

Halato-Telechelic Polymers. 8. Dependence of the Viscoelastic Behavior on the Prepolymer Molecular Weight

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ABSTRACT: The viscoelastic behavior of halato-telechelic polymers (HTP) depends largely on the prepolymer molecular weight, as evidenced by magnesium α,ω -dicarboxylatopolydienes at 296 K. At carboxylato group contents lower than 0.7 mol % ($\bar{M}_n > 2 \times 10^4$), the relaxation of the long and entangled polymeric backbone obeys a WLF type of temperature dependence. The ionic interactions act essentially as thermoreversible cross-links responsible for a dramatic extension of the rubber-like plateau. The time-temperature reducibility disappears at increasing ion concentration, because of the occurrence of a further relaxation characteristic of the ionic component. At sufficiently short prepolymer length ($\bar{M}_n = 4600$ for polybutadiene), the relaxation of the ionic aggregates is only evidenced with an Arrhenius type of activation. It results that the ion aggregation depends not only on the electrostatic interactions (nature of the ion pairs and polarity of the medium) but also on the ion content and the extent of entanglement of the polymeric backbone (considered above its T_g).

Introduction

In recent years, there has been a great deal of interest in the viscoelastic behavior of ionomers.¹⁻⁴ The properties of commodity polymers (polyethylene, polystyrene, polybutadiene, and EPM) are indeed greatly modified by the incorporation of ionic groups which induce a cross-linking effect by aggregation into multiplets and possibly into clusters. In ionomers, the ion pairs are more or less randomly attached onto the polymeric backbone, and their aggregation is limited by steric hindrance imposed by chain segments. Under these conditions, multiplets, i.e., aggregates containing exclusively ion pairs, cannot grow into large entities, but at high enough ion concentrations, they can loosely associate into clusters, i.e., large heterogeneous aggregates of high ion density organic material. Comprehensive studies of the physical state of ionomers, based on viscoelastic and X-ray investigations, are, however, at variance and subject to different interpretations.

To gain a more straightforward analysis of the general behavior of ion-containing polymers, we have given attention to halato-telechelic polymers (HTP), which result from the complete ionization of both ends of telechelic polymers and behave as significant model compounds.⁵⁻⁹ The viscoelastic properties of halato-telechelic polybutadienes have been investigated in solution¹⁰ and in the bulk^{11,12} but at constant and low prepolymer molecular weight ($\bar{M}_n = 4600$). An attractive time-temperature reducibility is observed, whereas a secondary relaxation is evident and unambiguously attributed to the ionic component. This paper reports the bulk viscoelastic behavior of HTP based on carboxytelechelic polyisoprene, the molecular weight of which ranges between 7000 and 70000. The rheological features of the nonneutralized α,ω -dicarboxylic acid prepolymers will also be considered to appreciate the effect of H bonding between the acid end groups.

Experimental Section

Carboxy-telechelic polyisoprenes were anionically prepared in tetrahydrofuran at -78°C . Tetramer of sodium α -methylstyrene was used as difunctional initiator of the isoprene (10 wt %) polymerization. The living macrodianions were deactivated by excess anhydrous carbon dioxide,¹³ and the final polymer was isolated by precipitation into acidified methanol. The polyisoprene microstructure was characterized by 65% 3,4 units and 35% 1,2 units. The glass transition temperature of this type of prepolymer

Table I
Dependence of the WLF Constants C_1 and C_2
(Referred to 296 K) on the Molecular Weight (\bar{M}_n) of
 α,ω -Dicarboxylic Acid Polyisoprenes

\bar{M}_n	C_1	C_2, K	f_{296}	$\alpha_f \times 10^4, \text{K}^{-1}$
69 000	12.6	156	0.035	2.20
36 000	12.0	168	0.037	2.15
20 000	11.4	143	0.039	2.67
15 500	11.1	143	0.040	2.74

was 263 K, its heterodispersity was lower than 1.2, and the mean number of carboxylic acid groups per chain was about 1.95. Five samples of different molecular weight (\bar{M}_n) were prepared: 69 000, 36 000, 20 000, 15 500, and 7000. Carboxy-telechelic polyisoprenes were quantitatively neutralized by magnesium methoxide, barium methoxide, and dibutylberyllium, as described in detail elsewhere.^{8,10} The dynamic mechanical behavior in bulk was investigated by means of an RMS-7200 Rheometrics mechanical spectrometer with plate-and-plate geometry (plate diameter, 500 mm; plate-to-plate distance, 2 mm); temperature regulation was better than 0.5°C .

