Halato Telechelic Polymers. XVI - Viscoelastic Properties of α,ω-Transition Metal Carboxylato Polybutadiene

J. Horrion, R. Jérôme, and Ph. Teyssié

Laboratory of Macromolecular Chemistry and Organic Catalysis, University of Liège, Sart Tilman, B6, B-4000 Liège, Belgium

To whom correspondence should be addressed.

A low molecular weight carboxy-telechelic polybutadiene (Mn = 4,000) 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.1 Similarly, modifications of traditional polymers by groups able to coordinate to transition metal salts is also an effective way to crosslink the polymer thermoreversibly.2 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.3

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.4-10 Indeed, the well-de-
fined although largely variable distances between the terminal interacting ion pairs make their association less restricted by the polymer chain. In the series of neutral carbonyl alkylthio polydienes, small angle X-ray scattering (SAXS) has shown that the dipolar asso- ciation of ion pairs results in multiplet formation, primarily governed by the configura- tion of the polymer between the ionic groups. 14,15 viscoelastic properties of both car- bonylated10,11,13,16,19 and sulfonated21,22 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 (Ea) of such a relaxation is related to the val- ency (n) and ionic radius (r) of the cation according to the following equation: 13

\[ E_a = 85.3n^2r \]  

[1]  

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

The situation changes dramatically when alka- line and alkaline-earth cations are substi- tuted by transition metal cations. Although the terminal carbonylalkylpolydienes of telechelic polydienes still tend to be associated, electrostatic interactions do not play a decisive role any more. Rather, the stability of transition ele- ments to form complexes with ligands, e.g., car- bonylalkynes, and their coordination number appear to be the key parameters controlling the end-groups association. That general conclu- sion results from a previous study of the solu- tion behaviour of a,a-transition metal carbo- nylalkylpolydienes. 16 It has been re- ported that telechelic 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 telechelic solutions, although a rise in viscosity is noted when the polymer concentration is raised. A lower coordination number of these cations and/or non-three-dimensional structure of their com- plexes are the most likely reasons of solution properties of a,a-transition metal carbo- nylalkylpolydienes. 16,18 In order to get a better insight into the role played by the transition metal cations in rela- tion to metal carbonyl alkyl-end groups, a vis- coelastic study of salts of Cu(II), Fe(III), Cd(II), Ni(II), Cu(II), and Mn(II) of telechelic carbo- nylalkylpolydienes (Me = 4,400) was under- taken and is reported here.  

EXPERIMENTAL

Carboxy-telechelic polybutadiene commerci- ally available from BF Goodrich (Hycar CTB 2000x156), with Me = 4,400, Mw/Mn = 1.6; func- tionality equals 2.0 and cis/trans vinyl ratio equals 20/80; was used as received.  

Transition metal acetates were commercial crystalline products [CuAc2.5H2O, NiAc2.5H2O, CoAc2.5H2O, MnAc2.5H2O]. The carboxy-telechelic polybutadiene was dis- solved in previously dried toluene (5 wt%) and added to a stoichiometric amount of metal acetate (1 salt molecule per telechelic molecule) previously dissolved in methanol or acetic acid (102 mol·L-1). The solvent and the acidic solution were removed from the reaction mixture by toluene azotropic distillation. The distillation was re- peated until the neutralization of the acid end- groups was complete. 16 The iron(III)-containing sample resulted from the end-neutrali- zation of carboxy-telechelic polybutadiene with iron(III) 2-propanol under anhydrous condi- tions. Synthesis of the iron alkoxide and the neutralization technique were reported else- where. 16 The toluene samples were dried under vacuum until there was no further weight re- duction.  

The dynamic mechanical properties were studied using a Rheometrics Mechanical Spectrometer (RMS-7200) fitted with a plate and plate geometry (plate diameter 2.5 cm). The G' and G" values were measured in the fre-
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 carboxylated telechelic PBD neutralized with alkaline and alkaline earth cations. 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 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. 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 which maximum reflects the strength of the network formed by the association of metal carboxylate end-groups. As a third common characteristic, the shift factors 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\(\eta\) vs. 1/\(T^\alpha\) plots and it is reported in Table 1 for the transition metal cations under consideration.

![Figure 2. Partial master curves of storage (G') and loss (G'') shear moduli for \(\alpha,\omega\)-Cu carboxylate polybutadiene (Mn = 4,000). Reference temperature: 300K (\(\Theta\) 300K, \(\Theta\) 300K, \(\Theta\) 317K, \(\Theta\) 298K, \(\Theta\) 338K).](image)

![Figure 3. Partial master curves of storage (G') and loss (G'') shear moduli for \(\alpha,\omega\)-Fe(III) carboxylate polybutadiene (Mn = 4,000). Reference temperature: 300K (\(\Theta\) 300K, \(\Theta\) 300K, \(\Theta\) 317K, \(\Theta\) 298K, \(\Theta\) 338K).](image)

**Table 1: Activation energy (Ea), equilibrium storage modulus (Goe) and average number of cations per aggregate (nag) for \(\alpha,\omega\)-transition metal carboxylate polybutadiene.**

<table>
<thead>
<tr>
<th>Metal</th>
<th>(Ea), kcal/mol</th>
<th>(Goe), MPa</th>
<th>(nag)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(\beta)</td>
<td>20.5</td>
<td>1.9</td>
<td>7.8</td>
</tr>
<tr>
<td>Fe(\beta)</td>
<td>19.7</td>
<td>1.4</td>
<td>3.5</td>
</tr>
<tr>
<td>Cd(\beta)</td>
<td>18.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ni(\beta)</td>
<td>20.0</td>
<td>2.0</td>
<td>8.1</td>
</tr>
<tr>
<td>Mn(\beta)</td>
<td>21.7</td>
<td>2.0</td>
<td>8.1</td>
</tr>
</tbody>
</table>

