Random ethyl acrylate–sulphonatopropylbetaine copolymers: 2. Dynamic mechanical properties

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The dynamic mechanical properties of ethyl acrylate–sulphonatopropylbetaine copolymers (zwitterionomers) and their stoichiometric blends with lithium perchlorate were examined as a function of temperature and frequency from the glassy to the melt zones. By comparing with the behaviour of classical microphase-separated ionomers, it could be concluded that the zwitterionomers both with and without added salt display the characteristics of microphase separation, thus supporting previous small angle X-ray studies. The slope of the modulus curves in the glass transition region decreases with increasing zwitterion content (up to ≈ 10 mol%), the loss tangent intensity decreases and the rubbery plateau modulus increases. The addition of the salt affects the glass transition zone relatively little, but significantly extends the range of the rubbery zone, indicating that the electrostatic interactions in the zwitterionic phase are stable to higher temperatures or lower frequencies than in the absence of salt. Furthermore, a second dispersion region is clearly evident. Time–temperature superposition is applicable to all the copolymers, with and without salt, in the range of conditions studied.

INTRODUCTION

In the first of this series of articles[1], preliminary results were reported of a structural study of a series of atactic random copolymers of ethyl acrylate (A) and diethyl-(2-methylacryloyloxyethoxy-2-ethyl)-1-(3-sulphopropyl) ammonium betaine (B). These copolymers were analysed in bulk by small angle X-ray scattering (SAXS)[1].
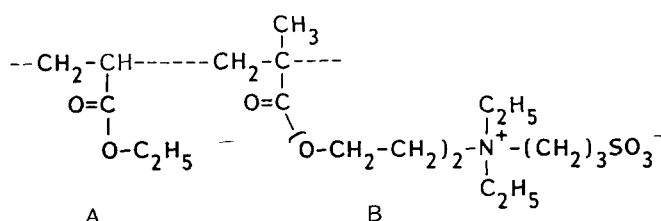
The diffusion curves of pure AB copolymers (molar fraction of B units $F_B < 0.40$) and of their stoichiometric amorphous blends with lithium perchlorate salt ($F_B \leqslant 1$, $LiClO_4/B = 1$) were tentatively attributed to partial microphase separation of the strongly dipolar zwitterions into microdomains of about 2 nm in diameter, assuming a spherical geometry. This segregation appears to be enhanced in the presence of the salt, which is assumed to be preferentially located in the zwitterionic domains.

The data were rationalized as reflecting a two-phase material with liquid-like order characterized by an average correlation distance between the microdomains of about 3–4 nm.

This interpretation is based on the structural analogy between random zwitterionic copolymers and the well known ionomers where a two-step segregation of the charged units into multiplets and clusters is said to occur[2-4]. The large dipole–dipole interactions in sulphonatoammonium betaine copolymers are assumed to play the same role as the more compact ion-pair interactions in ionomers. Such an analogy is supported by the extensive structural, mechanical and dielectric studies carried out by Graiver *et al.*[5-9] on polysiloxane dizwitterionomers bearing a similar sulphopropylbetaine function. It is therefore reasonable that microphase separation occurs in the AB copolymers, both with and without added salt. However, this conclusion requires corroboration and elucidation using other methods.

In particular, poly(ethyl acrylate) has a relatively high polarity (average dipole moment[10] $(\bar{\mu}/N)^{0.5} = 1.02\,D$, and dielectric permittivity[11] $\varepsilon = 7$ at 20°C). Thus, there may be microphase separation only at higher zwitterion contents or not at all, as seems to be the case in anionic[12,13] and cationic[14] poly(ethyl acrylate) ionomers, respectively. It also has a much higher glass transition temperature than polysiloxane, possibly higher than a potential transition due to a microphase.

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Since a two-phase structure should impart specific mechanical properties to the copolymers, in particular by introducing additional relaxations due to dipolar aggregation as is the case for many ionomers[2-4], such a study should be useful in clarifying the structure of the betaine materials. Therefore, the purpose of this paper is to present and analyse the dynamic mechanical properties of the sulphonatopropylbetaine AB copolymers of mostly low and some medium zwitterion content ($F_B < 0.50$) and of their stoichiometric blends with $LiClO_4$ ($F_B < 0.10$) in order to identify any features that may be correlated with the segregated structure suggested by the X-ray studies.

In the text the samples are denoted as follows: AB–8.8 is the random AB copolymer containing 8.8 mol% zwitterionic units B; AB'–8.8 is the same copolymer blended with a stoichiometric amount of $LiClO_4$, ($B' = B + LiClO_4$, $[LiClO_4]/[B] = 1$).

EXPERIMENTAL

Synthesis and preparation of polymers

The copolymers were synthesized by radical copolymerization of monomers A and B as described elsewhere[15]. Their stoichiometric blends with $LiClO_4$ were obtained by evaporation of their dilute solution in methanol for $F_B < 0.1$ and in trifluoroethanol for higher B content. All samples were dried at elevated temperatures (80–100°C) under 10^{-2} torr (≈ 1.3 Pa) for several hours before storage and/or further processing.

Samples for dynamic mechanical measurements were moulded under vacuum and moderate pressure (a few atmospheres) at about 60°C above T_g for the copolymers and about 100°C above T_g for their blends with $LiClO_4$. Either rectangular or disk geometry was used, depending on the experiment. The brittleness of the samples of high zwitterion content made their moulding impracticable, thereby restricting the mechanical measurements to samples of relatively low zwitterion content.

Differential scanning calorimetry (d.s.c.)