Results and Discussion

The dynamic mechanical behavior of the nonneutralized carboxy-telechelic polyisoprenes was first investigated by means of the Rheometrics mechanical spectrometer between 296 and 351 K, except for the lowest molecular weight sample ($\bar{M}_n = 7000$), the fluidity of which is too high to enable significant measurements. The time-temperature reducibility is verified for both the storage (G') and loss (G'') moduli, and Figures 1 and 2 show the resulting partial master curves at 296 K. These curves correspond to the viscous flow region but also to the occurrence and extension of the rubberlike plateau as the molecular weight increases. The shift factors a_T obey the WLF equation (eq 1, Figure 3), which means that the thermorheological be-

$$\log a_T = -\frac{C_1(T - T_0)}{C_2 + T - T_0} \quad (1)$$

havior of the carboxy-telechelic polyisoprenes is controlled by the free volume concept. Table I summarizes the values of the C_1 and C_2 coefficients of the WLF equation at 296 K, chosen as the reference temperature (T_0). The free volume fraction at 298 K (f_{298}) and the volume expansion coefficient (α_f) are calculated and reported also in Table I. Both f_{298} and α_f have reasonable values which slightly

Table II
Dependence of the Equilibrium Storage Modulus (G_e) and the Average Molecular Weight between Entanglements (\bar{M}_e) on the Molecular Weight of α,ω -Dicarboxylic Acid Polyisoprenes

\bar{M}_n	$(\tan \delta)_{\min}$	ω (s ⁻¹) at ($\tan \delta$) _{min}	$G_e \times 10^{-5}$, Pa	\bar{M}_e	$\bar{n}_e - 1$	$\bar{M}_n/(\bar{n}_e - 1)$
69 000	0.33	1.3	2.5	9800	6.0	11 000
36 000	0.49	13	2.9	8600	3.2	11 000
20 000	0.76	16	3.3	7500	1.7	12 000
15 500	0.85	50	4.1	6100	1.5	10 000

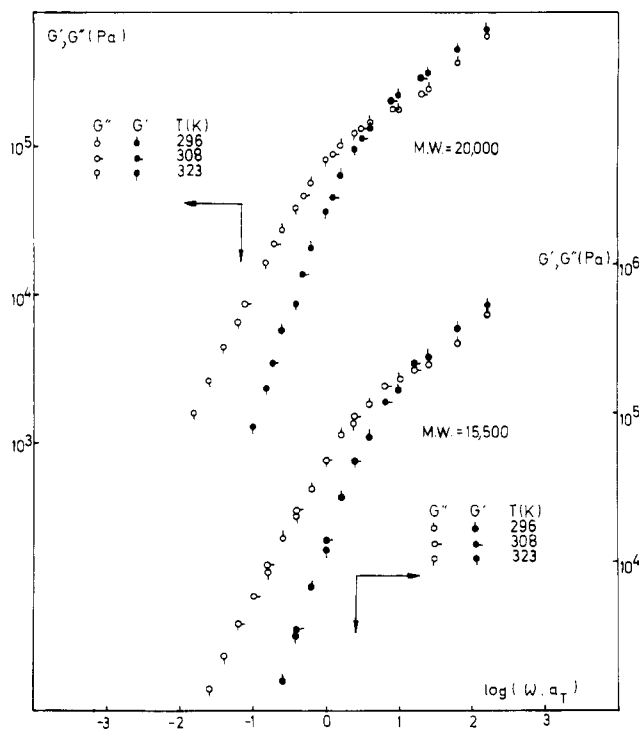


Figure 1. Partial master curves of shear storage and loss moduli of α,ω -dicarboxylic acid polyisoprenes. $\bar{M}_n = 15\,500$ and $20\,000$, respectively. Reference temperature: 296 K . Only half the experimental points of each isotherm are plotted on the figure.

increase as the molecular weight decreases, i.e., as the acid end group concentration increases.

