

# Halato Telechelic Polymers. XVI - Viscoelastic Properties of $\alpha,\omega$ -Transition Metal Carboxylato Polybutadiene

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A low molecular weight carboxy-telechelic polybutadiene ( $M_n = 4,600$ ) behaves as a thermorheologically simple polymer when the end-groups are neutralized with a series of transition metal cations like Cd, Cu(II), Fe(III), Ni, Co, and Mn. On the basis of the dynamic mechanical properties of the carboxylated telechelic polymers, two classes of cations can be distinguished according to their ability to efficiently stabilize a chain network. Polybutadiene containing Co, Ni, and Mn carboxylates behaves like a cured rubber, whereas Fe(III), Cu(II), and Cd carboxylate end-groups show a decreasing efficiency in contributing to the elasticity of the polymer. Such behaviour is induced by the structure of the coordinative complexes which are formed by the d orbital containing cations with carboxylate end-groups and possibly with double bonds of the polymeric backbone.

## Keywords

Ionomers; Networks; Polybutadiene; Rheology; Telechelic Polymers; Transition Metals

## INTRODUCTION

Viscoelastic properties of organic materials are usually strongly modified by grafting of low percentages of mutually interacting groups to the constitutive macromolecules. Chemical modification of a hydrophobic polymer by a small percentage (<10 - 15 mol%) of ionic groups - such as metal carboxylates, metal sulfonates or quaternary ammonium salts - is known to promote the thermoreversible crosslinking of the material which is referred to as an ionomer.<sup>1</sup> Similarly, modifications of traditional polymers by groups able to coordinate to transition metal salts is also an effective way to

crosslink the polymer thermoreversibly.<sup>2</sup> It must also be pointed out that the degree of miscibility of two otherwise immiscible polymers can be largely controlled by specific interactions, e.g., hydrogen bonding, acid-base interactions, complex formation, or promoted by mutually interacting groups selectively attached, one on each polymeric partner.<sup>3</sup>

In order to have a better understanding of the process of intermolecular associations, various studies on model systems, particularly on model ionomers, have been undertaken during the last decade. Due to the selective localization of ionic groups at both ends of linear chains, halato-telechelic polymers have been studied as models for ionomers.<sup>4-20</sup> Indeed, the well-de-

finned although largely variable distances between the terminal interacting ion pairs make their association less restricted by the polymer chain. In the series of metal carboxylate telechelic polydienes, small angle X-ray scattering (SAXS) has shown that the dipolar association of ion pairs results in multiplet formation, primarily governed by the configuration of the polymer between the ionic groups.<sup>14,15</sup> Viscoelastic properties of both carboxylated<sup>9,10,11,13,16,19</sup> and sulfonated<sup>21,22</sup> telechelic polymers are found to resemble thermorheologically simple polymers, and partial master curves show the presence of a secondary relaxation characteristic for thermal dissociation of ionic aggregates. The activation energy ( $E_A$ ) of such a relaxation is related to the valency ( $n$ ) and ionic radius ( $r_i$ ) of the cation according to the following equation:<sup>16</sup>

$$E_A = 85.3n/r_i \quad [1]$$

An increase in the cation valency usually promotes the formation of a more stable network because of electrostatic interactions.<sup>13,16</sup> Moreover, the equilibrium storage modulus shows that the bigger the alkaline-earth cation, the more extensive is the ion pair association.<sup>10,13</sup> In contrast, the degree of association goes through a maximum when the radius of alkaline cations increases. Indeed, sodium carboxylates provide telechelic polybutadiene with the highest elasticity, which makes it comparable to the calcium counterpart.<sup>16</sup>

The situation changes dramatically when alkaline and alkaline-earth cations are substituted by transition metal cations. Although the terminal carboxylate groups of telechelic polybutadiene still tend to be associated, electrostatic interactions do not play a decisive role any more. Rather, the ability of transition elements to form complexes with ligands, e.g. carboxylates, and their coordination number appear to be the key parameters controlling the end-groups association. That general conclusion results from a previous study of the solution behaviour of  $\alpha,\omega$ -transition metal carboxylato polybutadiene.<sup>18</sup> It has been reported that toluene solutions jell rapidly upon increasing concentrations when the counterion is Ni, Co, or Mn, i.e., cations which exhibit the most common six-fold coordination. In contrast,

Cu(II), Cd(II), Hg(II), and Fe(III) cations are unable to promote the gelation of toluene solutions, although a rise in viscosity is noted when the polymer concentration increases. A lower coordination number of these cations and/or non-three-dimensional structure of their complexes are the most likely reasons of solution properties of  $\alpha,\omega$ -transition metal carboxylate polybutadiene.

In order to get a better insight into the role played by the transition metal cations in relationship to metal carboxylate end-groups, a viscoelastic study of salts of Cu(II), Fe(III), Cd(II), Ni(II), Co(II), and Mn(II) of telechelic carboxylated polybutadiene ( $M_n = 4,600$ ) was undertaken and is reported here.

## EXPERIMENTAL

Carboxy-telechelic polybutadiene commercially available from BFGoodrich (Hycar CTB 2000x156), with  $M_n = 4600$ ,  $M_w/M_n = 1.8$ ; functionality equals 2,0 and cis/trans/vinyl ratio equals 20:65:15, was used as received.

