

Halato-telechelic Polymers. XIV. Solution Behavior of α,ω -Divalent Transition Metal Dicarboxylato Polybutadiene

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Synopsis

A procedure is described which allows α,ω -dicarboxylic acid polybutadiene to be end-neutralized using a stoichiometric amount of a transition metal acetate. In a nonpolar solvent, the solution viscosity of this new class of carboxylato telechelic polymers depends on the neutralization degree of the acid end groups in such a way that the progress of the neutralization may be compared with that of a polycondensation reaction. In contrast to Cu(II), the Zn, Ni, Co, and Mn carboxylate endgroups promote very early gelation of toluene solutions when the polymer concentration increases. The particular behavior of Cu(II) can only be explained by a difference in the coordination number compared with the other elements of the first transition series. The dependence of the solution viscosity on the atomic number of the element cannot be completely accounted for so far. Nevertheless, an electrostatic association of the cupric carboxylate end groups can be disregarded, since the solution viscosity is independent of the polarity of the solvent in the range of 2.28–7.28 D.

INTRODUCTION

To modify a common polymer with a low percentage of metal carboxylate or sulfonate pendant groups is a well-known means of improving its bulk properties.¹⁻⁴ Because of their very poor solubility in most usual solvents, the solution behavior of such polymeric materials—namely ionomers—has been overlooked. In solvents with a low dielectric constant, electrostatic interactions between ionic groups lead to ion pairs which build up an insoluble three-dimensional polymer network. However, solubility can be restored when small amounts of a polar compound are added to the nonpolar solvent, thus solvating the ion pairs and preventing any further association.⁵ Among other examples, Lundberg et al. have investigated the solution behavior of polystyrene⁶⁻¹¹ and EPDM^{12,13} carrying Na sulfonate groups randomly distributed along the chain. When dissolved in a hydrocarbon containing a suitable amount of an alcohol, those ionomers unexpectedly show a sharp rise of the solution viscosity upon increasing temperature.⁶ This can be explained by the low temperature solvation of the sulfonate groups by the cosolvent and its rapid desolvation at a high-enough temperature. The degree of polystyrene sulfonation is a major factor in the ion pair association.^{9,10} Indeed, a reversible change from intramolecular to intermolecular interactions takes place at a critical concentration which is mainly dependent on the sulfonate content. It must be pointed out that, in all foregoing examples, nonpolar solvents

are good solvents of the modified polymer. In a polar good solvent, the polymeric backbone may be modified by a limited percentage of ionic groups before insolubilization takes place; the greater the polarity of the solvent, the more extensive the ion modification of the polymer can be while maintaining solubility.^{7,8} Grafting a hydrocarbon polymer with a few percents of ionic groups is instrumental in promoting the dissolution in a polar nonsolvent; e.g., polystyrene as such is insoluble in dimethylsulfoxide but dissolves when containing 1.7% sulfonate groups.⁸ As a rule, the ionic groups randomly attached to hydrocarbon chains either prevent the polymer from dissolving in nonpolar solvents or make the solubilization easier in polar nonsolvents. Finally, when an ionomer is soluble in a solvent of high dielectric constant (dimethylformamide, ethyleneglycolmonomethylether), a typical polyelectrolyte behavior is observed and the hydrodynamic volume depends on the nature of the counterion.^{14,15} Further details on the solution behavior of ionomers can be found in a recent review.¹⁶

The solution behavior of halato-telechelic polymers is especially interesting as they have been designed as models for the more complex ionomers.^{17,18} In halato-telechelic polymers, the ionic groups are selectively attached at both ends of linear chains. This allows the precise control of their mutual spacing and makes the association process less complex because of much less restriction by the polymer chain when the ion pairs are brought together. α,ω -Dicarboxylic acid polybutadiene end-neutralized by alkaline-earth cations has been thoroughly investigated. The most striking behavior in nonpolar solvents is that gelation occurs at as low a polymer concentration as 1 or 2 wt%.^{18,19} As expected, a polar cosolvent hinders gelation so that the sol-gel transition is less sharp and occurs at higher polymer concentrations. The same effect is observed when the temperature increases, but thermally induced modifications are reversible. The bigger the alkaline-earth cation is, the more delayed is the gelation process. Similarly, the gelation concentration is all the more small as the polymer molecular weight is high, and an experimental relationship— $C_{\text{gel}} = kM_n^{-0.5}$ — has been reported.²⁰ k is constant for a given polymer and accounts for an increase in C_{gel} when the chain cross-section increases.²¹ Gelation also depends on the molecular weight distribution since the sharpness of the sol-gel transition decreases as the polydispersity index increases.¹⁸ Finally, at polymer concentrations smaller than C_{gel} either a homogeneous sol is observed or a phase demixing takes place when the electrostatic interactions are strong enough.^{19,21} Further data on the solution behavior of sulfate^{22,23} and sulfonate^{24,25} telechelic polymers are also available and complete the foregoing information. As a conclusion, halato-telechelic polymers provide a rather clear insight into the ion pair association process and emphasize how it depends on the molecular features of the polymeric backbone.

In the series of carboxylato-telechelic polymers, the essentially ionic alkaline earth carboxylates have been considered so far. The question is now how much the dissociation of carboxylate groups is modified when the metal carboxylate bonds are less ionic and more coordinative. A partial answer should be found in the solution behavior of a series of carboxylato-telechelic polymers containing divalent transition metal cations instead of divalent

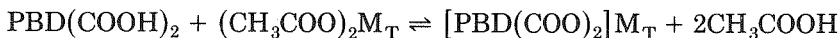
alkaline earth cations. This paper reports a general procedure for the quantitative conversion of carboxylic acid end groups into transition metal carboxylates. Emphasis will be placed upon the solution behavior of transition metal carboxylato-telechelic polybutadiene in relation to the degree of neutralization of the end groups, the polarity of the solvent, and the cation characteristics.

