# Solution Behavior of $\alpha,\omega$-(Dimethylamino)polyisoprene Coordinated to Transition Metal Salts

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ABSTRACT: Coordination of the amino end groups of a telechelic polymer to transition-metal salts has been found to modify profoundly the solution behavior of that material. In toluene, the relative viscosity increases rapidly with concentration, in a way that depends on the transition metal. The coordination ability of the metal cations has been observed to be as follows: Ni < Co < Fe < Cu. The sharpness of the increase in viscosity upon increasing polymer concentration can be significantly reduced in a polar solvent and more effectively in a solvent able to compete with the amino end groups for the coordination sites of the transition metal. Moreover, the viscosity effect, and accordingly the association of the amino end groups, appears to be maximum at a Cu/amine molar ratio of 1. Any change in this ratio between 0.33 and 1.25 causes a drop in the solution viscosity. Empirical equations have been derived to fit the experimental hydrodynamic behavior.

## Introduction

The main physicomechanical properties of organic materials are known to be modified by grafting to the constitutive macromolecules' low percentages (<10-15 mol %) of ionic groups, such as metal carboxylates, metal sulfonates, and quaternary ammoniums salts. The superiority of ionomers over the nonionic precursors results from the electrostatic interactions of the ions pairs attached onto the polymer backbone.[1-3] An alternative to the ionomers might be to replace the ionic groups by other types of mutually interacting groups. In particular, the chemical modification of a polymer by a small percentage of groups that can coordinate to transition-metal salts is an effective way to cross-link a polymer thermoreversibly.[4-6] Although a wide variety of ligands is available, most of the polymers are modified by an amine. Bulk properties of this type of material have been investigated,[4-6] and more recently growing attention has been paid to the solution behavior[7-15] initially investigated in the 1960s.[16] It is worth noting that ligand-modified polymers rapidly become insoluble in nonpolar solvents upon complexation with transition-metal salts. The content of the interacting groups is generally higher than 5 mol %, and these materials form a gel in hydrocarbons, as the ionomers do. It is, however, known that the addition of a low percentage of solvating agent to a gelified ionomer is an effective way to dissolve it completely.[17]

As previously reported, halato telechelic polymers have been proposed as models for the more complex ionomers in which the ionic groups are randomly distributed along the polymeric chain.[2] Thus $\alpha,\omega$-carboxylic acid telechelic polymers have been neutralized with various metal cations in order to have a better insight into the ion-pair association that takes place in an environment of low polarity.[18-20] At very low polymer concentration (<1 g/dL), neutralization of the acid end groups has no significant effect on the solution behavior of the polymeric backbone. However, an increase in the polymer concentration causes an asymptotic rise of the solution viscosity and ultimately the formation of a three-dimensional network. The gelation is observed at concentrations as low as 2 wt % for $\alpha,\omega$-alkaline-earth carboxylatopolybutadiene ($\bar{M}_n$ = 4.6 kg/mol) in toluene at 25 °C. It has been proposed that a transition occurs from intramolecular association of the ionic end groups to a network of intermolecular associations when the polymer concentration increases.[21] Fluorescence measurements have clearly shown that intramolecular interactions prevail in the low polymer concentration regime.[22] Moreover, the sol-gel concentration has been found to be proportional to the reciprocal square root of the molecular mass.[18,19] Gelation has also been reported for other telechelic polymers such as $\alpha,\omega$-metal sulfonate and sulfate polymers in solvents of low dielectric constant.[23-28]

This paper addresses the possibility for association of the amino end groups of a telechelic polyisoprene coordinated to transition-metal salts. Copper, iron, nickel, and cobalt cations are, for instance, known for their ability to form rather strong coordination bonds with amino compounds.[29] The viscosimetric behavior of this new type of telechelic polymer will be investigated in relation to the polarity of the solvent and the metal to amine molar ratio. Results will be compared with the well-known behavior of halato telechelic polymers, i.e., their purely ionic counterparts.

## Experimental Section

**$\alpha,\omega$-(Dimethylamino)polyisoprene.** The anionic polymerization of isoprene was performed in previously flamed and nitrogen-purged glass reactors equipped with rubber septums. Hypodermic syringes and stainless steel capillaries were used to handle liquid products under a nitrogen atmosphere.

Tetrahydrofuran (THF) was dried by refluxing over sodium-benzophenone and distilled under a nitrogen atmosphere. Isoprene was dried over calcium hydride at room temperature and distilled under reduced pressure. It was finally mixed with $n$-BuLi and distilled just before use. 1-Chloro-3-(dimethylamino)propane (DMAPC) resulted from the neutralization of DMAPC·HCl by sodium hydroxide in water. DMAPC was recovered by repeated extractions with diethyl ether. It was dried over anhydrous sodium sulfate and calcium hydride, respectively, for at least 3 days. It was finally distilled just before use.

$\alpha,\omega$-(Dimethylamino)polyisoprene, noted as $PIP(NMe_2)_2$ (Me = $CH_3$), was anionically prepared in THF, at -78 °C. Sodium naphthalene was used as a difunctional initiator. It was previously prepared by reacting naphthalene with an excess of sodium

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in anhydrous THF. The living macrodianion was deactivated by an excess of anhydrous DMAPC and precipitated into methanol. The $PIP(NMe_2)_2$ was purified by three successive precipitations from THF into methanol.

Molecular weight was precisely controlled by the monomer/initiator molar ratio in agreement with a living polymerization mechanism. It was measured by size-exclusion chromatography (SEC) referring to a calibration curve with polystyrene standards. Molecular weight and polydispersity were calculated as $\bar{M}_n$ = 22.5 kg/mol (in polystyrene) and $\bar{M}_w/\bar{M}_n = 1.2$. Assuming two amino groups per PIP chain, titration molecular weight was determined as $\bar{M}_t$ = 19.5 kg/mol by potentiometric titration of the dimethylamino end groups using perchloric acid (0.02 mol/L) in a 9/1 toluene/methanol mixture. Knowing that the SEC ratio of polyisoprene to polystyrene molecular weights is usually 0.8, $\bar{M}_n$ was calculated as 18 kg/mol for the PIP chains. From this $\bar{M}_n$ value and the titration result, $PIP(NMe_2)_2$ was found to be end-capped by 1.85 amino groups.

