attempt to make long fibers of coordination polymers having unique properties, either alone or as composites. Our aim is to obtain species with improved solubility, flexibility, high thermal stability, and extended conjugation.

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Registry No. 1, 19691-23-7; $[Zr(tsb)]_n$, 77274-52-3; $Zr(sal)_4$, 65531-97-7; TAB, 3204-61-3; Hsal, 90-02-8; H_4tsb $(3\text{-}MeO)_4$ derivative, 96482-27-8; H_4tsb $(5\text{-}MeO)_4$ derivative, 96482-26-7; 3-methoxysalicylaldehyde, 148-53-8; 5-methoxysalicylaldehyde, 672-13-9; 5-bromosalicylaldehyde, 1761-61-1; 2-hydroxy-1-naphthaldehyde, 708-06-5.

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Halato-Telechelic Polymers. 11. Viscoelastic Behavior of α,ω-Dicarboxylatopolybutadiene Based on Group 4 Metal Ions

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ABSTRACT: In nonpolar solvents, α,ω-alkaline and -alkaline-earth dicarboxylatopolybutadiene ($\bar{M}_n$ 4600) leads to gel formation at concentrations as low as 1.5 g dL^{-1}. However, any polar additive, i.e., water or alcohol, has a depressive effect on the metal–carboxylate association and the resulting gelation. The use of group 4 metal ions is an efficient way to overcome this drawback. Cross-linking of the carboxy-telechelic polymer is then promoted by a group 4 metal (Ti, Zr, Ce) alkoxide used in excess vs. the acid end groups. When the unreacted alkoxide groups are hydrolyzed into metal oxoalkoxide groupings, the gelation occurs in the presence of the alcohol formed as a byproduct and the required humidity of the medium. Cross-linking efficiency depends on the size of the group 4 cation just like in the series of alkaline and alkaline-earth cations. The deformation mechanism is controlled by the stability of the metal–carboxylate bonds and by the mean number of chain ends attached to the metal oxide aggregates. In this respect, excess alkoxide is a key parameter to impart to the solutions a broader range of rheological properties. Viscous solutions are observed at a metal-to-chain molar ratio of 0.5, whereas increasing excess of metal alkoxide is responsible for a shear-thickening behavior and finally for elastic gels.

Introduction

A few decades ago, macromolecular chemistry enjoyed a new expansion thanks to the development of multiphase polymeric materials. Indeed, the advent of block copolymers and more especially of thermoplastic elastomers opened up bright prospects for both scientists and tech-

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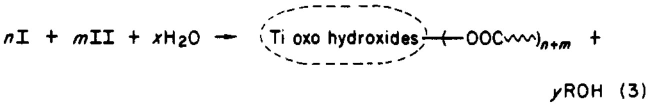
nologists. As a consequence, great efforts have been devoted to the development of block copolymers,[1,2] polymer alloys,[3] and ion-containing polymers.[4-6] These materials have the distinctive feature of combining in an additive way the main characteristics of their two (or more) components. In this respect, the ion-containing polymers, more commonly known as "ionomers", display dramatic improvements in their physicomechanical properties due to the thermolabile interactions of the ionic groups they contain. It is worth recalling that the ionic groups of ionomers are randomly attached as pendant groups to the polymeric backbone. So, the polymeric segments counteract the intermolecular interactions of the ionic groups and limit their importance. Halato-telechelic polymers are a particular and quite attractive type of ionomer. Their ionic groups are indeed selectively attached at each end of linear chains and accordingly suffer only limited restrictions in their mutual interactions. The investigation of solution and bulk properties of carboxylato-telechelic polymers has given a new insight into the role played by the ionic groups in the control of the polymer properties.[7-18]

The synthesis of representative halato-telechelic polymers requires the quantitative transformation of the chain ends into ionic groups in order to reach as high performances as possible and to avoid the presence of more than one type of interchain associative binding. In previous papers, we have reported the end neutralization of α,ω-dicarboxylic acid polydienes in solution by a stoichiometric amount of alkaline-earth alkoxides.[7,10,18] Thanks to the high reactivity of the neutralizing agent and the continuous removing of the reaction subproduct (alcohol), the quantitative conversion of carboxylic acid into metal carboxylates is easily achieved. The same procedure applies when the alkaline-earth alkoxide is replaced by an alkoxide of alkaline metals, divalent transition metals (Cu, Zn, ...), and trivalent metals like Al and Fe.[10,16]

Especially in the case of alkaline and alkaline-earth metals, the ionicity of the metal–carboxylate bond is high and the ion-pair association in nonpolar environment is sensitive to the presence of small amounts of polar compounds (water, alcohol, ...).[10,18] Care has therefore to be taken to avoid chemical substances able to solvate the ion pairs and to limit the extent of their association. Recently, we have reported that a stoichiometric amount of a group 4 metal alkoxide was unable to quantitatively neutralize the polymer acid end groups, resulting in the absence of any cross-linking effect.[15] This means that the four alkoxy groups of a tetravalent metal (Ti, Zr, ...) cannot be replaced by a polymeric carboxylate; probably besides lower reactivity, steric hindrance is a major reason for this failure. Nevertheless, the chain ends can be quantitatively neutralized by using an excess of tetravalent metal alkoxide, e.g., one metal per chain end or two metals per linear chain (eq 1). The association of the chain ends into multifunctional (≥3) cross-links or aggregates is finally triggered by the hydrolysis of the alkoxy groups in excess (eq 2 and 3).