The glass transition temperatures were measured with a Perkin–Elmer DSC-2 apparatus, using 15–20 mg samples in sealed aluminium pans. The heating and cooling sequences that were systematically adopted, and repeated until reproducible scans were obtained, were as follows: heating up to 130°C at a rate of 20°C min^{-1}, annealing for 10 min at this temperature, cooling at a rate of 40°C min^{-1} to a low temperature, the value of which depended on the polymer, and annealing for 5 min at this temperature. The transition temperature was determined as the midpoint of the baseline shift ($\Delta C_p/2$). The width of the transition range was estimated by $\Delta T = T_1 - T_2$, where T_1 and T_2 are the intersections of the extrapolated glassy and liquid baselines with the tangent to the thermogram inflection point.

Dynamic mechanical measurements

One set of experiments was performed on rectangular specimens using the Polymer Laboratories dynamic mechanical thermal analyser (DMTA) in tensile bending mode with the dual cantilever at five frequencies (0.3, 1, 3, 10 and 30 Hz) as a function of temperature. The heating rate was fixed at 0.7°C min^{-1} and a strain of $\times 4$ (nominal

peak-to-peak displacement of 64 μm) was applied. The environmental chamber was constantly flushed with prepurified nitrogen. After moulding under vacuum and before measurement, all samples were stored under reduced pressure in a desiccator containing P_2O_5.

A second set of experiments was performed using the Rheometrics mechanical spectrometer RMS-605 (RMS), equipped with computerized control and data acquisition. Two transducers with different torque ranges (0.2 and 1.0 N m) were used, the choice depending on the temperature and zwitterion content of the samples, in order to measure dynamic moduli between 10^2 and 10^7 Pa. The environmental chamber was constantly flushed with nitrogen. Temperature analysis on rectangular specimens (48 × 9 × 3 mm) was carried out from -80°C to $T_g + 20$°C at three frequencies (1, 10, 100 rad s^{-1}), with a temperature step of 3 or 5°C and a thermal soak time of 4 min. Isothermal frequency analysis of disk specimens was carried out at various temperatures ranging from $T_g + 38$°C to 120°C in the frequency range 0.01 to 100 rad s^{-1} between parallel plates 25 mm in diameter. The disk specimens, initially 15 mm in diameter and 3 mm thick, were pressed between the plates at 150°C before measurement in order that the samples match the plates in diameter.

RESULTS AND DISCUSSION

Glass transition temperature

The d.s.c. results, along with the weight average degrees of polymerization (DP_w) of the various copolymers and homopolymers, are given in *Table 1*. Note that the first d.s.c. scan of some of the copolymer samples showed two baseline shifts. The higher temperature shift (in the range of 60–90°C for $F_B < 0.10$) is poorly defined and strongly dependent on the thermal history of the samples; it vanishes after the first thermal cycle. The lower temperature transition, identified as the T_g of the material, is reproducible to within ± 1°C in subsequent scans following the first cycle. From the table, it is evident that the glass transition temperatures of the AB copolymers (as well as the transition widths at low zwitterion content) are an increasing function of zwitterion content. If sample AB-15 is omitted, the T_g variations in the

Table 1 Weight average degrees of polymerization ($\overline{DP_w}$), d.s.c. glass transition temperatures (T_g), and their widths (ΔT), for homopolymers (A) and (B), copolymers (AB) and the AB blends with $LiClO_4$ (AB')

Sample	$\overline{DP_w}$	AB		AB'	
		T_g (°C)	ΔT (°C)	T_g (°C)	ΔT (°C)
A[a]	1000	-13	8		
A[b]	1000	-8	9		
A[c]	1000	-5	9		
A[d]	1000	7	12		
AB-2.1	710	-11	10	-9	9
AB-5.6	600	-2	20	-3	24
AB-8.8	780	7	32	6	27
AB-15	760	8	19	8	24
AB-25	500	48	19	57	25
B[e]		133	16	144	26

[a] Literature data[16]
[b–d] $[LiClO_4]/[A] = 0.04, 0.08$ and 0.13, respectively
[e] Literature data[17]

composition range studied may be described approximately by the linear relation, $T_g = 2.6F_B - 16$, with a correlation coefficient of 0.97.

It is instructive to compare the effects of added salt on the T_gs of the homopolymers and of the copolymers. Addition of $LiClO_4$ to homopolymer A, poly(ethyl acrylate), up to a molar fraction of 0.13, yields amorphous blends (as judged from wide angle X-ray scattering patterns[18]) with progressively increasing T_g values. This phenomenon has been observed previously in other polymer–salt amorphous blends[2]. It may be explained by the decrease in average segmental mobility due to coordination of the lithium cation by the carbonyl functions in the polymer. In contrast, the presence of $LiClO_4$ has negligible influence on the glass transitions of the AB' blends compared to that of the precursor AB copolymers, the only exception being the sample with the highest zwitterion content for which the T_g enhancement is significant. This parallels the observation that addition of $LiClO_4$ to the homo-poly(zwitterion) B raises its T_g value by only 11°C, or about 0.1°C per mol% of salt[17]. In view of these comparisons, it can be affirmed that in the amorphous AB' systems it is the zwitterionic units B that preferentially solvate the $LiClO_4$ ion pairs. It follows that these ion pairs are heterogeneously distributed in the AB matrix, no doubt because such a distribution optimizes the available electrostatic interactions.