**Complexation of the Amino Groups.** $PIP(NMe_2)_2$ was dissolved in toluene (5 wt %), to which was added dropwise a methanol solution of $CuCl_2{\cdot}2H_2O$, $FeCl_3{\cdot}6H_2O$, $CoCl_2{\cdot}6H_2O$, and $NiCl_2{\cdot}6H_2O$, respectively (0.2 mol/L), with vigorous stirring maintained for at least 24 h. Polymers complexed with the transition-metal salts were recovered by solvent distillation and dried under vacuum for several days at room temperature. The Cu to dimethylamino end-group ratios ($x$) were 0.33, 0.5, 0.75, 1.0, and 1.25, respectively. All the other transition-metal salts were used in a metal/dimethylamine molar ratio of 0.5. The samples will be quoted by the symbol of the polymer (PIP), followed by the metal (Cu, Fe, Co, or Ni) and the metal/end-group molar ratio ($x$).

**Viscosimetry.** Relative viscosity ($\eta_{rel}$) was determined at 25 ± 0.1 °C in a thermostated bath using a dilution viscometer, equipped with a sintered-glass filter to prevent any dust particles from penetrating into the capillary tube, and capped to prevent evaporation of solvent and exposure to air. $\eta_{rel}$ is the ratio of solution ($t$) to solvent ($t_o$ flow times, which were measured repeatedly in order to ascertain the reproducibility of the data. $\eta_{red}$ is the reduced viscosity, i.e., the ratio of specific viscosity ($\eta_{rel}{}^{-1}$) over the concentration ($C$ in g/dL).

## Results and Discussion

**Effect of the Transition-Metal Cation.** $Cu^{II}$, $Fe^{III}$, $Co^{II}$, and $Ni^{II}$ cations were selected for their ability to be coordinated to amino groups. It is, however, worth noting that information about complex formation is available mainly for aqueous media and few data have been reported in nonpolar and/or nonsolvating organic solvents.[26] This is a consequence of the insolubility of the complexes in low polarity media. Thus, there is a severe limitation to understand the solution behavior of the complexed $PIP(NMe_2)_2$ in a nonpolar solvent, since structural features and stability of the metal/amine complex, e.g., in water, cannot necessarily be extrapolated to hydrocarbons.[30]

Figure 1 shows that the relative viscosity of $PIP(NMe_2)_2$ in toluene is increased by complexation to a transition-metal salt to an extent that depends on the transition metal. Cu seems to be the most effective cation in promoting the intermolecular associations responsible for an increase in the solution viscosity and thus in the apparent molecular weight of the polymer. In fact, the increase in the solution viscosity must clearly be attributed to the coordination of amino end groups to transition-metal cations. Since the solution viscosity of PIP chains free from amino end groups remains unmodified upon the addition of copper chloride or iron chloride, coordination of the double bonds of PIP to the transition-metal cation can be precluded as a possible contribution to the effect observed in Figure 1. As a result of the poor tendency of $Ni^{II}$ to form a complex with a tertiary amine, $NiCl_2$ partly precipitates from the polymer solution in toluene at 25 °C. According to Figure 1, the complexation ability decreases in the order Cu > Fe > Co > Ni.

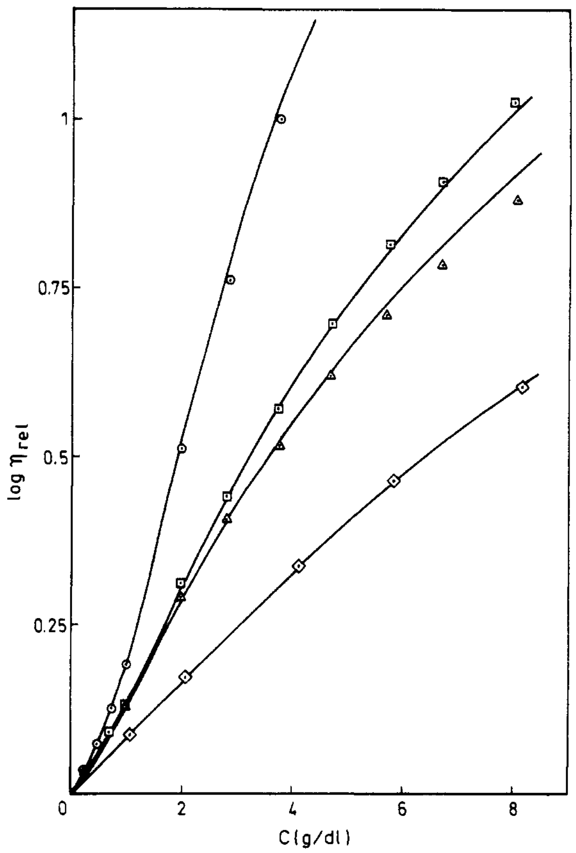

**Figure 1.** Relative viscosity against polymer concentration for $PIP(NMe_2)_2$, complexed with $CuCl_2$ (⊙), $FeCl_3$ (⊡), and $CoCl_2$ (▲) ($x$ = 0.5), as well as for the uncomplexed polymer (◈), in toluene.

In contrast to the solution behavior of $\alpha,\omega$-metal carboxylato and sulfonato polymers, complexation of the amino end groups of $PIP(NMe_2)_2$ is unable to promote gel formation. Consistently, the logarithm of the relative viscosity shows a sigmoid type of concentration dependence (Figure 1) instead of an asymptotic increase as observed when the concentration of carboxylato telechelic polymers in a nonpolar solvent increases.[18,19] This solution behavior is in sharp contrast to the gelation exhibited by traditional ionomers. It implies that the mean degree of coordinative association of the amine end groups increases initially as the polymer concentration increases. Indeed, the relative viscosity of $PIP(NMe_2)_2$ in toluene increases upon complexation with $CuCl_2$ ($x$ = 0.5) by a factor of 2.3 and 5 at a polymer concentration of 2 and 4 $g{\cdot}dL^{-1}$, respectively (Figure 1). In order to account for the absence of gelation, the initial phase of growing association must slow down and finally level off before any stable three-dimensional network is formed.