In Table II are gathered the values of the storage modulus corresponding to the minimum value of $\tan \delta$ ($\tan \delta = G''/G'$) and considered as the equilibrium storage modulus G_e . By applying the theory of rubber elasticity (eq 2), it is possible to calculate the average molecular weight

$$\bar{M}_e = RT\rho/G_e \quad (2)$$

between entanglements (\bar{M}_e). ρ is the density, estimated to be 0.9 .

As eq 2 is valid for an ideal network with tetrafunctional cross-links, it is interesting to note that \bar{M}_e decreases regularly with the prepolymer molecular weight (Table II). This type of behavior clearly demonstrates the cross-linking effect of the carboxylic acid end groups. Furthermore, the last two columns of Table II remove from the entanglement spacing the maximum possible contribution of the end-group association.¹⁴ Assuming that all end groups associate to form trifunctional (or higher) cross-links, there are $n + 1$ entanglement points per n temporary elastic chain segments on a molecule. Since two of the entanglements are due to associating ends, the number of mid-molecule entanglements is given by $\bar{n}_e - 1$, where $\bar{n}_e = \bar{M}_n/\bar{M}_e$. The spacing of the mid-molecule entanglements ($\bar{M}_n/(\bar{n}_e - 1)$) appears to be almost independent of the molecular weight and strongly supports the end-chain association. However, the interactions of the acid end groups are not sufficiently powerful to be re-

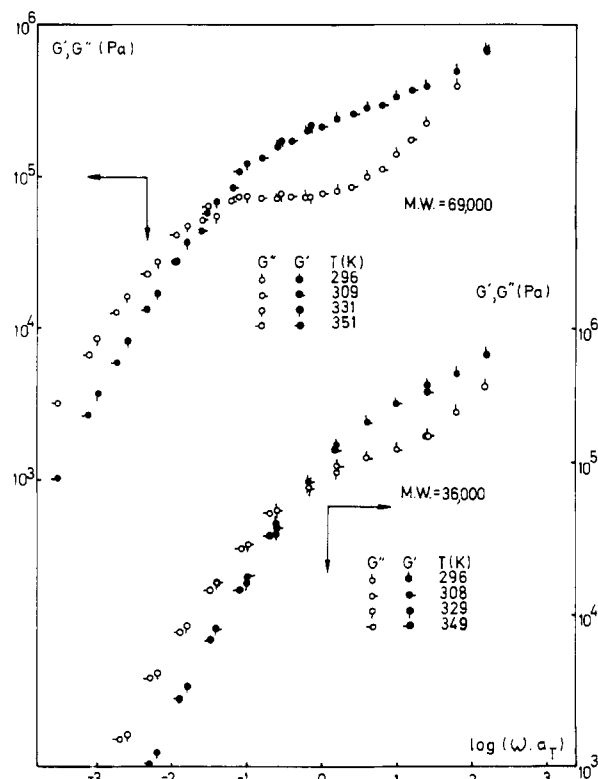


Figure 2. Partial master curves of shear storage and loss moduli of α,ω -dicarboxylic acid polyisoprenes, $\bar{M}_n = 36\,000$ and $69\,000$, respectively. Reference temperature: 296 K . Only half the experimental points of each isotherm are plotted on the figure.

