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Halato-Telechelic Polymers. VII. Viscoelastic Behavior of α,ω -Divalent Cation Dicarboxylato Polybutadiene

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Synopsis

Ba, Ca, Mg, and Zn short-length carboxylato-telechelic polybutadienes ($\bar{M}_n = 4,600$) exhibit thermorheological simplicity. A secondary relaxation characteristic of ionic aggregates obeys an Arrhenius type of activation, the energy of which is in inverse proportion to the ionic radius of the cation, whereas the mean size of the ionic aggregates is proportional to it. The glass transition of the carboxy-telechelic polybutadiene is quite independent of the degree of neutralization and of the subsequent phase separation by the metal cations. The increase in cation size favors the growth of the multiplets into layered structures. Two sets of relaxation times are reported for the smallest alkaline-earth cation (Be). They suggest the existence of small multiplets unable to grow except into clusters.

INTRODUCTION

During the last fifteen years, growing attention has been paid to the study of ion-containing polymers in the solid state. The advent of ionomers and, more especially, the commercialization of Surlyn by Du Pont in 1964 have promoted research to satisfactorily explain the unique properties of this type of polymer.^{1,2} Ionomers are very tough, strong materials that are easily processed by conventional techniques such as injection molding and extrusion. These attractive characteristics result from the association in a thermally reversible network of ionic groups more or less randomly attached to a hydrophobic polymeric backbone (polyethylene, polystyrene, EPDM, etc.). The mechanism of the ion aggregation process is complex mainly because of steric hindrance by polymer chain segments as pendant ion pairs are brought together. Extensive viscoelastic and x-ray studies support the idea that below a critical ion concentration multiplet formation occurs, whereas above the critical value ion clustering takes place.³ According to Eisenberg,⁴ multiplets consist of a maximum of eight ion pairs, but clusters contain some chains and a large number of ionic groups. In any case, it is very difficult to propose a detailed description of the state of aggregation of ions and associated hydrophobic polymer molecules in ionomers, and there is no agreement on their solid-state morphology.⁵

In previous papers we have reported that halato-telechelic polymers (HTPs), resulting from the complete ionization of both ends of telechelic polymers, are very helpful model compounds to study the behavior of ions attached to a polymeric matrix.⁶⁻⁸ In 1969, Otocka et al.⁹ reported that the solution and bulk

viscosity of carboxylic-acid-terminated polybutadiene increased markedly upon neutralization with monovalent and divalent bases. They related this observation to the apparent molecular weight, considering the association of the terminal salts as "polymerizing" the difunctional prepolymer. At the present time, the view of Otocka et al. that the ionized groups do not aggregate but form simple dipole-dipole bonded pairs is quite obsolete. Moudden et al.¹⁰ and Broze et al.⁸ have indeed studied similar materials by small-angle x-ray scattering and have concluded that the ionic groups aggregated within a probably short-range lamellar structure. The ion aggregation is supported by thermodynamic arguments^{4,11} and is qualitatively confirmed by the gelation of HTP in nonpolar solvents¹² and by the viscoelastic properties of their concentrated solutions.¹³

This paper presents the results of an investigation of the solid-state behavior of HTP, and more especially of the viscoelastic properties of a series of α,ω -alkaline-earth dicarboxylato polybutadiene, the length of the butadiene prepolymer (PBD) being kept constant.

EXPERIMENTAL

The samples used in this work were the same as those used in previous studies, especially in the study of the viscoelastic behavior of concentrated HTP solutions.¹³ The carboxy telechelic polybutadiene commercialized by Goodrich under the trademark Hycar CTB 2000 \times 156 (\bar{M}_n 4,600 and $\bar{M}_w/\bar{M}_n = 1.8$) was neutralized in dry benzene as described elsewhere.¹² Then benzene was removed as judged by a constant sample weight. Differential thermal analyses were performed with a Du Pont 990 thermal analyzer. A Gehman torsion pendulum was used to record isochronal (10 s) curves of torsion modulus versus temperature. The dynamic mechanical properties were investigated by means of a Rheometrics mechanical spectrometer (RMS-7200) fitted with plate-and-plate geometry, whereas the steady-flow viscosity was measured with cone-and-plate geometry.