**Effect of the Solvent.** Figure 2 shows the concentration dependence of the reduced viscosity of PIP/Cu 0.5 dissolved in various solvents: toluene, toluene/methanol (98/2 vol %), THF, and toluene/pyridine (98/2 vol %) at 25 °C. For the sake of comparison, the reduced viscosity of the uncomplexed PIP, in toluene and THF, has also been plotted in Figure 2. Similar to carboxylato telechelic polymers,[19] the solution viscosity of complexed $PIP(NMe_2)_2$ decreases when the dielectric constant of the solvent increases. Moreover, the additon of methanol, known to be a solvating agent of ionic groups, decreases the strength of the end-group interactions and this all the more greater the polymer concentration. This obser-

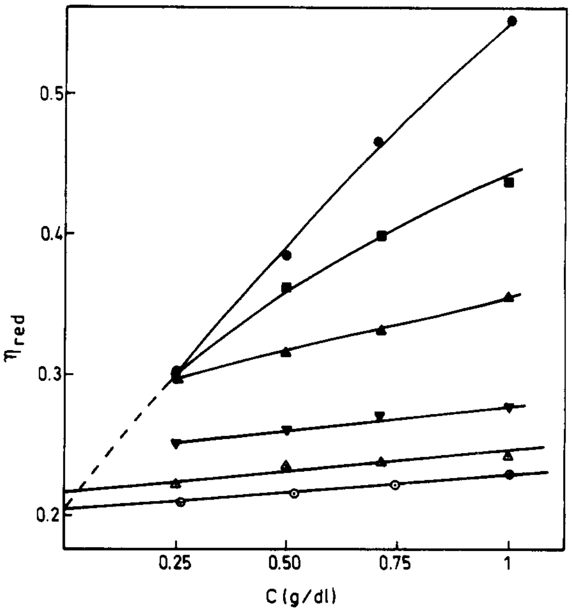

**Figure 2.** Reduced viscosity against polymer concentration for $PIP(NMe_2)_2$ in various solvents: open symbols, uncomplexed; filled symbols, complexed with $CuCl_2$, $x = 0.5$) toluene (⊙,●); THF (△,▲); toluene/methanol (98/2) (■); toluene/pyridine (98/2) (▼).

vation is consistent with the presence of more than one metal salt per aggregate. $CH_3OH$ would be expected to compete with the dipolar interactions of salt molecules ($Cu^{2+}Cl_2^-$ ion triplets) within the aggregates and accordingly favors a decrease in the mean degree of association. Furthermore, the polarity of the solvent may also affect the complexation constant and, hence, the percentage of amino end groups that are complexed to metal cations.[30]

It can be shown that the reduced viscosity is clearly perturbed by the ability of the cosolvent to compete with the amino end groups in its complexation to $Cu^{II}$ cations. The addition to toluene of 2% (v/v) pyridine causes dramatic change in the $\eta_{red}$ vs concentration plot. The decrease in $\eta_{red}$ is substantial compared to that caused by the addition of 2% (v/v) methanol to toluene. An increase in the dielectric constant ($\epsilon$) of the medium cannot account for the experimental data, since the dielectric constant of the toluene/pyridine mixture should be much less than that of toluene/methanol (at 25 °C; $\epsilon$ = 32.6 for methanol and 12.3 for pyridine), which is in contrast to the experimental observations. Aromatic amines, such as pyridine, are well-known ligands of transition-metal cations,[29] and furthermore their molar abundance is 200 times higher than that of the tertiary amines attached to PIP chains. Undoubtedly, some amino end groups are displaced from the coordination sphere of Cu cations by pyridine, thereby decreasing the mean degree of association of the PIP chain ends. Lundberg has also reported that aliphatic amines are more effective than alcohols in decreasing the solution viscosity of zinc sulfonate EPDM ionomers.[17]

The nature of the competing amine is a key parameter. As an illustration, ethylenediamine, i.e., a chelating agent of $Cu^{II}$ cations, was added to a solution of PIP/Cu 0.5 in toluene (1 mol of diamine/mol of $Cu^{2+}$). The reduced viscosity diminished to the value reported for the uncomplexed PIP under the same experimental conditions. Clearly, ethylenediamine, used in the same molar amount as $PIP(NMe_2)_2$, has quantitatively displaced the dimethylamino end groups of PIP from the coordination sites of $Cu^{II}$.

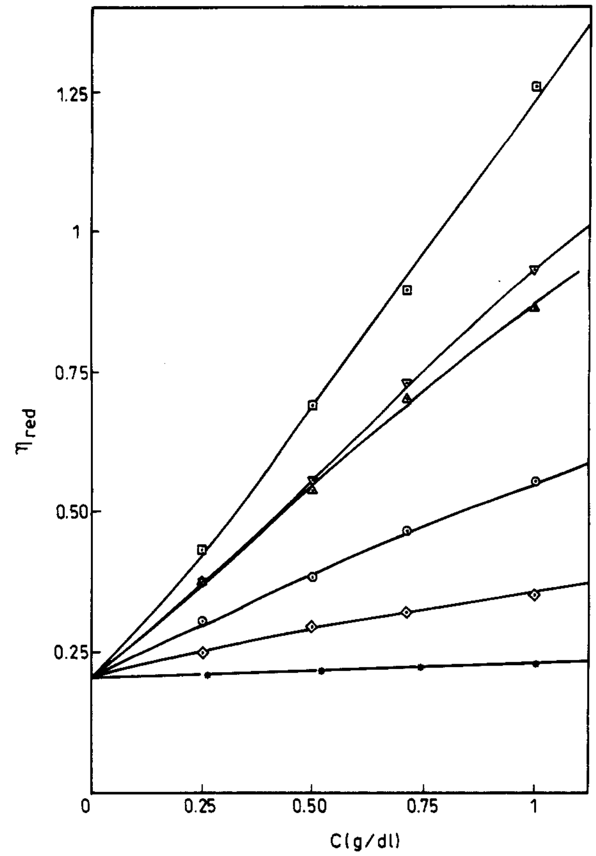

**Figure 3.** Reduced viscosity against polymer concentration for $PIP(NMe_2)_2$, complexed with $CuCl_2$ using different Cu/amine molar ratios, in toluene: $x = 0.33$ (◈), $x = 0.5$ (⊙), $x = 0.75$ (△), $x = 1.0$ (⊡), and $x = 1.25$ (▽), as well as for the uncomplexed polymer (*).