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 counterion, whereas PBD-Cd behaves in a similar manner to telechelic PBD bearing as weakly associating dipoles as Rb and Cs carboxylate. 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 - a constant valency - associated with the carboxylate anion. 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 (0.86 Å) is comparable similar to Cd(II) (0.92 Å) and Ca (1.00 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 carboxylate polybutadiene.
chain network. When Fe(III) carboxylates are studied, EXAFS measurements show that majority of the iron of PBD-Fe is present as co-bridged trimers which constitute base-functional crosslinking points. 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. 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:

\[
\text{Eq [2] was derived from the Rouse theory of rubber elasticity in which the functionality of crosslinks is assumed to be } \frac{6}{5} \text{. In the networks under investigation, the actual functionality is not 4 but corresponds to the average number of chains emanating per aggregate of end-groups, i.e., } (\nu N_{\text{avg}}) \text{ where } N_{\text{avg}} \text{ is the amount of cations per aggregate and } \nu \text{ is the valency of the cation. Furthermore, } M_w \text{, the molecular weight of the prepolymer, was approached to the molecular weight between crosslinks, } p \text{ the density, } R \text{ the gas constant, } T \text{ the absolute temperature and } G_0 \text{ the equilibrium modulus.}
\]

Although \( N_{\text{avg}} \) 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 carboxylate PBD has been reported elsewhere and gives credence to such conclusion. Since transition metal carboxylates do not associate predominantly by electrostatic interactions, carboxylates have to be considered as ligands for the bridging 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(OOC-CH\(_2\))\(_2\)\(_2\)(H\(_2\)O)\(_2\) which suggests the presence of monatomic bridging groups. 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 carried 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.

\[
\text{Figure 5. Comparison of the partial master curves of } G' \text{ for } \nu \text{, and carboxylate polybutadiene (M, } 4,600) \text{ neutralized with Cu, Mg, Cd, and Ca, respectively. Reference temperature: } 301 \pm 1 \text{K.}
\]

\[
\text{Figure 4. Shift factor } (\text{log } G') \text{ versus reciprocal temperature } T \text{ for copper (Cu), iron (Fe), and cadmium (Cd) carboxylato polybutadiene.}
\]

\[
\text{Figure 3. Storage (G') and loss (G'') shear moduli versus frequency for } \nu \text{, and carboxylato polybutadiene (M, } 4,600) \text{ at 376K.}
\]

\[
\text{Figure 2. Relaxation time spectra for } \nu \text{, and Cu and Fe(III) carboxylato polybutadiene (M, } 4,600) \text{ at 300K.}
\]
very well for the storage moduli of PBD-Ni and PBD-Mn, the G' isotherms do not fit so closely. Finally, plots of \( \log a \) 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.

As has been reported elsewhere, the dynamic mechanical behaviour of PBD-Ni and \( a, a'-\text{Ni} \) carboxylate polymethylene (PBD-Ni) of the same molecular weight has been compared and a stronger network is formed when the polymer contains double bonds.\(^\text{22}\) Such behaviour is explained as relative to the coordination of double bonds of PBD and the \( a, a' \)-orbitals of the transition metal.

The exceptionally high elasticity that Mn, Ni, and Co impart to carboxylate telechelic PBD as compared with Cu, \( a \), Cu, and Fe (III) should thus be attributed to much greater stability of the coordinative complexes formed by these hexacoordinated ions not only 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 situations 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 a qualitative agreement with the mechanical properties reported for transition metal containing polyurethane ionomers.\(^\text{28}\) Nevertheless, the activation energy reported for bulk PBD-Co, PBD-Ni, and PBD-Mn is unaffected by the addition of a spolar solvent of PBD.\(^\text{18}\) Thus, in contrast to aggregates with the carboxylate ions 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 situations might account for the extreme broadness of the classical maximum in G'.

Figure 9. Partial master curves of storage (\( G' \)) and loss (\( G'' \)) shear moduli for \( a, a'-\text{Mn} \) carboxylate polyethylene (M, \( = 4,600 \)). Reference temperature: 300K (\( \odot \) 300K, \( \odot \) 308K, \( \odot \) 318K, \( \odot \) 328K, \( \odot \) 338K, \( \odot \) 348K, \( \odot \) 358K).

Figure 8. Partial master curves of storage (\( G' \)) and loss (\( G'' \)) shear moduli for \( a, a'-\text{Ni} \) carboxylate polyethylene (M, \( = 4,600 \)). Reference temperature: 300K (\( \odot \) 300K, \( \odot \) 318K, \( \odot \) 328K, \( \odot \) 338K, \( \odot \) 348K, \( \odot \) 358K).

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 Cu, Cu, and Fe counterparts at the same temperature (300K), Ni, Mn, and Co containing telechelic PBDs are much more elastic materials (Figures 1, 2, 3, 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 temperatures 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 (Figure 8) and PBD-Mn (Figure 9) are compared to those of PBD-CO (Figure 2), the former samples behave like cured rubbers up to temperature as high as 576K (Mn) and 476K (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-CO. It must also be pointed out that although the time-temperature equivalence works...
REFERENCES


ACKNOWLEDGEMENT

The authors are indebted to the Services de la Programmation de la Politique Scientifique for financial support. Most of the viscoelastic measurements have been carried out using a Rheometrics Dynamic Mechanical Analyzer made available by a grant from the Fondation de la Recherche Scientifique (F.N.R.S.).

© ChemTec Publishing

1181-9610/92/$0.00+0.70

© ChemTec Publishing
1181-9610/92/$0.00+0.70