$$\sim\!\mathrm{COOH} + \mathrm{Ti(OR)_4} \rightarrow \underset{\mathrm{I}}{\sim\!\mathrm{COO{-}Ti(OR)_3}} + \mathrm{ROH} \qquad (1)$$

$$2\mathrm{I} + \mathrm{H_2O} \rightarrow \underset{\mathrm{II}}{\sim\!\mathrm{COO{-}Ti(OR)_2{-}O{-}Ti(OR)_2{-}OOC}\!\sim} + 2\mathrm{ROH} \qquad (2)$$



$$n\mathrm{I} + m\mathrm{II} + x\mathrm{H_2O} \rightarrow (\text{Ti oxo hydroxides}) \!\!-\!\!(\!-\mathrm{OOC}\!\sim\!)_{n+m} + y\mathrm{ROH} \qquad (3)$$

$y = 3n + 4m$ and $y/2 \leqslant x \leqslant y$

Unlike alkaline and alkaline-earth carboxylate end groups, the chain-end association proceeds no longer through electrostatic interaction of metal–carboxylate ion pairs but through the chain attachment to metal oxo hydroxide aggregates via a metal–carboxylate bond (eq 3). As tetravalent metal–carboxylate bonds are essentially covalent, they are practically insensitive toward water and alcohol, which explains the synthesis of representative halato-telechelic polymers through the pathway described by eq 1–3. In conclusion, the neutralization of α,ω-dicarboxylic acid polymers by an excess of tetravalent metal alkoxides is quite attractive because thermoreversibly cross-linked polymers are prepared without bothering about avoiding water, which in fact is now a required reagent, and without necessarily removing the alcohol formed as the reaction subproduct (eq 1–3).

This paper reports a thorough investigation of solution and bulk properties of carboxylato-telechelic polybutadiene ($\bar{M}_n$ 4600) based on Ti, Zr, and Ce. The effect of the metal-to-chain molar ratio will be taken into account as well as the nature of the metal itself.

Experimental Section

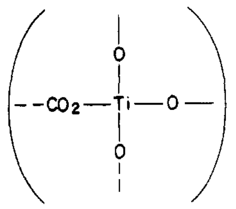
Zirconium *n*-propoxide and titanium(IV) isopropoxide were used as received from Ventron and Aldrich, respectively. Cerium *n*-butoxide was prepared by reference to the method reported by Bradley et al.[19]

The neutralization of the α,ω-dicarboxylic acid polybutadiene commercialized by B. F. Goodrich under the trademark Hycar CTB 2000X156 ($\bar{M}_n$ 4600) took place in solution (5 or 10 wt %) in nonanhydrous solvents (toluene or aromatic oil). The calculated amount of metal(IV) alkoxide was added to the polymer solution under vigorous stirring. Depending on the metal(IV) alkoxide-to-polymer molar ratio, a viscous or gellike solution was obtained in a few minutes. Either the solutions were studied as obtained or the solvent was distilled off under reduced pressure and the bulk polymer was finally dried under vacuum up to constant weight.

The dynamic mechanical behavior was investigated with a Rheometrics mechanical spectrometer (RMS-7200). Steady-flow viscosity was measured by using cone–plate geometry. The plate diameter was either 5.0 or 7.2 cm for the less viscous solutions; the cone angle (β) was 0.04 rad. Dynamic mechanical properties were investigated with the plate–plate geometry (plate diameter 5.0 cm; plate-to-plate distance 0.2 cm). A Gehman torsion pendulum was used to record isochronal (10 s) variation of torsion modulus vs. temperature.

Results and Discussion

Viscoelastic Behavior of Bulk Oxy Titanium and Zirconium α,ω-Dicarboxylatopolybutadiene. When a short-length α,ω-dicarboxylic acid polybutadiene ($\bar{M}_n$ 4600) is neutralized by an excess of titanium or zirconium alkoxide (Ti or Zr/PBD = 2.0) under nonanhydrous conditions, a nonsticky and gummy material is obtained. The shear storage (G') and loss (G'') moduli vs. frequency (ω) isotherms, recorded from 296 up to 380 K, can be shifted horizontally vs. log ω with respect to a reference isotherm (296 K) so as to form a single curve (Figure 1). The time–temperature equivalence works therefore very well in this studied range of temperature and frequency. The partial master curves obtained at 296 K corresponds to the rubberlike plateau ending with the viscous flow region. The maximum in G'', which is not observed for the nonneutralized α,ω-dicarboxylic acid polybutadiene,[14,16] is to be attributed to a secondary relaxation of the oxy metal carboxylates



$$\left(-\!-CO_2\!-\!\overset{\overset{|}{O}}{\underset{\underset{|}{O}}{Ti}}\!-\!O\!- \right)$$

As $(T_0 - T)/\log a_T$ vs. $T - T_0$ is not a straight line (Figure 2), the WLF equation and accordingly the free volume concept are not applicable to this secondary relaxation. Figure 3 shows that an Arrhenius-type temperature dependence is well suited to the oxy titanium carboxylates containing polybutadiene, which is not the case with the Zr equivalent. In the case of Ti, an activation energy of 14.3 kcal mol^{-1} is calculated. It practically has the same value as that reported for α,ω-dicarboxylatopolybutadiene based on Ba and Al (15 kcal mol^{-1}).[14,16]

From Figure 1, it is clear that the efficiency of zirconium alkoxide to cross-link the acid-terminated polybutadiene is higher than that of titanium alkoxide. The modulus of the rubberlike plateau, i.e., the strength of the formed network, is higher for Zr than for Ti. In other words, at a constant metal-to-chain molar ratio, the mean number of chain ends attached to an aggregate of oxy metal carboxylates depends on the metal and, more especially, increases with the ionic radius of the metal (r_{Ti} = 0.68 Å, r_{Zr} = 0.80 Å). Although smaller, the aggregates formed by oxy titanium carboxylates are more stable than those constituted with Zr ones, as assessed by the lower frequency at the maximum in G''. Accordingly, the relaxation spectrum calculated by the first-order approximation of Ninomiya and Ferry[20] is displaced toward longer relaxation times from Zr to Ti (Figure 4).