Transition metal acetates were commercial crystalline products [CuAc<sub>2</sub>.H<sub>2</sub>O; NiAc<sub>2</sub>.5H<sub>2</sub>O; CoAc<sub>2</sub>.4H<sub>2</sub>O; MnAc<sub>2</sub>.4H<sub>2</sub>O, and CdAc<sub>2</sub>.2H<sub>2</sub>O].

Carboxy-telechelic polybutadiene was dissolved in previously dried toluene (5 wt%) and added to the stoichiometric amount of metal acetate (1 salt molecule per telechelic molecule) previously dissolved in methanol or acetic acid ( $10^{-2}$  mol×L<sup>-1</sup>). The solvent and the acetic acid formed as the neutralization by-products were removed from the reaction mixture by toluene azeotropic distillation. The distillation was repeated until the neutralization of the acid end-groups was complete.<sup>18</sup> The iron(III)-containing sample resulted from the end-neutralization of carboxy-telechelic polybutadiene with iron(III) 2-propoxide under anhydrous conditions. Synthesis of the iron alkoxide and the neutralization technique were reported elsewhere.<sup>23</sup> The final samples were dried under vacuum until there was no further weight reduction.

The dynamic mechanical properties were studied using Rheometrics Mechanical Spectrometer (RMS-7200) fitted with plate and plate geometry (plate diameter 2.5 cm). The  $G'$  and  $G''$  values were measured in the fre-

quency range  $10^{-4}$  -  $100$  rad×sec<sup>-1</sup>; the covered temperature range was a function of the strength of the neutralized polybutadiene, typically being in the range 25 - 100°C. The partial master curves were constructed by superposing the  $G'$  and  $G''$  curves at different temperatures along the frequency axis by a factor  $a_T$ .

## RESULTS AND DISCUSSION

Except for Cd, all the investigated cations belong to the first transition series of the periodic table of elements and their atomic number increases regularly: Mn (25), Fe (26), Co (27), Ni(28), and finally Cu (29). For the sake of comparison, cations have been used in the same oxidation state (II). Iron is, however, an exception because of the easy oxidation of Fe(II) to Fe(III). Iron(III) might, however, be useful to estimate the effect adequate to the valency increase of the transition metal cation. For convenience, the studied samples will be designated as PBD-M, where PBD stands for polybutadiene and M for the metal cation.

By reference to the solution behaviour, the bulk rheological properties of the  $\alpha,\omega$ -transition metal carboxylate PBD will be discussed in relation to the ability of the cation to jell (Mn, Co, Ni) or inability to jell (Fe, Cu, Cd) toluene solutions.

### Viscoelastic Behaviour of Cu(II), Cd(II), and Fe(III) Salts of Carboxy-telechelic PBD

As mentioned in the *Introduction*, the Cu(II), Cd(II), and Fe(III) were found to increase the viscosity of the carboxylated telechelic PBD in toluene and decahydronaphthalene (DHN). Although the increase in viscosity could be very sudden, particularly for Cu(II), no gelation was ultimately observed.<sup>18</sup> When 10 wt% solutions in DHN were compared at room temperature, the efficiency in stabilizing intermolecular associations decreased from Fe(II) to Cu(II) and finally to Cd(II).<sup>18</sup> Indeed, the PBD-Cd solution was too fluid for reliable values of the storage ( $G'$ ) and loss ( $G''$ ) shear moduli to be measured. In contrast, the isothermal dependence of  $G'$  and  $G''$  on frequency ( $1$  to  $100$  rads<sup>-1</sup>) could be recorded for the PBD-Cu solution at 298K - but

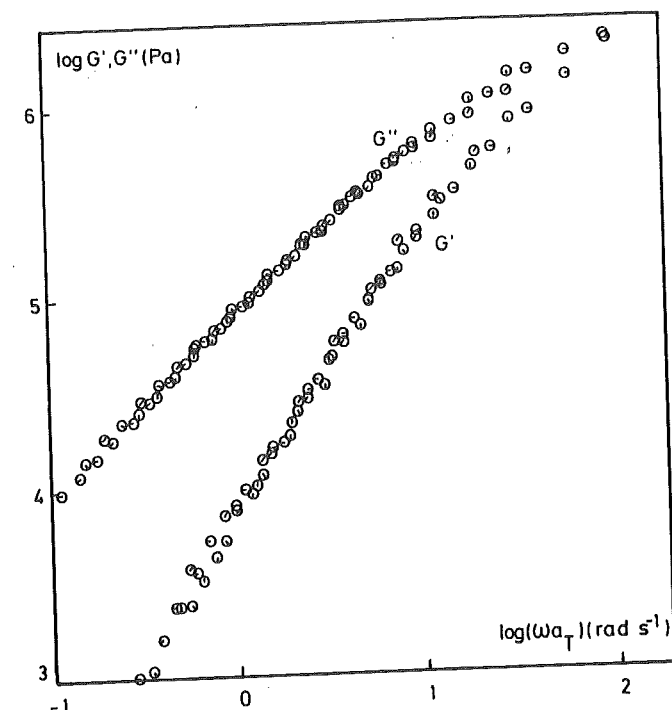


Figure 1. Partial master curves of storage ( $G'$ ) and loss ( $G''$ ) shear moduli for  $\alpha,\omega$ -Cd carboxylato polybutadiene ( $M_n = 4,600$ ). Reference temperature: 300K (○ 301K, ○ 308K, ○ 313K, ○ 319K, ○ 325K, ○ 331K, ○ 336K).

not at a higher temperature - and supported a purely viscous behaviour. The  $G'$  values were actually smaller than  $G''$  and rapidly decreasing at decreasing frequencies. Finally, in the same frequency range, a partial master curve was obtained for the PBD-Fe solution from isotherms measured between 298 and 328K. At the reference temperature of 298K, a rubbery plateau emerged at the highest frequencies and the transition to the viscous flow regime (maximum in  $G''$ ) was observed at ca.  $10$  s<sup>-1</sup>.