RESULTS

The differential thermal analysis clearly shows the glass transition of the butadiene prepolymer ($T_g = 193$ K), which is the same whatever the nature of the divalent cation. This result agrees with the previous observation of Otocka et al.⁹ The ion content is, however, rather low (2.3% mol), but in styrene ionomers, the incorporation of 2% mol of ionized units is responsible for a significant increase of T_g (4°C).³

The isochronal (10 s) torsion modulus-temperature curves confirm that T_g is independent of the cation (Fig. 1). It is noteworthy that a rubberlike plateau is observed, although the un-neutralized PBD is a viscous liquid at room temperature and cannot be processed into samples suitable for torsion modulus measurements. Thus the carboxylato end groups act as efficient crosslinking agents at least below 273 K. The curves for Ca- and Mg-containing materials are quite similar. However, the substitution of Be for Ba is responsible for a drop of about one order of magnitude in the plateau modulus. Nevertheless no flow

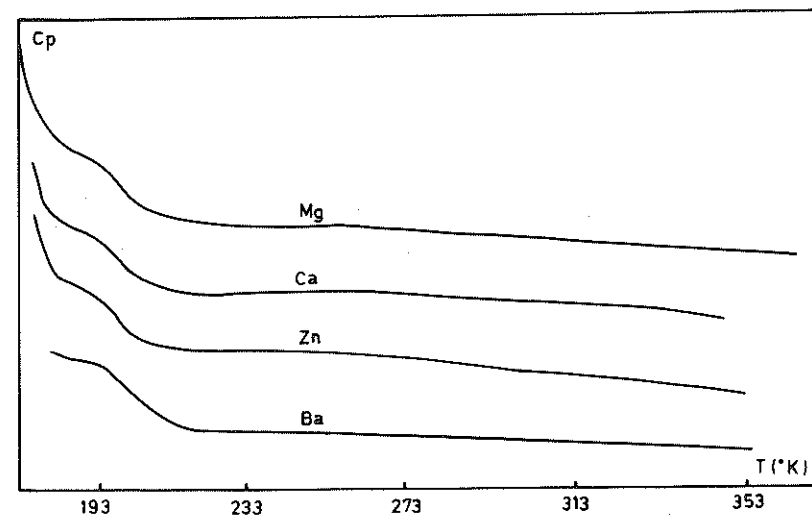


Fig. 1. Differential thermal analysis of a series of α,ω -divalent cation dicarboxylato polybutadienes ($\bar{M}_n = 4,600$).

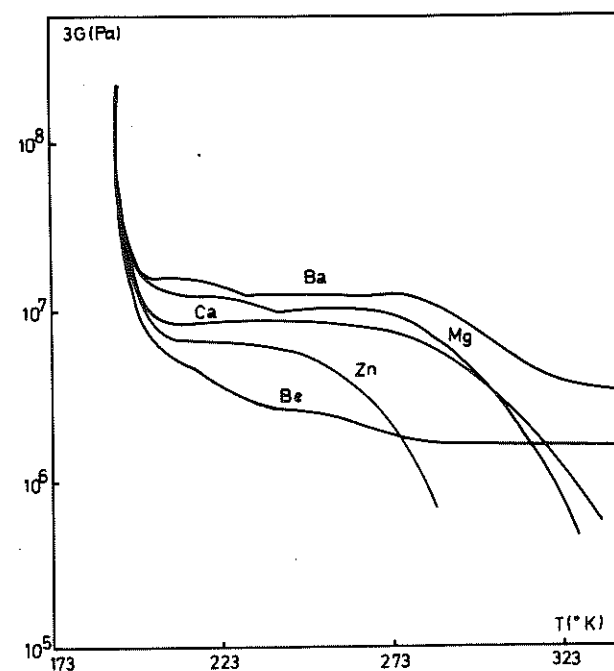


Fig. 2. Isochronal (10 s) torsion modulus vs. temperature for a series of α,ω -divalent cation dicarboxylato polybutadienes ($\bar{M}_n = 4,600$).

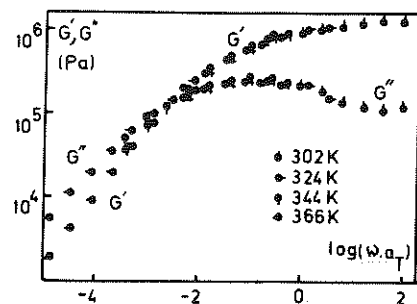


Fig. 3. Master curves of storage (G') and loss (G'') moduli vs. reduced frequency for α,ω -Mg dicarboxylato polybutadiene ($\bar{M}_n = 4,600$). Reference temperature 302 K. For the sake of clarity, only half the experimental points of each isotherm are plotted on the figure. Isotherms measured at 313, 334, and 354 K confirm the time-temperature equivalence.

