molar concentration of the chain fragments between entanglements, C_e (mol/m^3). The concentration C_e is related to the correlation length, ξ , of the polymer solution by $C_e \approx 1/\xi^3$. In a good solvent, $\xi \approx C^{-3/4}$, with the concentration C in g/L .²⁹ Consequently, the plateau modulus is also concentration dependent. For flexible chains (both equilibrium polymers and covalently bonded polymers), this dependency is approximately:^{19,30,31}

$$G_0 \cong \frac{k_B T}{\xi^3} \approx C^{9/4} \quad (4)$$

where k_B is the Boltzmann constant.

For wormlike micelles, Cates et al. developed a model for the dynamical properties that also takes into account the breaking and reassembly of chains.^{19,20} In this model, the relaxation of reversible polymers can be described by two time scales: the reptation time, τ_{rep} , and the lifetime of a chain, τ_{break} . The reptation time is the time needed for an entangled polymer to diffuse out of its imaginary tube.³¹ This tube is made up of the network made by all of the other entangled polymer chains, which makes diffusion only possible in the direction of the tube. τ_{break} is the lifetime of a chain of mean length before it breaks into two pieces.²⁰ When breaking is fast as compared to reptation ($\tau_{\text{break}} \ll \tau_{\text{rep}}$), the relaxation time is given by

$$\tau \cong (\tau_{\text{rep}}\tau_{\text{break}})^{1/2} \approx C^{5/4} \quad (5)$$

According to the model of Cates,^{32,33} the relaxation time τ scales with the concentration with an exponent of $5/4$. The zero-shear viscosity η_0 is related to the relaxation time τ and the plateau modulus G_0 by

$$\eta_0 = G_0\tau \approx C^{3.5} \quad (6)$$

and η_0 scales with the concentration with an exponent of 3.5 in the fast breaking regime.

The relaxation time τ is also related to a reaction rate constant k . The reaction involved in relaxation is a combination of

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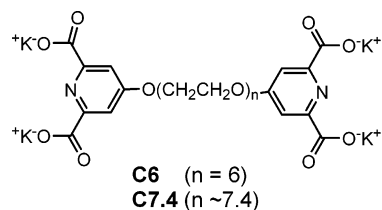


Figure 1. Schematic representation of bifunctional ligands **C6** and **C7.4**.

reptation and dissociation of the coordination bonds, yielding a single relaxation time (eq 5). In the fast breaking regime, the reaction is therefore a first-order reaction. Even when water molecules assist in the breaking of the coordination bonds, the reaction rate is a pseudo first-order reaction, because the water concentration is constant ($k_{\text{observed}} = k \cdot [\text{H}_2\text{O}]$). Nevertheless, if we assume that the process is a first or pseudo-first-order process, k_{obs} can be described by

$$k_{\text{obs}} = 1/\tau \quad (7)$$

The Arrhenius equation gives the relation of k_{obs} and the activation energy E_a as a function of the temperature:

$$k_{\text{obs}} = A e^{-E_a/RT}$$

or

$$\tau = A^{-1} e^{E_a/RT} \quad (8)$$

with A as the preexponential factor.³⁴ Both the activation energy and the preexponential factor can be divided into the contributions of reptation and breaking of the chains using eq 5: $A = (A_{\text{rep}} \cdot A_{\text{break}})^{1/2} \approx C^{-5/4}$ and $E_a = (E_{a,\text{rep}} + E_{a,\text{break}})/2$. So, E_a is the arithmetic mean of the activation energies of reptation and breaking of the chains and should not depend on the concentration.

For cross-linked systems, no theoretical scaling exponents as a function of concentration have been published yet. However, some experimental data are reported of the scaling exponents of wormlike micelles (CTAB) in which intermicellar branching occurs at high salt concentration by Khatory et al.²⁵ The branching of these wormlike micelles leads to a reduction of the zero-shear viscosity and scaling exponents different from those predicted by Cates for linear reversible chains. The scaling exponents found at a salt concentration of 1.5 M are: $\eta_0 \approx C^{2.42}$, $\tau \approx C^{0.57}$, and $G_0 \approx C^{1.85}$. Relaxation can occur by sliding of the linear chains along the cross-links through viscous flow of the surfactant molecules. Due to this flow, the reptation process can still take place but the reptation time decreases, because the large number of possible paths for reptation accelerates the curvilinear motion of the cylinders between two free ends.³⁵

II. Results and Discussion

Bifunctional ligands **C6** and **C7.4** (Figure 1) were used to form complexes with neodymium(III) ions in aqueous solution.