As an extension of that previous study, the viscoelastic properties of the bulk PBD-Cu, PBD-Cd, and PBD-Fe samples have been measured as illustrated in Figures 1 to 3.

Although the isothermal dependence of  $G'$  and  $G''$  on frequency has been investigated in a limited temperature range of ca. 35K, the successive isotherms can be superposed with a maximum overlap (Figures 1-3). At the refer-

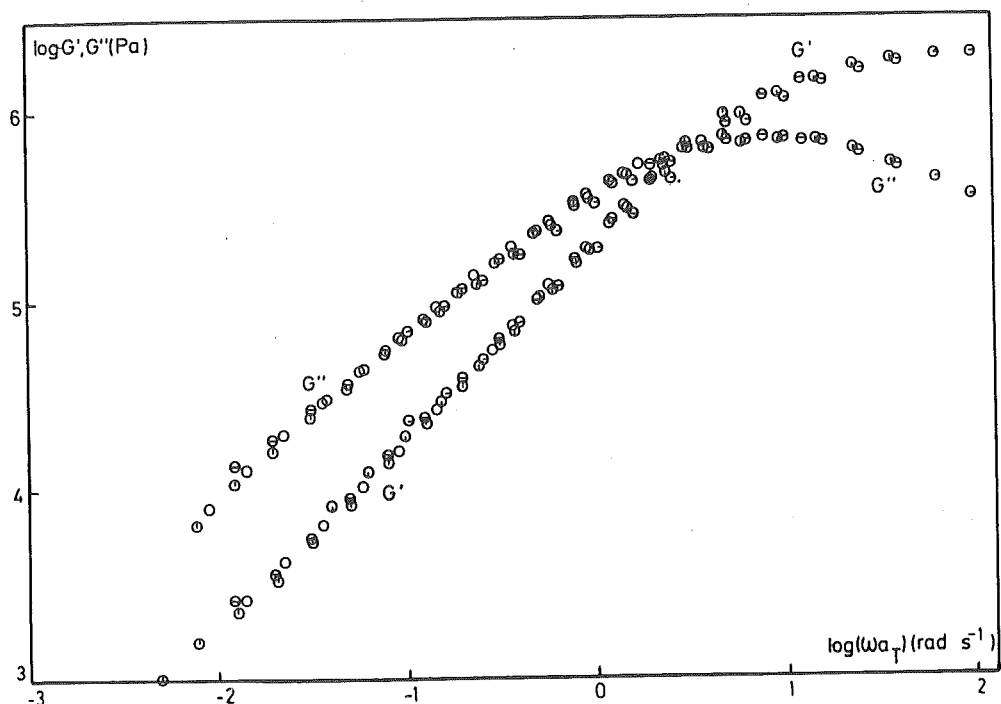


Figure 2. Partial master curves of storage ( $G'$ ) and loss ( $G''$ ) shear moduli for  $\alpha,\omega$ -Cu carboxylato polybutadiene ( $M_n = 4,600$ ). Reference temperature: 301K ( $\ominus$  301K,  $\odot$  308K,  $\ominus$  319K,  $\odot$  325K,  $\odot$  336K).

ence temperature of 301K, the terminal zone of PBD-Cd is observed in the experimentally accessible frequency range from 0.1 to 100  $\text{rad s}^{-1}$  (Figure 1). Under the same conditions of temperature and frequencies, PBD-Cu exhibits the end of the rubbery plateau in addition to the viscous flow regime (Figure 2). Thus, in the same way as in solution, Cu carboxylates are more effective than Cd carboxylates in promoting and stabilizing the association of the end-groups of telechelic PBD. Figure 3 convincingly shows that PBD-Fe manifests a much stronger network system than PBD-Cu at the same reference temperature. The terminal region only appears at and below  $10^{-2} \text{ rad s}^{-1}$ , i.e., frequency range in which the complex shear modulus of PBD-Cu is too small to be measured accurately. Clearly, there is a remarkable analogy in the effect induced by Fe, Cu, and Cd on

the origin of intermolecular associations, as reflected by a shift of the terminal zone towards lower frequencies at a constant reference temperature and very often by the occurrence of the rubbery plateau in a frequency range where the original PBD is purely viscous.<sup>5,10</sup> In the latter case, a secondary relaxation is observed as shown in Figures 2 and 3, which is characteristic of the disruption of a chain network. The frequency at that maximum reflects the strength of the network formed by the association of metal carboxylate end-groups. As a third common characteristic, the shift factors ( $a_T$ ) obey an apparent Arrhenius-like dependence on temperature as reported in Figure 4 for Cu, Cd, and Fe. The activation energy of the secondary relaxation process is easily calculated from the slope of the  $\log a_T$  vs.  $1/T$  plots and it is reported in Table 1 for the transition metal cations under consideration.

the viscoelastic behaviour of the carboxylated telechelic PBD in solution and in the bulk state.