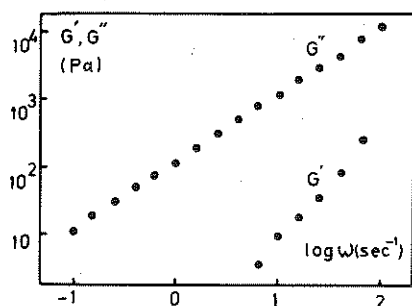


Fig. 4. Dynamic storage and loss moduli of carboxy-telechelic polybutadiene ($\bar{M}_n = 4,600$) vs. angular frequency at 302 K.

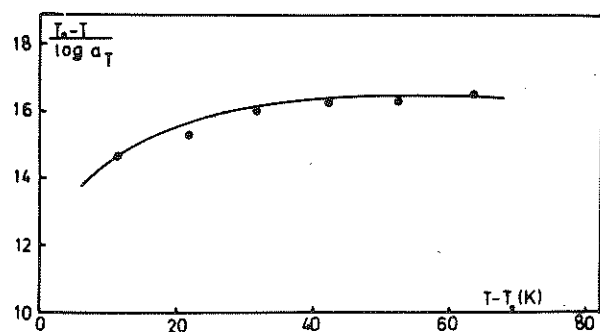


Fig. 5. Test of the WLF equation for α,ω -Mg dicarboxylato polybutadiene ($\bar{M}_n = 4,600$; $T_0 = 302$ K).

is observed below 343 K for either Be or Ba cations. At 393 K, the torsion modulus of α,ω -Ba dicarboxylato PBD is still higher than 10^6 Pa and this material remains completely soluble in toluene containing a few percent of methanol. Zn carboxylates form a much weaker pseudonetwork: the rubbery plateau is indeed much shorter, the ionic crosslinks start to yield above 243 K, and the modulus drops off very rapidly at 273 K.

The rheological behavior of 10-wt % solutions of α,ω -alkaline-earth dicarboxylato PBD in xylene has been reported elsewhere.¹³ Two main points are

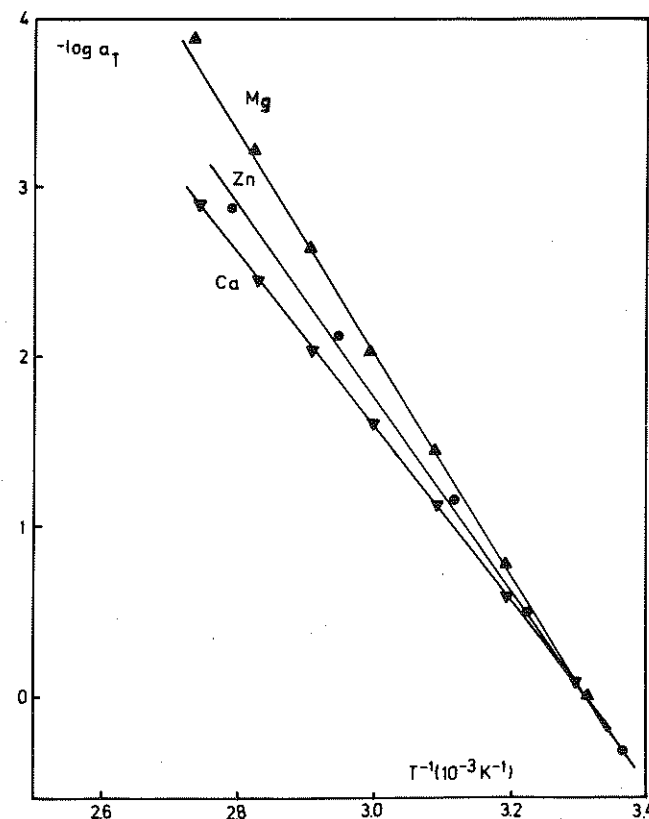


Fig. 6. Shift factors a_T vs. $1/T$ for α,ω -Mg, Ca, and Zn dicarboxylato polybutadienes ($\bar{M}_n = 4,600$).