The rheological behavior of α,ω-dicarboxylatopolybutadiene based on Ti and Zr is quite similar to that reported for the corresponding alkaline earth α,ω-dicarboxylatopolybutadiene.[14] In the latter case, the smaller the alkaline-earth cation, the longer the mean relaxation time and the lower the equilibrium storage modulus. The similar viscoelastic behavior could mean that, in both cases, the deformation mechanism corresponds to the thermoreversible rupture of the metal–carboxylate bonds and/or multiplets. The only disturbing point here is the apparent discrepancy displayed by the secondary relaxation of the oxy zirconium carboxylates with respect to an Arrhenius-type activation process. The least-squares regression correlation coefficient (R^2) has been calculated as 0.9928 and 0.9057 for the Ti and Zr systems, respectively.

A second anomaly is observed in the isochrone (10 s) torsion modulus vs. temperature curve of oxy zirconium α,ω-dicarboxylatopolybutadiene (Figure 5). As expected, the modulus of the oxy titanium carboxylates containing polybutadiene is lower than that of its Zr equivalent, whereas an earlier viscous flow is reported for the rubberlike plateau modulus at temperatures higher than 243 K. This phenomenon might be explained by a stress release due to a rearrangement of the aggregates during heating. The torsion modulus vs. temperature curves are indeed recorded from low up to high temperatures on samples molded at 373 K. As a softer material and smaller aggregates result from the substitution of Zr by Ti, the stress concentration during cooling from the melt could accordingly be avoided. In conclusion, zirconium α,ω-dicarboxylatopolybutadiene exhibits some unexpected features which could be due to a nonequilibrium aggregation of the oxy zirconium carboxylates and/or to the occurrence of at least two different thermally activated processes in the investigated range of temperature and frequency.

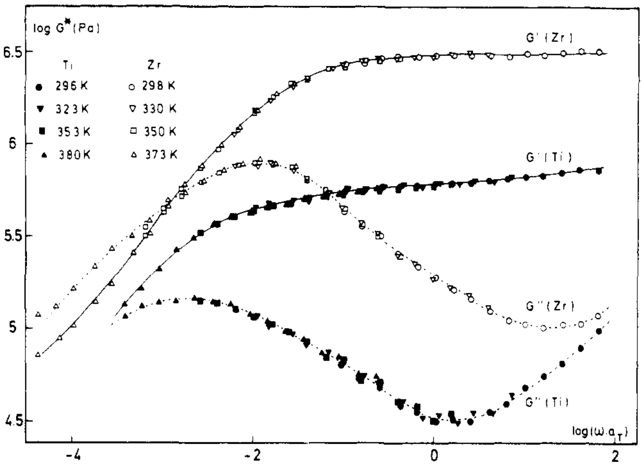


Figure 1. Partial master curves of shear storage (G') and loss (G'') moduli of bulk oxy titanium and zirconium α,ω-dicarboxylatopolybutadiene ($\bar{M}_n$ 4600) (Me/chain = 2.0). Reference temperature: 296 K.

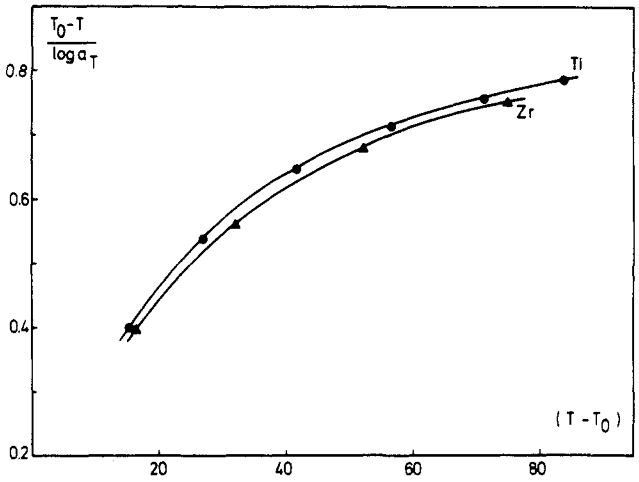


Figure 2. $(T_0 - T)/\log a_T$ vs. $T - T_0$ for bulk oxy titanium and zirconium α,ω-dicarboxylatopolybutadiene ($\bar{M}_n$ 4600) (Me/chain = 2.0). Reference temperature (T_0) is 296 K and a_T is the shift factor.