Figures 1 to 3 show obvious similarities with the partial master curves which have been previously reported for the carboxy-telechelic PBD neutralized with alkaline and alkaline earth cations.<sup>10,16</sup> First, all these metal carboxylate telechelic PBDs behave as thermorheologically simple polymers. Secondly, compared to the unneutralized telechelic PBD, the presence of metal carboxylate end-groups is at

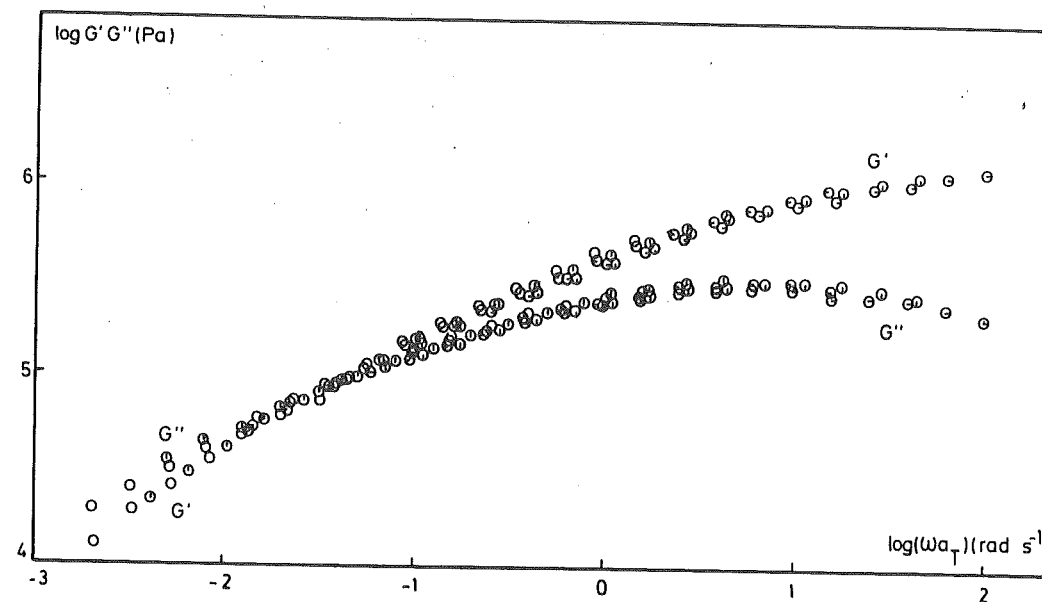


Figure 3. Partial master curves of storage ( $G'$ ) and loss ( $G''$ ) shear moduli for  $\alpha,\omega$ -Fe(III) carboxylato polybutadiene ( $M_n = 4,600$ ). Reference temperature: 300K ( $\ominus$  300K,  $\odot$  309K,  $\ominus$  317K,  $\odot$  328K,  $\odot$  338K).

Table 1

Activation energy ( $E_A$ ), equilibrium storage modulus ( $G_e$ ) and average number of cations per aggregate ( $n_{avg}$ ) for  $\alpha,\omega$ -transition metal carboxylato polybutadiene.

Metal	$E_A$ , kcal/mol	$G_e$ , MPa	$n_{avg}$
Cu <sup>2+</sup>	20.5	1.9	7.8
Fe <sup>3+</sup>	19.7	1.4	3.5
Cd <sup>2+</sup>	18.0	-	-
Ni <sup>2+</sup>	20.0	2.0	8.1
Mn <sup>2+</sup>	21.7	2.0	8.1

When alkaline-earth carboxylates are compared to carboxylates of Cu and Cd of the same valency, there is a striking difference in the strength of the intermolecular associations. For instance, at the same reference temperature, PBD-Cu shows a maximum of  $G''$  at a frequency which is higher by approximately one or two decades for PBD-Ca and PBD-Mg, respectively (Figure 5). The difference is still more pronounced when Cd (Figure 1) is considered,

rather than Cu. Actually, partial master curves of  $G'$  and  $G''$  versus reduced frequency of PBD-Cu are quite comparable to those reported for the monovalent K counterpart,<sup>16</sup> whereas PBD-Cd behaves in very similar manner to telechelic PBD bearing as weakly associating dipoles as Rb and Cs carboxylates.<sup>16</sup> When the mutual interactions of metal carboxylates is of an electrostatic origin, the strength of these interactions is governed by the dipolar moment of the ion pairs and particularly by the ionic radius of the cation - of a constant valency - associated with the carboxylate anion.<sup>10</sup> Thus, the association of metal carboxylates is strengthened when the cation radius decreases. Since the ionic radius of Cu(II) (0.72 Å) and Mg (0.66 Å) is comparable similar to Cd(II) (0.92 Å) and Ca (0.99 Å), these pairs of cations should provide carboxy-telechelic PBD with similar viscoelastic properties. The experimental observations (Figure 5) do not confirm such prediction and rather indicate that the intermolecular associations of carboxylated telechelic PBD proceed through a different mechanism when divalent transition metal cations are used instead of alkaline earth ones. The influence of solvent polarity on solution viscosity of  $\alpha,\omega$ -metal car-