Note that the above d.s.c. results provide no real evidence for phase separation, in contrast to recent data on an ampholytic ionomer for which a higher temperature transition does seem to have been detected[19]. The existence of a single well defined T_g value and its variation with composition in the AB and AB' systems are typical of the behaviour of simple homogeneous copolymers and blends. However, this observation is no different from what is normally shown by d.s.c. data on ionomers which are known to be microphase-separated; these also show only one transition[2]. If the experience with ionomers is applicable to the zwitterionic systems, dynamic mechanical studies ought to shed greater light on the question of microphase separation in the latter.

One additional point relating to d.s.c. results that should be made suggests that microphase separation of some kind may certainly be expected in the copolymer systems described here. Poly(ethyl acrylate) films doped with 5.9 wt% of triethylammoniumsulphopropylbetaine $((C_2H_5)_3-N^+-(CH_2)_3-SO_3^-$, melting point $\approx 290°C$), which can be considered a model for the B units in the AB copolymer, are clearly not homogeneous according to d.s.c. and optical studies. That is, the T_g of the doped film is not significantly shifted from that of the pure polymer, and the crystalline zwitterionic microdomains in the doped film remain birefringent up to 275°C (5.9 wt% corresponds to 0.027 molar fraction of zwitterions). These observations demonstrate that the zwitterions are not solvated by ethyl acrylate, thus indicating that the B co-units in the AB copolymers would tend to segregate within the ethyl acrylate matrix to the extent possible given the copolymeric nature of the material.

Dynamic mechanical temperature scans

DMTA results in the form of Young's storage moduli (E') and loss tangents (tan δ) as a function of temperature at a frequency of 1 Hz are shown in *Figures 1–4*. From *Figure 1*, it is apparent that the transition zone of the
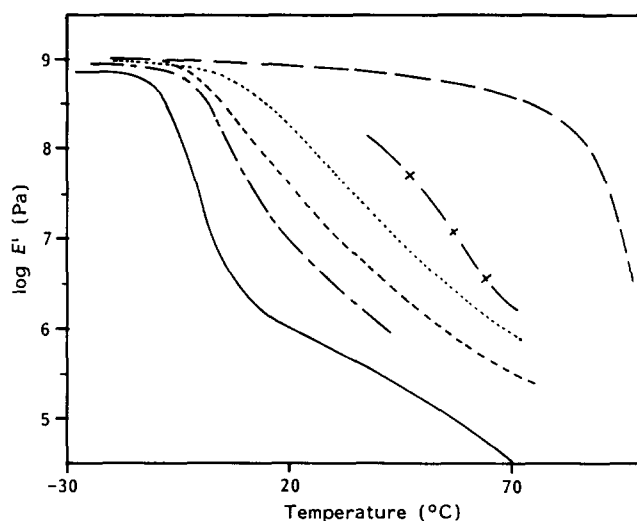

Figure 1 Storage Young's modulus at 1 Hz against temperature for the AB copolymers. Zwitterion content in order of increasing T_g: 2.1, 5.6, 8.8, 10.4, 22, 42 mol%
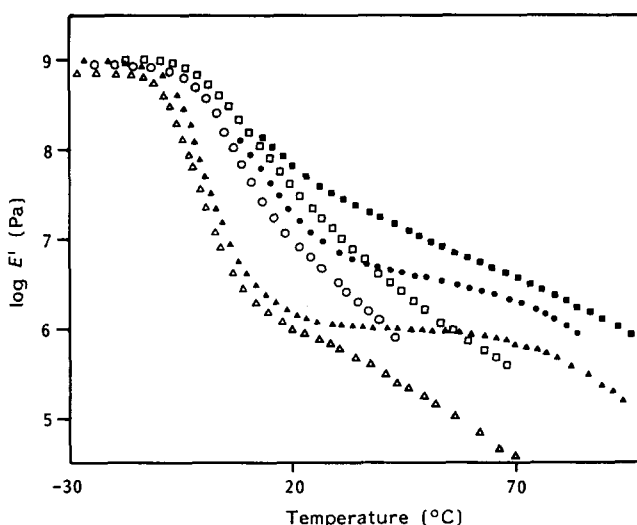

Figure 2 Storage Young's modulus at 1 Hz against temperature for AB copolymers and their blends with $LiClO_4$ (AB'): △, ▲ AB–2.1, AB'–2.1; ○, ● AB–5.6, AB'–5.6; □, ■ AB–8.8, AB'–8.8
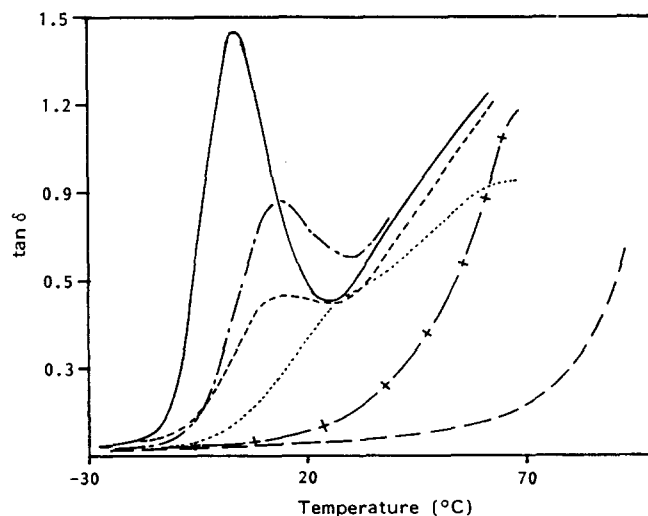

