Halato-telechelic polymers. XIII. Viscoelastic properties and morphology of low molecular weight polybutadiene bearing alkaline carboxylate end-groups

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When end-capped by alkaline carboxylate groups, a low molecular weight polybutadiene ($\bar{M}_n = 4600$) behaves as a thermorheologically simple polymer. A secondary relaxation characteristic of the thermal dissociation of the ionic domains is observed in agreement with an Arrhenius-type temperature dependence. Although alkaline carboxylates generally impart a less elastic behaviour to polybutadiene than alkaline earth carboxylates, sodium carboxylate end-groups enjoy a very large degree of association in contrast to all the other alkaline and alkaline earth carboxylates. As a result, sodium carboxylates stabilize a polymer network as efficiently as calcium carboxylates, in spite of the difference in cation valency. The main structural features deduced from dynamic mechanical measurements are supported by the phase morphology as investigated by SAXS. Sodium carboxylates are observed to form the biggest ionic domains with an approximate radius of 12 Å, and to promote light dimensional extension of the chains in agreement with the larger interdomain distances.

INTRODUCTION

Since Surlyn has been discovered by Du Pont de Nemours Co., much research has been done on the modification of common polymers by a low percentage of metal carboxylates or sulphonates[1-6]. In an environment of low dielectric constant, the ionic groups are recognized to form ion pairs which associate into multiplets. However, their more or less random distribution along the polymeric backbone prevents the multiplets growing extensively, and the only way to further decrease the free energy of the system is their aggregation into 'clusters'. This two-phase morphology is responsible for the thermoreversible crosslinking of the polymer and governs its main physical and rheological properties. Although thermodynamic arguments favour the cluster hypothesis[7], the actual structure of the ionic domains is still subject to controversy and structure–property relationships are severely lacking. In order to overcome these drawbacks, halato-telechelic polymers (HTPs) have been designed as models for ionomers[8-11]. As ionic groups are selectively attached at both ends of the linear chains, their association is much easier and a better defined and simpler morphology is involved.

Small-angle X-ray scattering measurements (SAXS) have indicated the formation of multiplets, each of which are surrounded by a volume free from ionic interactions with other partners in a liquid-like structure[11]. In the investigated range of ion pair concentrations (0.37–2.12 carboxylates per 100 monomers) and temperatures (25–200°C), no critical value for cluster formation has been observed. Furthermore, a carboxylato-telechelic polybutadiene (PBD) of low molecular weight (4600) shows a very clear-cut thermorheological behaviour since master curves can be built from individual isotherms, and exhibit a secondary relaxation attributed to the ion pair association[10,12,13]. That relaxation obeys an Arrhenius type of activation, and the activation energy is inversely proportional to the cation size in the series of alkaline earth cations. The equilibrium storage modulus, which directly depends on the mean number of carboxylate groups per multiplet, shows that the bigger the cation, the more extensive is the ion pair association.

So far, the association of alkaline carboxylate ion pairs in these HTPs is not documented, although electrical measurements stress a very significant decrease in the stability of the ion pair association when alkaline earth carboxylates are substituted by alkaline ones[14]. It is the purpose of this paper to investigate the dynamic mechanical properties of a low molecular weight PBD

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end-capped by alkaline carboxylates, and to compare both the activation energy for the secondary relaxation characteristic of the ionic association and the mean size of the corresponding ionic domains with the values reported for the same polymer carrying alkaline earth carboxylate end-groups. Attention will also be paid to a possible change in the phase morphology in going from alkaline earth to alkaline cations. As a convention, α, metal dicarboxylato PBD will be designated at PBD-M, where M is the metal cation.

EXPERIMENTAL

The α,ω-dicarboxylic acid PBD, Hycar™ CTB 2000 × 156 ($\bar{M}_n$: 4600; functionality: 2,00 and $\bar{M}_w/\bar{M}_n = 1.8$), was kindly supplied by B. F. Goodrich. The carboxylic acid end-groups were quantitatively neutralized using stoichiometric amounts of freshly prepared Li, Na and K methanolate, respectively. The preparation of metal methanolates, and the neutralization procedure are described elsewhere[8]. The acetates of the biggest alkali metals, i.e. Rb and Cs, were also used as neutralizing agents of the carboxylic acid end-groups. A toluene solution of Hycar™ was added with a solution of Rb or Cs acetate in methanol; the molar ratio of carboxylic acid to alkali metal was one. Both methanol and the acetic acid formed as by-products of the neutralization process were removed from the reaction medium by repeated azeotropic distillation of toluene. The equilibrium of the neutralization reaction was accordingly displaced towards the quantitive formation of the metal carboxylato-telechelic PBD, whereas a possible solvation of the ion pairs by methanol or acetic acid was avoided as much as possible. In a final stage of purification, possible traces of these volatile components were evaporated under reduced pressure until there was no further weight reduction of the end-neutralized PBD. The i.r. analysis of the latter assessed the complete conversion of the carboxylic acid groups into metal carboxylate groups. The dynamic mechanical properties were investigated with a Rheometrics Mechanical Spectrometer (RMS 7200) fitted with a plate and plate geometry, whereas the steady flow viscosity was measured using a cone and plate geometry.

Glass transition temperatures were determined by differential thermal analysis using a Dupont 990 thermal analyser. SAXS experiments were performed at LURE-DCI, Orsay, at beam-line D-11. Both facilities and treatment of the data have been described elsewhere[11].