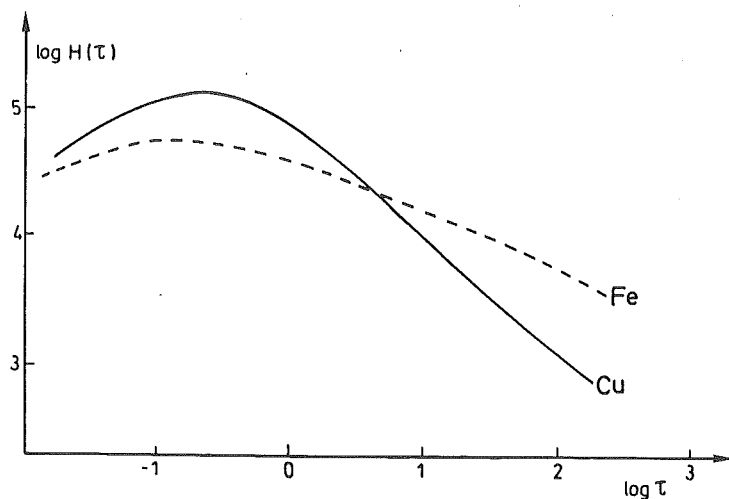


Figure 6. Relaxation time spectra for  $\alpha,\omega$ -Cu and Fe(III) carboxylato polybutadiene ( $M_n = 4,600$ ) at 300K.

$$n_{avg} = \frac{4M_n G_e}{v\rho RT} \quad [2]$$

Eq [2] was derived from the Rouse theory of rubber elasticity in which the functionality of crosslinks is assumed to be 4. In the networks under investigation, the actual functionality is not 4 but corresponds to the average number of chains emanating per aggregate of end-groups, i.e.,  $(v n_{avg})$  where  $n_{avg}$  is the amount of cations per aggregate and  $v$  is the valency of the cation. Furthermore,  $M_n$ , the molecular weight of the prepolymer, was approximated to the molecular weight between crosslinks,  $\rho$  is the density,  $R$  gas constant,  $T$  the absolute temperature and  $G_e$  is the equilibrium modulus.

Although  $n_{avg}$  is at least two times smaller for Fe(III) compared with Cu(II) (Table 1), Fe(III) carboxylates are clearly more effective than Cu(II) carboxylates in imparting elastic properties to PBD. This is reflected by the broader set of relaxation times typical for the aggregates of iron carboxylates compared to those of copper car-

chain network. When Fe(III) carboxylates are studied, EXAFS measurements show that majority of the iron of PBD-Fe is present as oxo-bridged trimers which constitute hexa-functional crosslinking points.<sup>23</sup> Furthermore, Mössbauer spectroscopy suggested the presence of supermagnetic fine particles, which implies the association of some of the trimers to give larger aggregates. This is also in a qualitative agreement with SAXS measurements.<sup>14,15</sup> Interestingly enough, all these direct observations give confirmation of the functionality of the crosslinks, estimated as being equal to 3.5 (Table 1) from the equation below:

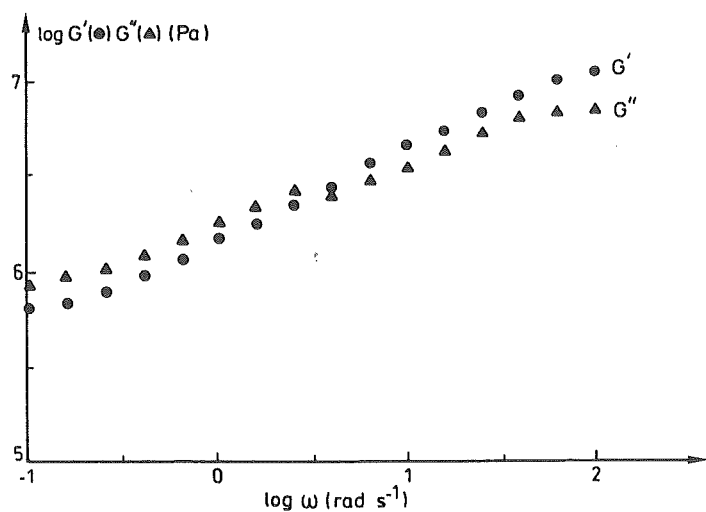


Figure 7. Storage ( $G'$ ) and loss ( $G''$ ) shear moduli versus frequency for  $\alpha,\omega$ -Co carboxylato polybutadiene ( $M_n = 4,600$ ) at 376K.

monomeric and/or dimeric Cu complexes, the combination of which ultimately stabilizes the

relaxation times typical for the aggregates of iron carboxylates compared to those of copper car-

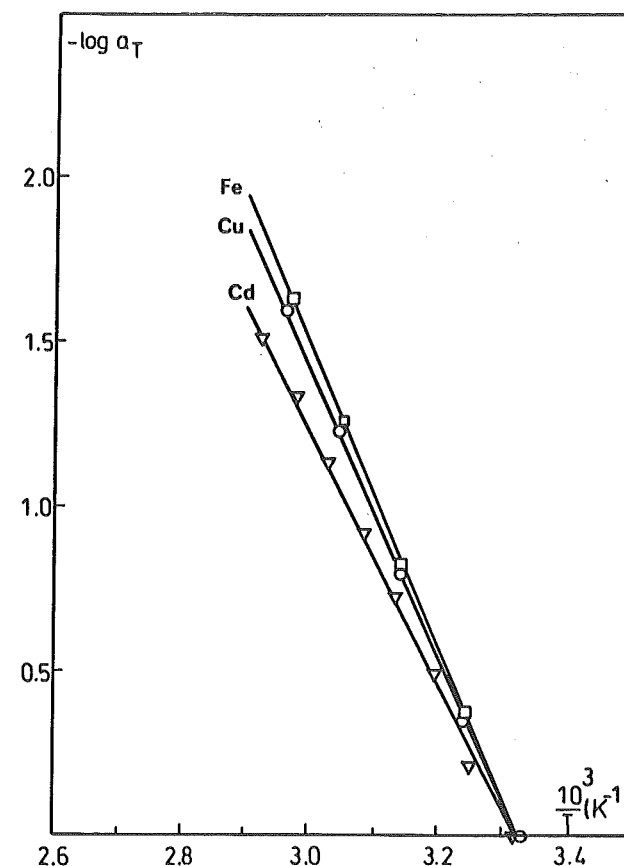


Figure 4. Shift factors ( $-\log a_T$ ) versus reciprocal temperature  $1/T$  for copper (O), iron (□), and cadmium (∇)  $\alpha,\omega$ -carboxylato polybutadiene.