It is noteworthy that the plot of $\eta_{red}$ vs concentration in the 98/2 (v/v) toluene/pyridine mixture is parallel to that reported in pure toluene for the $PIP(NMe_2)_2$ precursor (Figure 2). With comparison of these two plots, it appears that only a very low degree of association persists in the presence of pyridine, independent of the polymer concentration at least up to 1 $g{\cdot}dL^{-1}$. It must be noted that no significant difference has been observed in the solution behavior of the uncomplexed $PIP(NMe_2)_2$ in toluene and in the 98/2 toluene/pyridine system. Moreover, the PIP amine precursor and the same PIP devoid of terminal amine groups display exactly the same viscosity dependence on polymer concentration in the investigated solvents.

**Effects of the Cu/Amine Molar Ratio.** Variation of the reduced viscosity with polymer concentration is plotted in Figure 3 for $PIP(NMe_2)_2$ complexed with various amounts of copper chloride, i.e., Cu/amine molar ratios ($x$) of 0.33, 0.5, 0.75, 1.0, and 1.25, respectively. Surprisingly enough, the intermolecular associations appear to be the most extensive when each amino end group is associated with one Cu cation. It is difficult to understand, on the basis of strictly coordinative interactions, why the most extensive association of the end groups occurs at a 1/1 $Cu^{2+}$/amine stoichiometry. Such a situation would be expected to occur at a stoichiometry ($x$ ratio) lower than 1. However, although $Cu^{2+}$ is usually coordinated with four amino ligands in water,[14] it may not be concluded that the same coordination number prevails in toluene, since the dielectric constant can affect the complexation constants, as it has been described above.[30]

Last, but not least, a polymeric amine is a very crowded ligand, and it may well be this that accounts for the

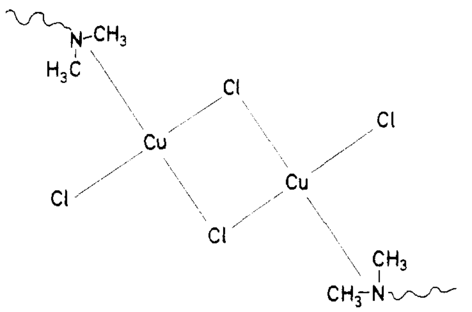

**Figure 4.** Structure proposed for $CuCl_2$ dimers for a Cu/amine molar ratio of 1.

decrease in coordination number. If each amino end group is coordinated to one $CuCl_2$ molecule, then the tendency of the PIP chain ends to associate mutually should be less hindered than when the Cu/amine ratio is less than 1. On the other hand, $\mu$ complexes may be formed for a $x$ ratio of 1, as tentatively schematized in Figure 4, thus allowing the chains to extend up to an infinite value. In fact, such $CuCl_2$ dimers have been reported for poly(styrene-4-vinylpyridine) coordinated with $CuCl_2$.[31] Moreover, it is possible for such dimers to interact through electrostatic attractions, again increasing the apparent molecular weight of the PIP chains, i.e., the solution viscosity. Therefore, a second type of interactions, notably dipolar interactions, may be contributing to the association of the amino end groups, as has been previously suggested. Lundberg reported similar observations for EPDM grafted with zinc sulfonate groups in which associations between $Zn^{2+}$ cations and aliphatic amines or styrene/vinylpyridine copolymers are the most effective at a unitary Zn/amine molar ratio.[15,17] Similarly, the modification in the dynamic mechanical properties of PIP-$(NMe_2)_2$ ($\bar{M}_n$ = 5 kg/mol), upon addition of $CuCl_2$, is the highest at a 1/1 Cu/amine molar ratio.[32]

**Treatment of the Viscosity Data.** Bodycomb and Hara have recently reported on the solution behavior of $\alpha,\omega$-metal carboxylatopolybutadienes in THF. These authors have proposed a method to evaluate the mean degree of association of the end groups as long as gelation does not occur.[33] It is assumed that the partial association of the end groups results in aggregates of macromolecules that behave as a single macromolecule of a higher molecular weight and that mutually interact like traditional macromolecules. Therefore, the higher the polymer concentration, the higher the solution viscosity; and this is related to the apparent molecular weight, i.e., the weight of the aggregate, and its interactions with other aggegates. Furthermore, the average size of the molecular aggregates changes with polymer concentration. In agreement with the Huggins equation (eq 1), the procedure assumes that the size of the aggregates persists to infinite dilution and is therefore characterized by an intrinsic viscosity, which, of course, changes with the concentration[33]

$$\eta_{\text{red}} = [\eta] + k'[\eta]^2 C \tag{1}$$

where $[\eta]$ is the intrinsic viscosity and $k'$ is the Huggins constant characteristic of a polymer–solvent–temperature system.

Equation 1 is linear for the uncomplexed polymer and allows $k'$ and $[\eta]_0$, i.e., $[\eta]$ of the uncomplexed polymer, to be determined. By a least-squares fit, $k'$ and $[\eta]_0$ have been found to be 0.45 and 0.21 dL·g$^{-1}$, respectively. Equation 1 can be reformulated in such a way that the dependence of $[\eta]$ on concentration $C$ can be calculated in the case of the complexed telechelic PIP (eq 2) where $[\eta]_{\text{ag}}$

$$[\eta]_{\text{ag}} = \frac{-1 + (1 + 4k'C\eta_{\text{red}})^{1/2}}{2k'C} \tag{2}$$

is the intrinsic viscosity of $PIP(NMe_2)_2$ complexed to a transition-metal salt and $k'$ is the Huggins constant for the uncomplexed polymer.