C6 has a spacer length of exactly 6 ethylene oxide units. **C7.4** consists of a mixture of molecules with an average spacer length of 7.4 ethylene oxide units as determined by ¹H NMR.

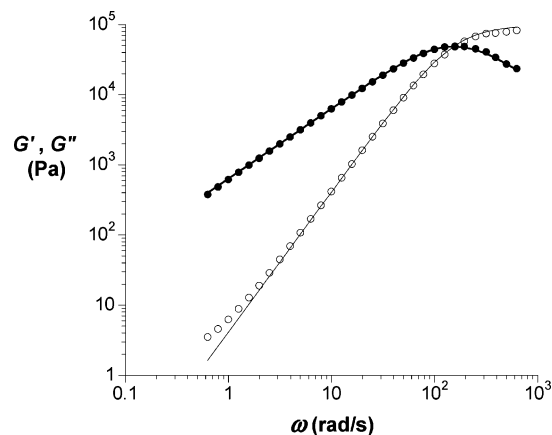


Figure 2. Storage modulus (○) and loss modulus (●) as a function of the angular frequency ω for a solution of 500 g/L of **C7.4** and 0.7 equiv of $\text{Nd}(\text{NO}_3)_3$ in 100 mM PIPES buffer pH 5.4 at 20 °C. Curves are fits to the Maxwell model, eqs 1 and 2.

Neodymium ions can bind to three of these ligand groups. The complexation constants of the subsequent binding of three 2,6-pyridine-dicarboxylic acid molecules to one Nd^{3+} ion are: $K_1 = 10^{8.78}$, $K_2 = 10^{6.72}$, and $K_3 = 10^{5.06}$ as reported by Grenthe.²⁷

When ligands **C6** and **C7.4** were dissolved in an aqueous 1,4-piperazinebis(ethanesulfonic acid) (PIPES) buffer (pH 5.4, 100 mM) and mixed with a solution of 0.7 equiv of $\text{Nd}(\text{NO}_3)_3$ in the same buffer, a precipitate was formed initially, which gradually dissolved upon mixing in an ultrasonic water bath. We reported earlier that samples with 0.7 equiv of Nd^{3+} ions gave somewhat higher viscosities than those having a ratio of exactly $2/3$ at low concentrations (8–35 g/L) and therefore the ratio of 0.7 was also used here.¹³ The gels of both **C6** and **C7.4** showed only very little recovery in creep experiments, which means that the gels are still liquidlike. The gels formed with **C7.4** were completely transparent after about 24 h of mixing. The gels formed with **C6** were slightly turbid. This difference is probably caused by a small difference in the polarity of the compounds. **C6** is a little less polar than **C7.4**, and this may lead to incomplete dissolution of the coordination complexes in water at the concentrations used in this study. We also tried to form gels with **C4** and **C5** (same compounds, but with a spacer length of only 4 and 5 ethylene oxide units, respectively), but in these systems, despite initial gelation, always a precipitate was formed after approximately half an hour at concentrations above 100 g/L. Solutions at lower concentrations of all compounds (**C4**–**C7.4**) with a Nd^{3+} /bifunctional ligand ratio of 0.7 were transparent. The viscosity of these solutions at low concentration increased with increasing concentration and had a maximum when the Nd^{3+} /bifunctional ligand ratio was between 0.67 and 0.71.¹³

(a) Concentration Dependence. The rheological characteristics of solutions of both ligands with Nd^{3+} were measured as a function of frequency at different concentrations. Figure 2 shows the storage modulus (G') and the loss modulus (G'') as a function of the angular frequency (ω) for a **C7.4** gel with 0.7 equiv of $\text{Nd}(\text{NO}_3)_3$ at 20 °C at a concentration of 500 g/L (concentration of ligand and $\text{Nd}(\text{NO}_3)_3$ together). The curves show that the gel has typical viscoelastic properties. At low frequency, the loss modulus dominates, while at higher frequencies the storage modulus dominates and levels off toward a plateau value. Figure 3 shows G'' as a function of G' in a so-