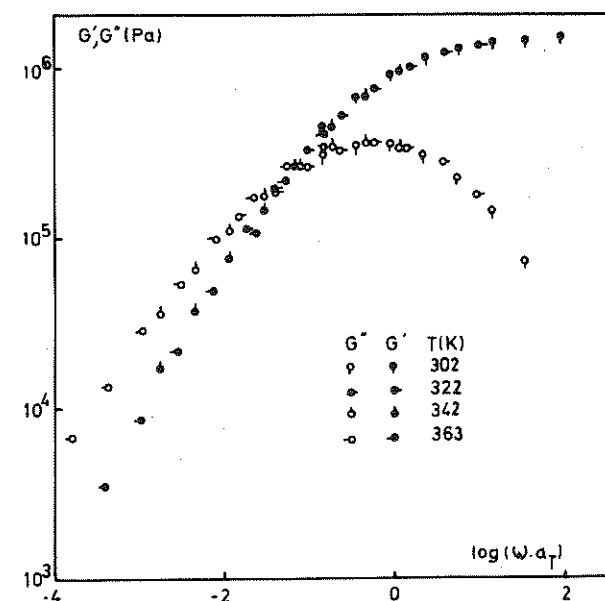


Fig. 7. Master curves of storage (G') and loss (G'') moduli vs. reduced frequency for α,ω -Ca dicarboxylato polybutadiene ($\bar{M}_n = 4,600$). Reference temperature 302 K. Isotherms measured at 302, 334, and 353 K confirm the time-temperature equivalence.

to be recalled: the thermorheological simplicity of these solutions, and the occurrence of a secondary relaxation unequivocally due to the ionic component. In bulk, the same materials display rheological properties formally similar to those observed in solution. Figure 2 shows the thermorheological simplicity of α,ω -Mg dicarboxylato PBD; the time-temperature equivalence works very well for both the storage (G') and loss (G'') modulus in the studied range of temperatures (302–370 K) and frequencies. The resulting partial master curves at $T_0 = 302$ K correspond to the end of the rubberlike plateau followed by viscous flow. The maximum of G'' , which is not observed for the un-neutralized PBD (Fig. 3), accordingly results from a secondary relaxation of the ionic component. The WLF equation does not fit the experimental shift factors a_T ; indeed, no linear relationship is obtained by plotting $(T_0 - T)/\log a_T$ vs. $T - T_0$ (Fig. 4). While the secondary relaxation activation process does not obey a free-volume relation, it is well characterized by an Arrhenius type of temperature dependence (Fig. 5). Ca and Zn dicarboxylato PBDs exhibit the same general behavior as the Mg equivalent (Fig. 5). The shear complex modulus of the Ba equivalent can be measured between plate and plate only at temperatures higher than 373 K. The isotherm recorded at 396 K is plotted in Figure 6, where G' is higher than G'' over a broad range of frequencies. Unfortunately, because of the poor thermal stability of PBD, it was hazardous to measure a series of isotherms at higher temperatures. However, the Newtonian melt viscosity of this compound measured between cone and plate over a limited range of temperature (368–383 K) also has an Arrhenius type of dependence (Fig. 7); this is also true for Mg and Ca equivalents. The dynamic behavior of α,ω -Be dicarboxylato PBD is more complex as discussed in detail below, and the measurement of its Newtonian melt viscosity was difficult to approach. Except for the Be derivative, for which information is uncomplete, the deformation of α,ω -alkaline-earth dicarboxylato PBD is again clearly controlled by the dissociation of the ionic aggregates, as reported for solutions.¹³

The activation energies have been calculated either from a plot of $-\log a_T$ vs. $1/T$ (Mg, Zn, Ca), or from the temperature dependence of the melt viscosity (Mg, Zn, Ca, Ba); values calculated by each of these techniques are in close agreement (Table I). The variation of the activation energy with the ionic radius is quite different in bulk and in solution (10% in xylene) (Fig. 8). The effect of the solvent in decreasing the bulk activation energy tends to be more pronounced as the cation size increases. The smallest alkaline-earth cation (Be) gives rise to a halato-telechelic polybutadiene exhibiting much more elastic behavior, but also a more complex relaxation mechanism than that displayed by the other alka-

TABLE I
Activation Energy of the Secondary Relaxation Observed in α,ω -Divalent Cation Dicarboxylato Polybutadiene ($\bar{M}_n = 4,600$)