Thus, $[\eta]_{\text{ag}}$ can be calculated at any concentration for which the experimental value of $\eta_{\text{red}}$ is known. $[\eta]_{\text{ag}}$ can be correlated to an apparent molecular mass, $M_{\text{ag}}$, by virtue of Flory's equation (eq 3) where $K$ is a constant and

$$[\eta]_{\text{ag}} = K\alpha^3(M_{\text{ag}})^{1/2} \tag{3}$$

$\alpha$ is the (viscosity) expansion coefficient. Equation 4 is the expression of the degree of aggregation, DA, as defined by Bodycomb and Hara

$$\text{DA} = M_{\text{ag}}/M_{\text{o}} \tag{4}$$

where $M_{\text{o}}$ is the molecular weight of the individual PIP macromolecule. From eqs 3 and 4, the expression

$$\text{DA} = ([\eta]_{\text{ag}}/[\eta]_{\text{o}})^2 \tag{5}$$

is obtained provided that $K$ and $\alpha$ are assumed to be the same for both the aggregates and the single molecule. This is a reasonable approximation since Lantman et al.[34] have reported recently that individual ionomer molecules associate into molecular aggregates without significant changes in individual size. Both the knowledge of $[\eta]_{\text{o}}$ and the dependence of $[\eta]_{\text{ag}}$ on concentration allow the variation of DA with concentration to be established.[33] In accordance with the calculation procedure proposed by Bodycomb and Hara, the experimental data of viscosity reported in Figures 1–3 have been converted into DA data as shown in Figures 5–7, respectively. Although DA values are not the actual mean numbers of PIP extremities associated together, plots of Figures 5–7 allow us to discuss on a comparative basis the effect of the main experimental parameters on the coordination of the amine end groups on transition-metal salts.

Plots of DA vs $C$ show much more clearly than the viscosity curves how the PIP chain ends associate. An initial phase of rapid association is followed by a substantial slowing down as the polymer concentration increases; above 1 or a few wt %, depending on the transition metal (Figure 5), the solvent (Figure 6) and the metal/amine ratio (Figure 7), the average degree of association levels off. This behavior is in sharp contrast to the exponential dependence of DA on the polymer concentration observed by Hara et al. for $\alpha,\omega$-metal carboxylatopolybutadiene in THF at 25 °C (eq 6).

$$\log \text{DA} = \beta C \tag{6}$$

$\beta$ is dependent on the metal carboxylate end groups and reflects at what point aggregation occurs as the polymer concentration is increased.[33] The early leveling off in the DA plot that is clearly shown in Figures 5–7 is consistent with the absence of gelation exhibited by the solutions of complexed dimethylamino telechelic PIP. It should be mentioned that the shape of the DA vs $C$ curves provides valuable qualitative information on the association mechanism but not a quantitative analysis of the association process.

On an empirical basis, it has been found that eq 7 fits the DA values in toluene (and toluene/methanol) very closely where $b$ and $k$ are independent constants that

$$\log \text{DA} = b(1 - e^{-kC}) \tag{7}$$

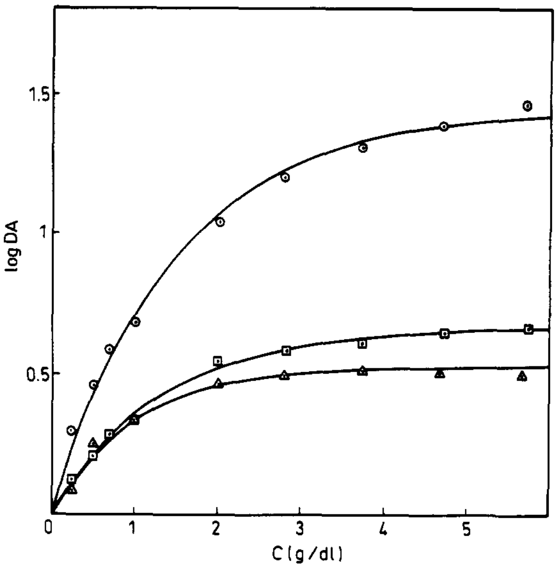

**Figure 5.** Degree of aggregation against polymer concentration for PIP(NMe$_2$)$_2$, complexed with CuCl$_2$ (⊙), FeCl$_3$ (⊡), and CoCl$_2$ (▲) ($x$ = 0.5), in toluene. The full line curve is the theoretical prediction from eq 7.

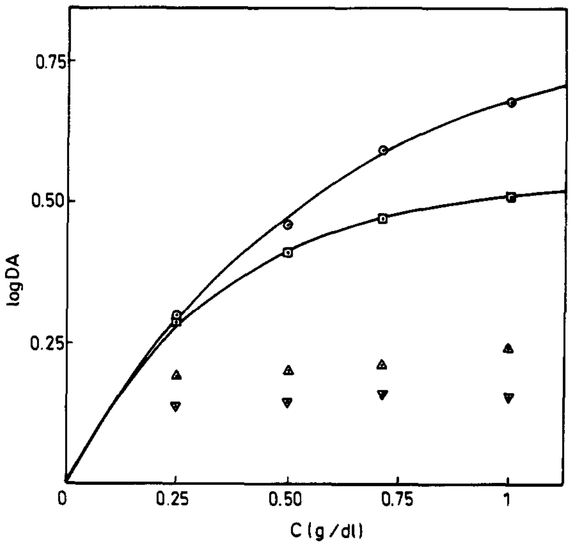

**Figure 6.** Degree of aggregation against polymer concentration for PIP(NMe$_2$)$_2$/Cu 0.5 in various solvents: toluene (⊙), toluene/methanol (98/2) (⊡), THF (▲), toluene/pyridine (98/2) (▼). The full line curve is the theoretical prediction from eq 7.

have been calculated by a least-squares fit and which are listed in Table I. The log DA vs $C$ curves, determined using eq 7 and the data of Table I, are plotted in Figures 5–7. A very good fit between the experimental data and theoretical predictions from eq 7 is shown. From eqs 1, 5, and 7, it is also possible to predict the concentration dependence of $\eta_{\mathrm{red}}$ and log $\eta_{\mathrm{rel}}$, i.e., the experimental data reported in Figures 1 and 3 (eqs 8 and 9)

$$\eta_{\mathrm{red}} = [\eta]_{\mathrm{o}} \exp(W/2) + [\eta]_{\mathrm{o}}^2 k' C \exp(W) \qquad (8)$$

$$W = b(\ln 10)(1 - e^{-kC})$$

$$\log \eta_{\mathrm{rel}} = \log (1 + C\eta_{\mathrm{red}}) \qquad (9)$$

Once again the fit between the theoretical curve and the measured values is excellent and supports the validity of eq 7.