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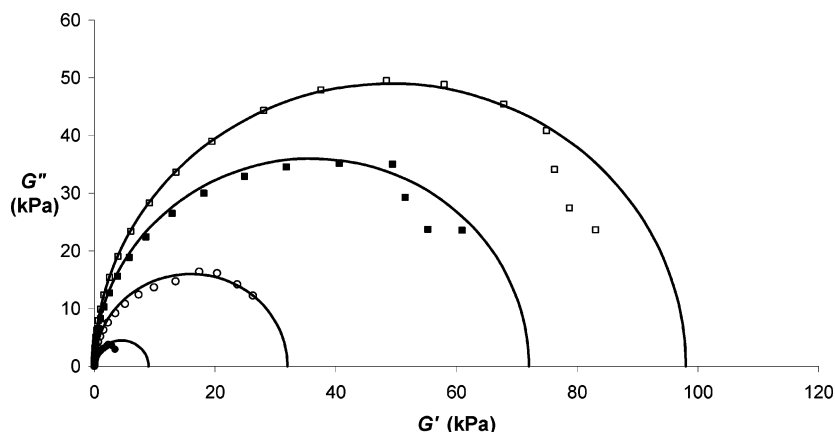


Figure 3. Cole–Cole plots of G' and G'' data for **C7.4** and 0.7 equiv of $\text{Nd}(\text{NO}_3)_3$ at 20 °C of 181 g/L (●), 308 g/L (○), 400 g/L (■), and 500 g/L (□) in 100 mM PIPES buffer pH 5.4 solutions. The semicircular curves correspond to the Maxwell model, eqs 1 and 2.

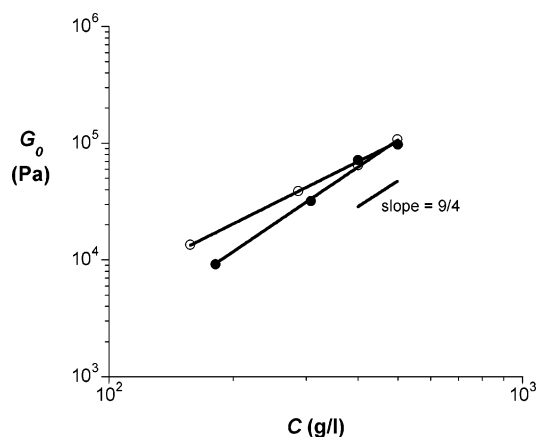


Figure 4. Plateau modulus (G_0) as a function of concentration for **C6** (○) and **C7.4** (●) with 0.7 equiv of $\text{Nd}(\text{NO}_3)_3$ in 100 mM PIPES buffer pH 5.4 at 20 °C.

called Cole–Cole plot for different concentrations of **C7.4** at 20 °C. The solid lines in Figures 2 and 3 correspond to the fits of the Maxwell model. The shapes of the curves measured for **C6** are comparable to those of **C7.4**.

As can be seen, the rheological behavior of the system can be described very well by the Maxwell model over a frequency range, which extends beyond $\omega = 1/\tau$. In Figure 3, G_0 corresponds to the diameter of the semicircle and depends on the concentration. At high frequency, a small deviation from the Maxwell model is found, which is common for reversible polymers and wormlike micelles.^{18,25,30,32,33} This deviation is usually interpreted as a crossover to a different dynamical regime, where other relaxation modes are important. Whether the same explanation for the deviation can be given for this system is not clear, because G'' decreases faster as compared to G' than in other reported systems.