Figure 3 Loss tangent at 1 Hz against temperature for the systems of *Figure 1*
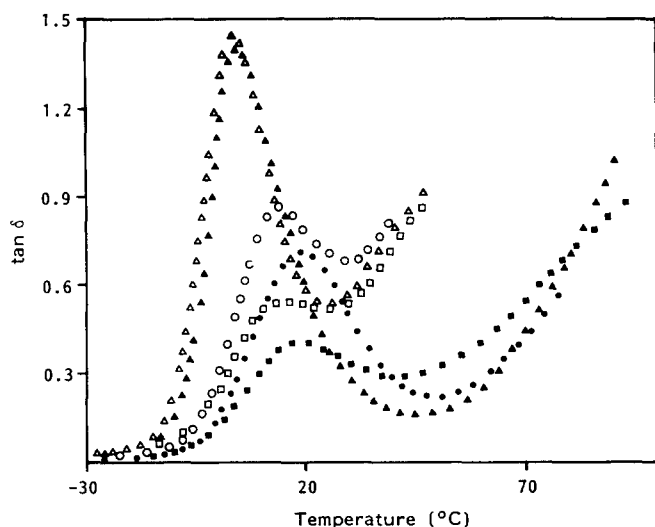
Figure 4 Loss tangent at 1 Hz against temperature for the systems of *Figure 2*

Figure 1, it is apparent that the transition zone of the copolymer AB generally increases in temperature with increasing zwitterion content. Furthermore, its slope decreases with increasing zwitterion content up to *ca.* $F_B = 0.10$, after which the transition range appears to narrow again, confirming the variation in transition widths seen by d.s.c.

A similar increase in the temperature and width of the transition zone is observed in the AB' system ($F_B < 0.10$) as shown in *Figure 2*. Significantly, when AB and AB' systems of equal zwitterion contents are compared (*Figure 2*), it is clear that the rubbery zone is extended considerably by the presence of the $LiClO_4$ salt. This is especially evident for $F_B = 0.021$, for which a rubbery plateau extending over 50°C exists in the AB' sample where virtually none exists in the AB sample. That is, whereas the presence of the salt affects the glass transition temperature very little, it retards the attainment of the flow zone by $\approx 50°C$ for the lower zwitterion content samples. The rubbery zone also shows an increase in modulus with increasing copolymer content in the AB' systems studied.

The loss tangent data corresponding to the curves of *Figures 1* and *2* are shown in *Figures 3* and *4*. Although the base width of the glass transition is influenced relatively little by the copolymer content and by the presence of the salt, its height clearly decreases with increasing zwitterion content for the samples with lower F_B values. (It may or may not be significant that the peak maxima for $F_B = 0.056$ and 0.088 are located at practically identical temperatures, in contrast to the d.s.c. T_g data.) The presence of $LiClO_4$ seems to decrease the peak intensities a little.

Apparent Arrhenius activation energies for the glass transitions were calculated from the variation in temperature of the loss tangent maxima as a function of frequency. For $F_B < 0.10$, these energies show a decrease with increasing zwitterion content for both the AB and AB' systems (-280, -210, -160 and -270, -230, -180 kJ mol^{-1} for AB and AB', respectively, with F_B in the order 0.021, 0.056 and 0.088). However, for a given zwitterion content, the presence or absence of $LiClO_4$ has little effect. It is interesting to compare this result with the variation of the apparent activation energies for the T_g relaxation as a function of ion content for a styrene

ionomer measured dielectrically[20]. The activation energies in that case initially decrease with increasing ion content, attain a minimum, and then increase.

The above data point to the existence of some kind of microphase separation in the zwitterionomers. The phenomena described can be compared to that shown by typical ionomers characterized by microphase separation, as follows. Generally, the glass transition zone of the modulus curves increases in temperature and broadens in width; the rubbery zone is enhanced in intensity as well as in its high temperature range; and the T_g loss tangent decreases in intensity with increasing ion content[2–4]. All these features are shown by the zwitterionomers, with the largest effects as far as the rubbery zone is concerned being shown by the $LiClO_4$-containing samples.

In contrast, an ionomer which does not show the effects of microphase separation, or in which the ionic interactions are thermally labile above the main transition zone, displays a sharp transition in the storage modulus curves (typical of an ordinary homopolymer) whose temperature increases with ion content, but whose slope does not vary with ion content[14,21]. Furthermore, the rubbery zone shows no significant increase in intensity; and the loss tangent curves show a single, narrow, high intensity transition.
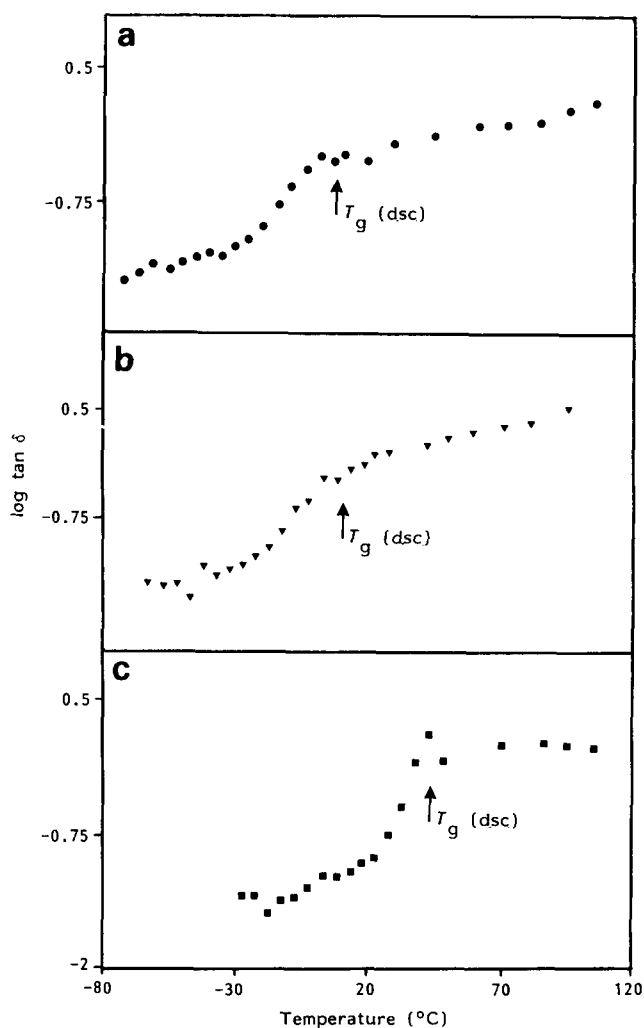
Figure 5 presents loss tangent data obtained with the