RESULTS AND DISCUSSION

Dynamic mechanical properties

The end-neutralization of α,ω-dicarboxylic acid PBD has no noticeable effect on the glass transition temperature; this observation was previously reported for alkaline earth and group IVb metal cations[12-15] and can be extended now to alkaline metal cations.

The valency of the metal cation at the carboxylate end-groups has, however, a dramatic effect on the viscoelastic properties of PBD. Although the conversion of the acid end-groups into Li carboxylates obviously increases the storage modulus of the telechelic PBD, *Figure 1* shows that a further significant change occurs when Mg is substituted for Li, i.e. a divalent cation of the same ionic

radius (0.66 Å). In a frequency range extending from 10^{-1} to 10^2 rad s^{-1}, the viscous flow of PBD-Li observed at 299 K disappears in favour of a rubbery plateau when PBD-Mg is considered at 302 K. It means that, all other conditions being kept constant, increasing the cation valency results in a stabilization of the three-dimensional polymer network through electrostatic interactions of carboxylate end-groups. As discussed later, this conclusion cannot be extended to divalent or higher valency transition metals whose carboxylates are less ionic (more coordinative) than those of alkaline and alkaline earth metals and thus do not lend themselves to a reliable comparison[16]. The effect of the valency of alkaline earth cations on the viscoelastic properties of PBD-M is quite consistent with a previous investigation of their electrical behaviour[14]. A marked decrease in the conductivity of α,ω-dicarboxylic acid PBD is observed when neutralized with alkaline earth cations, probably as a result of trapping impurity charge carriers by thermally stable ionic aggregates (at least up to 350 K). With alkaline cations, on the contrary, an increase of conductivity occurs above 273 K, due to the thermal breaking of unstable aggregates.

A thorough analysis of the viscoelastic behaviour of PDB-Li is interesting. Isotherms ranging from 299 to 338 K have been measured in the frequency range from 10^{-1} to 10^2 rad s^{-1}. Unfortunately values obtained at temperatures higher than 338 K were too weak to be reliable, whereas the lack of a cooling device prevented any reliable measurements below 299 K. *Figure 2* shows
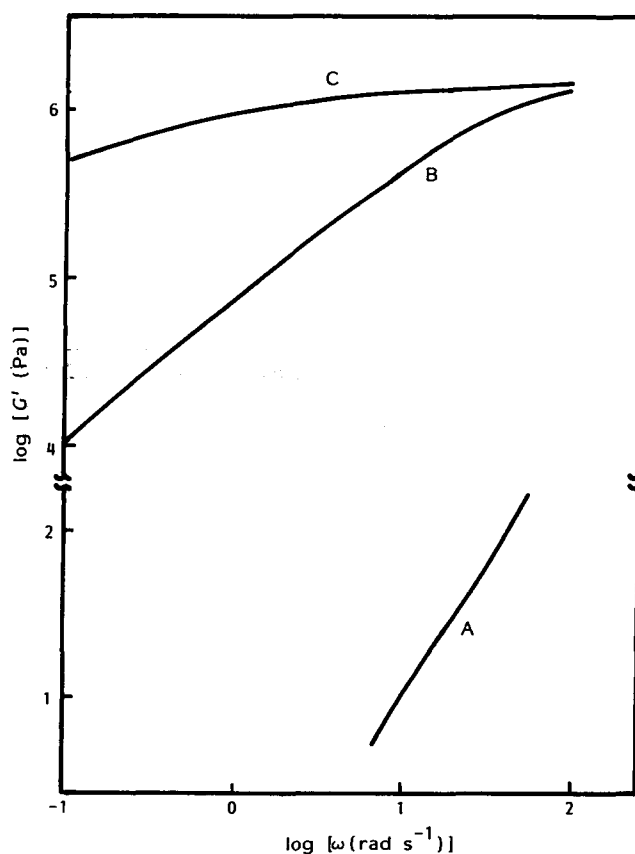