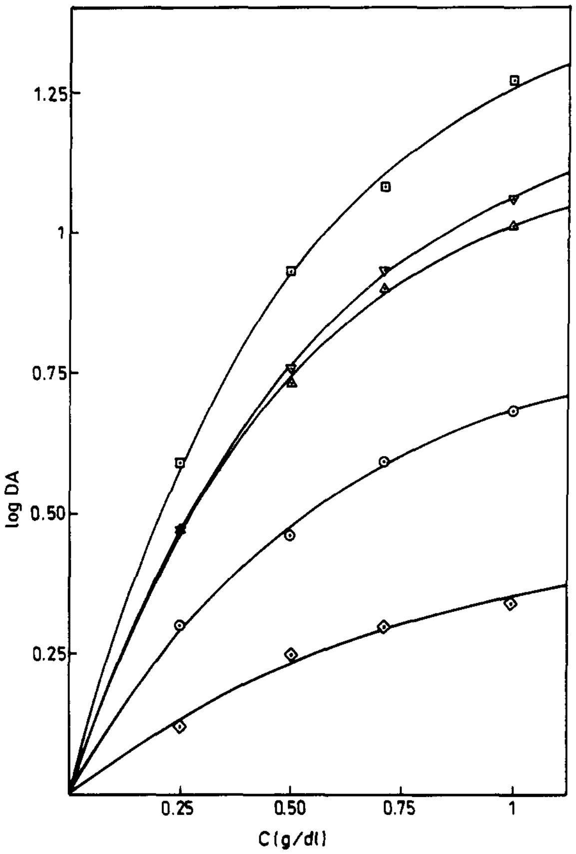

**Figure 7.** Degree of aggregation against polymer concentration for PIP(NMe$_2$)$_2$, complexed with CuCl$_2$ using different Cu/amine molar ratios, in toluene: $x$ = 0.33 (◆), $x$ = 0.5 (⊙), $x$ = 0.75 (▲), $x$ = 1.0 (⊡), $x$ = 1.25 (▼). The full line curve is the theoretical prediction from eq 7.

**Table I**

| samples | $b$ | $k$ | DA$_{\mathrm{max}}$[a] | $C_{\mathrm{ip}}$,[b] g/dL |
|---|---|---|---|---|
| PIP/Cu 0.5[c] | 1.44 | 0.68 | 28 | 1.15 |
| PIP/Fe 0.5 | 0.66 | 0.77 | 4.6 | 1.45 |
| PIP/Co 0.5 | 0.53 | 1.01 | 3.4 | 1.23 |
| PIP/Cu 0.33 | 0.48 | 1.33 | 3 | 1.03 |
| PIP/Cu 0.5[d] | 0.83 | 1.70 | 6.8 | 0.89 |
| PIP/Cu 0.75 | 1.17 | 2.03 | 15 | 0.77 |
| PIP/Cu 1.0 | 1.44 | 2.06 | 27 | 0.74 |
| PIP/Cu 1.25 | 1.25 | 1.88 | 18 | 0.80 |

[a] DA$_{\mathrm{max}}$ = $10^b$. [b] $C_{\mathrm{ip}}$ = $C$ at the inflection point of the log $\eta_{\mathrm{rel}}$ vs $C$ plot calculated from eq 14 (Appendix (2)). [c] Parameters calculated from data of Figure 5. [d] Parameters calculated from data of Figure 7.

The accuracy of the $k$ and $b$ values is obviously dictated by the number of experimental data available. In order to obtain highly accurate values of $k$, as many data as possible are required in the concentration range where the curvature of the log DA vs $C$ plot is maximum, whereas $b$ is determined essentially by data at relatively high concentrations, i.e., in the plateau region of log DA vs $C$. This remark is substantiated by the $b$ and $k$ values reported in Table I for the PIP/Cu 0.5 sample, as calculated from two series of measurements. As already pointed out, $b$ and $k$ values have essentially a comparative meaning for samples characterized under the same experimental conditions (concentration range and number of measurements). Within the limits of that restriction, the values of $b$ determined for the PIP(NMe$_2$)$_2$ samples complexed with various metal/amine molar ratios ($x$) show that $b$ passes through a maximum at $x$ = 1 when $x$ increases from 0.33 to 1.25.

According to eq 7, DA is equal to $10^b$ upon extrapolation to infinite concentration. From this point of view, the highest value of DA ($DA_{max}$) may be approximated as reported in Table I. This also means that $b$ is related to the maximum number of macromolecules associated per aggregate. Furthermore, it is worth pointing out that increasing values of $k$ correspond to a more pronounced curvature in the log DA vs $C$ curve, in agreement with eq 7. $k$ can thus be related to the ability of the chain end groups to participate in intermolecular associations when the polymer concentration increases.

Finally, another characteristic feature of interest in eq 7 is that plots of DA vs $C$ exhibit an inflection point at $C = k^{-1} \ln (b \ln 10)$ (Appendix (1)). It should be recalled that the log $\eta_{rel}$ vs $C$ curves also have a typical sigmoid shape, suggesting that an initial intramolecular association of the end groups disappears rapidly in favor of intermolecular interactions. However, in the concentration range corresponding to the inflection point, the rise in the aggregate size decreases and levels off more or less rapidly. By applying eqs 8 and 9 to the data, the concentration at the inflection point of the log $\eta_{rel}$ vs $C$ curves ($C_{ip}$) was determined (Appendix (2)) and these are collected in Table I. They are consistent with the experimental curves plotted in Figure 1, corroborating again that eq 7 closely reflects the solution behavior of the complexed $PIP(NMe_2)_2$ samples investigated in this study.