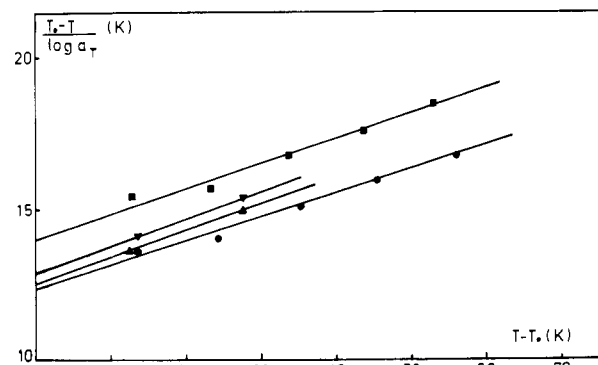


Figure 3. $(T_0 - T)/\log a_T$ vs. $T - T_0$ for α,ω -dicarboxylic acid polyisoprenes of different molecular weight: (●) $\bar{M}_n = 69\,000$; (■) $\bar{M}_n = 36\,000$; (▲) $\bar{M}_n = 20\,000$; (▼) $\bar{M}_n = 15\,500$.

sponsible for significant aggregation of the carboxylic acid groups together with the occurrence of a characteristic relaxation process. In other words, the potential H bonds between acid end groups are not sufficiently strong to perturb the time-temperature reducibility of the polymeric backbone in the investigated range of molecular weight.

Once the carboxy-telechelic polyisoprenes are neutralized by magnesium methoxide, their shear complex modulus increases, and consequently the dynamic mechanical properties of the lowest molecular weight ($\bar{M}_n = 7000$)

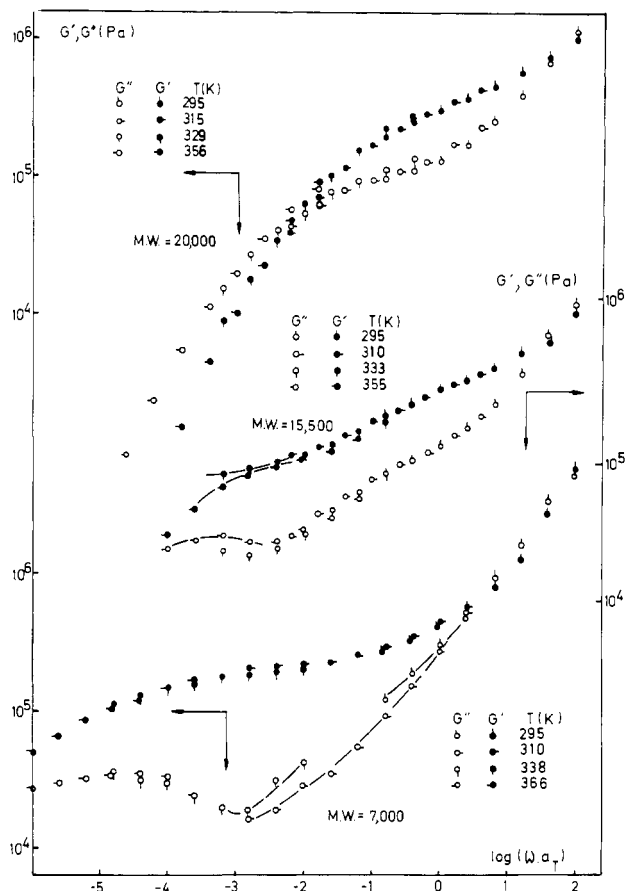


Figure 4. Partial master curves of storage and loss moduli of magnesium α,ω -dicarboxylatopolyisoprenes based on the 20000 molecular weight prepolymer. Partial pseudomaster curves for the same material based on prepolymers of low molecular weight: 15500 and 7000, respectively. Reference temperature: 295 K. For clarity, only part of the experimental data are reported in the figure.