Figure 1 Shear storage modulus (G') *versus* frequency for (A) α,ω-dicarboxylic acid polybutadiene ($T = 302$ K), the end-neutralized polymer containing (B) Li ($T = 299$ K) and (C) Mg ($T = 302$ K) as a counter-cation, respectively
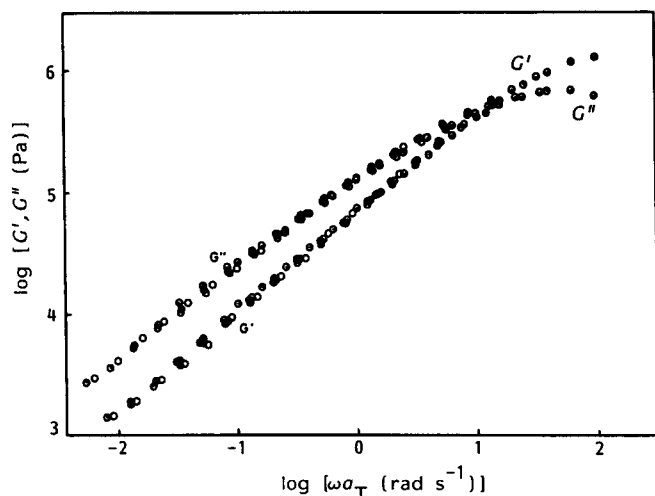
Figure 2 Master curves of storage (G') and loss (G") moduli *versus* reduced frequency for α,ω-Li dicarboxylato-polybutadiene ($M_n = 4600$). Reference temperature = 299 K (⊖, 299 K; ⊕, 310 K; ⊖, 319 K; ⊕, 328 K; ○, 338 K)
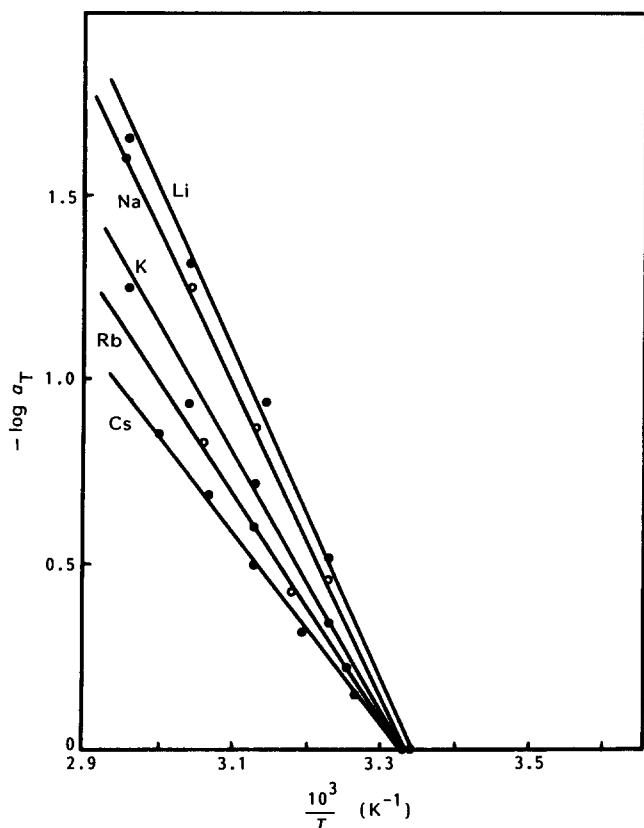

Figure 3 Log a_T (shift factor) vs. $1/T$ for α,ω-alkaline dicarboxylato-polybutadiene ($M_n = 4600$)

the master curves of both storage (G') and loss (G") shear modulus *versus* frequency. Since the maximum in G" is not observed for the unneutralized telechelic PBD[10], it has to be attributed here to a secondary relaxation of the ionic domains. The same has been previously observed for the α,ω-alkaline earth dicarboxylato PBD[12]. The question arises now whether the shift factors corresponding to the secondary relaxation follow an Arrhenius type temperature dependence or if they are of a WLF type. *Figure 3* clearly shows that the shift factors used to obtain the master curves of *Figure 2* are consistent

with an Arrhenius equation. Clearly, the secondary relaxation corresponds to the thermoreversible dissociation of the ionic domains, and at 299 K the viscous flow is activated at frequencies smaller than 10^2 rad s⁻¹. The steady flow viscosity of PDB-Li has also been measured at three different temperatures and its dependence on the shear rate is typical of a rheothinning material: the Newtonian behaviour observed at low shearing is followed with a drop in viscosity at increasing shear rates (*Figure 4*). The activation energy associated with the secondary relaxation process, calculated from the slope of *Figure 3*, was 85 kJ mol⁻¹. The close agreement with the value of 84 kJ mol⁻¹ (*Figure 5*) derived from the thermal dependence of the Newtonian shear viscosity also indicates that the secondary relaxation is somehow related to the thermal dissociation of the ionic domains which allows the PBD chains to flow. A substantial decrease in the activation energy of the secondary relaxation is reported while going from PBD-Mg (127.5 kJ mol⁻¹ (ref. 12)) to PBD-Li, which agrees with the previous conclusion that weaker interactions occur between carboxylate groups when associated with Li instead of Mg.

The investigation of the viscoelastic properties of α,ω-dicarboxylato PBD has been extended to the other alkali metal cations. Whatever the cation, the low molecular weight PBD-M is a thermorheologically simple polymer; a master curve can be built by horizontally shifting successive curves of log G' (G") *versus* log ω with respect to a reference curve. At a constant reference temperature, PBD-Li and PBD-K (*Figure 6*) exhibit a very similar rheological behaviour in the same frequency range. The frequency at which the curves of log G' and log G" *versus* log ω cross over is almost constant, although the maximum in G" is better defined for PBD-K than for PBD-Li. The situation is very different with Na, the ionic radius of which lies between that of Li and K (*Figure 7*). PBD-Na is indeed an essentially elastic material since G'
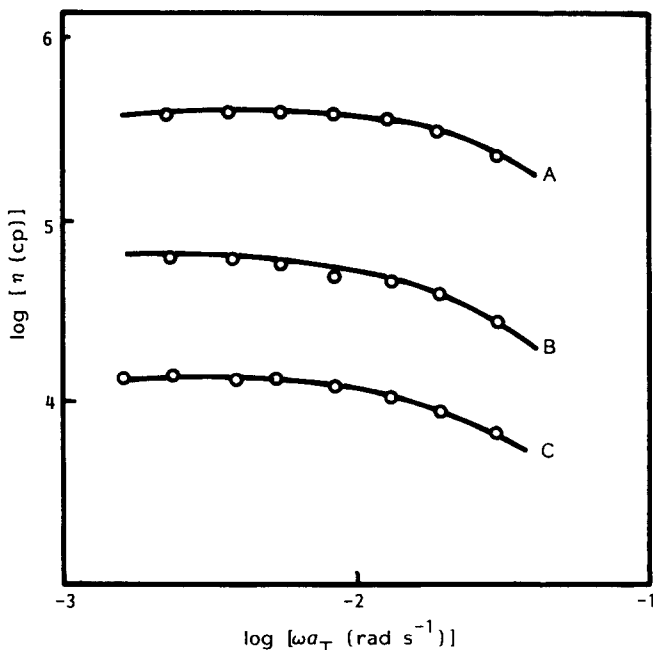