Cation	Ionic radius (Å)	E_{act} (kcal mol ⁻¹)
Ba	1.34	15
Ca	0.99	24
Zn	0.74	25.5
Mg	0.66	30.5

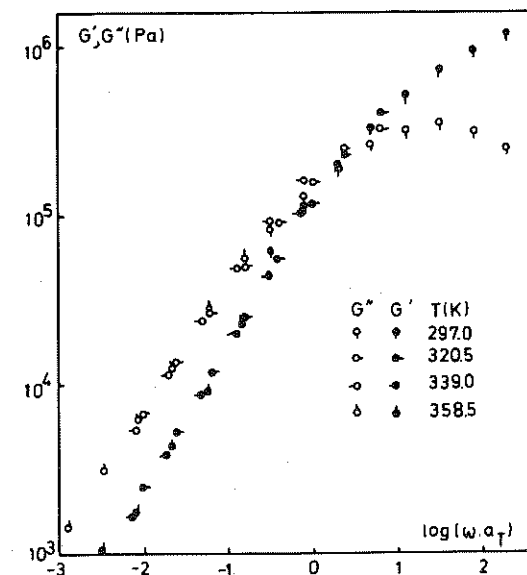


Fig. 8. Master curves of storage (G') and loss (G'') moduli vs. reduced frequency for α,ω -Zn dicarboxylato polybutadiene ($\bar{M}_n = 4,600$). Reference temperature 302 K. Isotherms measured at 310 and 339 K confirm the time-temperature equivalence.

line-earth equivalents. A pseudo-master-curve has, however, been obtained by shifting the isotherms along both axes simultaneously (Fig. 9). The pseudo-shift-factors apparently still fit an Arrhenius-type law. Two sets of relaxation times are now observed (Fig. 9); the first one (corresponding to about 0.5 s) is responsible for an increase of the storage modulus by a factor of 2, whereas the longer relaxation times (2×10^3 s) are characteristic of more stable cross-

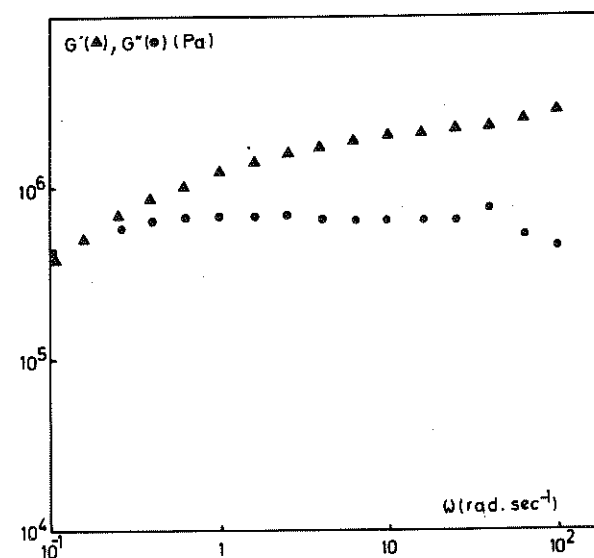


Fig. 9. Dynamic storage and loss moduli of α,ω -Ba dicarboxylato polybutadiene ($\bar{M}_n = 4,600$) at 396 K.

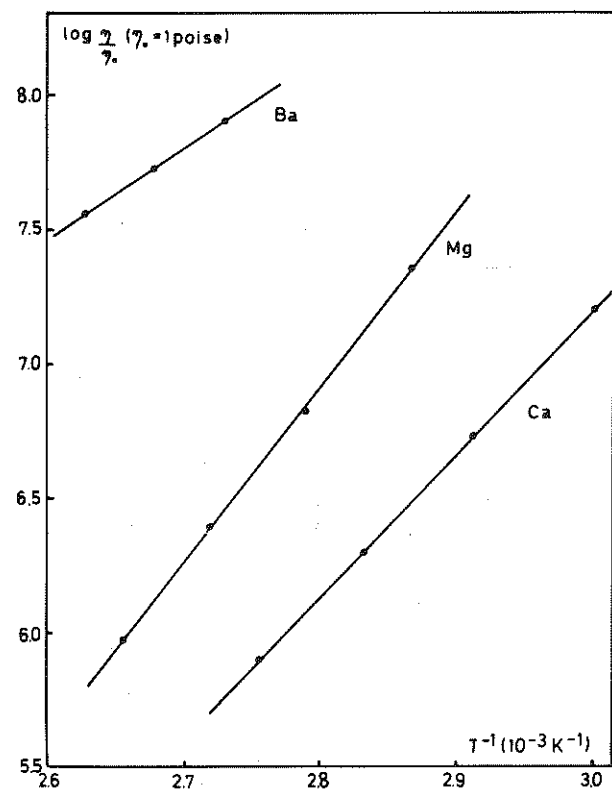


Fig. 10. Newtonian melt viscosity vs. temperature for α,ω -Ba, Ca, and Mg dicarboxylato polybutadienes ($\bar{M}_n = 4,600$).