Table III
WLF Parameters for Magnesium α,ω -Dicarboxylatopolyisoprenes Based on Prepolymers, the Molecular Weight of Which Equals or Exceeds 2×10^4

\bar{M}_n	T_{ref}, K	C_1	C_2, K	f_{298}	$\alpha_f \times 10^4, K^{-1}$
69 000	302	10.9	139	0.039	2.88
36 000	302	10.0	153	0.042	2.85
20 000	315	7.7	83	0.045	6.80

sample can now be characterized. From the shear moduli measured at different frequencies (10^2 – 10^6 rad·s $^{-1}$) and temperatures (295–366 K), it appears that the time–temperature superposition is applicable to magnesium α,ω -dicarboxylatopolyisoprenes only when the molecular weight of the prepolymer is equal to or higher than 2×10^4 (Figures 4 and 5). For these samples, the WLF equation is verified, and the characteristic parameters are calculated and reported in Table III. In the range of molecular weights higher than 2×10^4 , the free volume theory is valid (Figure 6) independently of the neutralization of the carboxy-telechelic polyisoprenes; the salt form is only characterized by higher values of f_{298} and α_f compared to those of the corresponding acid form (Tables I and III). This observation is probably due to the modification in the packing of the end chains. Indeed, when the aggregate size increases, the packing density of the end chains distributed at the surface decreases. As the hydrogen interactions (carboxylic acids) induce expectedly smaller size association at 298 K, compared to the corre-

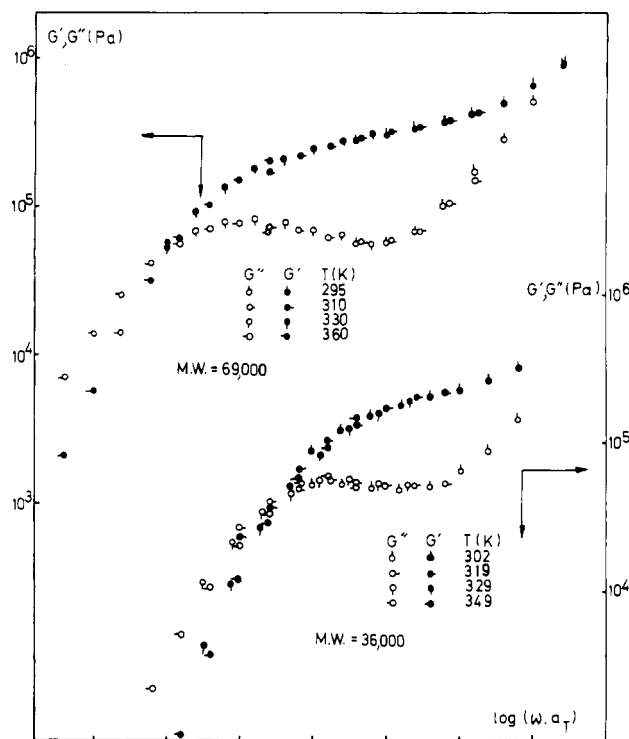


Figure 5. Partial master curves of storage and loss moduli of magnesium α,ω -dicarboxylatopolyisoprenes based on prepolymers of high molecular weight: 36000 and 69000, respectively. For clarity, only part of the experimental data are reported in the figure. Reference temperature: 295 K.

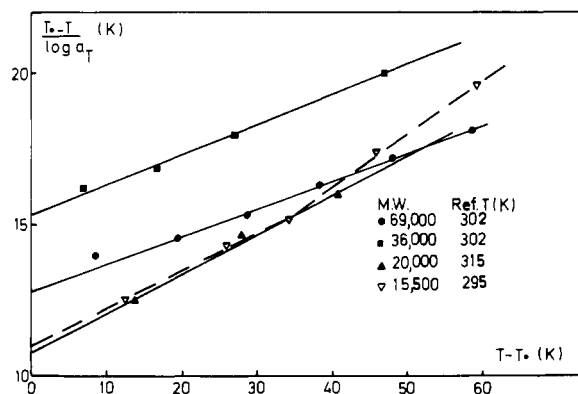


Figure 6. $(T_0 - T)/\log a_T$ vs. $T - T_0$ for magnesium α,ω -dicarboxylatopolyisoprenes based on prepolymers of various molecular weight.