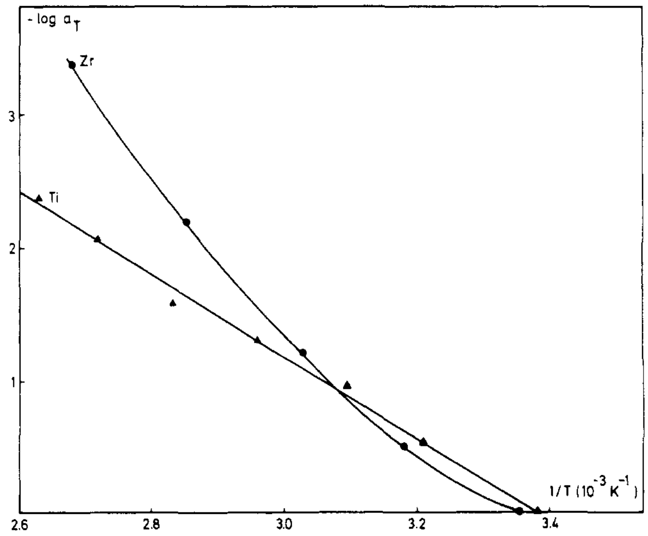


Figure 3. Shift factors a_T vs. $1/T$ for bulk oxy titanium and zirconium α,ω-dicarboxylatopolybutadiene ($\bar{M}_n$ 4600).

Viscoelastic Properties of Solutions of Oxy Metal(IV) α,ω-Dicarboxylatopolybutadiene. As previously reported,[7,10,18] the addition of a stoichiometric amount of an alkaline, alkaline earth, or trivalent metal (Fe^{III}, Al)

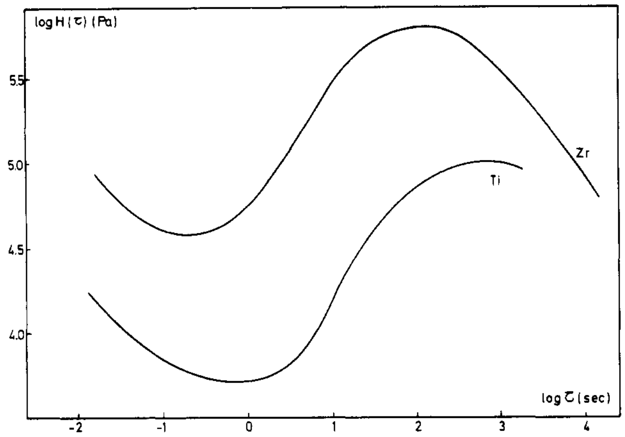


Figure 4. Relaxation time spectra for bulk oxy titanium and zirconium α,ω-dicarboxylatopolybutadiene ($\bar{M}_n$ 4600) at 296 K.

alkoxide ($\mathrm{Me(OR)}_n$) into a carefully dried solution of α,ω-dicarboxylic acid polybutadiene (OR/COOH = 1) in a nonpolar solvent results in a noticeable gelation as soon as the alcohol formed is removed from the solution. Under similar conditions, the use of a tetravalent metal (Ti, Zr, Ce) alkoxide is responsible for only an increase in the solution viscosity.[15] According to our recent observations, it is impossible to remove from the reaction medium much more than half the theoretical amount of alcohol (ROH) corresponding to the quantitative neutralization (eq 4).

$$n{\sim\sim}\mathrm{COOH} + (n/4)\mathrm{Me(OR)_4} \rightarrow (n/4)\mathrm{Me(OOC{\sim\sim})_4} + n\mathrm{ROH} \quad (4)$$

Nevertheless, the use of an excess of metal(IV) alkoxide (OR/COOH > 1) followed by a humidity intake into the reaction medium leads to a regular increase of the solution's viscosity vs. time, i.e., to a rheopectic-like behavior promoted by water.[15] Depending on the rate of the water intake, the gelation is more or less rapidly observed although the alcohol formed is not distilled off from the solution. Equations 5 and 6 represent the elementary steps

$$\underset{\mathrm{I}}{{\sim\sim}\mathrm{COO{-}Ti(OR)_3}} + \mathrm{H_2O} \rightarrow \underset{\mathrm{III}}{{\sim\sim}\mathrm{COO{-}Ti(OR)_2OH}} + \mathrm{ROH} \quad (5)$$

$$\mathrm{I} + \mathrm{III} \rightarrow {\sim\sim}\mathrm{COO{-}Ti(OR)_2{-}O{-}Ti(OR)_2{-}OOC}{\sim\sim} + \mathrm{ROH} \quad (6)$$

of the gelation process, described by eq 1–3. The properties of the solutions or gels, prepared as described hereabove, have been systematically studied in the presence of the alcohol and under nonanhydrous conditions. All the rheological investigations have been performed on systems the properties of which have reached a reproducible value. This situation is reached quickly (a few hours) after the neutralization and a prolonged exposure to the air has no relevant effect. The effect of parameters like excess of alkoxide over carboxylic acid to be neutralized, nature of the tetravalent metal, polymer concentration, and temperature has been analyzed in a systematic way as discussed hereafter.

Metal-to-Chain Molar Ratio. The effect of the excess alkoxide used in the neutralization of α,ω-dicarboxylic acid polybutadiene ($\bar{M}_n$ 4600) has been investigated in an aromatic oil as solvent; 10 g $\mathrm{dL^{-1}}$ solutions were neutralized by the stoichiometric amount of zirconium alkoxide (i.e., Zr/chain = 0.5) and by a twofold (Zr/chain = 1.0), threefold (Zr/chain = 1.5), and fourfold excess (Zr/chain = 2.0) of alkoxide, respectively.