linking entities. Figure 10 clearly shows that the distribution of the relaxation times is related to the cation size; the width of this distribution increases as the ionic radius decreases from Ca to Mg and it finally splits for Be. It must be stressed that the two-axis shift as used in the superposition for the Be-based HTP does not allow the interpretation of the results in terms of a relaxation time spectrum. Nevertheless the existence of two types of ionic aggregates remains quite conceivable in that case.

From the storage moduli master curves it is also possible to determine the equilibrium storage modulus G_e of the α,ω -alkaline-earth dicarboxylato PBD (Table II): the larger the cation size, the higher the G_e , and the stronger the

TABLE II
Equilibrium Storage Modulus G_e and Mean Number of Cations per Ionic Aggregate \bar{n} of α,ω -Alkaline-Earth Dicarboxylato Polybutadiene ($\bar{M}_n = 4,600$)

Cation	$G_e \times 10^6$ (N/m ²)	\bar{n}
Be	0.8	3.3
Mg	1.2	5.0
Ca	1.6	6.6
Ba	2.4	9.1

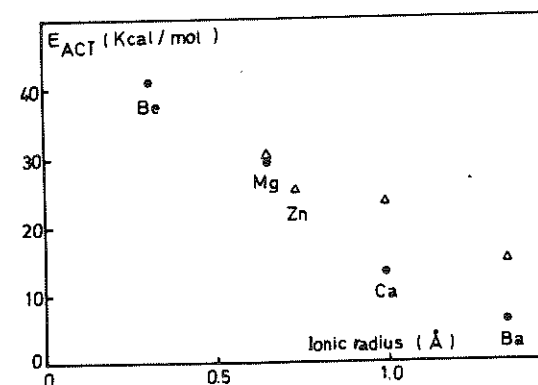


Fig. 11. Dependence of the activation energy of the ionic radius for a series of α,ω -alkaline-earth dicarboxylato polybutadienes ($\bar{M}_n = 4,600$) in bulk (Δ) and in 10% solution xylene (\bullet).

network formed. The theory of rubberlike elasticity establishes, as a first approximation, a simple relationship between G_e and the average molecular weight between entanglements (M_e) for an ideal network with tetrafunctional crosslinks¹⁴:

$$M_e = RT\rho/G_e$$

where ρ is the density of the crosslinked polymer. Our HTPs are based on a short butadiene prepolymer ($\bar{M}_n = 4,600$) which is not at all entangled: accordingly M_e may be approximated by the \bar{M}_n of the prepolymer. As the functionality of the crosslinks in HTP is the mean number of chains emanating per ionic aggregate, this parameter can be expressed by $\bar{n}v$ where \bar{n} is the mean number of cations per aggregate and v the cation valency. Thus

$$\bar{n} = 4\bar{M}_n G_e / vRT\rho$$

The calculated values of \bar{n} are summarized in Table II and plotted in Figure 11. Without giving an absolute meaning to these values (ρ has been approximated by 0.9 whatever the cation), it is clear that the mean size of the ionic aggregates increases inversely with the electrostatic interactions. Indeed, Ba carboxylato end groups favor the less stable (Table I) but large-sized ionic associations (Table II), the reverse being true for Be. It is meaningful that a lamellar structure is more clearly evidenced by SAXS⁸ as the ionic radius increases. These experimental observations support the hypothesis that the cation size and its related steric and electrostatic effects are really determinant in the phase separation process.

