Dielectric behaviour of carboxylato- and sulphonato-telechelic polydienes

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Linear polydiene chains selectively end-capped by an ionic group have been investigated by dielectric spectroscopy in relation to both polydispersity and the glass transition temperature (T_g) of the polymer and nature of the dipolar end groups. An α-relaxation associated with the micro-Brownian motion of chain segments is systematically observed. When the chain length distribution is broad the structure of the α-relaxation is complex and reflects an incomplete segregation of ionic and non-ionic components. The thermal dissociation of the ionic multiplets allows unpaired carboxylate groups to be released (Σ phenomenon); it is observed as a large relaxation process when it occurs at a temperature much higher than T_g (e.g. 100°C) and when carboxylate end groups are associated with alkaline cations (excluding alkaline earth cations). When the glass transition of the matrix and the thermal dissociation of the multiplets interfere, the situation is more complex: the α-relaxation is observed at a temperature lower than expected; and the Σ phenomenon is no longer detected (in the usually investigated temperature range) although an unexplained low amplitude relaxation is noted beyond the α-relaxation.

(Keywords: spectroscopy; dielectric behaviour; polydienes; ionomers; telechelics)

INTRODUCTION

Dielectric spectroscopy is a very convenient method for characterizing polymeric materials containing polar groups or polarizable moieties. Ion-containing polymers, usually known as ionomers, comprise permanent dipoles able to interact with an electrical field and able to reveal structural transition in the material by a change in the dielectric polarization. The electric response of ionomers is therefore expected to provide information on local motions – and thus local structures – and molecular dynamics. A paper by Boiteux in 1987 reviewed the main contribution of dielectric spectroscopy to the characterization of ionomers[1].

During the last decade special attention has been paid to the synthesis and characterization of model ionomers, i.e. linear chains selectively end-capped by an ionic group and termed halato-telechelic polymers[2–4]. Two papers have focused on the dielectric behaviour[5] and relaxation and conductivity properties[6] of such model ionomers. The first study dealt with the carboxy-telechelic polybutadiene (PBD) commercialized under the trade mark 'Hycar CTB' by B. F. Goodrich and usually neutralized by a molar excess of monovalent metal hydroxide or divalent metal oxide, respectively[5]. Two dielectric loss peaks were reported at 10 kHz when both monovalent (Na, K) and divalent (Mg, Zn) cations were used in a two-fold molar excess (*Figure 1*). The lower temperature peak was observed as a shoulder at ~ −55°C whatever the cation and it was tentatively correlated with the β-mechanical relaxation (glass transition) of the PBD matrix, although a possible contribution of water molecules was not disregarded. The second relaxation was designated as the α-relaxation, it was cation dependent and assigned to the glass transition of ionically concentrated phases. The α-relaxation was observed at a higher temperature for Na and K (~30°C) and referred to as α_U. The relaxation attributed to Mg and Zn (or α_L) was reported at ~ −20°C. The α_U- and α_L-relaxations were assumed to be related to clusters and multiplets, respectively, meaning that Na and K cations would favour clustering in contrast to Mg and Zn cations which would mainly participate by forming multiplets.

Later on, thermally stimulated depolarization (t.s.d.c.) and polarization (t.s.p.c.) methods were used as complementary tools in the characterization of metal carboxylato-telechelic PBD. Hycar CTB was neutralized by alkaline (Na, K, Li) and alkaline earth (Ba, Ca, Mg) alkoxides under anhydrous conditions[6]. The degree of neutralization ranged from 20 to 100% and the investigated temperature ranged from −100 to 30°C. The precursor acid prepolymer (Hycar CTB) exhibited a t.s.d.c. curve characterized by two distinct peaks which were labelled α and ρ (*Figure 2*). The low temperature α peak was close to the glass transition temperature (T_g)

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(-75°C) and ascribed to micro-Brownian motions of chain segments. Characteristics of the ρ peak at ~ -30°C were in agreement with a charge-carrier migration over macroscopic distances. Upon increasing neutralization of the acid end groups, particularly above 40%, the shape and position of the α peak remained unchanged whereas its amplitude decreased whatever the cation valency. This was attributed to the formation of highly symmetrical and thus dielectrically inactive species (multiplets) by the metal carboxylate end groups. From 80 to 100% neutralization, a new relaxation appeared in the α region. At high temperature, the electrical behaviour of the carboxylato-telechelic PBD was strongly dependent on the metal cation. In the presence of alkaline earth cations, both t.s.d.c. and t.s.p.c. curves supported a decrease in the number of charge carriers as the degree of neutralization was increased. For instance, the ρ peak became exceedingly weak for 100% neutralization, suggesting that impurity charge carriers were trapped into or at the boundaries of thermally stable carboxylate aggregates. When alkaline earth cations were substituted by alkaline ones, a Σ peak was observed in the t.s.d.c. spectrum. It was >60 times more intense than the α peak for 100% neutralization samples and it was observed in the range from 0 to 20°C depending on the cation. Polarization experiments also revealed the Σ phenomenon which was related to a molecular relaxation process involving isolated, highly dipolar carboxylate groups. Thus, in contrast to the alkaline earth carboxylates, the alkaline ones appeared to be associated into less stable aggregates the thermal breaking of which occurred above T_g and was responsible for a spectacular increase in conductivity.