sponding electrostatic interactions (metal carboxylates), f_{298} would accordingly be higher in the neutralized telechelic polymers. Furthermore, at decreasing molecular weight, the effect of chain ends increases and explains the differences in f_{298} and α_f values reported in Tables I and III, respectively. When the molecular weight of the carboxy-telechelic polyisoprenes is lower than 2×10^4 , the time–temperature superposition no longer works satisfactorily. Attempts to form master curves by shifting the individual isotherms in the usual manner are unsuccessful. Small vertical shifts improve the overlap through the whole range of frequencies; nevertheless a single curve cannot be constructed as shown by Figure 4. The thermorheological complexity suggests the occurrence of at least two differently activated relaxation processes. A second relaxation mechanism may be expected when the concentration of the carboxylato groups is sufficient to form a new type of phase and to exhibit a further deformation mode; this concentration would experimentally be observed around

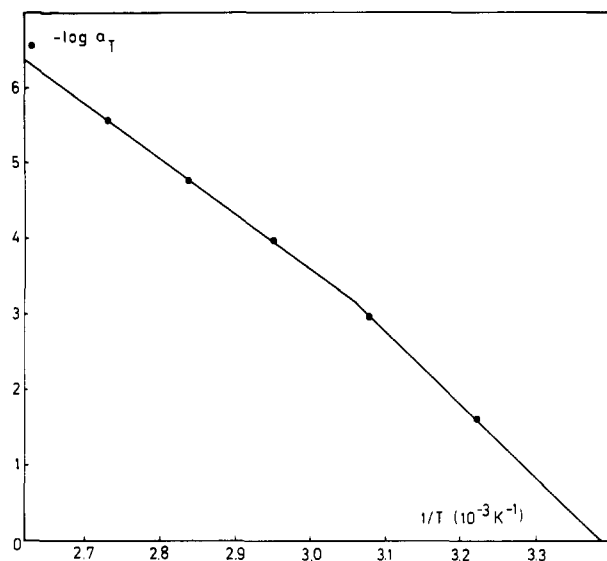


Figure 7. $-\log a_T$ vs. $1/T$ for magnesium α,ω -dicarboxylatopolyisoprene ($\bar{M}_n = 7000$).

0.7 mol %, in agreement with a critical molecular weight of 2×10^4 . In that respect, the pseudomaster curve of the magnesium α,ω -dicarboxylatopolyisoprene ($\bar{M}_n = 7000$; Figure 4) shows a minimum value at $2 \times 10^{-3} \text{ s}^{-1}$ corresponding to a further set of relaxation times around $4 \times 10^4 \text{ s}$. The polyisoprene of $\bar{M}_n = 15\,500$ displays a similar but less pronounced behavior. This situation is not at all surprising as magnesium α,ω -dicarboxylatopolybutadiene with a lower molecular weight ($\bar{M}_n = 4600$) exhibits only one relaxation process unambiguously attributed to the ionic component.^{6,10} Furthermore, an Arrhenius type of activation is observed, with an activation energy of $30.4 \text{ kcal}\cdot\text{mol}^{-1}$. When $-\log a_T$ is plotted vs. $1/T$ for magnesium α,ω -dicarboxylatopolyisoprene ($\bar{M}_n = 7000$), a broken line is obtained but the slope of the straight-line segment at the higher temperatures allows for calculating an activation energy of $33.4 \text{ kcal}\cdot\text{mol}^{-1}$, in rather good agreement with the above-mentioned value (Figure 7).

Conclusively, the dynamic mechanical behavior of the magnesium α,ω -dicarboxylatopolybutadiene ($\bar{M}_n = 4600$), elsewhere discussed, is now well completed by that of this series of polyisoprenes (\bar{M}_n ranging from 7000 to 70 000). The effect of the ionic end groups can accordingly be clearly discussed in relation with their relative abundance. At concentrations of the carboxylate groups lower than 0.7 mol %, the intrinsic rheological properties of the polymeric backbone remain practically unmodified and the ionic interactions act essentially as thermoreversible cross-links by formation of small multiplets homogeneously distributed in the polymeric matrix. The time-temperature reducibility is therefore observed, and the relaxation of the polymeric backbone is evidenced with a WLF type of temperature dependence. At higher ion concentrations, the metal carboxylates give rise to a phase separation process, quite similar to the ion clustering reported in ionomers,^{1,12} and a characteristic relaxation appears, resulting in a thermorheological complexity. At sufficiently short prepolymer length, the relaxation of the ionic aggregates overtakes that of the polymeric backbone, at least for unentangled polybutadiene, whose T_g is very low (193 K) compared to the reference temperature (302 K).⁶ An Arrhenius type of temperature dependence is then observed.