DISCUSSION

In comparison with ionomers, halato-telechelic polymers have the great advantage of displaying a well-characterized behavior as illustrated by their thermorheological simplicity (Figs. 2 and 8). In a hydrophobic matrix, the ionic end groups associate into entities the relaxation of which is clearly evidenced and can be studied in relation to the metal cation. For Ba, Ca, Mg, and Zn, the relaxation of the ionic aggregates follows an Arrhenius type of activation (Fig. 5)

in which the thermoreversible dissociation of these species controls the deformation of this type of ion-containing polymer. As far as Be is concerned, two sets of relaxation times are evidenced and the rheological behavior is a little more complex owing to the existence of two different kinds of ionic aggregates, probably obeying the same activation type, i.e., thermally induced ion pair dissociation. As expected, the activation energy increases with increased electrostatic interaction, i.e., proportionally to the reciprocal ionic radius of the metal cation. It may be observed that the addition of solvent can decrease the activation energy more easily as the ion pairs are less interacting (Fig. 8).

Attached at both ends of a macromolecule, the carboxylato groups seem to be largely independent of each other, and their association has no significant effect on the glass transition of the polymeric carrier (Fig. 1). This is an important difference between HTP and ionomers for which the ion segregation into a separate phase is drastically limited by the chain segments. According to Eisenberg, multiplets containing a maximum of eight ion pairs are expected in ionomers and these multiplets cannot grow into two- or three-dimensional arrays but can only give rise to loosely interacting aggregates or clusters.⁴ In HTP, phase separation appears to be mainly controlled by the features of the ion pairs. In the particular case of the carboxylato groups, the size of the metal cation is of great importance; perhaps surprisingly, the largest size aggregate would be formed in the case of the biggest alkaline-earth cation, which displays the lowest electrostatic interactions. This trend supports the hypothesis that the association of the ionic groups is not severely impeded by polymer chains. In the alkaline-earth cation series, Ba and Be display extreme sizes. The heights of the corresponding rubbery plateau are indeed quite different, with the larger aggregates being formed by Ba carboxylates (Fig. 1). Nevertheless the association of both Ba and Be carboxylates is responsible for a pronounced delay in the occurrence of viscous flow (Fig. 1), but for fundamentally different reasons. Be

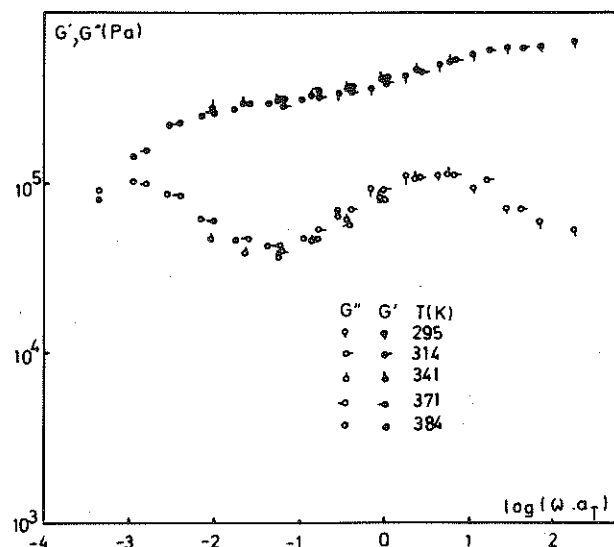


Fig. 12. Pseudomaster curves of storage and loss moduli vs. reduced frequency for α,ω -Be dicarboxylato polybutadiene ($\bar{M}_n = 4,600$). Reference temperature 302 K. The isotherms measured at 302, 324, and 357 K confirm the time-temperature equivalence.

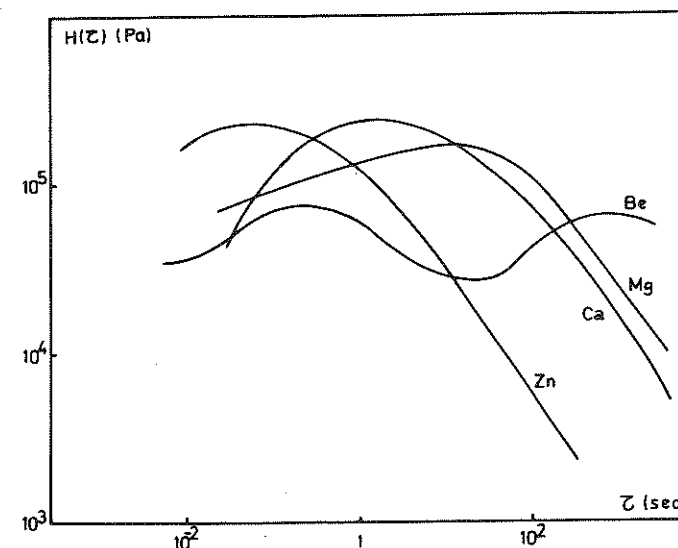


Fig. 13. Relaxation time spectra for α,ω -Ca, Mg, Zn, and Be dicarboxylato polybutadienes ($\bar{M}_n = 4,600$) at 302 K.