EXPERIMENTAL

Carboxy-telechelic polybutadiene commercially available from BF Goodrich (Hycar CTB 2000 \times 156) with $\bar{M}_n = 4.600$; $\bar{M}_w/\bar{M}_n = 1.8$, functionality = 2.01, and *cis/trans*/vinyl ratio = 20 : 65 : 15 was used as received.

Transition metal acetates were commercial crystalline products containing a well-defined number of water molecules in the crystal [CuAc₂ · H₂O, NiAc₂ · 5H₂O, CoAc₂ · 4H₂O, MnAc₂ · 4H₂O, CdAc₂ · 2H₂O], except for HgAc₂ which was an anhydrous salt. Metal acetates were previously dissolved in methanol or in acetic acid when insoluble in the former solvent (10⁻² mol L⁻¹). Carboxy-telechelic polybutadiene was dissolved in previously dried toluene (5 wt%) and added with the stoichiometric amount of metal acetate, i.e., 1 mol of salt or two acetate anions per telechelic molecule. The solvent of the metal acetate solution (methanol or acetic acid) and the acetic acid formed as neutralization product were removed from the reaction mixture by toluene azeotropic distillation. Briefly, toluene was partially (ca. 50%) distilled off under reduced pressure, freshly dried toluene was added into the reaction medium and a further distillation run was performed. The recovered acetic acid was determined by potentiometric titration with tetramethylammonium hydroxide in a 90% benzene/10% methanol mixture. It was observed that the acetic acid due to the quantitative neutralization reaction was completely removed when the volume of distilled toluene was at least equal to that of the initial reaction mixture. Nevertheless, the distillation run was repeated three times in order to eliminate as much as possible the molecules (H₂O, methanol, acetic acid) that solvate the metal carboxylate end groups. After the third distillation run, the polymer was dried under vacuum at room temperature until no weight reduction was observed.

Solution viscosity was measured using a Desreux-Bischoff viscometer²⁶ immersed in a thermostated bath (25°C). Solutions were prepared using solvents previously dried by refluxing over calcium hydride (benzene, toluene, chlorobenzene, decahydronaphthalene) or benzophenone sodium (tetrahydrofuran). The dynamic mechanical behavior of 10 gdL⁻¹ solutions in decahydronaphthalene was investigated with a Rheometrics mechanical spectrometer (RMS-7200) equipped with the plate-plate geometry (plate diameter 5.0 cm, plate-to-plate distance 0.2 cm). IR spectra were recorded on a Perkin Elmer 197 spectrometer.



Typically, a solution of the carboxy-telechelic polybutadiene in toluene is added with the stoichiometric amount of a transition metal (M_T) acetate

previously dissolved in methanol or in acetic acid if required. After stirring for 10 min, a sample of the reaction mixture is withdrawn and the polymer recovered by solvent evaporation and drying under vacuum. The IR analysis clearly shows that the carboxyl stretching band of the carboxylic acid at 1710 cm^{-1} disappears in favor of a new broad absorption characteristic of the carboxylate anion between 1550 and 1590 cm^{-1} depending on the metal (Fig. 1). It means that the conventional technique of toluene removal and final drying of polybutadiene is efficient enough to displace the equilibrium of the neutralization reaction towards the expected metal carboxylato-telechelic polymer and to remove the major part of the acetic acid by-product. The same conclusion holds when polybutadiene is recovered by precipitation into methanol followed by drying in vacuo. The actual structure of the carboxylic acid at both ends of polybutadiene ($\text{HOOC}-(\text{CH}_2)_2-\text{C}(\text{CH}_3)(\text{CN})-$) provides the end groups with an acidity greater than that of acetic acid accounting for the ease of the neutralization reaction; it is indeed known that the model of the end groups, i.e., $\text{CH}(\text{CH}_3)(\text{CN})-(\text{CH}_2)_2-\text{COOH}$, is more acid ($\text{pK}_a = 4.51$) than acetic acid ($\text{pK}_a = 4.75$).²⁹

As explained in the experimental part, the final α,ω -transition metal dicarboxylato polybutadiene is extensively purified by repeated toluene azeotropic distillation. In that way, methanol used as solvent of the metal acetate, acetic acid and water of crystallization of the acetate are already removed before drying the bulk material in vacuo. This new, easy, and well-controlled technique of neutralization has been applied for the synthesis of polybutadiene end-capped with divalent Zn, Cu, Ni, Co, Mn, Cd, and Hg carboxylates, respectively.

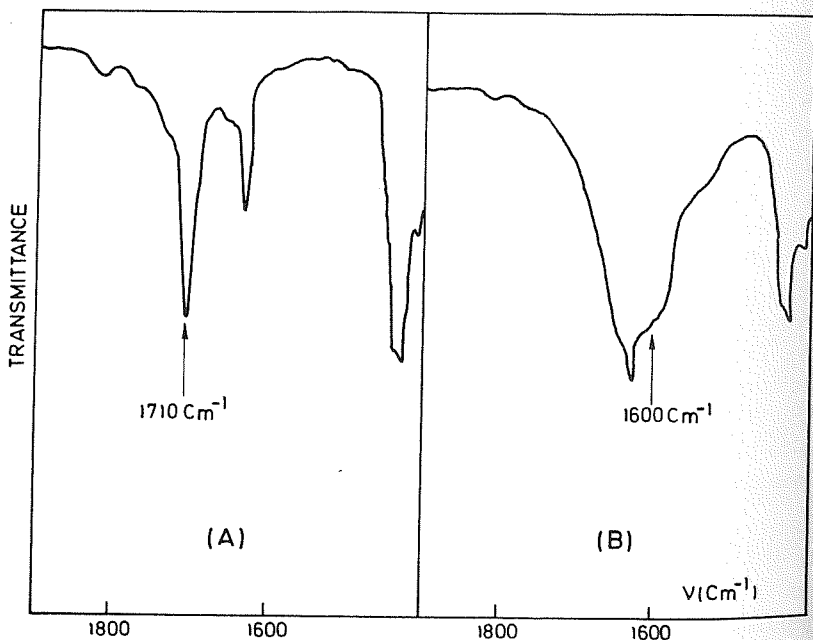


Fig. 1. Infra-red spectroscopy of α,ω -dicarboxylic acid polybutadiene: (A) before neutralization, (B) after reaction with the stoichiometric amount of cupric acetate ($\text{COOH}/\text{acetate} = 1$).