Figure 4 shows the concentration dependence of G_0 for both **C6** and **C7.4** with Nd^{3+} . The data for compound **C7.4** can be fitted by $G_0 \approx 0.03C^{2.4}$ (Pa) and for compound **C6** by $G_0 \approx 1.75C^{1.8}$ (Pa). The scaling exponent of 2.4 for **C7.4** agrees well with the theoretical scaling exponent $9/4$ for linear polymers. This is an indication that the effective cross-links observed in the high-frequency rheological experiments are predominantly entanglements. The slope of 1.8 for **C6** deviates from $9/4$. The slope of **C6** corresponds, however, well to the scaling exponent found experimentally for cross-linked wormlike micelles men-

Table 1. Average Molecular Weights between Effective Cross-Links (M_e) for Various Concentrations of **C7.4**/ Nd^{3+} and **C6**/ Nd^{3+} Solutions

C (g/L) C7.4 / Nd^{3+}	M_e (kg/mol)	C (g/L) C6 / Nd^{3+}	M_e (kg/mol)
181	49	157	35
308	23	287	18
400	14	400	15
500	12	498	11

tioned in the Introduction.²⁵ Yet because the solutions of **C6** are a little turbid, the system may be partially precipitated so that part of the material does not contribute to the polymer network. Hence, comparing the data for this system to theory or other experiments might be questionable. However, the different behavior of **C6** could not be caused only by partial dissolution of the coordination complexes. In that case, the curves in Figure 4 (and also in Figures 5 and 6) would be horizontal, because at concentrations above the solubility product no additional molecules dissolve. Most likely, the difference in behavior between **C6** and **C7.4** is due to the difference in the spacer length. However, it cannot be excluded that the difference in polydispersity is relevant as well.

From the plateau modulus, the molecular weight between effective cross-links was calculated using eq 3. The M_e values are summarized for various concentrations of both the **C6** and the **C7.4** systems in Table 1. The large values for M_e indicate that we do not have many effective cross-links (the molecular weight of a bifunctional ligand plus one metal ion including counterions is about 1.1 kg/mol).

The Maxwell model applies well for a large frequency range (considerably beyond $\omega = \tau^{-1}$, see Figures 2 and 3), which is an indication that the system is fast breaking ($\tau_{\text{break}} \ll \tau_{\text{rep}}$). The relaxation times τ are concentration dependent (Figure 5), and our experiments are in very good agreement with the model of Cates for compound **C7.4** ($\tau \approx 4 \times 10^{-6}C^{1.2}$). The scaling of **C6** with an exponent of 0.7 corresponds again very well with the one found experimentally for the cross-linked wormlike micelles ($\tau \approx 8 \times 10^{-5}C^{0.7}$). However, the different scaling could also be attributed to its incomplete dissolution.

Although the exponents for τ are comparable to those found experimentally for linear hydrogen-bonded reversible polymers, the absolute relaxation times are much smaller.^{5,11} The relaxation time is build up by two contributions: τ_{rep} and τ_{break} (eq 5). In our system, τ_{break} may be much smaller due to the role of the

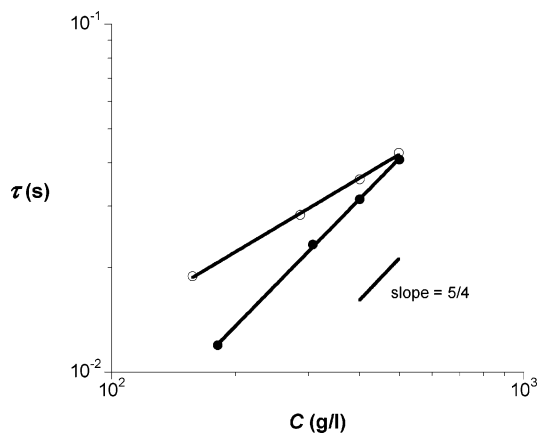


Figure 5. Relaxation time (τ) as a function of concentration for **C6** (○) and **C7.4** (●) with 0.7 equiv of $\text{Nd}(\text{NO}_3)_3$ in 100 mM PIPES buffer pH 5.4 at 20 °C.

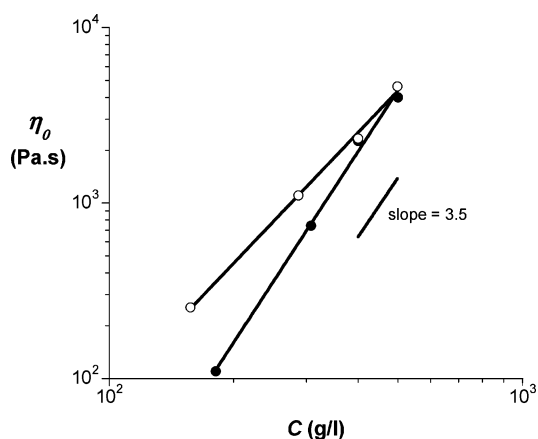


Figure 6. Zero-shear viscosity (η_0) as a function of concentration for **C6** (○) and **C7.4** (●) with 0.7 equiv of $\text{Nd}(\text{NO}_3)_3$ in 100 mM PIPES buffer pH 5.4 at 20 °C.