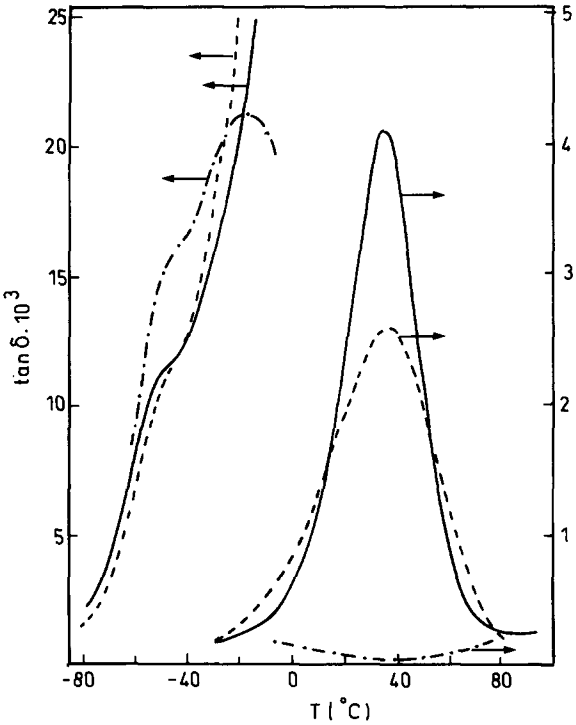

Figure 1 Thermal dependence of dielectric loss (tan δ) measured at 10 kHz for Hycar CTB neutralized with a two-fold molar excess of NaOH (——), KOH (– – –) and MgO (—·)[5,6]

Two conclusions have thus clearly emerged from dielectric measurements and t.s.d.c. and t.s.p.c. techniques: a low temperature relaxation is observed independently of the cation and neutralization degree and it is usually associated with the glass transition of PBD; and the thermal behaviour above T_g is strongly related to the cation valency. In this regard, there is an apparent lack of consistency between the interpretation of the dielectric results and the information provided by the thermally stimulated methods. This paper aims at reviewing the dielectric study in order to provide a unified view of the association of metal carboxylate groups in a polydiene matrix and the thermal stability of the related aggregates.

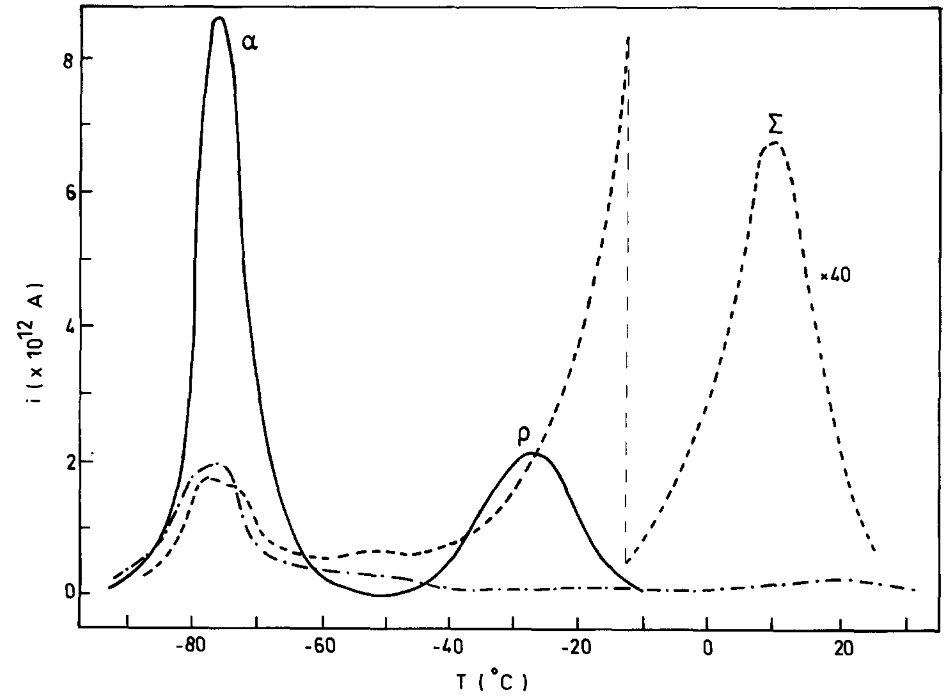

Figure 2 T.s.d.c. curves for Hycar CTB: unneutralized (——) and end-neutralized with sodium methoxide (– – –) and barium methoxide (–·–·–)

For the sake of comparison with previous t.s.d.(p.)c. measurements, the precursor Hycar CTB was neutralized by metal alkoxides under anhydrous conditions by using stoichiometric amounts of the metal reagent. In view of extending the comparison beyond the effect of the metal cation, an additional series of samples of a higher T_g (polyisoprene, PIP) has been prepared, the end groups of which are metal carboxylate and metal sulphonate, respectively.

EXPERIMENTAL

Carboxy-telechelic PBD commercially available from B. F. Goodrich (Hycar CTB 2000 × 156) was used. The main molecular characteristics were: $\bar{M}_n = 4600$; $\bar{M}_w/\bar{M}_n = 1.8$; functionality = 2.01; and *cis/trans*/vinyl ratio = 20/65/15.