Solution Behavior of α,ω -Cu Dicarboxylato Polybutadiene

The α,ω -dicarboxylic acid polybutadiene has been neutralized at levels of 25, 50, 75, and 100% of the acid end groups, respectively, using Cu acetate as the neutralizing agent; for convenience, the related polymers will be designated as PBD-Cu 25, PBD-Cu 50, PBD-Cu 75, and PBD-Cu 100, respectively. Figure 2 shows that the benzene solutions of both PBD-Cu 25 and PBD-Cu 50 at 25°C have a viscosity which is not very much greater than that of the unneutralized polymer. This is in sharp contrast to the completely neutralized polybutadiene which exhibits a very sharp increase in the relative viscosity at a polymer concentration as low as 2 wt%. The solution behavior of PBD-Cu 75 follows the same dependence on polymer concentration as PBD-Cu 100; the relative viscosity and accordingly the apparent molecular weight of PBD-Cu 75 are reasonably smaller than that of PBD-Cu 100 but comparatively much greater than PBD-Cu 50. This situation can be rationalized when the neutralization of α,ω -dicarboxylic acid polybutadiene by a divalent metal acetate is formally compared with the well-known polycondensation of two difunctional and mutually reactive organic molecules. Polycondensations proceed in a stepwise manner, with the molecular weight of the polymer increasing slightly with lower conversion. For instance, a yield of 90% leads to a degree of polymerization of 10. In contrast, the molecular weight increases dramatically during the last stage of the step polymerization, and the polymerization degree may exhibit a 10-fold increase while the yield goes from 90 to 99%. The apparent molecular weight of the neutralized carboxy-telechelic polybutadiene should follow the same trend as the neutralization degree of the acid end groups increases. Furthermore, the progress in the apparent hydrodynamic volume can be enhanced by the possible intermolecular association of the partially neutralized molecules; this effect is expected to be all the greater as the polymer concentration is high.

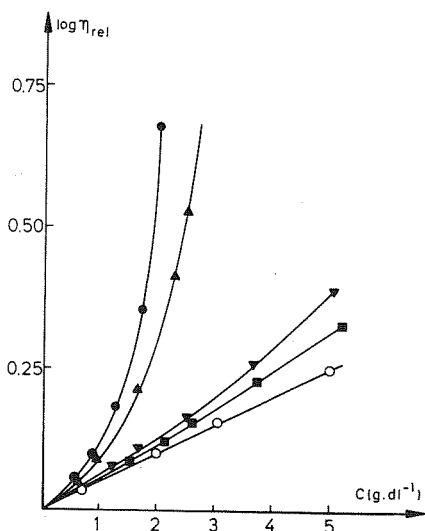


Fig. 2. Plot of the relative viscosity in benzene versus concentration for α,ω -dicarboxylic acid polybutadiene neutralized at different percentages with cupric acetate. Temperature: 25°C (O, unneutralized; ■, 25%; ▼, 50%; ▲, 75%; ●, 100%).

As stressed in the introduction, toluene solutions of polybutadiene end-capped by ionic alkaline earth carboxylates turn into a gel in the polymer concentration range where the relative viscosity of the PBD-Cu 100 solution increases very sharply. In spite of the same general solution behavior, PBD-Cu 100 is, however, unable to stabilize a three-dimensional polymer network in benzene. The Cu carboxylate end groups interact strongly enough to promote a dramatic increase of the apparent molecular weight of polybutadiene, but the average degree of intermolecular association is not great enough to impart elastic properties to the solution and no gel is observed even at much higher polymer concentrations (10 wt%). At first glance, a decrease in the ionicity of the metal carboxylate bond as due to the substitution of an alkaline earth cation by a transition metal cation such as Cu(II) could have a deleterious effect on the aggregation of the related groups in nonpolar solvents. Nevertheless, before a definite conclusion can be drawn, the behavior of a series of divalent transition metals should be investigated. Furthermore, the effect of the polarity of the solvent might shed light on the nature of the intermolecular association of the transition metal carboxylates.

Dependence of the Solution Behavior on the Nature of the Transition Metal

In the same way as the solution behavior of carboxylato-telechelic polybutadiene has been investigated for alkaline earth cations,^{18,19} elements of the first transition series (the acetates of which are available) have been considered in this study, i.e., in the sequence of increasing atomic number: Mn(25), Co(27), Ni(28), Cu(29), and Zn(30). All of these metal ions have been used in the same oxidation state +2. The relative viscosity of the related α,ω -transition metal dicarboxylato polybutadiene in toluene at 25°C has been plotted against polymer concentration (Fig. 3). In contrast to the unneutralized polybutadiene, all the polymers end-capped by transition metal carboxylates exhibit the same behavior, which is characterized by a very sharp increase in viscosity. This increase, however, occurs at increasing polymer concentration when the atomic number decreases. From a qualitative point of view, the concentration as defined by the vertical asymptote to the viscosity curve depends on the atomic number of the metal, i.e., in an opposite way when alkaline earth cations are compared with transition metals of period 4 of the periodic table of elements. In the family of alkaline earth cations, the experimental increase in C_{gel} as the ionic radius increases is simply accounted for by the weakening of the ion pairs and the related intermolecular dipole-dipole interactions. In the series of transition metals, the situation is not so clear because all these elements are close to each other. Actually, the radii of the elements from Mn through Cu are very similar, lying in the range of 1.15 to 1.17 Å. Similarly the ionic radii of the divalent cations do not change very much, although different values may be found in the literature depending on the coordination number of the metal, the nature of the ligands, and the determination technique. For instance, Mahan reports the following ionic radii for divalent cations: Mn, 0.80; Co, 0.74; Ni, 0.72; Cu, 0.72; and Zn, 0.74 Å.³⁰ Accordingly, no relation can be drawn between the polymer concentration