At 298 K, the aromatic oil displays a low steady-flow viscosity (0.75 ± 0.05 Pa s) and a fairly shear-thinning

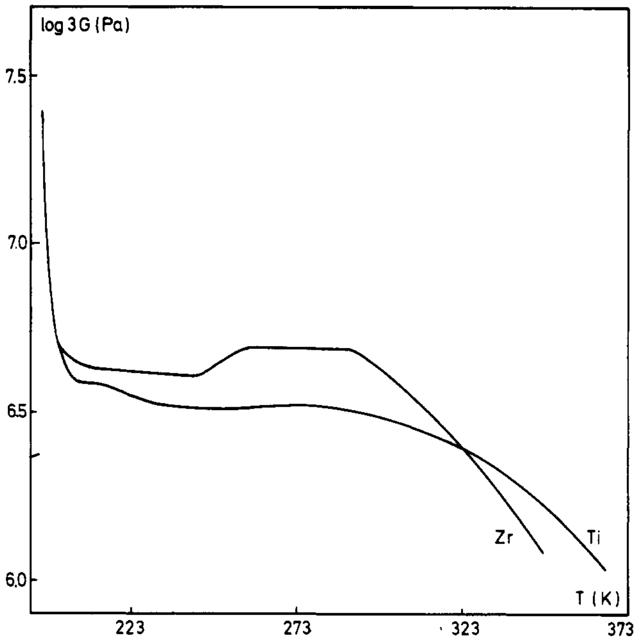


Figure 5. Isochronal (10 s) torsion modulus vs. temperature for bulk oxy titanium and zirconium α,ω-dicarboxylatopolybutadiene ($\bar{M}_n$ 4600).

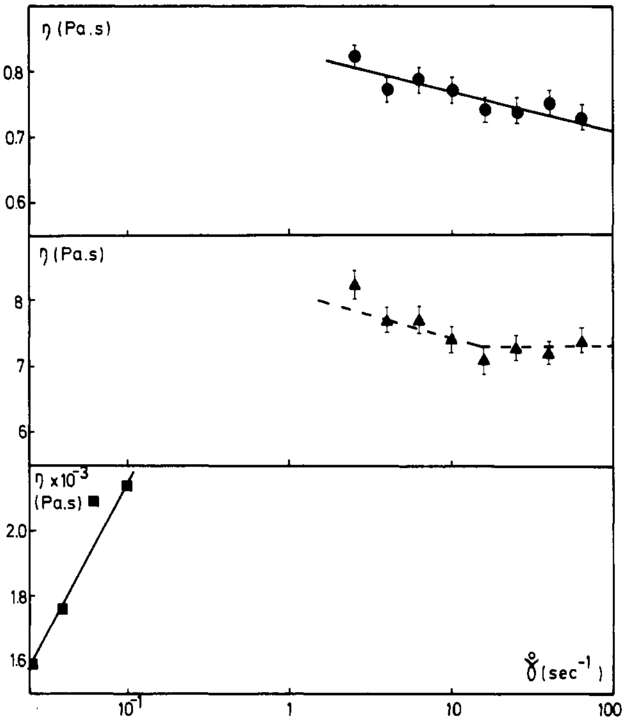


Figure 6. Steady-flow viscosity vs. shear rate ($\dot{\gamma}$) for 10 g $\mathrm{dL^{-1}}$ solutions of α,ω-dicarboxylic acid polybutadiene ($\bar{M}_n$ 4600) nonneutralized (●) and neutralized by zirconium alkoxide: Zr/chain = 0.5 (▲) and 1.0 (■), respectively. Solutions were prepared in an aromatic mineral oil and characterized at 298 K.

behavior (Figure 6). Viscosity increases from 0.75 (±0.05) up to 7.5 (±0.5) Pa s, on the addition of half a zirconium alkoxide molecule per telechelic chain. As shown in Figure 6, the rheofluidity of the oil is no longer observed at shear rates ($\dot{\gamma}$) higher than 10 $\mathrm{s^{-1}}$. A twofold excess of alkoxy groups has a dramatic effect on the viscosity which exceeds 10^3 Pa s at shear rates higher than 10^{-2} $\mathrm{s^{-1}}$, whereas the rheological behavior is now typically a shear-thickening one (Figure 6).

The shear storage and loss moduli vs. frequency curves of the 10 g $\mathrm{dL^{-1}}$ solutions are also reported at 298 K. From

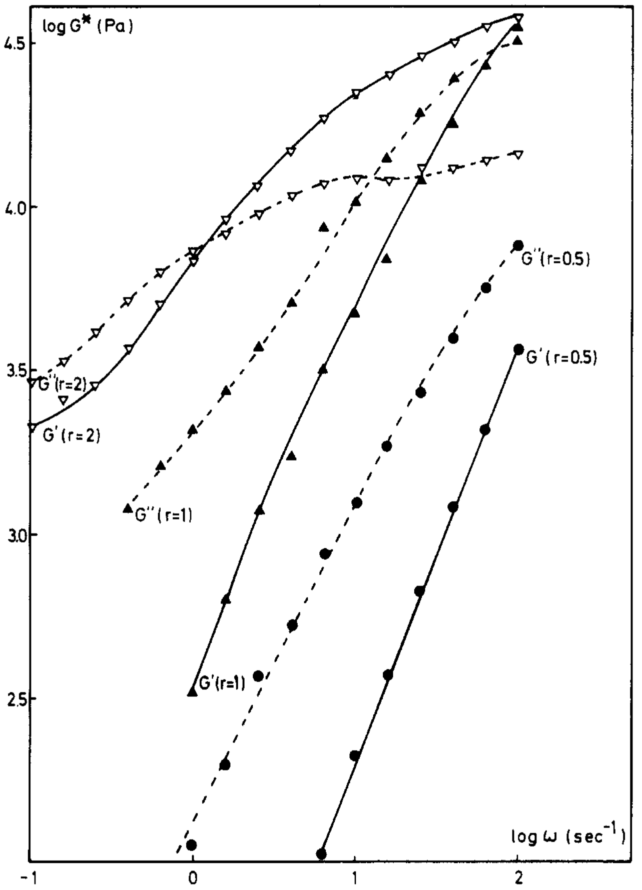


Figure 7. Shear storage (G') and loss (G'') moduli vs. frequency for 10 g dL^{-1} solutions of zirconium α,ω-dicarboxylatopolybutadiene ($\bar{M}_n$ 4600) in an aromatic mineral oil at various Zr-to-chain molar ratios (r). Temperature: 298 K.