Figure 4 Steady flow viscosity *versus* shear rate at (A) 297, (B) 319 and (C) 338 K for α,ω-Li dicarboxylato-polybutadiene ($M_n = 4600$)
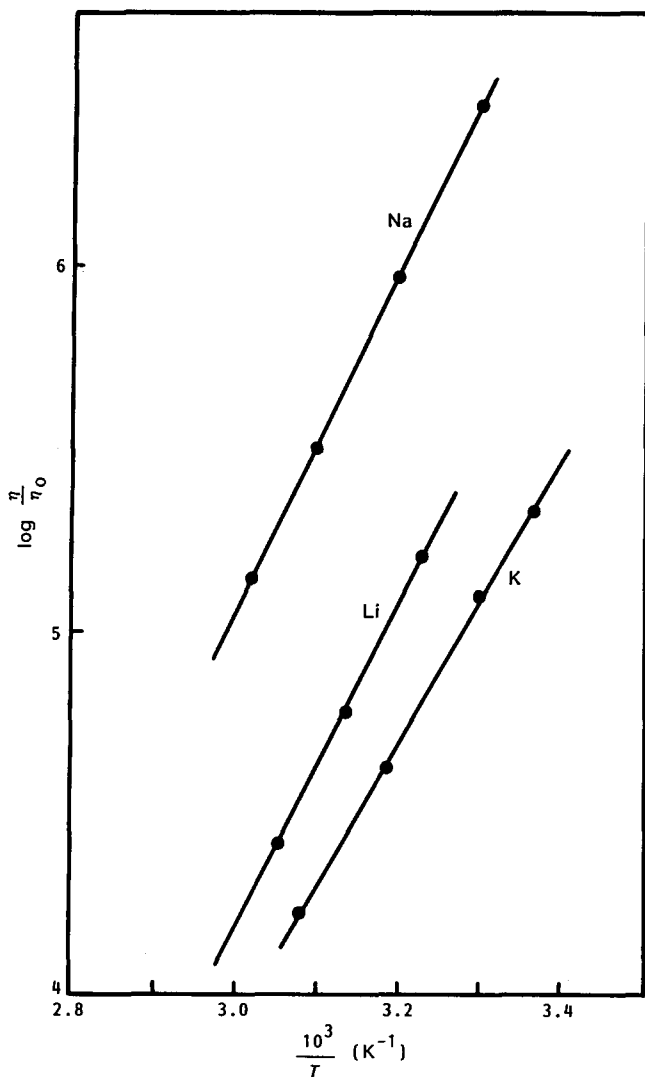
Figure 5 Thermal dependence of the Newtonian melt viscosity for α,ω-alkaline dicarboxylato-polybutadiene ($\bar{M}_n = 4600$)

becomes smaller than G'' two decades of frequency lower than for PBD-Li and PBD-K. Accordingly, the electrostatic interactions of Na carboxylate end-groups allow the rubbery plateau to extend over about three decades of frequency instead of only one when the chain ends are associated through K and Li carboxylates, all the other conditions being unmodified. Comparing with the response of α,ω-alkaline earth dicarboxylato PBD, it is found that, in spite of a lower valency of the cation, PBD-Na is as elastic as PBD-Ca[12] (*Figure 8*) and its behaviour is very close to that of PBD-Mg. Similarly the steady flow viscosity is quite consistent with the dynamic mechanical properties in emphasizing the unique behaviour of Na compared with Li and K (*Figure 5*). As a consequence, the beneficial effect of an increase in the metal valency (in going from Li to Mg) on the stability of the metal carboxylate interactions may not be a general rule even though the ionicity of the metal carboxylate bonds is comparable. Under the same experimental conditions, the biggest alkali metal cations (Rb and Cs) impart to the α,ω-dicarboxylic acid PBD a purely viscous behaviour, which limits the range of experimentally accessible temperatures and frequencies (*Figures 9* and *10*).

Table 1 summarizes activation energies as calculated from the thermal dependence of the shift factors used in

building master curves (*Figure 3*), and from the steady flow viscosity (*Figure 5*), when possible. No discrepancy is observed between the two series of values. As in the series of alkaline earth cations[12], the activation energy decreases as the ionic radius of the alkaline cations increases. A straight line is obtained when the activation energy (E_A) for both the monovalent and divalent cations is plotted *versus* the reciprocal ionic radius ($1/r_i$) (*Figure 11*). It must be stressed that Li is the only cation which does not obey the experimental equation $E_A = 85.5/r_i$. The discrepancy between the observed activation energy for Li carboxylates and the value expected from *Figure 11* is so great (42.5 kJ mol^{-1}) that it cannot be rationalized. Thus, except for the Mg–Li pair, the carboxylates of alkaline and alkaline earth cations of the same ionic radius, i.e. K–Ba and Na–Ca, exhibit electrostatic interactions of comparable strength.