Carboxy-telechelic PIP was anionically synthesized in tetrahydrofuran (THF) at −78°C. α-Methylstyrene sodium tetramer was used as a difunctional initiator. The living polyisoprenyl chains were end-capped by an average number of two α-methylstyrene units before deactivation. Depending on whether anhydrous carbon dioxide or carefully purified propanesultone was used as a deactivating agent, carboxylato- or sulphonato-telechelic PIP was obtained and finally recovered by precipitation into acidified methanol. $HClO_4$ was used to convert sodium sulphonate end groups to acid sulphonic ones. Telechelic PIP was purified by repeated precipitation in methanol from THF solution. When living polyisoprenyl chains were directly deactivated by propanesultone, the functionality in sulphonic acid was disappointing[7]. The previous end-capping of PIP by α-methylstyryl anions restored the situation and the functionality of telechelic PIP was then 1.9. Whatever the deactivating agent, $\bar{M}_n$ of the synthesized sample was 15 000 and $\bar{M}_w/\bar{M}_n = 1.15$. The sample was characterized by g.p.c. using a Waters 200, with the polymer dissolved in THF at 25°C. The molecular weight was calculated by use of polystyrene calibration standards and the universal calibration curve. The diene microstructure was determined by ^{1}H *FT* n.m.r. The spectra were acquired on a Brüker WP-200 at 200.13 MHz, with the polymer dissolved in $CDCl_3$. The vinylene peak of the 3,4-microstructural units was observed as a resolved multiplet at $\delta = 5.7$ ppm (relative to tetramethylsilane), while the vinyl protons of the 1,2- and 3,4-units gave rise to overlapping peaks at 4.84 and 4.63 ppm, respectively. No peaks were observed near 5.1 ppm, the resonance of the vinylene proton in 1,4-units. On the basis of peak areas, the microstructure was found to consist of 65% 3,4-addition, 35% 1,2-addition, and no 1,4-addition.

Functionality was determined by potentiometric titration of the acid end groups with a standard solution of tetramethylammonium hydroxide in a benzene–methanol (9/1) mixture.

Carboxy-telechelic polydienes were neutralized under strictly anhydrous conditions with stoichiometric amounts of freshly prepared metal alkoxides. The alcohol formed as a by-product was removed by repeated azeotropic distillation of the solvent (toluene)[8]. Sulphonic acid-telechelic PIP was neutralized under non-anhydrous conditions because of the instability of aliphatic sulphonic acids in the dry state. Metal acetates were used as neutralizing agents and the reaction equilibrium was displaced towards the neutralized material by distilling off the acetic acid formed as a by-product[9].

Final polymers were stabilized by Irganox 1010 (1 wt%) and dried under vacuum for 1 week at 25°C and a few hours at 120°C. They were compression moulded at 160°C for 15 min into 0.5 mm thick discs.

A Gehman torsion pendulum was used in order to record isochronal (10 s) curves of torsion modulus *versus* temperature. T_g was measured using a Perkin-Elmer DSC-1B microcalorimeter at a heating rate of 20°C min^{-1}. Dynamic mechanical properties of α,ω-Na carboxylato PBD were investigated by means of a dynamic mechanical thermal analyser (Polymer Laboratories) below the T_g and a Rheometrics mechanical spectrometer (RMS 605 S) with a parallel-plate geometry above T_g. Measurements were carried out at a frequency of 1 Hz and a heating/cooling rate of 2°C min^{-1}.

Dielectric measurements were carried out using Hewlett-Packard 4274-4275A multifrequency LCR meters connected to a Polymer Laboratory cell and driven by an Apple II computer. Samples were characterized in the frequency range from 100 Hz to 100 kHz at a heating rate of 1°C min^{-1} under dry nitrogen. Log f_m was plotted *versus* $1/T_m$ for each relaxation (where f_m and T_m were the frequency and temperature at the peak maxima in the dielectric loss, ε'', *versus* T curves). A straight line was usually observed, the slope of which allowed the activation energy to be calculated[1].

α,ω-Metal carboxylato PBD (Hycar CTB) will be designated as PBD-Met (where Met stands for the symbol of the metal cation) and α,ω-metal carboxylato and sulphonato PIP as PIP-C-Met and PIP-S-Met, respectively.

RESULTS AND DISCUSSION

α,ω-Metal carboxylato PBD (Hycar)

Figure 3 shows the temperature dependence of the dielectric loss tan δ (1 kHz) for α,ω-Na and K carboxylato PBD. Two regions clearly appear, the amplitudes of which differ by one order of magnitude. The loss peak observed in the low temperature range is less intense and results from the overlapping of two relaxations. These characteristics qualitatively correspond to the so-called α region in the t.s.d.c. curves for the same but independently prepared samples[6]. Moreover, the position of that complex loss peak in the temperature range is similar to that of the shoulder observed for PBD (Hycar CTB) overneutralized with NaOH and KOH[5]. Let us denote these two peaks by α_L and α_U, where L and U stand for lower and upper, respectively. The high temperature and more intense peak will be designated as Σ by analogy with the t.s.d.c. curves[6]. Its position also corresponds to the large relaxation observed at 30°C for the overneutralized samples[5].

There is thus a striking similarity between *Figure 3* and the t.s.d.c. curves for the end-neutralized samples containing K and Na cations (*Figure 2*), i.e. a complex α region and a Σ phenomenon. The similarity can also be extended to the tan δ *versus* temperature curves reported for the parent overneutralized samples (*Figure 1*), except for the structural complexity of the α region. It must be noted that t.s.d.c. data have been recorded at a frequency which is lower by three or four decades than the dielectric measurements of *Figures 1* and *3*, respectively.