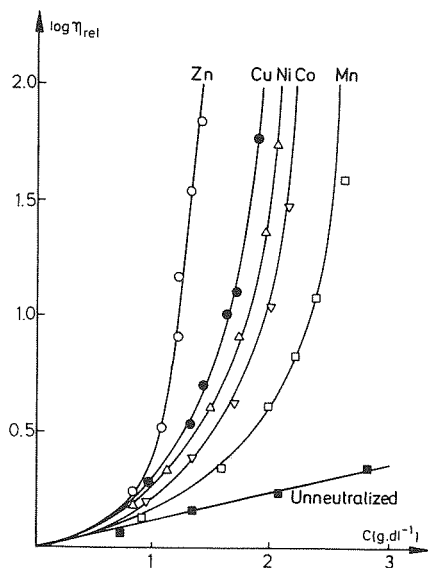


Fig. 3. Relative viscosity versus concentration for α,ω -dicarboxylic acid polybutadiene end-neutralized by acetates of elements of the first transition series. Solvent: toluene; temperature: 25°C.

at which the relative viscosity increases sharply and the average dimension of the cation. Thus, a possible electrostatic origin for the solution behavior reported in Figure 3 may be disregarded. Another intriguing observation is the very particular behavior of Cu compared with that of the other transition metal cations of the first series. Although the viscosity curve of PBD-Cu 100 cannot be distinguished from that of all the other α,ω -transition metal dicarboxylato polybutadienes regarding both the general shape and the relative position in the polymer concentration scale (Fig. 3), it is observed that the sharp increase in viscosity corresponds to a sol-gel transition excepted for solutions of PBD-Cu 100 that do not gellify but remain viscous beyond the dramatic viscosity rise. It is worth noting that most of the transition metals exhibit a sixfold coordination with an octahedral geometry. Nevertheless, a fourfold coordination is generally reported for Cu(II) with a square planar arrangement of the ligands (Jahn Teller effect). For instance, as a consequence of a lower coordination number of Cu(II), anhydrous cupric chloride and bromide consist of long chains of atoms, departing from the structure found in the dihalides of alkaline earth metals and the other metals of the first transition series. Assuming that this situation might be extended to the Cu(II) carboxylate end groups of polybutadiene and that carboxylates often have a bidentate structure, the end-neutralization of the short-length α,ω -dicarboxylic acid polybutadiene by Cu(II) cations should result in a linear macromolecule of very high molecular weight. The entanglements of very long chains could account for the solution behavior reported in Figure 3. This is partially supported by the microstructure of bulk PBD-Cu 50 and PBD-Cu 75 as investigated by EXAFS (extended X-ray absorption fine structure) and electron paramagnetic resonance.³¹ The local structure consists of both iso-

lated and dimeric complexes. The former behave as chain extenders ($\sim\text{C} \begin{array}{c} \diagup \text{O} \\ \diagdown \text{O} \end{array} \text{Cu}^{2+} \begin{array}{c} \diagup \text{O} \\ \diagdown \text{O} \end{array} \text{C} \sim$) while the latter would have a structure similar to that of Cu(II) acetate complexes and would link four end groups all together. Surprisingly enough, magnetic measurements show that the dimerization ratio decreases from 0.78 to 0.70 when the percentage of neutralization increases from 50 to 75%. Without anticipating the effect of the solvent on these structural features, it may be suggested that dimers stabilize a three-dimensional PBD network which could however be disrupted by too short a lifetime of the isolated complexes. Since the toluene solution of carboxylato-telechelic polybutadiene containing metal cations of the first transition series other than Cu(II) form homogeneous gels, the divalent Mn, Co, and Ni cations should exhibit the most common sixfold coordination. The behavior of Zn cations is however more complex, since this metal belongs to family II of elements consisting of Zn, Cd, and Hg. Since they have $2s$ electrons beyond filled d subshells, these three elements are not usually considered transition metals. However, they resemble transition elements in their ability to form complexes with ligands such as ammonia, cyanide, and halide anions. Although Zn dicarboxylato polybutadiene (PBD-Zn) exhibits a solution behavior in agreement with that observed for transition metals of period 4 as classified by decreasing atomic number (Fig. 3), Zn should be considered independently of the Mn, Co, Ni, and Cu series. Furthermore, its most common coordination number is four with a tetrahedral structure, which is, however, consistent with gelation of PBD-Zn solution in toluene.

Figure 4 reports the viscosity curves characteristic of group IIb elements (Zn, Cd, Hg) and shows the same trend as for the alkaline earth cations, since the rise in viscosity at increasing concentration is delayed as the atomic

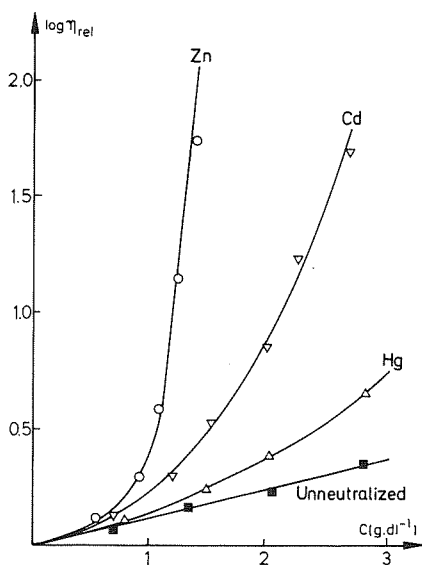


Fig. 4. Relative viscosity versus concentration for α,ω -dicarboxylic acid polybutadiene end-neutralized by acetates of elements of the IIb family. Solvent: toluene; temperature 25°C.