As pointed out elsewhere[10,12], the equilibrium storage modulus (G_e) allows the mean number of cations per
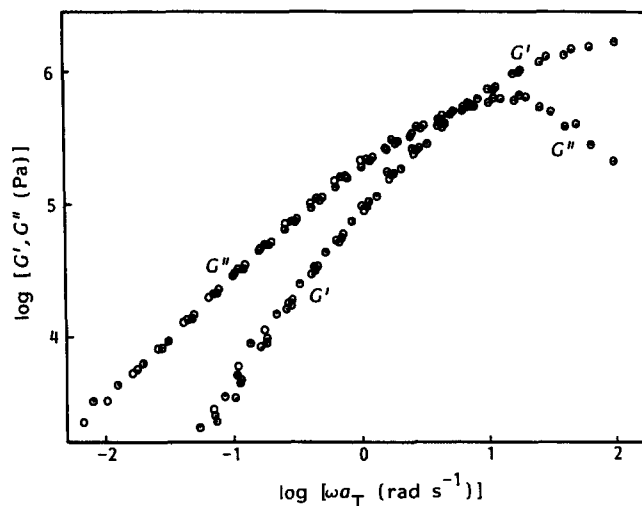

Figure 6 Master curves of storage (G') and loss (G'') moduli *versus* reduced frequency for α,ω-K dicarboxylato polybutadiene ($\bar{M}_n = 4600$). Reference temperature = 300 K ($\ominus$, 300 K; $\oplus$, 310 K; $\ominus$, 320 K; $\oplus$, 329 K; $\bigcirc$, 338 K)
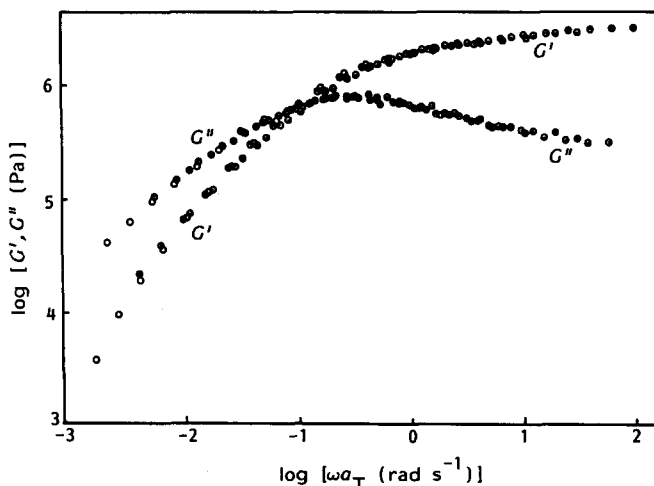
Figure 7 Master curves of storage (G') and loss (G'') moduli *versus* reduced frequency for α,ω-Na dicarboxylato-polybutadiene ($\bar{M}_n = 4600$). Reference temperature: 300 K ($\ominus$, 300 K; $\oplus$, 310 K; $\ominus$, 320 K; $\oplus$, 329 K; $\bigcirc$, 338 K)
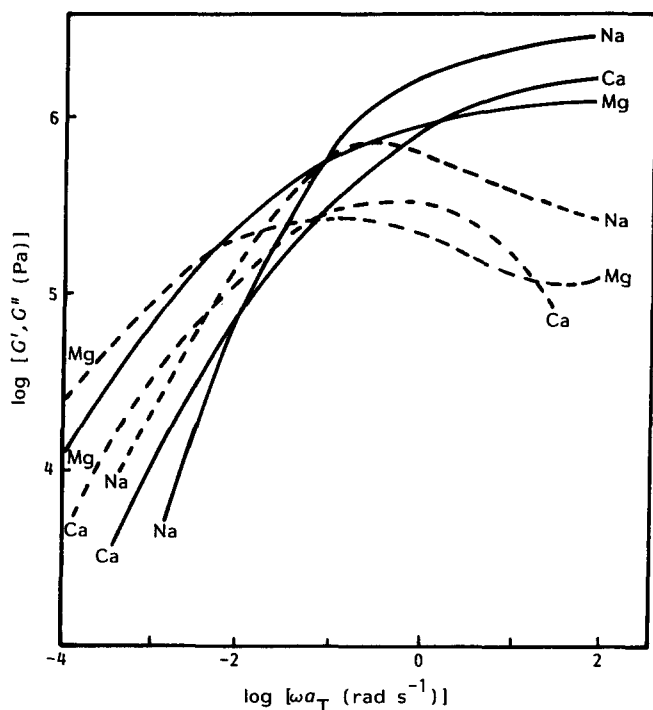
Figure 8 Comparative effect of Na, Ca and Mg on the master curves of storage (G') and loss (G") moduli of α,ω-dicarboxylato polybutadiene ($\bar{M}_n$ = 4600). Reference temperatures: Na (300 K, Ca (303 K) and Mg (302 K)
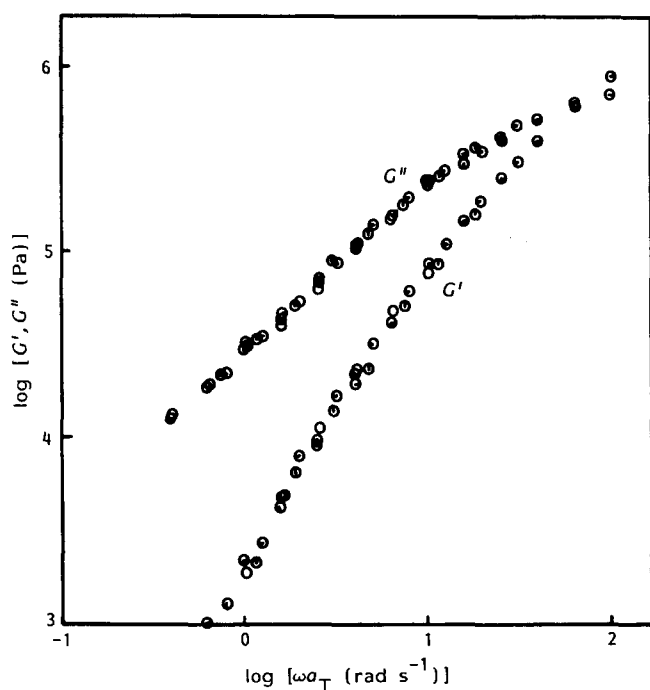
temperature, R the universal gas constant, v the cation valency, and $\bar{M}_n$ the molecular weight of the telechelic PBD (4600). This equation assumes that the polymer crosslinking is due to the dipole–dipole association of the end-groups at the exclusion of chain entanglements; the very short length of PBD makes this approximation reasonable. G_e is easily determined for PBD-Na, but can only be approximated for PBD-K by extrapolating the rubbery plateau to higher frequencies. Since the partial master curves of the other α,ω-alkaline dicarboxylato PBD mainly correspond to the viscous flow, G_e cannot be estimated (*Table 2*). Alkaline and alkaline earth cations of the same ionic radius are compared while considering the number of carboxylate anions per aggregate which is twice the value of n for alkaline earth cations. For K and Ba carboxylates, the mean degree of association is of the same order of magnitude as well as the strength of the electrostatic interactions. The much higher stability of the polymer network formed by PBD-Ba[12] compared with PBD-K has therefore to be attributed to the increase in the metal valency. In contrast to the strength of the ion pair interactions, the mean degree of association is much
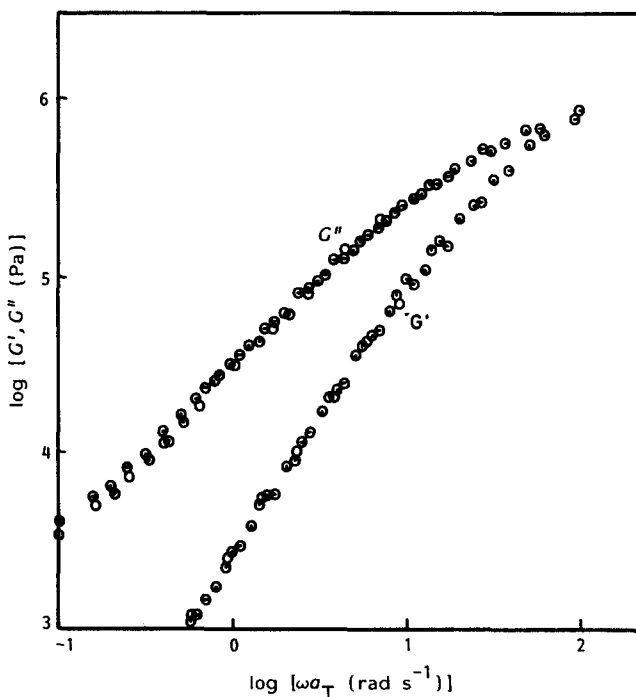