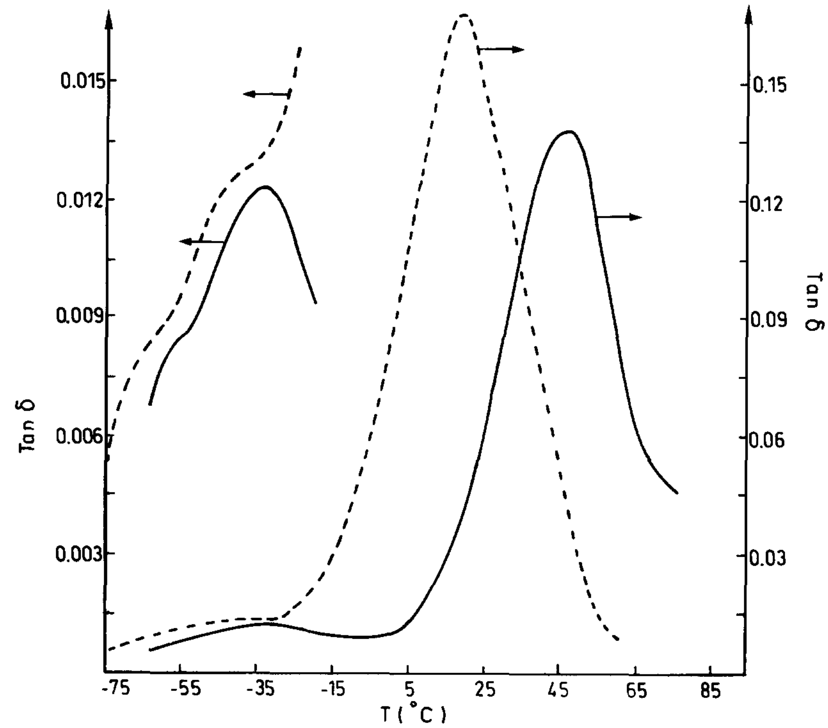

Figure 3 Tan δ *versus* temperature curves (1 kHz) for α,ω-Na (——) and -K (– – –) carboxylato PBD (Hycar CTB)

Table 1 Dielectric characteristics of α,ω-metal carboxylato PBD (Hycar CTB) at 1 kHz[a]

	T_{max} (°C)			Activation energy (kJ mol^{-1})		$\Delta\varepsilon$	
Cation	α_L	α_U	Σ	$\alpha_L + \alpha_U$	Σ	$\alpha_L + \alpha_U$	Σ
Na	−55	−32	46	88	185	0.30	3.95
K[b]	−61	−35	20	–	155	(0.40)	4.40
Mg	−55	−33		86		0.95	
Ba	−61	−42		84		0.25	

[a] P ($0 < P < 1$), the distribution of the relaxation times, is in the range of 0.6–0.7 whatever the relaxation

[b] The overlapping of α_U with α_L and Σ prevents the activation energy from being calculated. For this reason the value of $\Delta\varepsilon$ is approximate

Table 1 summarizes the main characteristic data that have been extracted from *Figure 3*. The temperature reported for the α_L and α_U peaks should be considered cautiously since these values are affected by the uneven overlapping of two (Na) or three peaks (K). That α_L and α_U appear at temperatures apparently depending on the cation might merely reflect some sensitivity to minor differences in the experimental conditions for the polymer neutralization and sample preparation, such as the presence of adventitious water molecules.

The attribution of the α region to micro-Brownian motions of chain segments has been convincingly supported by t.s.d.c. and t.s.p.c. studies[6]. The complex structure of that region is more likely the result of a heterogeneous association of the alkaline carboxylate end groups. According to a thorough analysis by small angle X-ray scattering, the ionic aggregates in halato-telechelic polydienes ($\bar{M}_n > 4600$) are adequately described as multiplets and there is no evidence for ionic clusters[10]. Referring to t.s.d.c. data, multiplets of alkaline and alkaline earth carboxylates should be highly symmetrical in order to account for the decrease in the dielectric activity of the α region when the acid end groups are progressively neutralized. This actually occurs although the dipole moment of unpaired sodium carboxylates (6 D) is higher than that of the carboxylic acids (1.7 D)[6]. $\Delta\varepsilon$ values in *Table 1* also support that only a restricted number of the potentially available dipoles contribute to the α relaxation(s). It is finally worth recalling that water swelling experiments have revealed a substantial effect of the molecular weight distribution of the polydiene backbone on the morphology of the related carboxylato-telechelics[10]. It is only when the chain length distribution is broad enough, as for Hycar PBD, that uniform uptake of water is observed, in contrast to the swelling of a thin surface layer when the distribution is narrow[10]. This observation points out that the transport of water is facilitated in the neutralized Hycar CTB by an incomplete separation of ionic and non-ionic monomers. Some ionic 'impurities' should be present, possibly unpaired dipoles and/or small and non-symmetrical multiplets. The complexity of the α region might thus be the consequence of a heterogeneous morphology in terms of size and symmetry (and thus resultant dipole moment) of the multiplets and opportunity for the metal carboxylate groups to be oriented by the electrical field. As it has already been mentioned, the magnitude of the Σ peaks is at least a decade bigger than that of the α region (*Figure 3*). This is supported by the $\Delta\varepsilon$ values (*Table 1*) and indicates that a great number of highly dipolar carboxylate groups contribute to the underlying relaxation process. There is an obvious agreement between the t.s.d.(p.)c. measurements (*Figure 2*) and the dielectric results (*Figures 1* and *3*). The Σ phenomenon [designated as α_U in the previous investigation of overneutralized (Na, K) samples] can really be rationalized by the thermal breaking of alkaline