number of the element increases. However, it is not reliable to correlate that parameter with the regular shift of the viscosity curves parallel to the concentration axis due to the uncertainty about the ionic radii; for instance, similar values are reported for Cd(II) and Hg(II), i.e., 0.92 Å.³² It is worth noting that Cd and Hg carboxylate end groups cannot promote the gelation of the toluene solutions, and the ability of Hg carboxylates to increase the solution viscosity is even very weak. This observation might be related to the structural analysis of $\text{Cd}(\text{O}_2\text{C}-\text{CH}_3)_2(\text{H}_2\text{O})_2$ and $\text{Hg}(\text{O}_2\text{C}-\text{CH}_3)_2[(\text{C}_6\text{H}_{11})_3\text{P}]$ which suggests the presence of monoatomic bridging acetate groups.^{33,34} Since the cation radius cannot account for the solution behavior of group IIb elements containing dicarboxylato polybutadiene, the cation's polarizing power, or its softness according to Pearson's terminology,³⁵ could be a determining parameter. It is well known that discrepancies from structures predicted by the ionic bonding model increase as cation's softness increases.³⁶ Accordingly, the strength of dipoles associated with group IIb element carboxylates should decrease from Zn to Cd and finally to Hg, as experimentally observed. In conclusion, the nature of the metal is a key point in the control of the solution behavior, but it is premature to offer an explanation as long as the structure of the transition metal carboxylate end groups and their possible aggregation are unknown.

In the foregoing discussion, the behavior of carboxylatotelechelic polybutadienes containing either an alkaline earth or a transition metal cation has been tentatively compared. The meaning of that comparison is, however, questionable, since the nature of the intermolecular interactions is most likely very different, although the macroscopic phenomena are quite comparable. The electrostatic origin of the gelation promoted by α,ω -alkaline earth dicarboxylato polybutadiene has been unambiguously demonstrated.¹⁸ Since transition metals are generally said to form less ionic compounds than alkaline earth elements, gelation should occur at higher polymer concentrations as long as the electrostatic interaction of ion pairs is the preferential mechanism for the end groups to associate. When observed, however, gelation occurs at the same polymer concentration range for both alkaline earth and transition metal cations (Table I). It means that the same effect is most likely promoted by two different mechanisms. This conclusion is supported by the influence of the solvent on the solution viscosity as discussed hereafter.

Effect of the Solvent Polarity on the Solution Behavior

As stressed in the introduction, any solvating agent of the ion pairs has a depressive effect on the strength of the electro-static interactions. This feature has been exploited in order to dissolve ionomers in nonpolar solvents. Similarly, the solution behavior of α,ω -alkaline earth dicarboxylato polymers has been shown to change dramatically either upon adding toluene with 1% methanol or increasing the dielectric constant of the solvent, e.g. THF is sufficiently polar to prevent gelation.¹⁸

The reduced viscosity of the PBD-Cu samples of different neutralization degrees has been measured in solvents of various dielectric constants: THF (7.28D), chlorobenzene (5.71D), toluene (2.44D) and benzene (2.28D). For the completely neutralized polymer, the same type of viscosity curve as shown

TABLE I
Critical Concentration for Gelation (C_{gel}) of Toluene Solutions of α, ω -Metal
Dicarboxylato Polybutadiene at 25°C

Cation	Ionic radius ^a (Å)	C_{gel} (gdL ⁻¹)
Zn	0.74	1.4
Cu	0.72	1.9 ^b
Ni	0.72	2.1
Co	0.74	2.2
Mn	0.80	2.5
Mg ^c	0.65	2.0

^aFrom Ref. 30.

^bSince the related solutions are essentially viscous whatever the polymer concentration, the vertical asymptote to the viscosity curve does not correspond to a sol-gel transition, and the 1.9 gdL⁻¹ has nothing to do with C_{gel} .

^cFrom Ref. 18 and 19.

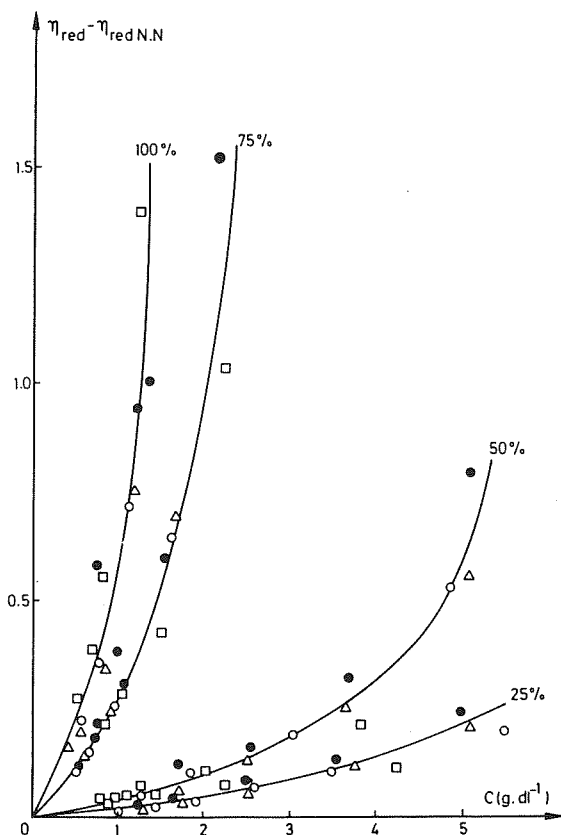


Fig. 5. Concentration dependence of the increase of the reduced viscosity of α, ω -dicarboxylic acid polybutadiene neutralized at different percentages by cupric acetate. Temperature: 25°C. Solvent: (●) toluene, (Δ) benzene, (□) THF, (○) chlorobenzene.