Figure 9 Master curves of storage (G') and loss (G") moduli *versus* reduced frequency for α,ω-Rb dicarboxylato-polybutadiene ($\bar{M}_n$ = 4600). Reference temperature: 300 K (⊖, 300 K; ⊕, 307 K; ⊝, 313 K; ⊙, 320 K; ○, 326 K)

Figure 10 Master curves of storage (G') and loss (G") moduli *versus* reduced frequency for α,ω-Cs dicarboxylato-polybutadiene ($\bar{M}_n$ = 4600). Reference temperature: 301 K (⊖, 301 K; ⊕, 313 K; ⊝, 319 K; ⊙, 325 K; ○, 332 K)

aggregate (n) to be determined according to the following equation.

$$n = 4\bar{M}_n G_e / v RT \rho \qquad (1)$$

where ρ is the density of the crosslinked polymer (as approximated by 0.9 for PBD), T the absolute

Table 1 Activation energy of the secondary relaxation observed in α,ω-alkaline dicarboxylato-polybutadiene ($\bar{M}_n$ = 4600)

Cation	Ion radius (Å)	Activation energy (kJ mol⁻¹)	
Li	0.66	85.0[a]	84.0[b]
Na	0.99	83.0[a]	82.5[b]
K	1.33	74.5[a]	73.0[b]
Rb	1.48	58.5[a]	_[b]
Cs	1.67	54.0[a]	_[b]

[a] As calculated from log a_T vs. $1/T$ plot (*Figure 3*)
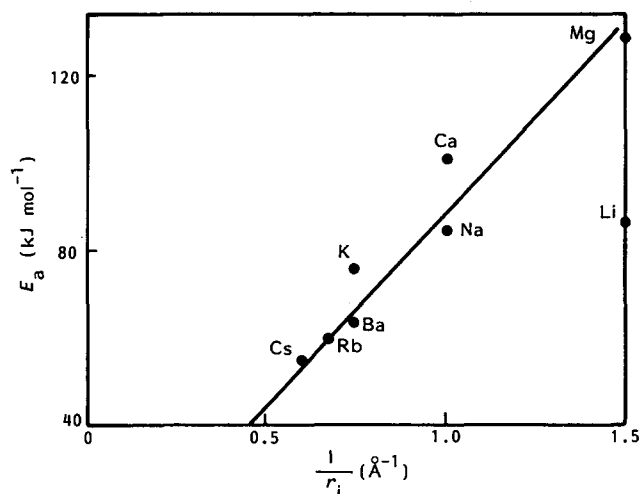[b] As calculated from log(η/η_0) vs. $1/T$ plot (*Figure 5*)