Figure 5 Loss spectra at 1 Hz against temperature for: (a) AB–8.8; (b) AB–15; (c) AB–25

RMS, with which higher temperatures could be attained than with the DMTA (albeit with less resolution). Although two transitions, one corresponding to the glass transition and one related to the microphase-separated regions, are not clearly evident, there is a slowly increasing plateau in the loss tangent from T_g to beyond 100°C. The lack of two distinct transitions contrasts with what is observed both with typical phase-separated ionomers[2] and with dizwitterionomer polysiloxanes[8]. However, it may be explained by exceeding broadness and relatively low intensity of the higher temperature transition and/or the relative closeness of the two transitions. Certainly, in the polysiloxanes having a similar zwitterion pendant chain, the higher temperature transition (*ca.* 50–80°C) is indeed very broad, but much higher in temperature than the matrix T_g, and therefore distinct[8]. The resolution or lack thereof is probably influenced to some extent by thermal history as well: the DMTA data for $F_B = 0.088$ in *Figure 4* do show a little better resolution of the T_g transition than the equivalent RMS data, whereas another DMTA scan for a separately moulded sample of $F_B = 0.088$ gave results similar to that shown in *Figure 5*.

Upon addition of LiClO$_4$, the transitions do appear to be somewhat better resolved (*Figure 6*). Again, this may be the result of a combination of 'improved' segregation of the zwitterionic units due to the presence of the salt (possibly leading to a narrower transition range) and of a larger temperature difference between the T_g and higher temperature transition.

Isothermal frequency scans

The variation of the shear storage and loss moduli, G' and G'', as a function of frequency over 3–3.5 decades was measured at various temperatures for the samples of lower zwitterion content. Master curves were constructed using $T_g + 38°C$ as the reference temperature, where the T_g is that determined by d.s.c. The isothermal frequency dependences of G' and G'' for AB'–5.6, along with the corresponding master curves, are shown in *Figures 7* and *8*, respectively. Complete superposition of both G' and G'' was possible using suitable horizontal shifts. The applicability of time–temperature superposition held for all the materials investigated. This leads to the conclusion that, in the temperature range of $T_g + 38°C$ to 100°C and in the frequency range studied, all the samples, both with and without added salt, are characterized by thermorheologically simple behaviour.

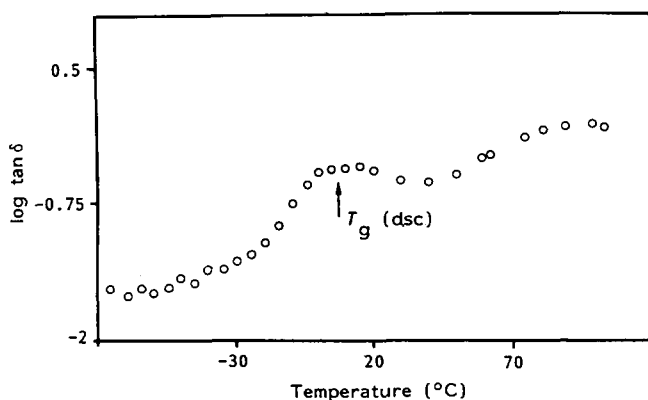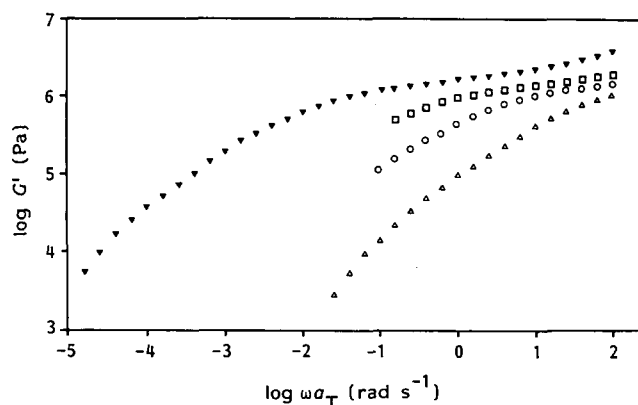The G' and G'' master curves that were determined for

Figure 7 Storage shear modulus against frequency at various temperatures and the corresponding master curve reduced to $T_g + 38°C$ for AB'–5.6: ▼, 32°C; □, 51°C; log $a_T = -1.4$; ○, 64°C, log $a_T = -2.4$; △, 85°C, log $a_T = -3.6$

