Poly(sulphopropylbetaines): 3. Bulk properties

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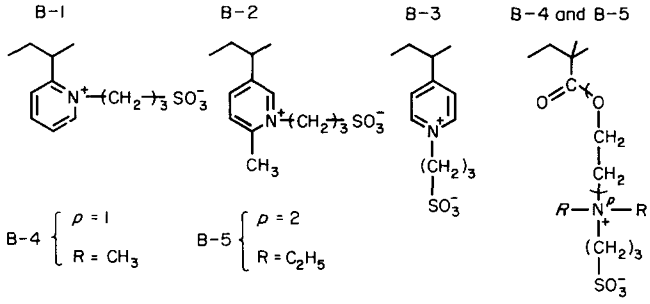
The bulk properties of a series of five atactic aliphatic and aromatic poly(sulphopropylbetaines) have been studied by u.v. and broad line n.m.r. spectroscopy, differential scanning calorimetry (d.s.c.), X-ray scattering (WAXS, SAXS) and thermally stimulated depolarization currents (t.s.d.c.). The high density in dipolar units $\equiv N^{\pm}-(CH_2)_3-SO_3^-$ affords a number of specific properties to these poly(zwitterions): very high glass transition temperatures (d.s.c., n.m.r.); (ii) a strong polarity typified by an apparent local dipole moment of about 5.5 D (u.v.) and a dielectric increment at $T_g > 1 \times 10^2$ (t.s.d.c.); (iii) the ability to dissolve $LiClO_4$ in stoichiometric amounts to yield amorphous microphase separated blends (WAXS, SAXS) without much change in chain dynamics (slight increase in T_g and in n.m.r. linewidth); (iv) a very high affinity for water which behaves as a very efficient plasticizer with 6.5 moles of 'unfreezable bound water' per monomeric unit.

(Keywords: poly(sulphopropylbetaines); bulk properties; $LiClO_4$–polymer blends; water–polymer interactions; glass transition temperature; dielectric relaxation)

INTRODUCTION

In the two preceding parts of this series the synthesis[1] and the dilute solution properties[2] of five atactic aliphatic or aromatic poly(sulphopropylbetaines) were described.



Because of the strongly dipolar structure of their zwitterionic lateral groups, these linear polymers display specific properties such as high chain rigidity and a very unusual and unique 'antipolyelectrolyte' behaviour characterized by an increasing chain expansion in water solution when the ionic strength is increased[2,3]. This paper describes a survey of some bulk properties of these representative poly(zwitterions) as studied by differential scanning calorimetry (d.s.c.), ultra-violet (u.v.) spectroscopy, X-ray scattering (WAXS and SAXS), broad line nuclear magnetic resonance (n.m.r.) spectroscopy and thermally stimulated depolarization currents (t.s.d.c.). The results will be discussed in relation to polarity, interactions with water and with inorganic salts such as $LiClO_4$, glass transitions and dielectric relaxation processes of the pure polymers or of their blends with $LiClO_4$. Some preliminary results have already been published[4,5].

EXPERIMENTAL

Polymers and salts

The polymers were obtained by radical initiated polymerization of the corresponding monomers in water solution as detailed elsewhere[1], and used without further fractionation. Their weight-average molecular weights were in the range 1×10^5–5×10^6 (see *Table 1*, below). In the following text symbols B refer to the betaine polymers, while symbols A refer to their tertiary amino precursors. All the polymers and the salt–polymer blends (NaCl or $LiClO_4$) were recovered by freeze-drying of their aqueous solution and dried at 60°C under 10^{-2} torr for at least 24 h before an experiment.

U.v. spectroscopy

Homogeneous films (thickness in the range 0.6–6 μm) of the various polymers doped with 0.005 mole fraction of 4-ethylpyridinium dicyanomethylide[6] were obtained by slow evaporation of their dilute solution in trifluoroethanol deposited on a quartz plate, followed by drying at 50°C under 10^{-2} torr for 24 h. The u.v. spectra of the films were recorded on a Cary 2300 spectrometer with an accuracy of about 0.1 nm at the λ_{max} of the long wavelength transition of the ylid.