In a nonpolar matrix, the aggregation of the ions is, of course, thermodynamically favored.⁹ However this trend is controlled by kinetic parameters, i.e., the chain mobility,

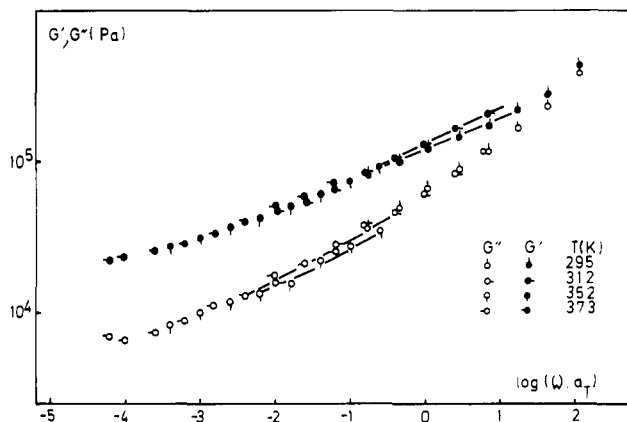


Figure 8. Partial pseudomaster curves of storage and loss moduli of beryllium α,ω -dicarboxylatopolyisoprene ($\bar{M}_n = 15\,500$). Reference temperature: 295 K.

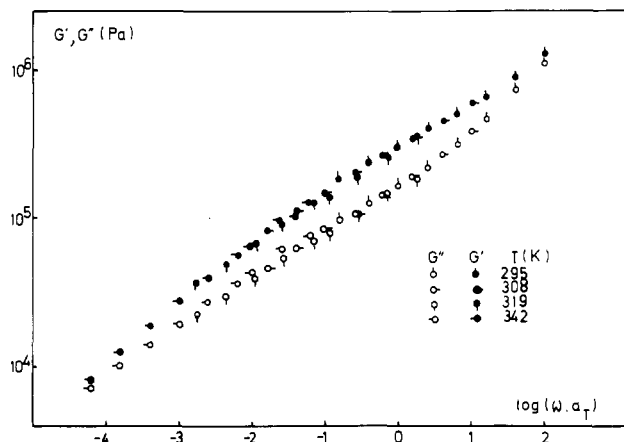


Figure 9. Partial pseudomaster curves of storage and loss moduli of barium α,ω -dicarboxylatopolyisoprene ($\bar{M}_n = 15\,500$). Reference temperature: 295 K.

Table IV
Average Relaxation Time ($\bar{\tau}$) for Barium, Magnesium, and Beryllium α,ω -Dicarboxylatopolyisoprenes ($\bar{M}_n = 15\,500$) at 295 K

cation	ionic radius, Å	$\bar{\tau}$, s
Ba ²⁺	1.35	20
Mg ²⁺	0.65	4×10^3
Be ²⁺	0.39	1×10^5

the effective ion concentration, and the extent of electrostatic interactions. The higher the molecular weight, the more pronounced the effect of the two latter parameters; indeed, the ion concentration decreases and the chain entanglement increases with increasing chain length. It is noteworthy that the halato-telechelic polydienes have been systematically investigated above their glass transition temperature (T_g). Furthermore, at constant prepolymer nature and molecular weight, the situation will be modified by the nature of the ion pairs and more especially by that of the metal carboxylates. Figures 8 and 9 show the partial pseudomaster curves ($T_0 = 295 \text{ K}$) relative to carboxy-telechelic polyisoprene ($\bar{M}_n = 15\,500$) neutralized with Be and Ba, respectively. The metal carboxylates are responsible for a dramatic extension of the rubberlike plateau compared to that exhibited by the nonneutralized equivalent (Figure 1). The ionic relaxation is not well pronounced and very widespread in the case of barium carboxylates but becomes more and more important as the cation radius decreases from Ba to Mg and finally to Be. From the pseudomaster curves, the average