in Figure 3 is observed whatever the solvent used, and the polymer concentration at which the reduced viscosity rises sharply is slightly dependent on the solvent, i.e.; 1.9% in toluene, 2.1% in benzene, 2.25% in chlorobenzene and 2.35% in THF. These values are however influenced by the specific polybutadiene-solvent interactions that might change from one solvent to another. In order to make the experimental results independent of that parameter, the difference between the reduced viscosity of the neutralized and the unneutralized polymer ($\eta_{red} - \eta_{red,NN}$) has been plotted versus the polymer concentration. For each neutralization degree, a single curve is reported whatever the dielectric constant of the solvent in the range of 2.28 to 7.28D (Fig. 5). These results convincingly support that Cu carboxylates do not promote electrostatic interactions between the poly-butadiene ends.

Effect of the Cation Oxidation State

In the first transition series, iron lies between Mn and Co; this element has been disregarded so far because of the easy oxidation of Fe(II) to Fe(III). Fe(III) might however be useful to estimate the effect due to an increase of the valence of the transition metal cation. Figure 6 shows that in spite of a lower oxidation state, Cu(II) is more instrumental than Fe(III) in increasing the solution viscosity and therefore the association of the original polybutadiene chains. Furthermore, like Cu(II), Fe(III) carboxylates do not stabilize a three-dimensional polybutadiene network in a nonpolar solvent. This is in sharp contrast to Al(III) carboxylates which are responsible for the gelation of the toluene solutions of the related telechelic polybutadiene. This example is

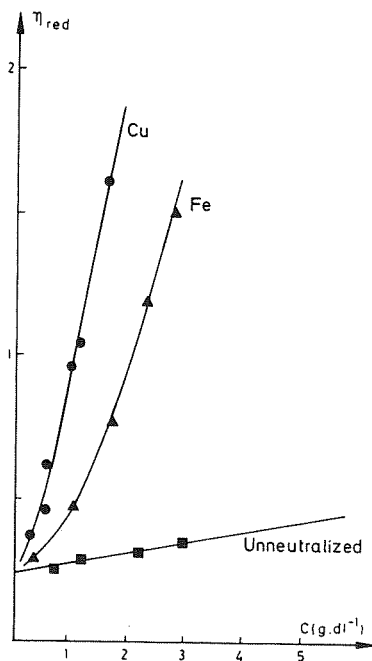


Fig. 6. Relative viscosity versus concentration for α,ω -dicarboxylic acid polybutadiene end-neutralized by cupric and ferric acetate, respectively. Solvent: toluene; temperature: 25°C.

additional evidence that when transition metals are considered, the mechanism for carboxylate end group interactions is very different from that followed by cations containing only *s* and *p* orbitals. For the sake of completeness, it must be mentioned that α,ω -Fe(III) dicarboxylato polybutadiene has been synthesized using Fe(III) isopropylate as the neutralizing agent,³⁷ according to the procedure as described earlier for alkaline earth cations.¹⁸ This procedure eliminates the presence of residual solvating agents, such as acetic acid, which is the main cause for the nongelation of the related solutions.

Behavior of Fe(III) alkoxide is very close to that of group IVb metal (Ti, Zr, Ce) alkoxides which, when used in stoichiometric amounts and under anhydrous conditions, react with carboxylic acid telechelic polymers without promoting a crosslinking effect.³⁸ This has been attributed to a possible steric hindrance of the alkoxide together with the opportunity for both end groups of telechelics to react with the same alkoxide molecule. Carboxy-telechelic polymers can, however, be crosslinked in a nonpolar solvent by Fe(III) alkoxide or a group IVb metal alkoxide used in excess versus the acid end groups: the solution turns into a gel upon the hydrolysis of the unreacted alkoxide groups into metal oxoalkoxide ones.³⁹

Viscoelastic Properties of 10 wt% Solutions in Decaline

From the dilute solution, the *d* orbitals containing metals can be classified into two classes according to their ability to gellify the solutions of the parent metal carboxylato-telechelic polymers or not: Mn(II), Co(II), Ni(II), and Zn(II) carboxylates are efficient gelling end groups, whereas Cu(II), Fe(III), Cd(II), and Hg(II) are only able to increase the solution viscosity with a decreasing efficiency from Cu(II) through Hg(II). In order to substantiate this conclusion merely based on visual observations, the viscoelastic properties of concentrated solutions (10 wt% in decahydronaphthalene) of the most representative α,ω -transition metal dicarboxylato polybutadienes have been investigated. Figure 7 shows the isothermal dependence of the storage (G') and loss (G'') shear moduli on frequency, at 25°C, for a cation of each class, i.e., Ni and Cu. It is obvious that the interactions of the Ni carboxylate end groups impart elastic properties to the solution since G' is largely independent of frequency in the investigated range of frequencies. All the other conditions being kept constant, substituting Cu for Ni is responsible for a purely viscous behavior as supported by G' values smaller than G'' and rapidly decreasing at decreasing frequencies.