X-Ray scattering

WAXS and SAXS measurements were carried out between 20 and 180°C with the usual experimental device[7] (monochromatic X-ray beam of $\lambda = 1.54$ Å). The scattered beams were recorded with a film or with a one-dimensional linear position detector for quantitative analysis.

Broad line n.m.r. spectroscopy

^1H n.m.r. was recorded at 60 MHz on a Brucker SXP

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Table 1 Molecular weights, apparent local dipole moments, glass transition temperatures and dielectric relaxations of the poly(sulphopropylbetaines) B and for their amino precursors A

Samples	A-1	A-2	A-3	A-4	A-5	B-1	B-2	B-3	B-4	B-5
$\bar{M}_w$ ($\times 10^{-5}$)	0.737	1.02	7.23	2.37	1.11	0.845	0.922	27.6	61.5	50.0
λ (nm)[a]	400.0	398.9	396.9	403.1	403.3	381.7	382.3	383.4	383.6	385.7
μ_D	2.9	3.0	3.3	2.4	2.4	5.7	5.6	5.5	5.5	5.1
T_g(°C)	104[b]	130[b]	142[b]	19[b]	−36	–[c]	–[c]	–[c]	–[c]	133
T(°C)[d]	103	128	149–164	15–40	−18	108	105	88–183	140	134
$\Delta\varepsilon$[d]	7	6	7	8–3		104	5.7	25–250	8.5	$>1\times10^2$

[a] Long wavelength of 4-ethylpyridinium dicyanomethylide embedded in the glassy polymer
[b] Literature data[24]
[c] $T_g > 250$°C, discoloration of the polymers
[d] Dielectric relaxation temperatures and corresponding dielectric permittivity increments $\Delta\varepsilon$ as observed in t.s.d.c.

spectrometer fitted with a high resolution Varian V3601 magnet stabilized by a 60 MHz proton external lock. The free induction decay (f.i.d.) signal was digitally transformed by a fast convertor Brucker BC 104 with a sampling frequency up to 10 MHz, and processed on-line with a BNC 12 Nicolet minicomputer. In all experiments, the sample temperature was monitored to within ±1°C. The second moment M_2 was derived from the f.i.d. following a 90° pulse (2–3 μs) by polynomial fitting[8]. The accuracy of the M_2 values derived from one temperature scan on a given sample is about $\pm 0.5\,G^2$. For measurements, the sample in powder form was dried further and degassed at 60°C under 5×10^{-5} torr for 18 h in the n.m.r. tube, which was then sealed.

Differential scanning calorimetry

D.s.c. experiments were performed on a Perkin-Elmer DSC-2 apparatus monitored by a microprocessor and interfaced with a computer data station, using 3–22 mg samples eventually pressed under 5 MPa. For the dry samples, the following heating–cooling sequences were systematically adopted and repeated (usually three times) until reproducible scans were obtained: heating up to 200°C at a rate of 20°C min^{-1}, annealing for 5 min at 200°C, cooling down to a low temperature, depending on the polymer, at a rate of 80°C min^{-1} and annealing for 5 min. For the study of water-plasticized polymers, the aluminium pan was first heated to 100°C with water to avoid any further reaction of water at the aluminium surface. The samples are prepared by adding known amounts of water to previously dried polymers (~3 mg) in the pan, which was then hermetically sealed; the amount of incorporated water was further checked after scanning by exhaustive drying of the polymer at 80°C under 10^{-2} torr for at least 24 h and determining the weight difference between the wet and dry samples. The following heating–cooling sequence at a rate of 10°C min^{-1} was always used: cooling down to −123°C, annealing for 5 min, heating up to 30°C and annealing for 5 min before repeating a second cycle. The glass transition temperature was measured at the mid-point of the baseline shift ($\Delta C_p/2$) with an accuracy of about ±1.5°C. The beginning and end of the glass transition were taken from the d.s.c. trace, as judged from the first deviation from the glassy baseline and the first attainment of the liquid baseline, T_b and T_e respectively. Furthermore, the intersections of the tangent at the thermogram inflection point (which is close to T_g) with the extrapolated glassy and liquid baseline were noted as T_1 and T_2 and used to estimate the sharpness of the transition ($\Delta T = T_2 - T_1$).