relaxation times corresponding to the ionic relaxation at 295 K have been estimated as mentioned in Table IV. These results confirm once more the electrostatic origin of the ion aggregation; the stability of large-size ionic aggregates is indeed inversely related to the cation radius or directly proportional to the electrostatic interaction forces. As pointed out by Eisenberg et al.² in ionomers and confirmed by us in HTP,⁸ the polarity of the medium has a great influence on the ion aggregation, but it appears from this study that the ion content, the nature of the ion pair, and the mobility of the polymeric backbone—and especially the extent of entanglements for polymers above T_g —also have a significant influence. It results therefore that the ion aggregation in detectable domains is kinetically controlled, similarly to the glass transition in amorphous polymers, and it will be hazardous to assess when the ion-containing polymers are really studied in their state of thermodynamic equilibrium.

Some aspects of the ion aggregation in polymeric matrices are also to be outlined as challenges for further study. First, what is the mean size of the ionic aggregates just sufficient to detect an ionic relaxation? Second, the large-size ionic aggregates are currently described as ionic clusters in ionomers,^{1,15} but which is it in halato-telechelic polymers? In that respect, ordered structures with a lamellar character have been reported in some carboxylato-telechelic polybutadienes and seem to be favored by large-size cations such as Ba and K.⁷

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Investigation of Short-Chain Branches in Polyethylene by Pyrolysis-GCMS

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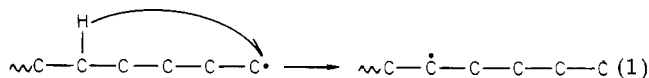
ABSTRACT: A novel pyrolysis-hydrogenation-GCMS technique has been developed and applied to branched polyethylenes of both the high-pressure and low-pressure varieties. The unique features of the technique are pyrolysis at low temperatures (360 °C) and low extent of pyrolysis of the sample (approximately 2% volatilized). This yields a high percentage of pyrolysis products pertaining to the branch points. Study of model ethylene- α -olefin copolymers shows that the pyrolysis products from branch points can be predicted solely by consideration of the possible carbon-carbon scissions α and β to the branch points. The variety of products from high-pressure polyethylene, however, is greater than that expected simply from the branch-formation mechanism proposed by Roedel and Willbourn. An expanded polymerization scheme has been formulated that includes the occurrence of intramolecular 1,3 hydrogen transfers as well as intramolecular 1,5 hydrogen transfers in the formation of short-chain branches.

Introduction

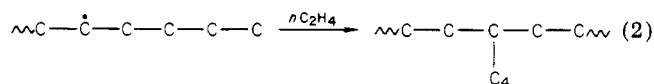
The short-chain branches in high-pressure polyethylene (HPPE) have been studied for a long time because of their influence on the physical properties of the product and because of their significance to the free radical polymerization mechanism. Various instrumental techniques have been used to determine the type and number of short branches. These include (a) infrared spectroscopy,¹ (b) carbon-13 NMR,²⁻⁷ (c) radiolysis-GC,⁸⁻¹⁰ (d) pyrolysis-GC,¹¹⁻¹⁶ and (e) pyrolysis-GCMS.¹⁷ These techniques have shown the presence of ethyl and *n*-butyl.

A theoretical mechanism for formation of short branches in the free-radical polymerization process was originally

proposed by Roedel.¹⁸ The growing polymer chain occasionally "back-bites" (intramolecular hydrogen transfer), producing a secondary radical site further down the chain.



The new radical site continues polymerization



The hydrogen abstraction was presumed to occur mostly on the fifth carbon as shown because this involves a sterically favored six-membered-ring intermediate. This mechanism, however, does not account for the other alkyl

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