boxylate PBD has been reported elsewhere and gives credit to such conclusion.<sup>18,24</sup>

Since transition metal carboxylates do not associate predominantly by electrostatic interactions, carboxylates have to be considered as ligands for the d orbitals containing cations, and the structure of the related complexes must play a major role in the end-group aggregation. Very weak mutual interactions of Cd carboxylates might be explained by structural analysis of a model compound:  $Cd(O_2C-CH_3)_2(H_2O)_2$  which suggests the presence of monoatomic bridging groups.<sup>25</sup> It is of course difficult to verify that the same situation prevails in Cd carboxylate containing PBD because of the problem in probing the local environment of Cd. Fortunately, that type of analysis has been car-

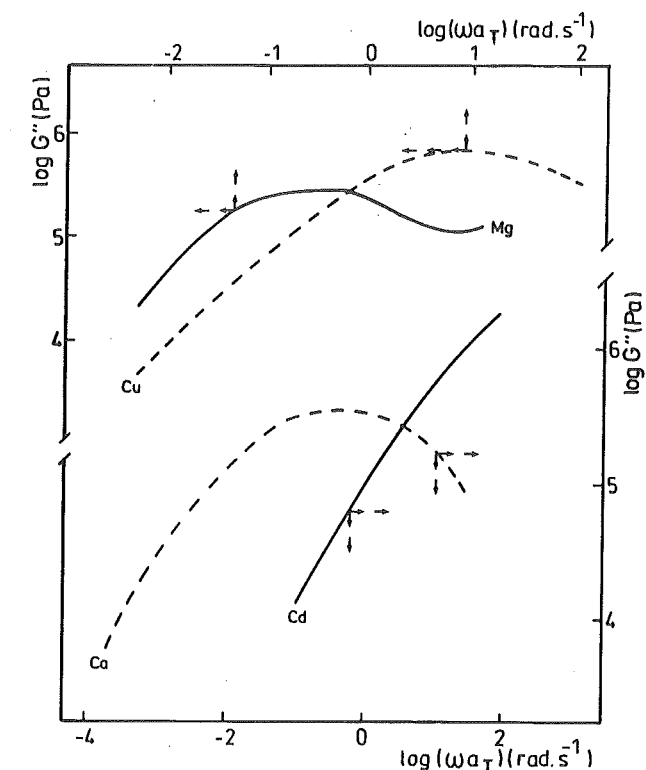
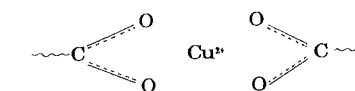


Figure 5. Comparison of the partial master curves of  $G''$  for  $\alpha,\omega$ -carboxylic acid polybutadiene ( $M_n = 4,600$ ) neutralized with Cu, Mg, Cd, and Ca, respectively. Reference temperature:  $301 \pm 1K$ .

ried out when Cu and Fe are the cations. Extended X-ray absorption fine structure (EXAFS) and electron paramagnetic resonance measurements have shown the presence of monomeric and dimeric copper complexes in PBD-Cu.<sup>26</sup>



which bond to the ends of 2 and 4 PBD chains, respectively. These complexes are at least partly associated into bigger aggregates since small angle X-ray scattering (SAXS) experiments revealed the existence of multiplets of an average radius of 6 Å.<sup>14,15</sup> From data of Figure 2, it appears that the set of relaxation times characteristic of the Cu carboxylate aggregates is of approximately 0.5 s, which is rather small and indicative of both the weakness of the bigger aggregates and the limited lifetime of the