Figure 11 Activation energy of the secondary relaxation observed in α,ω-metal dicarboxylato-polybutadiene ($\bar{M}_n = 4600$) plotted *versus* the atomic radii of alkaline and alkaline earth cations

Table 2 Equilibrium storage modulus (G_e) and mean number of cations $(\bar{n})$ and carboxylates $(\bar{n}_{COO^-})$ per ionic aggregate for α,ω-metal dicarboxylato-polybutadiene $(\bar{M}_n = 4600)$

Cation	Ionic radius (Å)	$G_e \times 10^{-6}$ (Nm^{-2})	$\bar{n}$	$\bar{n}_{COO^-}$
Na	0.99	3.8	29.5	29.5
K	1.33	2.0	16.5	16.5
Ca[a]	0.99	1.6	6.6	13.2
Ba[a]	1.34	2.4	9.1	18.2

[a] Reference 12

larger for Na than for Ca carboxylates; this explains why, in spite of a lower metal valency, these ion pairs impart to α,ω-dicarboxylic acid PBD the same behaviour as Ca carboxylates. Although a lack of data prevents the comparison of the association of Li and Mg carboxylates, two main effects are instrumental in improving the elastic behaviour of PBD-M when Mg is used as countercation rather than Li, i.e. the difference in both the metal valency and the strength of the ion pair interactions. Finally, the behaviour of Rb and Cs carboxylates is poorly documented except for the activation energy associated with the thermal dissociation of their aggregates. This information is compatible with the mainly viscous behaviour observed for the related carboxylato-telechelic PBD, but no decisive conclusion can be drawn since the characterization is too limited and both PBD-Rb and PBD-Cs have not been obtained in the same way as the other polymers.

The main conclusion of this additional research on carboxylato-telechelic PBD is that neutralized by either alkaline or alkaline earth cations, the α,ω-dicarboxylic acid PBD of 4600 molecular weight exhibits an interesting thermorheological simplicity that allows master curves to be obtained from individual shear modulus *versus* frequency isotherms. A secondary relaxation characteristic of the thermal dissociation of the ionic domains is systematically observed in agreement with an Arrhenius-type temperature dependence. When compared at constant cation size, the alkaline carboxylate groups impart a less elastic behaviour to

PBD than alkaline earth carboxylates and this can be rationalized in terms of a smaller valence of the cations. Two special situations have, however, to be emphasized. The strength of association of the Li carboxylate ion pairs is abnormally weak compared with that of all the other alkaline and alkaline earth carboxylates. This effect combined with a difference in the cation valency governs the respective elastic behaviour of PBD-Li and PBD-Mg. The most striking effect is the exceptionally large degree of association exhibited by Na carboxylates in contrast to alkaline earth and the other alkaline carboxylates. This unexpected situation provides PBD-Na with exceptional elastic properties compared with all the other alkaline carboxylates containing PBD; actually, Na carboxylates stabilize a polymer network as efficiently as Ca carboxylates in spite of the difference in cation valency. It is worth recalling that α,ω-alkaline dicarboxylato-PBDs exhibit a spectrum of thermally stimulated depolarization currents characterized by an α peak close to the glass transition temperature and a Σ peak with a very high intensity[14]. The Σ peak has been attributed to a molecular relaxation process of isolated, highly dipolar carboxylate groups resulting from the thermal break up of ionic associations above the glass transition temperature. Compared with Li, the Σ peak is 1.7-fold more intense for K, whereas a 3.3-fold increase in intensity is reported for Na. The Na carboxylate groups enjoy the greatest mobility and this feature might partially account for the highest degree of association as stressed by the dynamic mechanical method.

In conclusion, the dependence of both the activation energy of the viscous flow and the average size of the ionic domains on the ionic radius of alkaline earth cations is no longer observed when alkaline cations are considered. It means that the strength of the ion pair interactions and the opportunity for the ion pairs to associate extensively are dictated by the cation radius but not always in a predictable way.

Phase morphology

The question is now whether the differences reported in the dynamic mechanical behaviour can be supported by the phase morphology of the related materials. So α,ω-alkaline dicarboxylato PBD have been investigated by SAXS.

Figure 12 shows the scattering profile of PBD-Na, which is typical of all the PBD-alkaline samples investigated in this study. In agreement with previous observations[11,17], the carboxylic acid telechelic PBD does not exhibit any maximum in the SAXS pattern, whereas the neutralized form shows a well defined peak supporting the existence of some kind of ionic aggregates. The origin of the 'ionic peak' observed, whatever the cation, has been attributed to an interparticle interference in a model where a few ion pairs associate into ionic multiplets excluding organic material and where each multiplet is surrounded by a correlation hole from which all the ionic domains are excluded[11]. It means that the average distance between domains is mainly fixed by the chain length.