## Conclusions

Complexation of the amino end groups of a telechelic polyisoprene (18 kg·mol$^{-1}$) is responsible for a substantial increase in the solution viscosity in toluene at 25 °C. The log $\eta_{rel}$ vs concentration plots exhibit a sigmoidal shape, which has not been observed to date in traditional ionomers and which is consistent with the absence of any gelation process. All the other conditions being kept constant, the transition-metal salt used in the complexation process has a profound effect on the solution behavior. In the particular case of $CuCl_2$, the Cu/dimethylamine molar ratio ($x$) is a key parameter in the control of the solution viscosity, going through a maximum at $x = 1$ when $x$ varies from 0.33 to 1.25. The increase in the solution viscosity due to the complexation of the amino end groups to a transition-metal salt is affected by the polarity of the solvent. The addition of a complexing cosolvent (e.g., pyridine) to toluene has a deleterious effect on the aggregation of the complexed $PIP(NMe_2)_2$ chains, as the result of a competitive complexation to the transition-metal cation.

Empirical equations have been proposed that correlate closely both the experimental data of solution viscosity and the calculated degree of association to the polymer concentration.

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## Appendix

(1) The following equation applies:

$$\log \mathrm{DA} = b(1 - e^{-kC}) \tag{7}$$

If $a = b(\ln 10)$, then eq 7 becomes $\mathrm{DA} = \exp[a(1 - e^{-kC})]$. Therefore, the second derivative of DA is

$$\mathrm{d}^2\mathrm{DA}/\mathrm{d}C^2 = ak^2 \exp(a - ae^{-kC} - kC)(ae^{-kC} - 1)$$

At the inflection point of DA vs $C$, $\mathrm{d}^2\mathrm{DA}/\mathrm{d}C^2 = 0$. This is verified for $(ae^{-kC} - 1) = 0$; thus $C = k^{-1} \ln a = k^{-1} \ln [b(\ln 10)]$.

(2) Assuming down $a = b$ (ln 10), the first derivative of $\eta_{red}$ (cf. eq 8) is

$$\mathrm{d}\eta_{red}/\mathrm{d}C = [\eta]_o{}^2k' \exp[a(1 - e^{-kC})][1 + ake^{-kC}] + (1/2)ak[\eta]_o e^{-kC} \exp[(a/2)(1 - e^{-kC})] \tag{10}$$

The second derivative of $\eta_{red}$ is

$$\mathrm{d}^2\eta_{red}/\mathrm{d}C^2 = [\eta]_o{}^2k'ak \exp[a(1 - e^{-kC})]e^{-kC}[1 + ke^{-kC}(a - 1)] + (1/2)ak^2[\eta]_o e^{-kC} \exp[(a/2)(1 - e^{-kC})][(a/2)e^{-kC} - 1] \tag{11}$$

Equation 9 can be rewritten as follows:

$$\log \eta_{rel} = (1/\ln 10) \ln (\eta_{red}C + 1) \tag{12}$$

The first derivative of log $\eta_{rel}$ is

$$\frac{\mathrm{d} \log \eta_{rel}}{\mathrm{d}C} = \frac{1}{\ln 10} \frac{C(\mathrm{d}y/\mathrm{d}C) + Y}{yC + 1} \tag{13}$$

where $y = \eta_{red}$.

The second derivative of log $\eta_{rel}$ is

$$\frac{\mathrm{d}^2 \log \eta_{rel}}{\mathrm{d}C^2} = \frac{[(C(\mathrm{d}^2y/\mathrm{d}C^2) + 2(\mathrm{d}y/\mathrm{d}C)](yC + 1) - [C(\mathrm{d}y/\mathrm{d}C) + Y]^2}{(yC + 1)^2 \ln 10} \tag{14}$$

At the inflection point of log $\eta_{rel}$ vs $C$, $(\mathrm{d}^2 \log \eta_{rel}/\mathrm{d}C^2) = 0$. By use of eqs 10, 11, and 14 and a computer program, the concentration at the inflection point ($C_{ip}$) has been optimized to satisfy the condition $(\mathrm{d}^2 \log \eta_{rel}/\mathrm{d}C^2) = 0$.

## References and Notes

(1) Eisenberg, A.; King, M. *Ion Containing Polymers*; Academic Press: New York, San Francisco, London, 1977.
(2) McKnight, W. J.; Earnest, T. R., Jr. *J. Polym. Sci., Macromol. Rev.* **1981**, *16*, 41.
(3) Longworth, R. In *Developments in Ionic Polymers. 1*; Wilson, A. D., Prosser, H. J., Eds.; Applied Science Publishers, Ltd.; Essex, U.K., 1983.
(4) Kaneko, M.; Tsuchida, E. *J. Polym. Sci., Macromol. Rev.* **1981**, *16*, 397.
(5) Pomogailo, A. D.; Savostyanov, V. S. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1985**, *C25* (3), 375.
(6) Foxman, B. M.; Gersten, S. W. *Encycl. Polym. Sci. Eng.* **1985**, *4*, 175.
(7) Lekchiri, A.; Morcellet, J.; Morcellet, M. *Macromolecules* **1987**, *20*, 49.
(8) Barbucci, R.; Casolaro, M.; Corezzi, S.; Reginato, G. *Polymer* **1986**, *27*, 1986.
(9) Kratz, M. R.; Hendricker, D. G. *Polymer* **1986**, *27*, 1641.
(10) Kobayachi, S.; Hiroichi, K.; Tokunoh, M.; Saegusa, T. *Macromolecules* **1987**, *20*, 1496.
(11) Pappalardo, S.; Bottino, F.; Finocchiaro, P.; Mamo, A. *J. Polym. Sci., Part A* **1987**, *25*, 1793.
(12) Nagai, A.; Takahashi, A.; Komatsu, T.; Nakawaga, T. *Polym. J.* **1988**, *20*, 609.
(13) Potts, K. T.; Usifer, D. A. *Macromolecules* **1988**, *21*, 1985.
(14) Sen, A.; Weiss, R. A. *Polym. Mater. Sci. Eng., Prepr.* **1988**, *58*, 981.
(15) Lundberg, R. D.; Phillips, R. R.; Peiffer, D. G. *J. Polym. Sci., Polym. Phys. Ed.* **1989**, *27*, 245.
(16) Teyssié, Ph.; Decoene, C.; Teyssié, M. T. *Makromol. Chem.* **1965**, *84*, 51.
(17) Lundberg, R. D. *J. Appl. Polym. Sci.* **1986**, *31*, 1843.