Figure 7 it is obvious that the viscous behavior of the oil is not modified when $Zr(OR)_4$ is used at the rate of 0.5 Zr per chain. G' is indeed smaller than G'', which varies practically in direct ratio to the frequency. Furthermore, normal stresses are not detected. At Zr/chain = 1.0, a gel should be observed at frequencies higher than 63 s^{-1} and the purely viscous behavior disappears in agreement with the shear-thickening effect imparted by the continuous deformation mode. Normal stresses are now observed and the following experimental relations are reported for the primary normal stress difference and shear stress, respectively.

$$\sigma_{11} - \sigma_{22} = 2.5 \times 10^4 \dot{\gamma}^2 \tag{7}$$

$$\sigma_{12} = 3.4 \times 10^3 \dot{\gamma}^{1.2} \tag{8}$$

As the excess of $Zr(OR)_4$ increases, the intersection point of the storage and loss moduli vs. frequency curves appears at decreasing frequencies (10 and 1 s^{-1} at Zr/chain = 1.5 and 2.0, respectively). At the same time, the relative variation of G'' in the investigated frequency range decreases.

In conclusion, at constant polymer concentration, the neutralization of the acid end groups by an excess amount of $Zr(OR)_4$, followed by the hydrolysis of the excess alkoxide, provides the scientist with an efficient way to control the rheology of the medium. Neutralized in that way, carboxy-telechelic polybutadiene can impart to the solvent a large range of behavior, i.e., an increased viscosity (Zr/chain = 0.5), a shear-thickening behavior (Zr/chain = 1.0), or finally a more and more pronounced elasticity (Zr/chain > 1.5). These potentialities are well illustrated by the dependence of tan δ ($=G''/G'$) vs. frequency at different Zr/chain molar ratios (Figure 8).

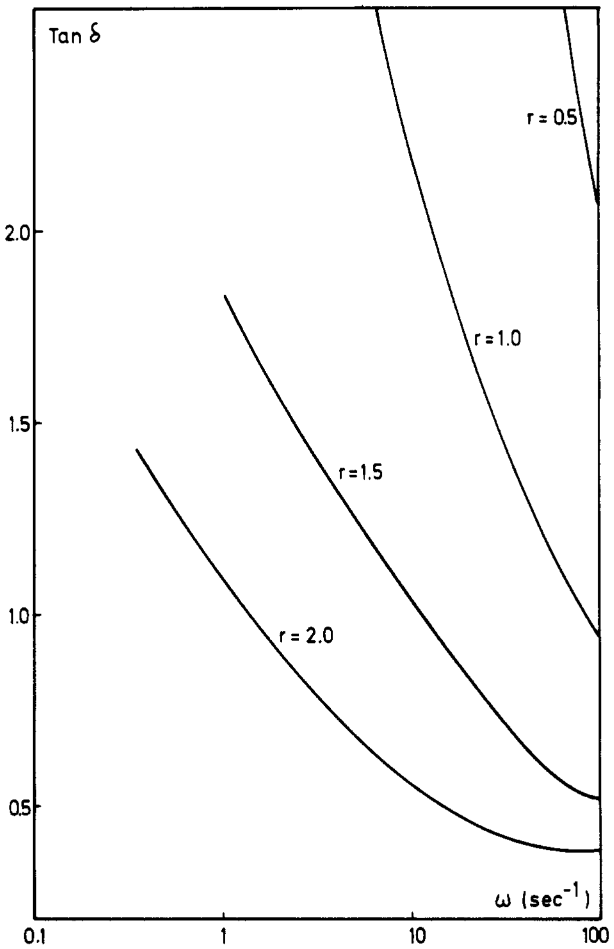


Figure 8. Loss tangent (tan δ) vs. frequency for 10 g dL^{-1} solutions of zirconium α,ω-dicarboxylatopolybutadiene ($\bar{M}_n$ 4600) in an aromatic mineral oil, at various Zr-to-chain molar ratios (r). Temperature: 298 K.

At Zr/chain = 1.0, the activation energy of the solution amounts to 5.9 kcal mol^{-1}; this means that the dynamic viscosity is reduced by half by a temperature increase of 23 °C between 273 and 373 K. It is noteworthy that the nature of the solvent is of prime importance. In particular, the nonneutralized polymer–solvent interactions should be large enough to prevent the polymer from demixing upon neutralization and resulting association of the carboxylic end groups.

Nature of the Tetravalent Metal. The short-length carboxy-telechelic polybutadiene has been neutralized in toluene (10 g dL^{-1}) by a fourfold excess (Me/chain = 2.0) of titanium, zirconium, and cerium alkoxide, respectively. The dynamic mechanical properties of these gels have been reported at 298 K (Figure 9). When titanium alkoxide is used as the neutralizing agent, a clear-cut elastic behavior is observed as G' is practically independent of the frequency in the investigated range, whereas G'' is significantly smaller and passes through a pronounced minimum. Cerium alkoxide is far less efficient than titanium alkoxide in imparting elastic properties to the gel. In the same frequency range, a viscous flow is now reported instead of a rubberlike plateau. An intermediate viscoelastic behavior characterizes the oxy zirconium carboxylates containing polymer. The end of a rubberlike plateau followed by the viscous flow region is indeed put in evidence.