The second characteristic of the scattering profiles has to be found in the strong forward scattering; this feature is shared by all the halato-telechelic polymers investigated so far[11,17] and is generally reported for ionomers[18]. This scattering at the lower angles can only be attributed to
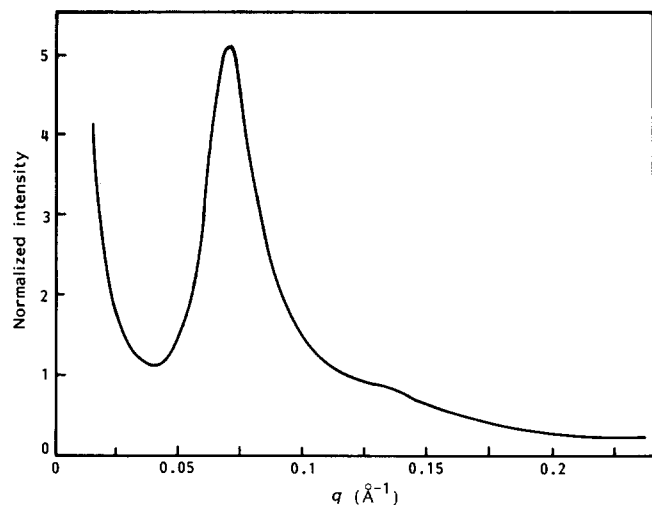
Figure 12 Normalized small angle X-ray scattering profile for α,ω-dicarboxylato polybutadiene neutralized with sodium

Table 3 SAXS data for α,ω-alkaline dicarboxylato-polybutadiene ($\bar{M}_n = 4600$)

Cation	Ionic radius (Å)	d (Å)	$\Delta q/q_{max}$	$R_D{}^a$ (Å)
Li	0.66	58.0	0.64	–
Na	0.99	79.0	0.36	–
K	1.33	71.6	0.33	11.1
Rb	1.48	64.0	0.35	–
Cs	1.67	65.0	0.39	–

^{a}Calculated from the asymptotic form of the scattered intensity[11] only when a sufficiently large range of scattering vectors has been investigated. Estimates of errors in the values R_D are ± 3 Å

scattering units with a characteristic size much larger than the interdomain distance. In the frame of the proposed model, it must be stressed that the end-to-end distance of the chain varies as $M^{1/2}$ while the distance should vary as $M^{1/3}$ for constant density. Accordingly, the spatial distribution of the domains throughout the specimen cannot be uniform, and these large-scale heterogeneities might be at the origin of the 'zero-order scattering'. The breadth of the SAXS intensity maximum relative to its position $(\Delta q/q_{max})$ is reported in *Table 3* and gives an indication of the dispersion of the Bragg distances (d), thus of both the interdomain distances and the size of the ionic domains. Except for Li which shows a much greater dispersion of d, $\Delta q/q_{max}$ is independent of the alkaline cation size. As for the activation energy of the viscous flow (*Figure 11*), Li makes itself conspicuous by some unusual morphological features.

Also in agreement with the SAXS profiles reported for alkaline earth carboxylato-telechelic PBD, the intensity in the tail of the scattering curves obeys Porod's law supporting that a sharp phase boundary exists between the ionic domains and the organic matrix. Finally a shoulder corresponding to a second order maximum is also reported, and this confirms previous observations of a weak higher order diffraction peak[11,17].

From the value of the scattering vector (q) at the scattering maximum, the distance between domains has been calculated by applying Bragg's law and reported in *Table 3*. Errors in the values of the distance between scattering domains may be estimated to 2 Å. Although d values calculated for the various alkaline cations are not very different from each other, they might be consistent with the same dependence on the ionic radius as that displayed by the elastic properties. It means that Na carboxylates provide PBD with the highest elasticity at 25°C, whereas the Bragg spacing is maximum for PBD-Na. When the capability of the metal carboxylates to stabilize a three-dimensional polymer network decreases, the Bragg distance varies qualitatively in the same way. This parallelism is still reinforced by Rb and Cs which show nicely superimposable master curves of G' and G'' versus reduced frequency (*Figures 9* and *10*) and are characterized by the same interdomain distance (*Table 3*). The experimental Bragg distance is actually of the same

order as the root mean square end-to-end distance of 70 Å for a PBD chain with a microstructure (71% *trans*, 25% *cis*, 4% vinyl) very close to that of the polymer investigated (65% *trans*, 20% *cis*, 15% vinyl)[19]. Qualitatively, it seems that the extension of the rubbery plateau of the physically crosslinked PBD brings an increase in the distance between the ionic domains, i.e. extension of the chain. This molecular feature should be a consequence of the electrostatic association of the chain ends into more effective crosslinking domains. For the Na carboxylate end-groups, the dynamic mechanical measurements result in the highest modulus of the rubbery plateau and therefore in the highest functionality of the crosslinks. That Na carboxylates are the most extensively associated ion pairs can also be supported by SAXS data. If ionic domains are assumed to be spherical and separated from each other by a distance d, a very simple relationship exists between the radius of the ionic domains (R_D) and d (equation (2))

$$R_D^3 = \phi \cdot 3d^3/4 \qquad (2)$$

where ϕ is the volume fraction of the ionic domains. Assuming that ϕ is not strongly dependent on the cation size but dominated by the much bigger carboxylate anion, R_D should be proportional to d. It means that, in the series of alkaline cations, Na carboxylates are most likely to form the biggest ionic domains, with an approximate radius of 12 Å. This value is estimated from equation (2) and the experimental radius of the ionic domains formed by K carboxylates (*Table 3*).

ACKNOWLEDGEMENT

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