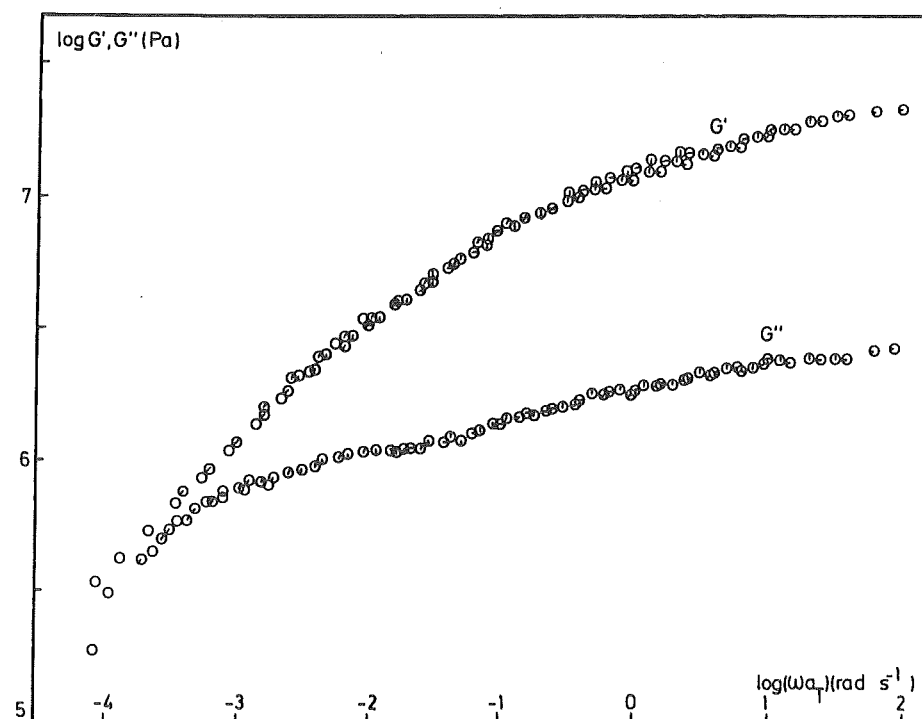


Figure 9. Partial master curves of storage ( $G'$ ) and loss ( $G''$ ) shear moduli for  $\alpha,\omega$ -Mn carboxylato polybutadiene ( $M_n = 4,600$ ). Reference temperature: 300K ( $\ominus$  300K,  $\odot$  308K,  $\ominus$  318K,  $\odot$  328K,  $\ominus$  337K,  $\odot$  348K,  $\ominus$  357K).

very well for the storage moduli of PBD-Ni and PBD-Mn, the  $G''$  isotherms do not fit so closely. Finally, plots of  $-\log a_T$  vs.  $1/T$  are linear and provide an activation energy for Ni and Mn in good agreement with the values reported for the other cations (Table 1). Nevertheless, a careful examination of these plots (Figure 10) may indicate that the experimental data fit two straight lines of a slightly different slope. These experimental observations may support the existence of two different types of mechanism of relaxation. In this regard, Co, Ni, and Mn are known to exhibit the most common six-fold coordination and to form complexes of an octahedral structure. However, two types of ligands are available:

- the carboxylates to which the cations are associated
- and the electron-rich double bonds of the PBD backbone.

with the carboxylate anions but also with the double bonds of PBD. Due to the abundance of these ligands, there are many possibilities for Mn, Ni, and Co to be coordinated, i.e., to participate in complexes of various stability, and such situation might account for the extreme broadness of the classical maximum in  $G''$ .

In spite of the deep difference in the viscoelastic properties of the two classes of transition metal cations investigated in this study, both the calculated activation energy and the estimated average size of the aggregates of metal carboxylates are essentially independent of the cation (Table 1). This is in a qualitative agreement with the mechanical properties reported for transition metal containing polyurethane ionomers.<sup>28</sup> Nevertheless, the activation energy reported for bulk PBD-Co, PBD-Ni, and PBD-Mn is unaffected by the addition of apolar solvent of PBD.<sup>18</sup> Thus, in contrast to aggre-

As has been reported elsewhere, the dynamic mechanical behaviour of PBD-Ni and  $\alpha,\omega$ -Ni carboxylate polyisobutylene (PIB-Ni) of the same molecular weight has been compared and a stronger network is formed when the polymer contains double bonds.<sup>27</sup> Such behaviour is explained as relative to the coordination of double bonds of PBD and the d-orbitals of the transition metal.

The exceptionally high elasticity that Mn, Ni, and Co impart to carboxylate telechelic PBD as compared with Cd, Cu and Fe(III) should thus be attributed to much greater stability of the coordinative complexes formed by these hexa-coordinated ions not only

boxylates (Figure 6). Actually, PBD-Fe and PBD-Cu differ from each other by the existence of much longer relaxation times in PBD-Fe. The latter must be attributed to the trimeric structure of the basic complexes formed by Fe(III) ions in contrast to monomeric and dimeric complexes of Cu(II) which are less effective in crosslinking of PBD chains. It is finally worth recalling that the association of Fe carboxylates is perturbed by the addition of apolar solvent of PBD since no gel is observed but rather a viscous solution.<sup>18</sup> In other words, the aggregates are unable to withstand the diluting forces of the network without being gradually destroyed. This observation must be related to the activation energy of the secondary relaxation, which decreases from 19.7 kcal $\times$ mol<sup>-1</sup> for the bulk PBD-Fe (Table 1) to 8-9 kcal $\times$ mol<sup>-1</sup> for a 10 wt% solution in DHN.<sup>18</sup>