The equilibrium storage modulus of the gels increases as the cation radius becomes larger (Table I). As already observed for the series of bulk alkaline-earth and oxy ti-

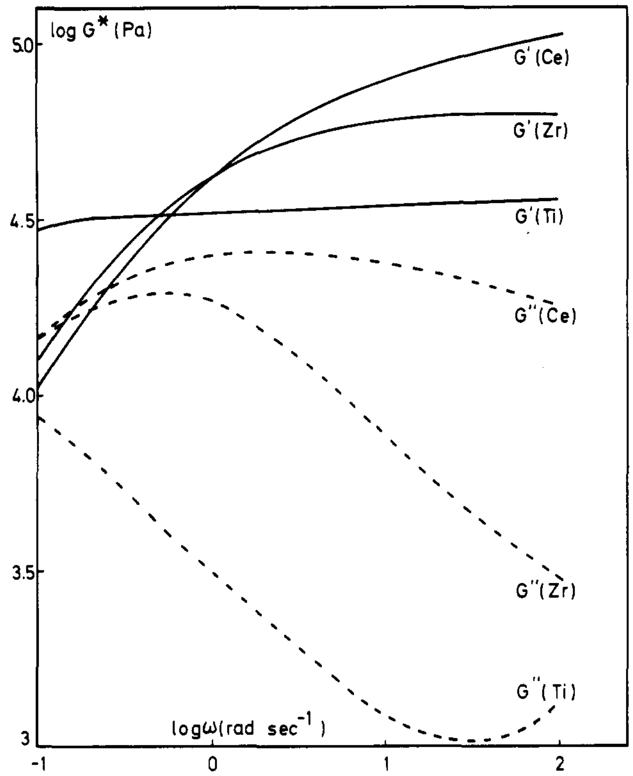


Figure 9. Shear storage (G') and loss (G'') moduli vs. frequency for 10 g dL^{-1} solutions of titanium, zirconium, and cerium α,ω-dicarboxylatopolybutadiene ($\bar{M}_n$ 4600) in toluene at 298 K (Me(IV)/chain = 2.0).

Table I
Equilibrium Storage Modulus (G_e) and Mean Relaxation Time (τ) of 10 g dL^{-1} Solution of Oxy Metal(IV) α,ω-Dicarboxylatopolybutadiene ($\bar{M}_n$ 4600) in Toluene at 298 K^a

metal	ionic radius (+4), Å	$10^{-4}G_e$, Pa	τ, s
Ti	0.68	3.5	±100
Zr	0.80	6.5	1.8
Ce	1.01	±12.0	0.25

^{a}Me/chain = 2.0.

tanium and zirconium α,ω-dicarboxylatopolybutadiene, the cross-linking efficiency is favored by an increase in the cation size. The larger the cation, the easier the association of the chain ends into bigger aggregates. On the other hand, the maximum in G'' corresponds again to a secondary relaxation of the oxy metal carboxylates and it controls the transition from the rubberlike plateau to the viscous flow region. The frequency at the maximum in G'' decreases from Ce to Zr and finally to Ti; in other words, the mean relaxation time (τ) connected with the viscous flow increases as the cation size decreases (Table I). There is again a great similarity between alkaline-earth and group 4 metal ions in the effect of the cation radius on the stability of the chain-end association. In conclusion, the cross-linking of neutralized carboxy-telechelic polybutadiene is controlled by the stability of the metal–carboxylate bonds in relation with the cation size as well for alkaline-earth as for group 4 metal ions. Of course, in the case of group 4 cations, the metal carboxylate groups are held together through metal oxo hydroxide groupings, while, in the case of alkaline-earth cations, the valency of the metal and the electrostatic interactions of the metal–carboxylate ion pairs are mainly responsible for the chain-end aggregation. It is noteworthy that the carboxy-telechelic polybutadiene end-neutralized with aluminum alkoxide behaves quite similarly to the corresponding oxy titanium carboxylates containing polymer (Ti/chain = 2.0) as well in bulk as in solution.[16] The high elastic behavior of gels based on these two materials means that the swelling proceeds preferentially by chain extension while keeping the chain-end association largely unmodified.

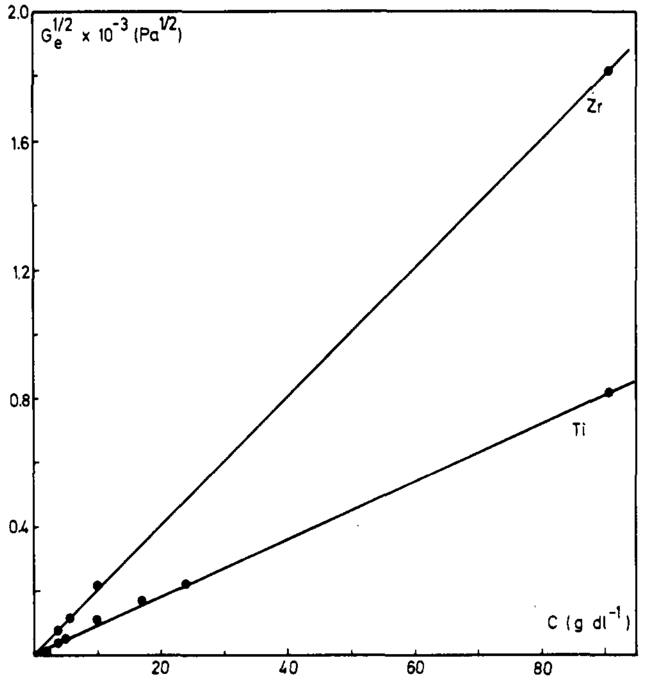


Figure 10. Equilibrium storage modulus (G_e) vs. concentration for solutions of titanium and zirconium α,ω-dicarboxylatopolybutadiene ($\bar{M}_n$ 4600) in toluene at 295 K. Metal/chain = 2.5.