solvent. The rheological properties of the hydrogen-bonded polymers reported were studied in organic solvents. These solvents do not play an active role in the breaking and recombination. Water, on the other hand, coordinates metal ions and stabilizes the free or partially bound metal ions, resulting in shorter relaxation times as compared to the hydrogen-bonded polymers in organic solvents. Whether τ_{rep} contributes also to smaller overall relaxation times in our system than in hydrogen-bonded polymers is harder to foresee, because τ_{rep} is related to the curvilinear diffusion coefficient, which depends among other things on the average chain length and the viscosity of the solvent.

Figure 6 shows the zero-shear viscosity η_0 as a function of concentration. The data can be fitted with a line of slope 3.6 for compound **C7.4** and 2.5 for compound **C6**. The scaling exponent predicted by Cates for linear reversible polymers is 3.5. Compound **C7.4** with Nd^{3+} corresponds again very well with this model. For compound **C6** and Nd^{3+} , all scaling exponents correspond nicely to the exponents found in cross-linked wormlike micelles. On the basis of these results, one might conclude that the **C6** system forms indeed a cross-linked network and the **C7.4** system forms linear chains.

Because neodymium ions bind to three ligand groups, one would expect the formation of cross-linked networks. A possible explanation, which reconciles the fact of three-fold coordinated



Figure 7. Schematic representation of linear chains formed by bifunctional ligands and lanthanide ions.

Nd^{3+} ions and the occurrence of linear chains of **C7.4**/ Nd^{3+} as suggested by the rheological results, may be the structure depicted in Figure 7. However, based on this structure, no good reason can be given why **C7.4** would give these linear chains and **C6** would not. The results indicate that **C6** rather forms cross-links than rings such as in Figure 7. However, in systems with transition metal ions, the formation of rings consisting of two **C6** molecules and two metal ions seemed well possible.¹² So, we still cannot exclude the explanation that **C6** gives different scaling exponents than **C7.4** due to partial precipitation in the **C6**/ Nd^{3+} system.

The results of the **C7.4**/ Nd^{3+} system can, however, be explained very well using the representation of linear chains in Figure 7. The ligands are known to form ringlike structures at low concentrations around transition metal ions.¹² When at the concentrations used for the measurements a reasonable amount of rings, such as in Figure 7, is still present, the solution may well behave as a solution of linear chains instead of a network. Unfortunately, it is very difficult to assess whether linear polymers, networks, or a combination of the two are present in our reversible system. With increasing concentration, the relative amount of rings is expected to decrease and the relative amount of cross-links is expected to increase. However, cross-linking is unfavorable because every cross-link yields an extra chain end (Figure 8). A chain end always has either an uncomplexed ligand group, a metal ion with free coordination sites, or a bifunctional ligand that forms a loop around one metal ion (monomer ring). These are all unfavorable, the first two possibilities for enthalpic reasons, the last for entropic reasons. Therefore, the branching of the chains is unfavorable and the formation of linear chains is more likely also at high concentrations. At very high concentrations, the branch points may connect two chains and not yield extra chain ends. However, to connect all possible branch points such as this, extremely high concentrations are needed, and this is not feasible in this system.

For comparison, we also prepared samples with Zn^{2+} ions instead of Nd^{3+} , which binds two ligand groups per metal ion and leads to the formation of linear chains and rings.¹² At a concentration of 500 g/L, a sample of **C7.4** with Zn^{2+} was completely liquidlike, whereas the Nd^{3+} samples gave viscoelastic materials. We also prepared samples with a concentration of 400 g/L of **C7.4** with Nd^{3+} and varying amounts of Zn^{2+} . The samples were prepared such that the amount of binding places on the metal ions was equal to the amount of binding groups. This is necessary because Zn^{2+} ions bind only two ligand groups, while Nd^{3+} binds three ligand groups. Both G_0 and η_0 (Figure 9a) decreased substantially with increasing percentages of Zn^{2+} . The relaxation time decreases only slightly with increasing percentages of Zn^{2+} (Figure 9b). Samples containing over 25% Zn^{2+} were completely liquidlike. So, we conclude that at a concentration of 400 g/L both the viscosity and the relaxation time decrease with decreasing amounts of trifunctional metal ions. A reason may be that the complexation constants for the binding of Zn^{2+} to the chelating group ($10^{6.4}$