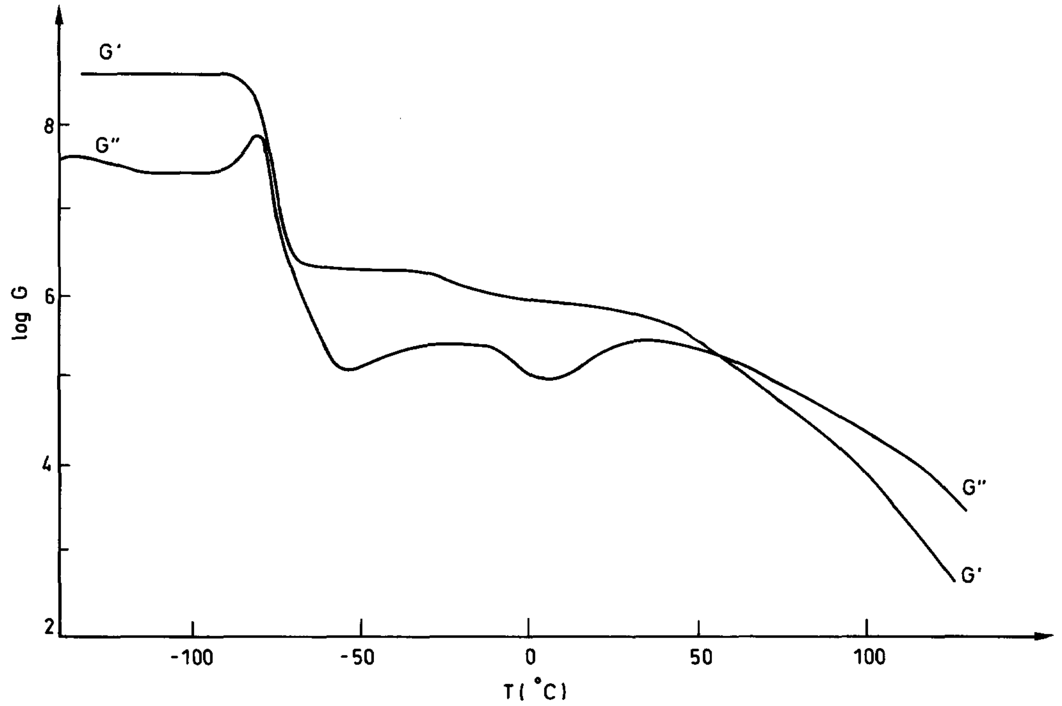

Figure 4 Thermal dependence of storage (G') and loss (G'') shear moduli (1 Hz) for α,ω-Na carboxylato PBD (Hycar CTB)

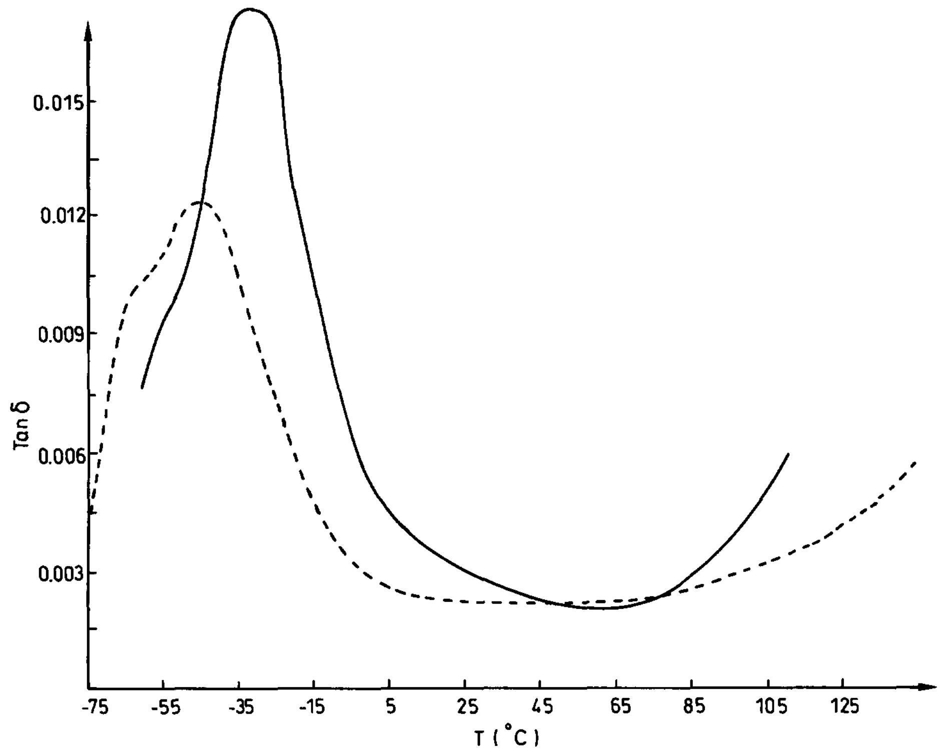

Figure 5 Tan δ *versus* temperature curves (1 kHz) for α,ω-Mg (——) and -Ba (---) carboxylato PBD (Hycar CTB)

carboxylate multiplets. Indeed, the thermal dependence of the storage (G') and loss (G'') shear moduli of α,ω-Na carboxylate PBD (Hycar CTB) clearly shows a mechanical relaxation in the range of 40°C which is nothing but the transition from the rubbery plateau to the viscous flow region, i.e. the thermal dissociation of the ionic domains (*Figure 4*). That the Σ peak corresponds to the disruption of the ionic multiplets is also supported by the higher temperature noted for Na compared to K. This is in agreement with the viscoelastic properties of the related samples which emphasize the stronger mutual interactions of the sodium carboxylate dipoles compared to the potassium counterparts[11].