Since the available mechanical spectrometer was not equipped with a cooling device, extra isotherms were recorded at temperatures higher than 25°C when the complex shear modulus was great enough to be measured accurately. In these conditions, several isotherms have been recorded up to 70°C for the cations of the first class, whereas Fe(III) is the only cation of the second class to have been successfully characterized in the same way. For all cations investigated, i.e., Mn, Ni, Co, and Fe(III), the time-temperature equivalence is verified allowing the related master curves to be built up for both G' and G'' . Figures 8–11 show that the usual procedure of shifting successive isotherms of $\log G'$ (or $\log G''$) versus $\log \omega$ horizontally with

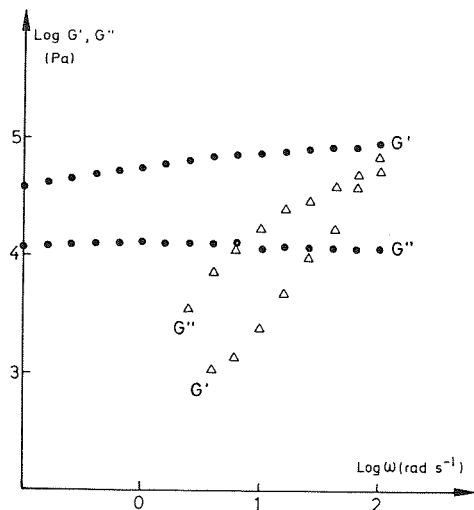


Fig. 7. Isothermal (25°C) dependence of the storage (G') and loss (G'') shear moduli on frequency for the 10 gdL⁻¹ solution in decahydronaphthalene of α, ω -dicarboxylato-polybutadiene containing Cu(II) (Δ) and Ni(II) (\bullet) as the counteranion, respectively.

respect to a reference isotherm makes them fit with a maximum overlap. A maximum in G'' at the end of the rubbery plateau is clearly observed when Fe(III) is the cation (Fig. 8); this maximum has to be attributed to the relaxation of the aggregates formed by the carboxylate end groups. In the presence of Co and Mn (Figs. 9 and 11) the maximum is very broad, whereas its observation in the same frequency range is prevented by the pronounced elasticity of the solution of α, ω -Ni dicarboxylato PBD. When Fe(III) is compared with the other transition metal cations (Mn, Ni, Co), it appears that the higher the elasticity of the solution, the broader the distribution of the relaxation times responsible for the occurrence of the viscous flow.

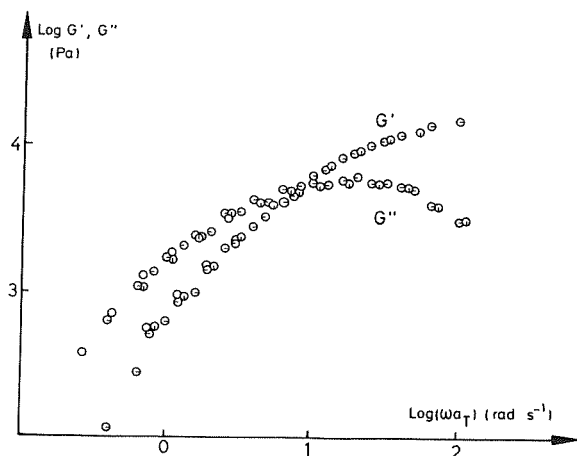


Fig. 8. Master curves of storage (G') and loss (G'') shear moduli versus reduced frequency for 10 gdL⁻¹ solution in decahydronaphthalene of Fe(III) α, ω -dicarboxylato polybutadiene (\bar{M}_n : 4600); reference temperature: 298 K. (\ominus) 298 K, (\oplus) 308 K, (\ominus) 318 K, and (\circ) 328 K.

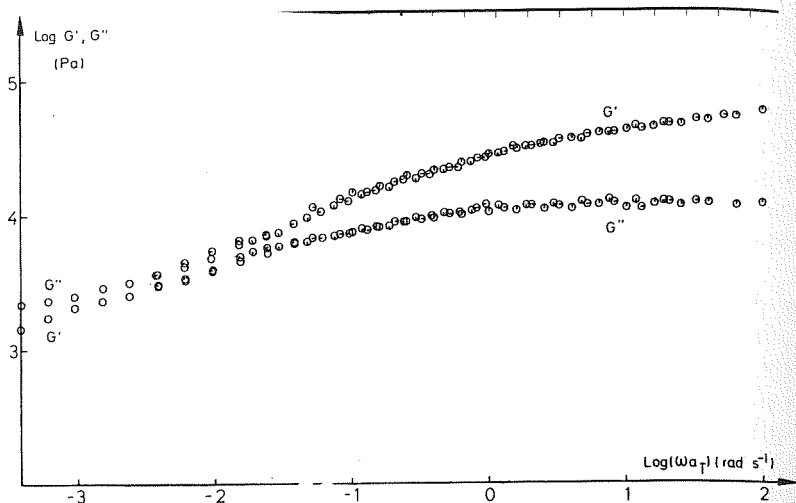


Fig. 9. Master curves of storage (G') and loss (G'') shear moduli versus reduced frequency for 10 gdL^{-1} solution in decahydronaphthalene of Co(II) α,ω -dicarboxylato-polybutadiene (\bar{M}_n : 4600); reference temperature: 305 K. (\circ) 305 K, (\square) 314 K, (\triangle) 323 K, (\diamond) 333 K, (\circ) 342 K.

At least in the investigated range, the shift factors plotted on a logarithmic scale versus the reverse of temperature support an apparent Arrhenius-like dependence (Fig. 12) from which the activation energy of the secondary relaxation process can be calculated. As shown in Table II, the activation energy does not change very much for cations in the first class, whereas it is significantly smaller for Fe(III) in agreement with the sharp difference observed in the solution behavior of PBD end-capped by carboxylates of each

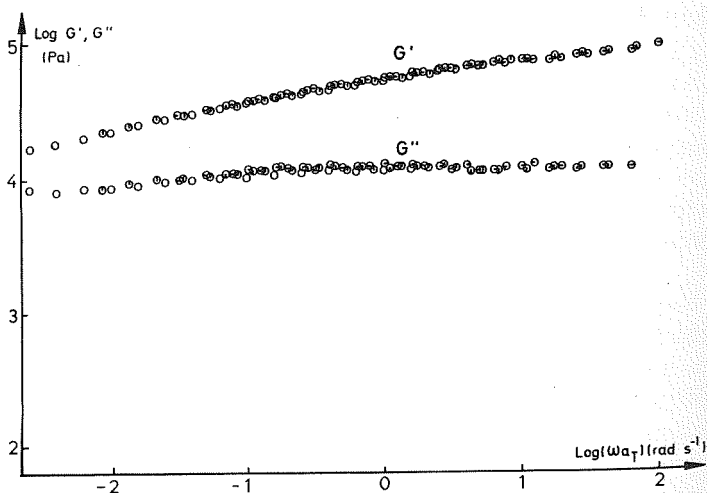


Fig. 10. Master curves of storage (G') and loss (G'') shear moduli versus reduced frequency for 10 gdL^{-1} solution in decahydronaphthalene of Ni(II) α,ω -dicarboxylato-polybutadiene (\bar{M}_n : 4600); reference temperature 304 K. (\square) 304 K, (\circ) 311 K, (\triangle) 321 K, (\diamond) 336 K, (\circ) 344 K.