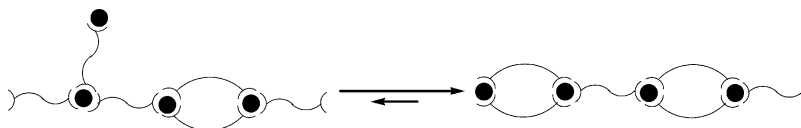


Figure 8. Branching leads to more chain ends. This favors the equilibrium toward linear chains.

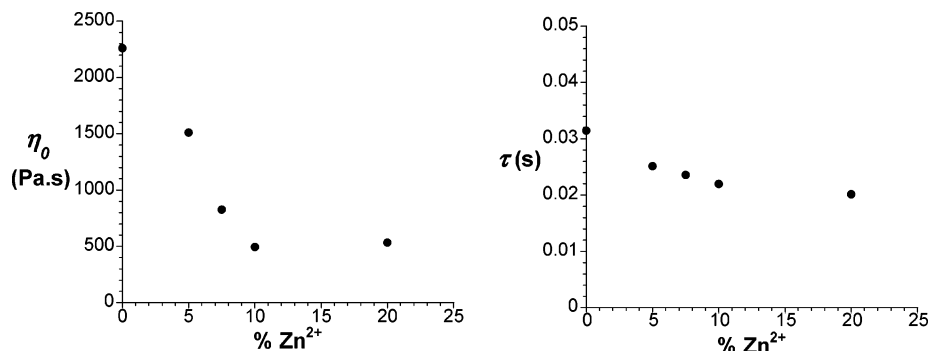


Figure 9. Dependence of η_0 and τ upon the % Zn^{2+} in a sample of 400 g/L **C7.4** and Nd^{3+} in 100 mM PIPES buffer pH 5.4 at 20 °C.

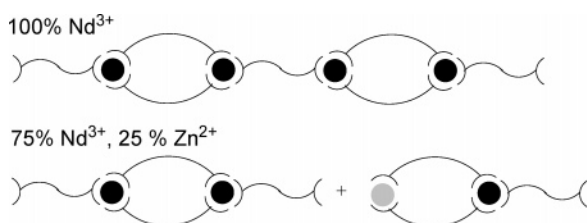


Figure 10. Schematic representation of the influence of the replacement of Nd^{3+} ions (black circles) by Zn^{2+} ions (gray circle).

and $10^{5.5}$) are smaller than the first two complexation constants of Nd^{3+} .²⁷ This will lower the average chain length and the solution viscosity. Yet the most important reason for lowering the viscosity is probably that the ligands are able to form rings around Zn^{2+} as well. Here, ring formation leads to chain ends as depicted in Figure 10. Such rings yield additional chain ends and hence reduce the average chain length. Transition metal ions added to a system consisting of terdentate bifunctional ligands and lanthanide ions might act as “chain stoppers” similarly to how monofunctional polymers do in solutions of bifunctional hydrogen-bonded polymers.^{26,36}

(b) Temperature Dependence. Besides the concentration dependence of the rheological properties, also a clear temperature dependence was observed. Figure 11 shows the storage and loss modulus as a function of temperature of **C7.4** and Nd^{3+} at a concentration of 400 g/L for a frequency of 100 Hz. The storage modulus decreases with increasing temperature. At about 37 °C, the loss modulus becomes larger than the storage modulus. At high temperatures, the mobility of the molecules increases but also the complexation constants between metal ions and ligands decrease, leading to smaller chains and eventually single molecules. Upon cooling, the storage and loss modulus return immediately to the same level as before the sample was heated, demonstrating the reversibility of the system.