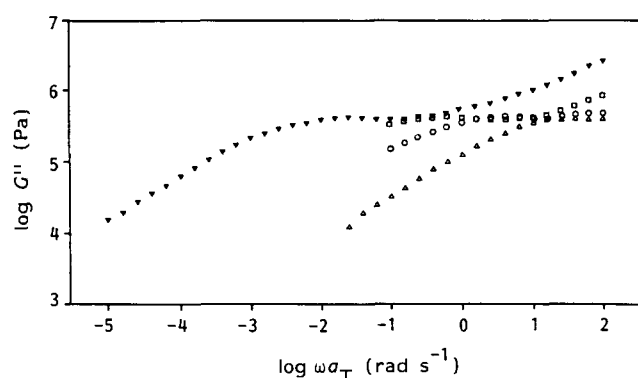**Figure 8** Loss shear modulus against frequency at various temperatures and the corresponding master curve reduced to $T_g + 38°C$ for AB'–5.6. For meaning of symbols see *Figure 7*

the samples of lower zwitterion content, with and without salt, as well as the reference homopolymer poly(ethyl acrylate), are shown in *Figures 9* and *10*, respectively. The incorporation of zwitterionic co-units into the homopolymer clearly affects the rubbery and flow behaviour. In particular, the moduli in the rubbery zone are increased by increasing zwitterion content, consistent with the hypothesis that the copolymers show a microphase-separated morphology. That AB–2.1 flows at lower frequencies than AB–5.6, leading to a crossover of their moduli curves, probably reflects the lower molecular weight of the latter (see *Table 1*); the copolymers AB–2.1, AB–8.8 and AB–15 have comparable molecular weights.

Addition of LiClO$_4$ to the copolymers does not particularly affect the height of the rubbery moduli compared to the same copolymer without salt; however, it extends the rubbery zone considerably, paralleling the DMTA results, and thus displaces the terminal zone to significantly lower frequencies. A distinct maximum in the reduced loss modulus curve at a frequency of ≈ -1.5 rad s^{-1} in log arithmetic units is evident for the samples of lowest zwitterion content. With increasing zwitterion content, this maximum seems to broaden and thus become less distinct, possibly reflecting a broader 'size' distribution of the microphase. The maximum may be associated with a transition or relaxation in the microphase that is presumably dominated by the zwitterion–salt interactions; these interactions become labile at low frequencies or high temperatures, thereby giving
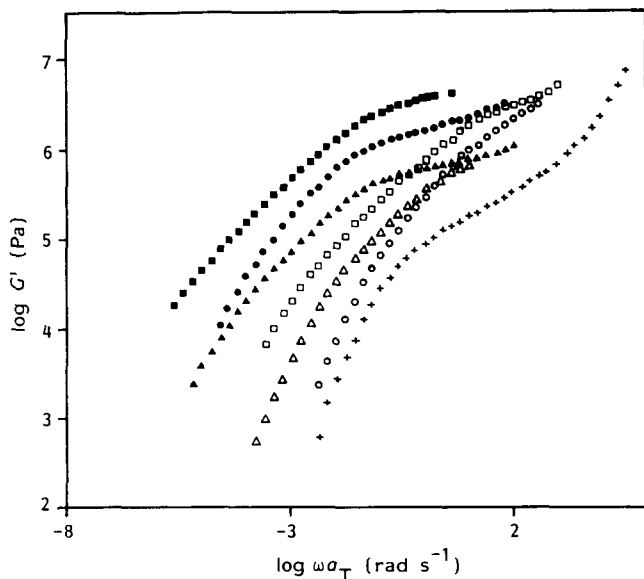

Figure 6 Loss spectra at 1 Hz against temperature for AB'–8.8

Figure 9 Storage shear modulus master curves reduced to $T_g + 38°C$ for poly(ethyl acrylate), A, and the AB and AB' zwitterionomers: +, A; △, ▲, AB–2.1, AB'–2.1; ○, ●, AB–5.6, AB'–5.6; □, ■, AB–8.8, AB'–8.8
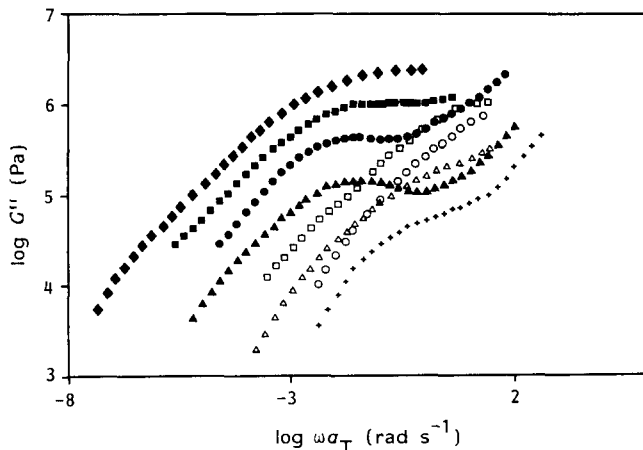

Figure 10 Loss shear modulus master curves reduced to $T_g + 38°C$ for poly(ethyl acrylate), A, and the AB and AB' zwitterionomers. ◆, AB'–15. For meaning of other symbols see *Figure 9*

rise to the maximum in question. The height of the moduli in the rubbery zone clearly increases with increasing zwitterion content (just as seemed to be the case for the corresponding copolymer without LiClO₄, but where the effect was less obvious); this can be attributed to an increasing total volume of the relaxing microphase-separated regions that results from increasing zwitterion content. It can be concluded that, essentially, incorporation of LiClO₄ into the AB copolymers raises the temperature range (or, equivalently, reduces the frequency range) of relaxations of the microphase-separated regions that are already present to about the same extent without the salt (though perhaps less well defined) at a given zwitterion content.