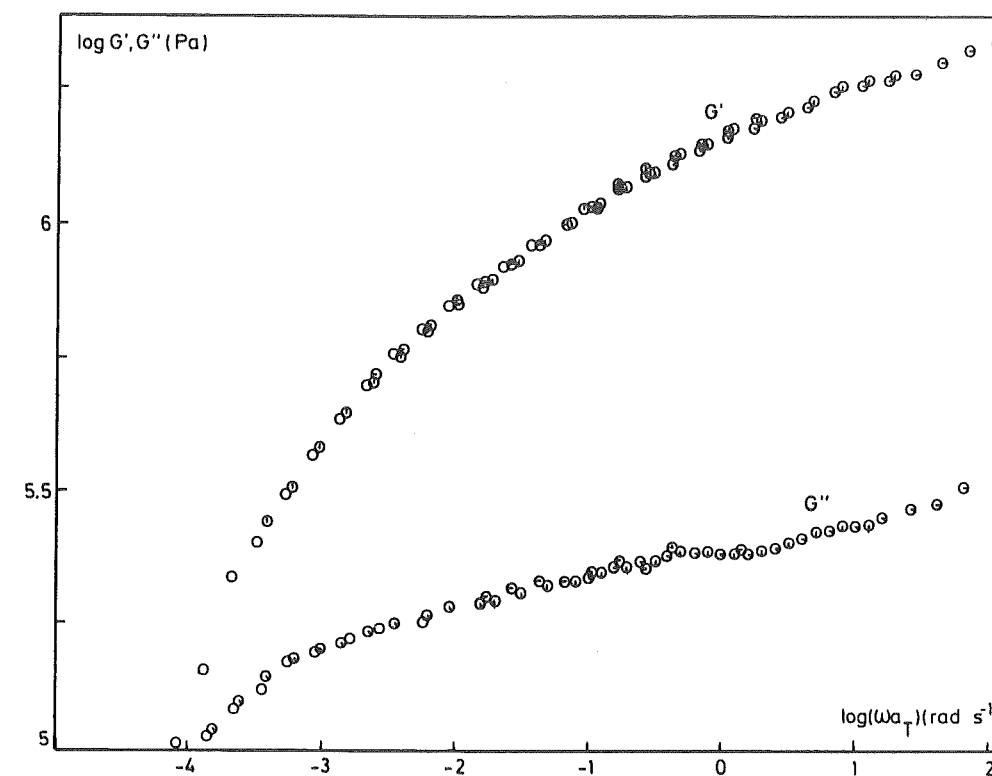


Figure 8. Partial master curves of storage ( $G'$ ) and loss ( $G''$ ) shear moduli for  $\alpha,\omega$ -Ni carboxylato polybutadiene ( $M_n = 4,600$ ). Reference temperature: 303K ( $\ominus$  303K,  $\odot$  317K,  $\ominus$  338K,  $\odot$  356K,  $\ominus$  366K,  $\odot$  376K).

### Viscoelastic Behaviour of Co(II), Ni(II), and Mn(II) Salts of Carboxy-telechelic PBD

From the solution behaviour in toluene, Mn(II), Co(II), and Ni(II) carboxylates have been classified as efficient gelling end-groups. Figures 7 and 8 illustrate the viscoelasticity of bulk PBD-Co, PBD-Ni, and PBD-Mn, respectively. Compared to Cd, Cu, and Fe counterparts at the same temperature (300K), Ni and Mn containing telechelic PBDs are much more elastic materials (Figures 1,2,3,8, and 9). The difference is still greater when Co is the cation, since the strength of PBD-Co is so high that the complex shear modulus has only been measured in a reliable way at 376K (Figure 7). The isothermal dependence of  $G'$  and  $G''$  on frequency has not been reported at higher tem-

peratures because of possible thermooxidation of PBD during measurement. Very clearly, the terminal zone of PBD-Co is not yet reached at 376K.

When the partial master curves of PBD-Ni (Figures 8) and PBD-Mn (Figures 9) are compared to those of PBD-Cu (Figure 2), the former samples behave like cured rubbers up to temperature as high as 357K (Mn) and 376K (Ni). Moreover, their  $G''$  partial master curves do not clearly indicate any characteristics of the relaxation of the carboxylate aggregates as it is reflected by a classical maximum in  $G''$  for PBD-Cu. It must also be pointed out that although the time-temperature equivalence works

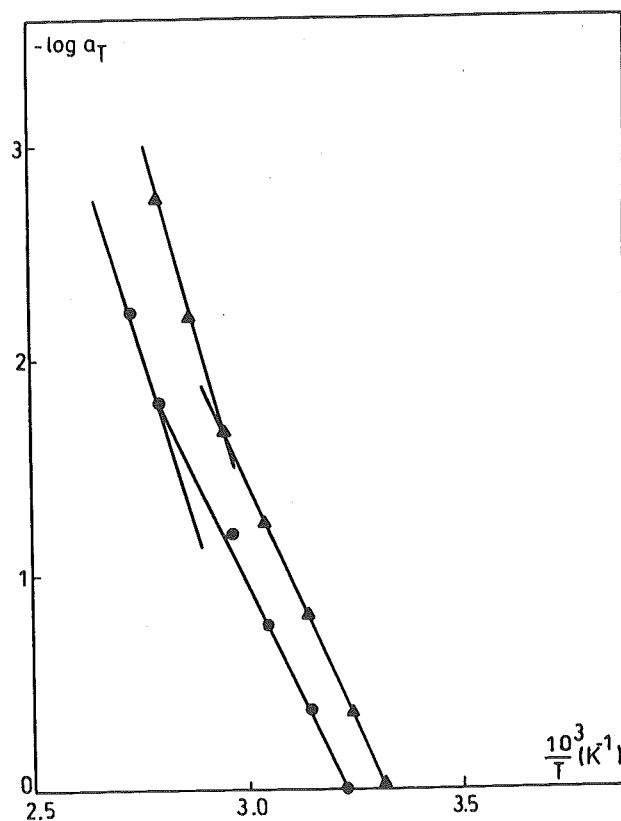


Figure 10. Shift factors ( $-\log a_T$ ) versus reciprocal temperature ( $K^{-1}$ ) for  $\alpha,\omega$ -Mn carboxylato polybutadiene ( $\blacktriangle$ ) and  $\alpha,\omega$ -Ni carboxylato polybutadiene ( $\bullet$ )

gates of Cu(II) and Fe(III) carboxylates, those derived from Co, Ni, and Mn withstand the retractive forces of the extended PBD chains without being disrupted significantly. This is supported by the gel state of the 10 wt% solution in DHN at 25°C.

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