Effect of Temperature. From the shear storage and loss moduli vs. frequency isotherms, it appears that the thermorheological simplicity of the bulk polymers is still observed in the presence of nonpolar solvents. The shift factors again obey an Arrhenius type of temperature dependence, and in the case of Ti (Ti/chain = 1.5), the activation energy has been calculated at different concentrations in toluene; it amounts to 6 kcal mol^{-1} at 5 g dL^{-1}, 8.9 kcal mol^{-1} at 10 g dL^{-1}, and 9.6 kcal mol^{-1} at 17 g dL^{-1}. It is therefore obvious that the thermoreversible dissociation of the Ti–carboxylate bonds is responsible for the occurrence of the viscous flow. As the activation energy increases with the polymer concentration, a parallel increase of the mean number of chain ends per aggregate can be assumed.

Effect of Polymer Concentration. At a constant metal-to-chain molar ratio of 2.5, the equilibrium storage modulus (G_e) has been measured at different polymer concentrations in toluene at 295 K. G_e is defined as the value of G' at the frequency for which G'' is minimum. Figure 10 shows a linear relationship between the square root of G_e (Pa) and the concentration (g dL^{-1}); eq 9 and 10 hold for Ti and Zr, respectively.

$$G_e^{1/2} = 9C \text{ for Ti} \qquad (9)$$

$$G_e^{1/2} = 20.2C \text{ for Zr} \qquad (10)$$

To explain this kind of dependence, it is helpful to refer to the theory of the rubberlike elasticity. As a first approximation, an ideal network with tetrafunctional cross-links is characterized by eq 11

$$G_e = RTC/M_e \qquad (11)$$

where C is the concentration of the cross-linked polymer (in bulk, C is the density of the vulcanizate) and M_e is the average molecular weight between entanglements. In this case, the very short length polybutadiene ($\bar{M}_n$ 4600) is not at all entangled and, accordingly, M_e may be approximated by $\bar{M}_n$. In halato-telechelic polymers, the functionality of the cross-links is really the mean number of chains emanating per ionic aggregate (υ). Equation 11 has therefore to be modified as follows:

$$G_e = \upsilon RTC/4(4600) \tag{12}$$

In a preceding paper, and for alkaline and alkaline earth carboxylate end groups, a linear dependence between the mean number of cations per aggregate and the concentration C was established.[10,11] If the same is true for the group 4 cations, υ should also be directly proportional to C and, according to eq 12, G_e should vary as the square of C. The experimental validity of eq 9 and 10 again supports a strong similarity between group 4 and alkaline-earth cations in halato-telechelic polymers.

Neutralization Procedure. It has to be stressed that aluminum alkoxide is a versatile neutralizing agent of carboxy-telechelic polybutadiene. It can indeed be used either in stoichiometric amount just like alkaline and alkaline-earth alkoxides or in excess in the same way as group 4 metal alkoxides. In both cases, an efficient cross-linking is reported.

The thermoreversible cross-linking of α,ω-dicarboxylic acid polybutadiene by an excess of group 4 metal alkoxide can also be performed under anhydrous conditions (dry solvent and atmosphere) but in the presence of a hydrated inorganic filler like alumina (10 wt % of the neutralized polymer). The hydration water of the mineral compound is sufficient to promote the hydrolysis of the alkoxide groups in excess; the final product exhibits a solution behavior quite similar to that of the polymer prepared according to the usual procedure, except for a higher shear complex modulus. That use of hydrated fillers is an attractive pathway to introduce a reinforcing agent into the vulcanizate. An appropriate choice of filler and metal alkoxide (i.e., alumina and aluminum alkoxide) could enhance favorable interactions between the cross-linked rubber and filler, and stabilize a fine dispersion of the latter, a point of obvious technological relevance.

The neutralization of carboxy-telechelic polymer by group 4 metal alkoxides is a very neat method to recover a hydrocarbon, like gasoline, floating upon water. A liquid telechelic polymer like short-length α,ω-dicarboxylic acid polybutadiene dissolves readily in the hydrocarbon and the addition of titanium or zirconium alkoxide triggers the gelation of the hydrocarbon layer which then can be neatly skimmed from the water. This could be an efficient method to fight some particular pollutions due to liquid hydrocarbons, considering that the critical concentration for gelation may be as low as 1.5 g dL^{-1}.

Finally, α,ω-carboxylic acid polybutadiene can be neutralized in the absence of solvent. The bulk polymer is then mixed with the required amount of group 4 metal alkoxide within a Brabender plastograph at 100 °C for 15 min. It is finally processed on a two-roll mill at 180 °C for 5 min giving rise to a product which displays practically the same modulus as that one of the polymer neutralized in solution and recovered after complete elmination of solvent.

It can be concluded that the thermoreversible cross-linking of telechelic polymers, as described in this paper, is potentially a very useful technique which is easily performed under very different experimental conditions.

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Registry No. Zirconium *n*-propoxide, 23519-77-9; titanium isopropoxide, 546-68-9; cerium *n*-butoxide, 78887-47-5.

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