Finally, the activation energy for the Σ relaxation is twice as high as the value calculated for the α process (*Table 1*), which is not surprising for the breaking and reformation of dipole–dipole interactions compared to a relaxation process of associated dipoles.

Figure 5 illustrates the temperature dependence of the dielectric loss tan δ for two alkaline earth cations (Mg and Ba). From the comparison of *Figures 3* and *5* and data in *Table 1*, there is no decisive effect of the cation on the characteristics of the α region. Two components are still observed in the temperature range from -60 to -30°C, the activation energy is independent of the cation (~ 85 kJ mol^{-1}) and $\Delta\varepsilon$ is <1 although slightly greater for Mg^{2+} than for the other cations. Upon substitution of alkaline by alkaline earth cations, the Σ phenomenon completely disappears as previously emphasized by t.s.d.(p.)c. measurements (*Figure 2*)[6]. This observation does not however mean that multiplets formed by alkaline earth carboxylates are not disrupted until 125°C. Indeed, isochronal (10 s) torsion modulus *versus* temperature curves have been reported for α,ω-Ba, Mg and Ca carboxylato PBD (Hycar CTB) and they show that these samples flow above room temperature[3], i.e. that the ionic multiplets are no longer able to sustain a mechanical deformation in that temperature range. Mechanical properties thus indicate that multiplets of alkaline earth carboxylates must be thermally unstable well below 125°C. Together with the dielectric results, this means that divalent cation containing ion pairs should be released as species of a zero or nearly zero dipole moment, supposedly as triplets. These triplets might however be in equilibrium with a set of doublets and anions. Upon increasing temperature, that equilibrium might be shifted towards the dielectrically active doublets and anions and account for an increase in tan δ at the highest temperatures (*Figure 5*).

$$\sim\sim COO^- \; M^{2+} \; {}^-OOC\sim\sim \;\rightleftharpoons\; \sim\sim COO^- \; M^{2+} + {}^-OOC\sim\sim$$

It may be concluded that the dielectric investigation of Hycar CTB samples neutralized by stoichiometric amounts of metal alkoxides under well-controlled conditions is in full agreement with the previously used t.s.d.(p.)c. methods. The former dielectric analysis of samples overneutralized by metal oxide or hydroxide can be now rationalized as follows. The shoulder observed on the low temperature side whatever the cation (~ -55°C at 10 kHz) belongs to the α region as well as the α_L peak (at -20°C, 10 kHz) characteristic of Mg- and Zn-containing samples (*Figure 1* for the Mg derivative). The so-called α_U which was observed at ~ 30°C for monovalent cations should be the expression of the Σ phenomenon. Let us finally point out that the absence of a Σ peak in the investigated temperature range when alkaline earth cations are considered does not support the thermal stability of the parent multiplets – as it was previously suggested[6] – but rather their dissociation into dielectrically inactive species.

α,ω-Metal carboxylato and sulphonato PIP ($\bar{M}_n = 15\,000$)

In a second series of experiments the possible effect of T_g of the polymeric matrix and the nature of the ion pairs on the dielectric behaviour of the polar end groups has been considered. Samples of PIP consisting mainly of 3,4- and 1,2-units have been synthesized and selectively end-capped by carboxylate and sulphonate groups, respectively. Na and Mg were selected as cations representative of the alkaline and alkaline earth series, respectively. The T_g of carboxylato and sulphonato-telechelic PIP has been measured by d.s.c. and observed at 10°C independently of the ionic end groups. The molecular weight of PIP ($\bar{M}_n = 15\,000$) is three times higher than that of Hycar CTB and the molecular weight distribution is narrower (1.15 *versus* 1.8). Finally an average of two α-methylstyrene units have been inserted between the PIP backbone and the ionic end groups in order to increase the otherwise too small functionality in sulphonic acid groups up to that of carboxylic acid ones (see Experimental).

Figure 6 illustrates the thermal dependence of tan δ at 1 kHz for α,ω-Na and -Mg carboxylato PIP. Only one peak is observed at 38°C for Mg, whereas two peaks are reported at 21°C and 60°C for Na. By analogy with the dielectric behaviour of Hycar CTB, only one type of dielectric relaxation is observed when an alkaline earth cation is associated with the carboxylate end groups. In

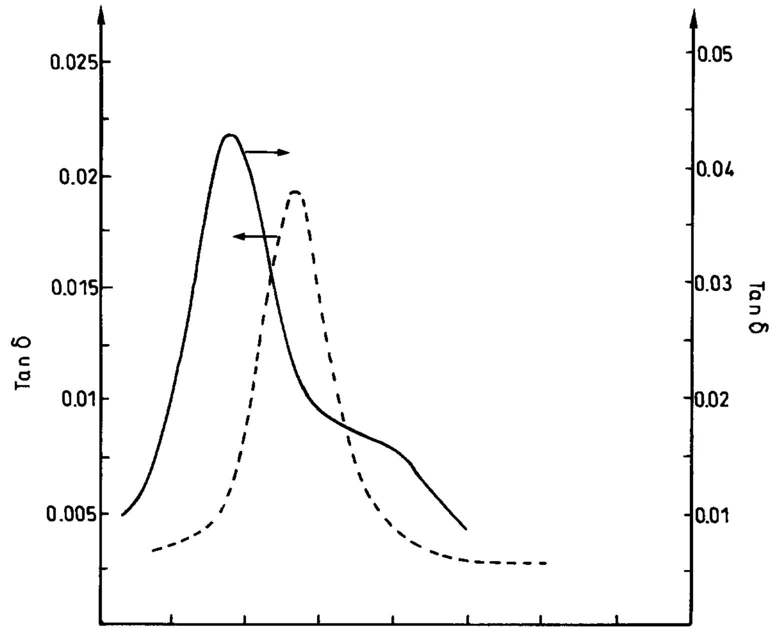

Figure 6 Tan δ *versus* temperature (1 kHz) for PIP-C-Na (——) and PIP-C-Mg (- - -)