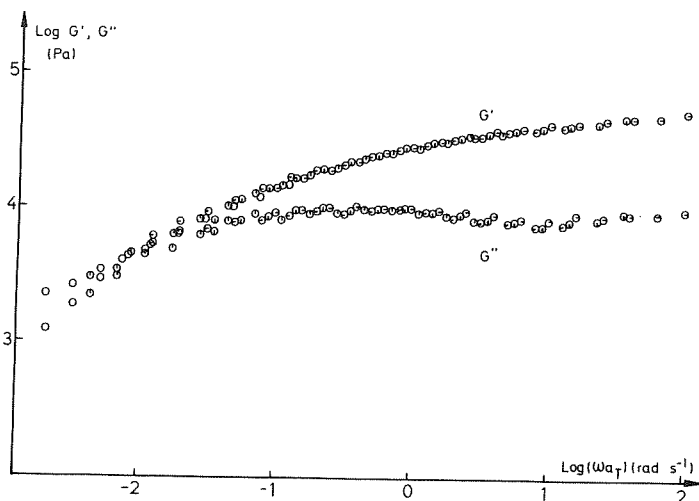


Fig. 11. Master curves of storage (G') and loss (G'') shear moduli versus reduced frequency for 10 g dL^{-1} solution in decahydronaphthalene of Mn(II) α,ω -dicarboxylato-polybutadiene (\bar{M}_n : 4600); reference temperature 303 K. (\circ) 303 K, (\odot) 308 K, (\ominus) 318 K, (\oplus) 329 K, (\oslash) 339 K.

type of cation. It is worth recalling that the solution behavior of Ti dicarboxylato PBD in toluene is quite similar to that reported in this paper and that an activation energy has been calculated which increases with the polymer concentration in the range of $5\text{--}17 \text{ g dL}^{-1}$.³⁹ The increase of the activation energy with the polymer concentration has been tentatively explained in terms of a parallel increase of the mean number of chain ends per aggregate.

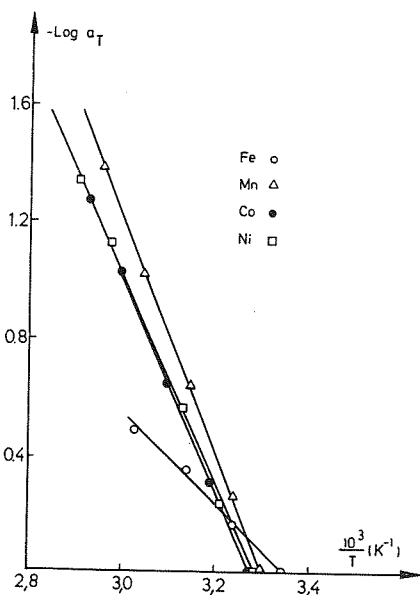


Fig. 12. Shift factors (a_T) versus $1/T$ for 10 g dL^{-1} solutions in decahydronaphthalene of Fe(III), Ni, Co, and Mn α,ω -dicarboxylato-polybutadiene (\bar{M}_n : 4600).

TABLE II
 Activation Energy of the Secondary Relaxation Observed in α,ω -Transition
 Metal Dicarboxylato Polybutadiene

Cation	Activation Energy Solution ^a	Bulk (kcal mol ⁻¹)
Cu(II)	b	20.5
Fe(III)	8.9	19.7
Cd	b	18.0
Mn	21.5	21.7
Ni	20.0	20.0
Co	20.1	b

^a10 wt% in decahydronaphthalene (decaline).

^bUndetermined.

In this regard, the viscoelastic behavior of α,ω -divalent transition metal dicarboxylato PBD has also been investigated in bulk and the activation energy of the secondary relaxation determined as for the related solutions. Indeed, the thermorheological simplicity of the solutions is still observed for the bulk material; these data will be thoroughly discussed elsewhere. From Table II it is clear that the activation process which makes the individual chains free to flow is insensitive to the addition of a nonpolar solvent when cations of the first class are considered and the polymer concentration remains higher than 10 wt%. The behavior of α,ω -Fe(III) dicarboxylato PBD is however different since the activation energy reported for the 10 wt% solution has increased while going to the bulk material. Quite interestingly the activation energy determined for bulk carboxylato-telechelic PBD is independent of the class to which the divalent transition metal belongs. In other words, the intermolecular interactions which promote and stabilize the association of the carboxylate end groups are largely independent of the transition metal considered in this study. The observation of two types of cations as derived from the solution behavior should be mainly related to the opportunity for the metal carboxylates to vary their association in solution. The increase of the mean degree of association of Cu, Fe(III), Cd, and Hg(II) carboxylates at increasing polymer concentration is expected to be slower compared with that of Mn, Ni, and Co carboxylate end groups.

The authors are indebted to the "Services de la Programmation de la Politique Scientifique" for financial support. They are also grateful to Professor C. Marco (University of Mons, Belgium) for his collaboration in the rheological study of the concentrated solutions. They thank M. Koenig for the measurements of solution viscosity.

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Received September 10, 1987

Accepted February 5, 1988