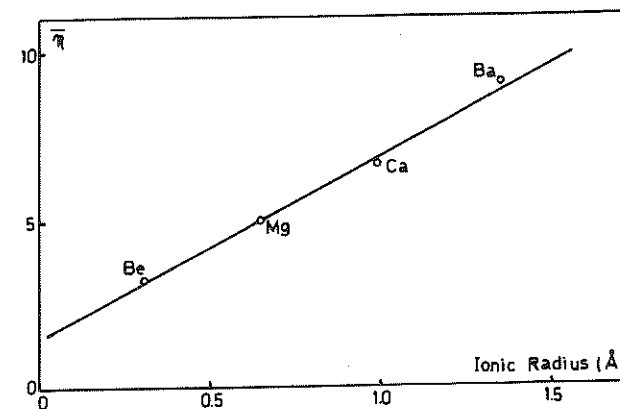


Fig. 14. Mean number \bar{n} of cations per ionic aggregate in α,ω -alkaline-earth dicarboxylato polybutadienes ($\bar{M}_n = 4,600$).

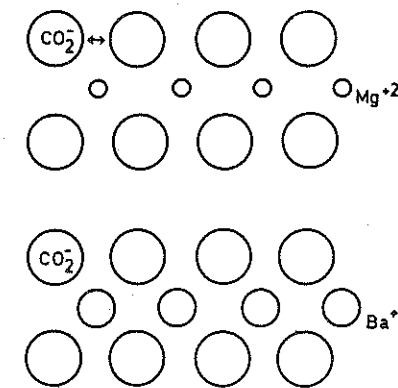


Fig. 15. Schematic representation of the arrangement of divalent metal carboxylates in a layered structure.

carboxylates form small and very tight aggregates thanks to the high electrostatic interactions they develop, whereas Ba carboxylates, which are less strongly interacting, favor a larger extension of the two-dimensional growth of multiplets into layered and localized structures.⁸ This could also account for the effects of solvent on activation energy reported in Figure 8. In the presence of a non-polar solvent, the swelling of HTP proceeds either by extension of the polymeric chains, while the aggregates of the carboxylate end groups remain largely unmodified, or by preferential dissociation of these aggregates. The former mechanism applies to the smaller-sized cations, for which the activation energy seems to be independent of the mixing of solvent. The effectiveness of the second pattern is manifest in Ca and Ba carboxylates, since the activation energy is significantly decreased by the mixing of xylene (90 wt %).

In order to give a consistent interpretation of the reported results, we suggest that bulky cations could be arranged in a two-dimensional layer (Fig. 12) without encountering major steric or electrostatic hindrance. In that respect, the structure of anhydrous Ba methacrylate consists of sheets of almost coplanar Ba ions bridged by the carboxylate groups to form an infinite two-dimensional polymer.¹⁵ The size of small cations and the higher electrostatic interactions then developed by the ion pairs could bring the neighboring carboxylate groups very close to each other. Spontaneous repulsive interactions between carboxylates would give rise to a distortion of the assumed lamellae and reduce their mean size and stability. In extreme cases, only multiplets could be formed, leading to a situation similar to that observed in ionomers but for extremely different reasons. In ionomers, the limited growth of the multiplets and their evolution into clusters is mainly due to steric hindrances in the polymeric carrier. In HTP the growth of the multiplets could be controlled through the characteristics of the interacting ion pairs independently of the polymeric backbone. This type of "ionomer" state is probably encountered in α,ω -Be dicarboxylate PBD for which the two observed sets of relaxation times could correspond to tight multiplets [$H(\tau) = 2000$ s] and clusters [$H(\tau) = 0.5$ s]. This assumption will have to be assessed by further experiments.

These conclusions are in sharp contrast to the pioneering work of Otocka et al.,⁹ which raised considerable doubt concerning ion aggregation and concluded that "the magnitude of interaction in the salt form was so great that differences between ions of different size or even valency were almost lost."

A separate paper will discuss the effect of the ionic content or prepolymer length on the rheological behavior of halato-telechelic polymers.

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