Increasing the temperature leads to a decrease in the relaxation time τ . Because ω is constant (100 Hz) during the temperature-dependent measurements, at each temperature τ can be calculated from G' and G'' using eqs 1 and 2. For all concentrations, the relaxation time drops until nearly zero at approximately 60

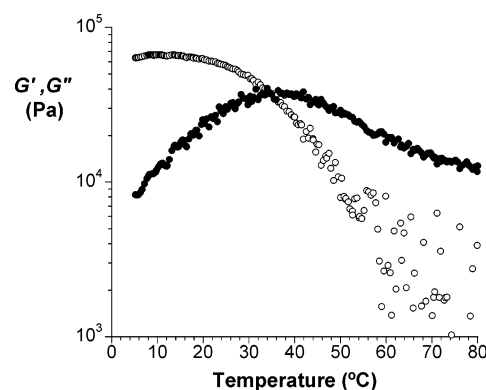


Figure 11. Storage modulus (\circ) and loss modulus (\bullet) as a function of temperature for a 400 g/L solution of **C7.4** and $\text{Nd}(\text{NO}_3)_3$ in 100 mM PIPES buffer pH 5.4 at a frequency of 627.7 rad/s and 1% strain.

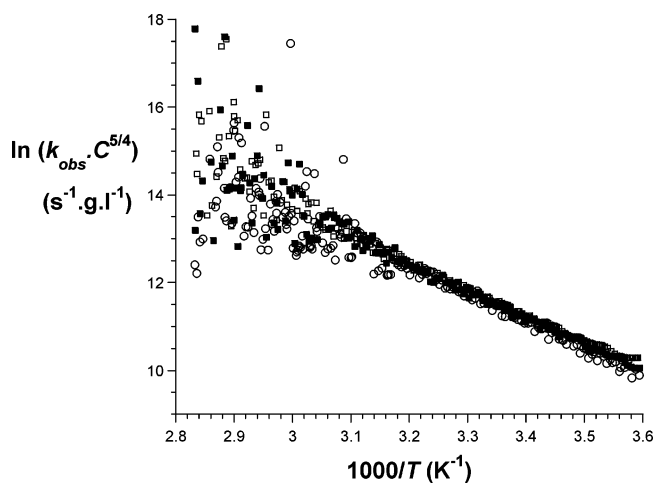


Figure 12. Arrhenius plot of $\ln k_{\text{obs}}$ against $1/T$ for **C7.4** and 0.7 equiv of $\text{Nd}(\text{NO}_3)_3$ normalized for a concentration of 308 g/L (\circ), 400 g/L (\blacksquare), and 500 g/L (\square) in 100 mM PIPES buffer pH 5.4 solutions.

°C (not shown). This means that with increasing temperature the sample loses its (visco)elastic properties and becomes a liquid.

From the relaxation times, the reaction rate, k_{obs} , was calculated (eq 7) as a function of temperature. In Figure 12, the Arrhenius plot is displayed for **C7.4** at three different

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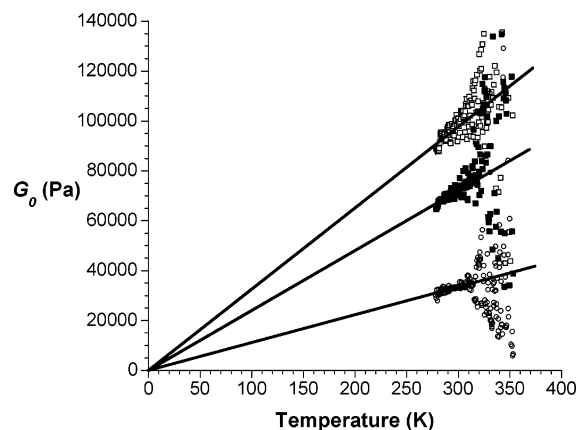


Figure 13. Plateau modulus as a function of temperature for **C7.4** and 0.7 equiv of $\text{Nd}(\text{NO}_3)_3$ of 308 g/L (○), 400 g/L (■), and 500 g/L (□) in 100 mM PIPES buffer pH 5.4 solutions.