Table 2 Dielectric characteristics of α,ω-metal carboxylato and sulphonato PIP at 1 kHz[a]

	T_{max} (°C)		Activation energy (kJ mol^{-1})		Δε	
Sample	α	α′	α	α′	α	α′
PIP-C-Na	21	60	143	154	0.38	0.11
PIP-C-Mg	38		156		0.32	
PIP-S-Na	34	80	167	153	0.32	0.08
PIP-S-Mg	30	100	160	115	0.25	0.08

[a] $P(0 < P < 1)$ is in the range of 0.55–0.65 for all the relaxations shown

the particular case of Hycar CTB the unique relaxation has been assigned to the glass transition of the matrix on the basis of both dielectric and t.s.d.(p.)c. measurements. The unique relaxation exhibited by α,ω-Mg carboxylato PIP should thus be the α-relaxation. Two main modifications in the dielectric response are however promoted by the substitution of Hycar CTB by PIP: the complex structure of the α region (*Figure 5*) has disappeared in favour of a quasi-symmetric peak (*Figure 6*); the activation energy has increased from ~86 to 156 kJ mol^{-1}, whereas Δε is not fundamentally different (*Tables 1* and *2*). The increase in activation energy might reflect a loss in mobility of the dipoles which are now attached to an intrinsically less flexible PIP chain through rigid and hindered α-methylstyrene units. That the α region in the PIP sample appears as a single peak gives consistency to the explanation for the complex structure when Hycar CTB is the matrix. In the latter case, it has been argued that the separation between ionic and non-ionic moieties was incomplete due to a broad molecular weight distribution. As a result, the phase morphology must be heterogeneous and species of a different dielectric activity be present in the matrix. The polydispersity of PIP is substantially smaller than that of Hycar CTB and water swelling experiments have confirmed a more complete segregation of ionic and non-ionic monomers[10]. Accordingly magnesium carboxylate dipoles are expected to be essentially equivalent in terms of environment (uniform multiplets) and dielectric activity.

Although the dielectric behaviour of α,ω-Mg carboxylato PIP is rather straightforward by reference to the properties of the Hycar CTB counterpart, the situation changes when Na is the counterion. It is worth recalling that two types of dielectric relaxations were displayed by α,ω-Na carboxylato PBD (Hycar): the complex α region on the low temperature side and the Σ peak associated with the dissociation of multiplets at higher temperatures. Although two peaks are observed when PIP is the polymeric backbone, it is out of the question to assign the higher temperature peak (designated as α′) to the Σ phenomenon. Indeed, the amplitude of that peak and the Δε value are very small and in sharp contrast to the Σ peak in the Hycar CTB sample (see *Figure 3* and *Tables 1* and *3* for Δε values). Incidentally, the activation energy is the same as the value calculated for the α peak in α,ω-Mg carboxylato PIP (*Table 2*). By comparison with the dielectric response of PIP bearing magnesium carboxylate end groups, the lower temperature peak for Na must be the α peak and designated as such. If this is so, the question arises why is the α peak observed more than 15°C earlier for Na than for Mg? Let us point out that the α relaxation is noted for α,ω-Mg carboxylato PIP (maximum at 38°C) in the same temperature range as the thermal dissociation of multiplets in α,ω-Na carboxylato PBD (Hycar) (Σ peak emerging at 5°C and maximum at 46°C; *Figure 3*). In the Hycar CTB matrix the α and Σ relaxations are very far from each other: the α relaxation occurs much earlier than the Σ phenomenon and the two relaxations do not interfere. This is no longer true in the PIP matrix and it is very difficult to state which relaxation occurs first. If it is multiplet dissociation the shift of the α peak towards lower temperatures might be accounted for. Indeed in a glassy matrix, the dipoles remain confined in the volume of the initial multiplets and they are continuously scrambling. The mobility of the dipoles might induce a premature micro-Brownian motion of the adjacent chain segments. It is interesting to note that the activation energy and the dielectric strength (Δε) are comparable for the α and α′ peaks and not different from the values calculated for the α relaxation in the α,ω-Mg carboxylato PIP sample (*Table 2*). The situation is thus complex when Na is the counterion and the set of α and α′ peaks has something to do (although not yet understood) with an excitation of the dipole mobility in the multiplets and the α relaxation of the chain segments. Let us summarize the situation as follows. When the dipole mobility is thermally excited, unpaired dipoles are easily released from the multiplets in the Hycar CTB matrix and the Σ phenomenon is observed; chain segments are indeed very mobile at a temperature higher than T_g by ~100°C. In the PIP matrix and in the time-scale of the dielectric experiment, the dipoles cannot escape from the multiplets because of the prohibitively high viscosity of the matrix. Kinetic considerations thus prevent the Σ phenomenon from being observed under static (mechanical) conditions. Actually, a mechanical (torsion) deformation is enough