*Macromolecules* **1990**, *23*, 1837–1841

(18) Broze, G.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1981**, *14*, 224.
(19) Broze, G.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1982**, *15*, 920.
(20) Broze, G.; Jérôme, R.; Teyssié, Ph.; Marco, C. *Macromolecules* **1983**, *16*, 996.
(21) Jérôme, R. Halato Telechelic Polymers: A New Class of Ionomers. *Telechelic Polymer: Synthesis and Applications*; Goethals, E., Ed.; CRC Press, Inc.: Boca Raton, FL, 1989; Chapter 11.
(22) Granville, M.; Jérôme, R.; Teyssié, Ph.; De Schryver, F. C. *Macromolecules* **1988**, *21*, 2894.
(23) Misra, N.; Banthia, A. K.; Mandal, B. M. *Eur. Polym. J.* **1979**, *15*, 943.
(24) Misra, N.; Mandal, B. M. *Macromolecules* **1984**, *17*, 495.
(25) Hegedus, R. D.; Lenz, R. W. *J. Polym. Sci., Polym. Chem.* **1988**, *26*, 367.
(26) Tant, M. R.; Wilkes, G. L.; Storey, R.; Kennedy, J. P. *Polym. Bull.* **1985**, *13*, 541.
(27) Foucart, M. Ph.D. Thesis, University of Liège, Belgium, 1988.
(28) Tant, M. R.; Wilkes, G. L.; Kennedy, J. P. *J. Appl. Polym. Sci.* **1989**, *37*, 2873.
(29) Ashcroft, S. J.; Mortimer, C. T. *Thermochemistry of Transition Metal Complexes*; Academic Press: London and New York, 1970.
(30) Reichardt, C. *Effet de Solvant en Chimie Organique*; Flamarion Science: Paris, 1969.
(31) Agnew, N. H. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 2819.
(32) Charlier, P.; Jérôme, R.; Teyssié, Ph.; Utracki, L. A. Accepted for publication in *Macromolecules*.
(33) Bodycomb, J.; Hara, M. *Polym. Bull.* **1988**, *20*, 493.
(34) Lantman, C. W.; McKnight, W. J.; Higgins, J. S.; Peiffer, D. G.; Sinha, S. K.; Lundberg, R. D. *Macromolecules* **1988**, *21*, 1339.

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# Cross-Polarization Magic Angle Spinning Carbon-13 Nuclear Magnetic Resonance Study of Linear Dextran Crystallized from Poly(ethylene glycol)–Water Solution at a High Temperature

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ABSTRACT: The solid-state structure of a synthetic linear dextran, which was crystallized at 160 °C from a mixture of water and poly(ethylene glycol), has been investigated by CP/MAS $^{13}$C NMR spectroscopy. The CP/MAS $^{13}$C NMR resonances narrow upon absorbing water without any change in chemical shifts, suggesting that some distortion of the molecular chains, which is produced by drying, may be relaxed upon the sorption of water. Each resonance line of wet dextran contains two components with $^{13}$C spin–lattice relaxation times, $T_{1C}$, of 170–203 and 8.0–11.4 s, which correspond to the crystalline and noncrystalline components, respectively. When the difference in $T_{1C}$ is used, separate spectra of the crystalline and noncrystalline components have been obtained. The line-shape analysis shows that the crystalline spectrum consists of six doublets with a 1:1 ratio corresponding to six carbon sites. These six doublets may originate from two different electronic environments produced by two different packing arrangements. The degree of crystallinity is approximately estimated to be 46% by the line-shape analysis, and the lamellar thickness is determined as 60 Å from SAXS. From these values the crystalline and noncrystalline thicknesses are assumed to be of the orders of 28 and 16 Å, respectively.

## Introduction

Native dextran ($\alpha$-1,6-glucan) is produced, for example, from saccharoses by *Leuconostoc mesenteroides*,[1] but it is not readily crystallizable because of the presence of branches. In contrast, linear dextran can be chemically synthesized by the polymerization of 1,6-dianhydro-2,3,4-tri-*O*-benzyl-$\beta$-D-glucopyranose following the debenzylation.[2] Chanzy et al.[3,4] have found that such a linear dextran can be crystallized from dilute solution in the form of lamellar single crystals, provided low molecular weight fractions are used. In addition, linear dextran exhibits two polymorphs; a "low-temperature" polymorph obtained below 100 °C and a "high-temperature" polymorph crystallized above 120 °C.[4–6] The principal difference between these polymorphs is that the high-temperature polymorph is anhydrous while the low-temperature crystalline form is hydrated.

In this paper we have investigated the solid-state structure of linear dextran, which was crystallized at 160 °C from dilute solution according to the previous method,[4] by cross-polarization (CP)/magic angle spinning (MAS) $^{13}$C NMR spectroscopy. The NMR analysis is based on the methods previously studied for the solid-state structure of $\alpha$-1,4- and $\beta$-1,4-glucans such as amylose[7,8] and cellulose.[9–14] The resolution enhancement of the resonance lines is made by measuring the NMR spectra in the presence of water. Then the contributions of the crystalline and noncrystalline components in the spectra are separately recorded by using the difference in $^{13}$C spin–lattice relaxation times ($T_{1C}$) between the two components. On the basis of these spectra and the $T_{1C}$ values, we discuss the crystalline and noncrystalline structures of the dextran sample.

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