concentrations. The curves are normalized for concentration to the power $^{5/4}$, which corresponds to the concentration dependence of τ and therefore also for $1/k_{\text{obs}}$. Due to normalization, the Arrhenius plots for different concentrations collapse onto one single curve. The intercept at $1/T = 0$ equals $\ln(A \cdot C^{5/4})$. Normalization for concentration has no effect on the slopes that correspond to the activation energy, E_a . Although a lot of scatter is present at high temperatures, the slope can easily be determined at lower temperatures. The slope yields an activation energy E_a of 49 kJ/mol, which is not very high. For the **C6**/ Nd^{3+} system, the exact same slope and thus the same activation energy were found. As discussed in section I(b), this activation energy E_a is the arithmetic mean of the activation energies of reptation and breaking of the chains. Because we cannot determine the values for the activation energy for reptation and breaking separately, we can only say that the activation energy for breaking is lower than 49 kJ/mol. A low value for the activation energy is realistic for a reversible process.

Besides the relaxation time, also the plateau modulus as a function of temperature can be determined assuming that the Maxwell model is valid over the whole temperature range. The plateau modulus G_0 can be calculated using eq 1 or 2, because ω is constant (100 Hz), τ was calculated, and G' and G'' were measured. The results are shown in Figure 13. The plateau modulus increases with temperature. This is in line with eq 3 if the amount of entanglements does not change with increasing temperature. From the slopes of the lines in Figure 13, the average molecular weight between the entanglements M_e can be calculated again. The M_e values found here from the slopes are the same as the values in Table 1.

III. Concluding Remarks

In conclusion, we presented here the rheological properties of reversible coordination polymers swollen in water. For **C7.4**,

the rheological properties fit nicely with the model of Cates for linear reversible polymers. Therefore, we conclude that we have mainly linear chains in our system by the formation of alternatively rings and connecting ligands (Figure 7). The addition of Zn^{2+} ions, which can bind only two ligand groups, yields solutions with a substantially decreased viscosity.

Temperature-dependent measurements of G' and G'' gave information about the changes in relaxation time and plateau modulus with temperature. Using the information of the relaxation time (or the rate constant), an activation energy of 49 kJ/mol was obtained at all concentrations for both the **C7.4**/ Nd^{3+} and the **C6**/ Nd^{3+} systems. The low value for the activation energy matches a reversible system. The temperature-dependent plateau modulus showed that the average molecular weight between effective cross-links or entanglements decreases with increasing concentration.

IV. Experimental Section

All commercial chemicals were obtained from Acros or Aldrich and were used as received. The synthesis of **C6** was reported in a recent paper,¹² and **C7.4** was prepared using the same method. For the spacer of **C7.4**, an oligo ethylene oxide (average M_n ca. 400) was used. The OH-groups were replaced by bromines using PBr_3 .³⁷ To purify the brominated ethylene oxides, the brominated ethylene oxides were extracted into diethyl ether. The longest ethylene oxides are more polar and are less easily extracted into the organic phase than the shorter brominated ethylene oxides. When we stopped extracting, we obtained a brominated ethylene oxide with an average of 7.4 ethylene oxide units and used this for the preparation of the final ligands according to the earlier described method.¹² Upon further extraction of the aqueous layer, longer brominated ethylene oxides can be obtained in the organic layer.

The number of the ethylene oxide units in the spacer of compound **C7.4** ranges between six and nine ethylene oxides. This was determined on the basis of the elution volume on a C18 reversed phase column and compared with similar monodisperse compounds (4,5,6,12 ethylene oxide units). Yield 21% (mp > 300 °C). ^1H NMR (D_2O): δ 3.44 (21.6H, m, CH_2O), 3.74 (4H, t, CH_2O), 4.18 (4H, t, CH_2O), 7.39 (4H, s, aromatic H). ^{13}C NMR (D_2O): δ 70.75, 71.04, 71.08, 72.10, 72.12, 72.33, 72.39, 115.41, 157.18, 169.31, 173.92.

All measurements were performed in a 100 mM 1,4-piperazinebis-(ethanesulfonic acid) buffer (PIPES), pH 5.4, and concentrations are given in weight per volume. The rheology experiments were performed on a TA Instruments AR1000-N rheometer using a cone-plate geometry (steel, 20 mm diameter with an angle of 1°). A solvent trap was used to prevent evaporation of the solvent. All experiments were performed at 1% strain. The temperature-dependent experiments were performed with a temperature ramp of 1 °C/min.

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