The increase in the rubbery plateau modulus with zwitterion content for both AB and AB' is shown graphically in *Figure 11*. The values plotted are in the form of G_N^o, the pseudoequilibrium modulus of the entanglement network, which is calculated by integration of G'' from $-\infty$ to either $\log(\omega_m a_T)$, where $\omega_m a_T$ is the

frequency corresponding to the maximum of $\log G''$ versus $\log \omega a_T$, or to the inflection point of $\log G''$ when no well defined maximum is observed[24]. That the values for AB and AB' copolymers fall approximately on the same line confirms that the presence or absence of LiClO₄ does not greatly affect the total relative volume of the zwitterionomer phase.

Note that the molecular weight effect seen for AB–5.6 compared to AB–2.1 is masked to a large extent by the presence of LiClO₄. There is no crossover of the curves for AB'–2.1 and AB'–5.6 in the frequency range investigated, as there is for the AB copolymers (although the G' curves clearly tend to this crossover at the lowest frequencies). The stronger, or more stable, electrostatic interactions in the AB' zwitterionomers thus effectively increase the apparent molecular weight of these systems well beyond the true molecular weight.

The shift factors used in constructing the master curves for AB–2.1, –8.8 and –15 and their blends with LiClO₄ are plotted in *Figure 12* in the form of $-\Delta T(\log a_T)^{-1}$ versus ΔT. For the pure copolymers, straight lines are obtained, indicating that the shift factors follow a single WLF type equation. They are essentially parallel and have higher values of $|-\Delta T(\log a_T)^{-1}|$ the lower the zwitterion content. Similar plots for the AB' copolymers are more complex. Two straight lines are needed to fit the data satisfactorily. This may reflect the two types of relaxation process, well separated, one due to the glass transition of the material, the other due to the zwitterion-containing microphase. Judging from the point of intersection of the pairs of lines, the latter process appears to dominate at temperatures above *ca.* 70, 90 and 90°C for AB'–2.1, –8.8 and –15, respectively. Similar complex behaviour was shown in the WLF analysis of the shift factors of (plasticized) microphase-separated ionomers[22] and pyridinium-containing butadiene ionomers[23].

The WLF constants, fractional free volumes and thermal expansion coefficients (calculated according to the free volume theory[24]) of the three copolymers and their LiClO₄ blends are listed in *Table 2*. For the salt-containing copolymers, the calculations were applied to the higher temperature linear portion only. Note that the extrapolated α_f and f_g values for the LiClO₄ blends are consistently lower than those for the AB copolymers. It is also interesting that the flow activation energies determined from the WLF constants show a trend opposite to that observed for the glass transition zone; i.e. the activation energies in the higher temperature range covered by the RMS experiments increase with
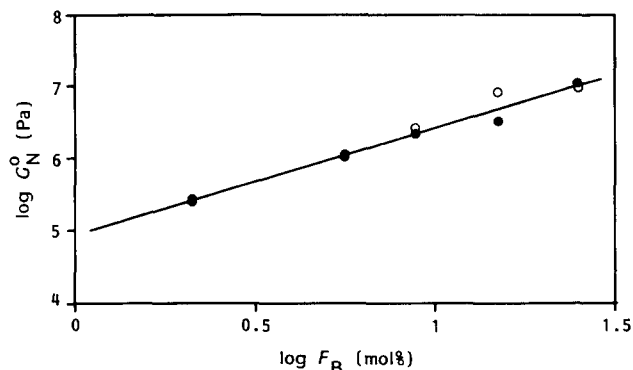

Figure 11 G_N^o against zwitterion content for the AB (○) and AB' (●) zwitterionomers

increasing copolymer content, both with and without added salt. (Again, these energies do not appear to differ significantly in the AB and AB' systems for a given copolymer content.) If reliable, this data supports the supposition of different relaxation processes in the T_g zone and in the rubbery-to-flow zone. The pyridinium-containing butadiene ionomers[23] also showed an inversion, at a particular temperature, of the direction of variation in the activation energies with ion content; it

was suggested that this temperature is the point at which sufficient thermal energy exists to induce bond interchange migration, and was thus identified as a second transition. It should be added that Salamone et al.[25] likewise reported increasing flow activation energies with increasing ion content for poly(n-lauryl methacrylate) ampholytic ionomers where the quaternized nitrogen and the sulphonate groups are on separate sidechains.

Finally, it seems reasonable that at higher F_B contents the zwitterionomer phase becomes the dominant phase. This may be related to the increasing sharpness in the slope of the modulus curves at T_g for $F_B < 0.1$, as shown in Figure 1. The matrix T_g may thus be considered to coincide with the transition due to the zwitterion-dominated phase at higher F_B content.

CONCLUSIONS

The dynamic mechanical properties of ethyl acrylate-sulphopropylammonium betaine copolymers (zwitterionomers) in the glass transition, rubbery and flow zones undergo increasing change with increasing zwitterion content. These changes strongly resemble the effects of increasing ion content on the mechanical properties of classical ionomers characterized by microphase separation. These results, obtained for relatively low zwitterion content only, thus confirm the two-phase structure suggested by small angle X-ray studies[1].