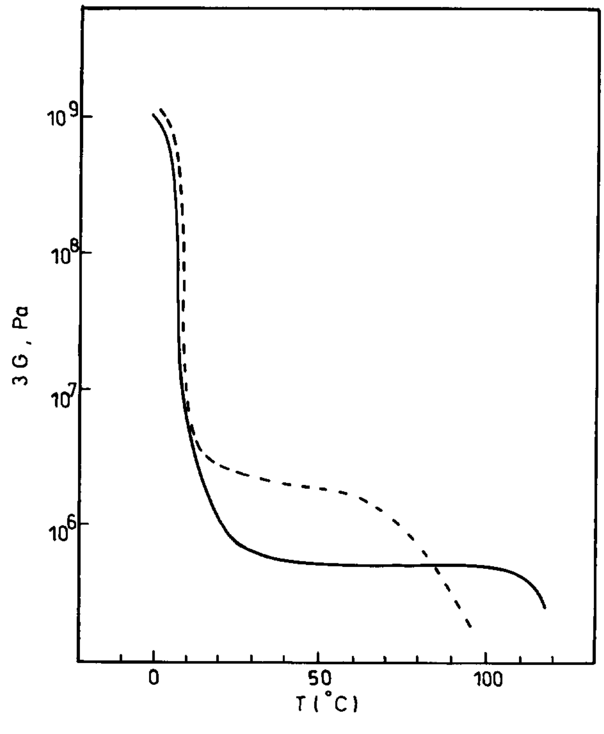

Figure 7 Isochronous (10 s) torsion modulus (3 G) *versus* temperature for PIP-C-Mg (– – –) and PIP-S-Mg (——)

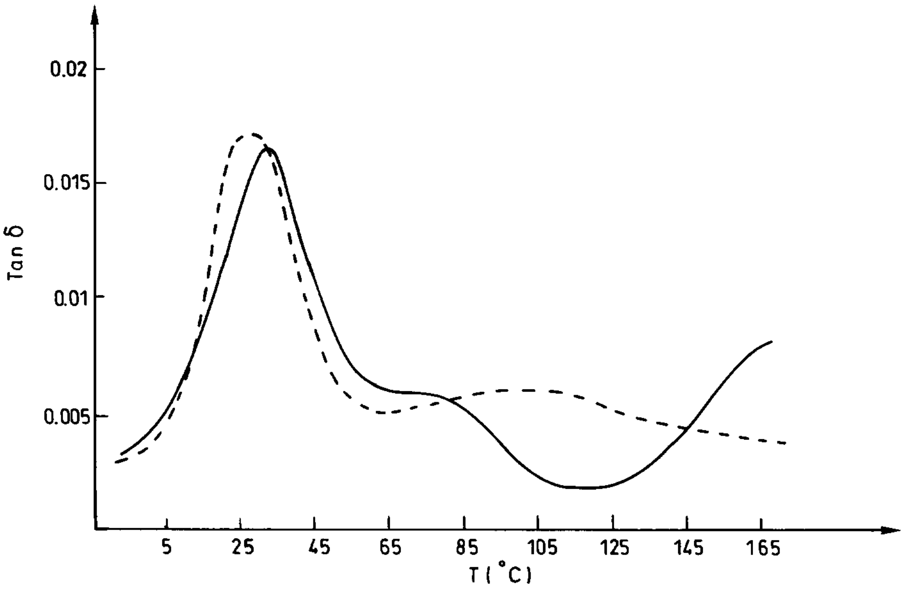

Figure 8 Tan δ *versus* temperature (1 kHz) for PIP-S-Na (——) and PIP-S-Mg (- - -)

to promote the occurrence of the viscous flow in the vicinity of 50°C as shown for α,ω-Mg carboxylato PIP (*Figure 7*).

The thermal dependence of tan δ is reported in *Figure 8* for α,ω-Na and Mg sulphonato PIP. The two curves show a low temperature peak, the position, the shape, the activation energy and the dielectric strength of which are very similar (*Table 2*). This peak has all the characteristics of the α peak of PIP ended with magnesium carboxylate groups. The α relaxation appears now to be independent of the cation in contrast to the carboxylate series. This observation lends support to the tentative explanation for the position of the α relaxation at a lower temperature for PIP-C-Na compared to PIP-C-Mg. Indeed, *Figure 7* shows that the thermal stability of the rubbery plateau is significantly enhanced when, for instance, magnesium carboxylate end groups are replaced by magnesium sulphonate ones; the excitation of the viscous flow is delayed by ~50°C. Thus going from metal carboxylate to metal sulphonate end groups keeps T_g (as measured by d.s.c.) constant and allows the α relaxation to manifest itself first and independently of the thermal excitation of the dipole mobility.

The origin of the additional α' peak is still unclear. The dielectric strength is very small (0.08) for Na and Mg and the activation energy is of the same magnitude as that of the α relaxation (although smaller for Mg). The α' peak for α,ω-Na sulphonato PIP is observed in a temperature range where the rubbery plateau is stable (up to ~100°C). A third relaxation emerges beyond 130°C, thus ~100°C above T_g ($T_{max} = 155$°C at 200 Hz) and might be the beginning of a Σ phenomenon. When magnesium sulphonate end groups are considered, T_{max} for the α' peak corresponds to the occurrence of the viscous flow (*Figure 7*) but it is so broad that it is very speculative to associate the dielectric and the mechanical relaxations to the same underlying phenomenon, i.e. the thermal dissociation of the multiplets. Additional measurements, and particularly investigations by t.s.d.(p.)c., are required to clear up the mechanism of the α' relaxation in sulphonato-telechelic PIP. That relaxation however appears to be associated with interacting dipoles.

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