The minor phase is presumably dominated by dipole–dipole interactions among the zwitterions for the pure copolymers and (additionally) by zwitterion–salt interactions for the copolymers blended with $LiClO_4$. D.s.c. data suggest that $LiClO_4$ is preferentially solvated by the zwitterionic units.

The addition of $LiClO_4$ to the AB copolymers considerably enhances the effect of the zwitterionic phase on the rubbery and flow zones, but influences the glass transition region relatively little. The latter is reasonable given the preferential solvation of $LiClO_4$ by the zwitterionic units and given the length of the zwitterionic sidechains, so that any decrease in the segmental mobility of these units due to the salt leaves the backbone relatively unaffected.

The effect of the presence of $LiClO_4$ at higher temperatures may be attributed at least in part to a greater stability of the electrostatic interactions in the minor phase that is induced by the salt. That is, whereas the interactions in the zwitterionic phase in the AB copolymers become labile not much above the T_g of the material, in the AB' systems this lability takes effect at higher temperatures (or lower frequencies), thus extending significantly the rubbery zone. The addition of salt
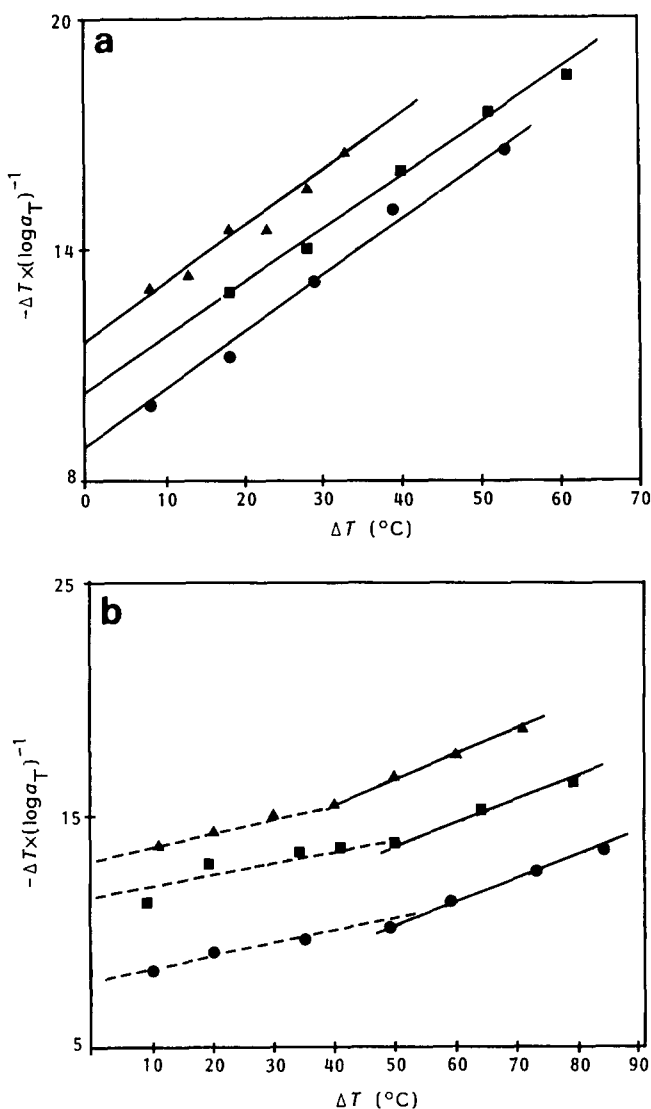

Figure 12 Temperature dependence of the shift factors (WLF test) used in constructing the master curves in Figures 9 and 10 for the (a) AB and (b) AB' zwitterionomers (B or B' contents: ▲, 2.1; ■, 8.8; ●, 15 mol%)

Table 2 WLF constants, thermal expansion coefficients α_f, and fractional free volumes f_g at T_g

Sample	T_0 (°C)	T_g (°C)	C_1^0 [a]	C_2^0 (K)[a]	C_1^g [b]	C_2^g (K)[b]	$10^4 \alpha_f$ (K^{-1})	f_g	R^c
AB–2.1	27	−11	7.1	82	13.1	44	7.5	0.033	0.965
AB–8.8	44	7	7.3	74	16.0	34	8.0	0.027	0.995
AB–15	45	8	6.6	58	18.2	21	11.4	0.024	0.996
AB'–2.1	30	−9	9.5	107	15.0	68	4.3	0.029	0.997[d]
AB'–8.8	44	6	11.2	106	17.5	68	3.7	0.025	0.999[d]
AB'–15	45	8	10.6	60	28.8	22	6.8	0.015	0.998[d]

[a] C_1^0, C_2^0, WLF constants at $T_0 = T_g + 38°C$
[b] C_1^g, C_2^g, WLF constants at T_g
[c] R, correlation coefficient
[d] For the higher temperature linear portion of $-\Delta T/\log a_T$ versus ΔT curve only

may also give rise to more efficient or better defined phase separation, possibly accompanied by a narrower transition zone in the mechanical properties for this phase. This seems indicated by the small angle X-ray scattering results[1], although the better definition of the small angle halo for the AB' systems may simply be due to the greater electronic contrast between the two phases that is induced by the $LiClO_4$ preferentially located in the zwitterionomer phase.

In conclusion, the zwitterionomers investigated have properties analogous to those of classical microphase-separated ionomers. Since these materials present much versatility in the choice of both the apolar and zwitterionic units and in the possible doping of the copolymers by a variety of metal salts, they should prove useful as alternatives to classical ionomers and should thus be of interest for both academic and technological purposes.

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