Thermally stimulated depolarization currents[9]

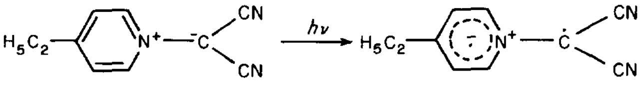
This method consists of measuring under defined heating scheme the currents generated by the release of a polarized state in a solid dielectric, and allows the analysis of molecular relaxations of the polymeric material.

T.s.d.c. and conductivity experiments were performed on a laboratory-built device operating under nitrogen, fitted with stainless steel electrodes, a CRC or Regukit d.c. power supply and a Keithley 616 electrometer[10]. Measurements were performed within the range −190 to 180°C at a constant heating rate of about 5°C min^{-1}. Moulding of the sample at 180–220°C is possible for the amino precursors A-1 to A-5 and for the polyzwitterion B-5. All the other polymers were pressed at room temperature under 40 MPa, except for the rubbery precursor A-5, which was applied directly to the electrodes. For metallization, silver or tungsten were evaporated under vacuum on sample surfaces and, in some cases, the polymers were silver-coated by painting. Poling of the discs of about 0.5–1.5 mm thickness was generally performed at various temperatures below 185°C under a field of 0.5 to 8×10^5 V m^{-1}.

RESULTS AND DISCUSSION

Polarity of the poly(sulphopropylbetaines) and solvation of salts

The polarity of the polyzwitterions in bulk may be estimated according to a solvatochromic method we have recently developed[6]. The transition energy E_T (kJ mol^{-1}) of the long wavelength absorption of the strongly dipolar 4-ethylpyridinium dicyanomethylide (formation of an intramolecular charge transfer complex) is very sensitive to polarity effects of its microenvironment, and this solvatochromic behaviour in liquid solvents was quantitatively analysed within the framework of the 'linear solvation energy relationships' proposed by Taft *et al.*[12,13].



$E_T(\text{kJ mol}^{-1}) = 284 + 21.6\pi^*$ for aprotic solvents[6], where π^* is an empirical polarity parameter of the solvent linearly correlated with its dipole moment μ in most cases[12]: $\mu_D = -0.1 + 4.3\pi^*$.

The polarity of bulk polymers doped with minute amounts of the ylid as a reporter probe may be identified with that of the solvents leading to the same transition

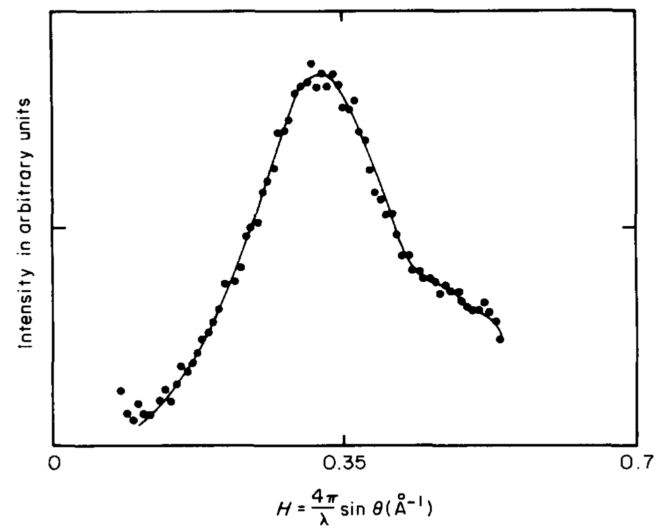


Figure 1 SAXS pattern of the amorphous stoichiometric blend $LiClO_4$/B-5 at room temperature

energy E_T: according to this approach, glassy polymeric films systematically appear more polar than the corresponding liquid solvents of the same chemical structure[11]. The 'apparent' local dipole moments of the poly(sulphopropylbetaines) are increased by a factor of nearly 2 with respect to those of their tertiary amino precursors (*Table 1*). Such behaviour is indeed quite expected: depending on its conformation either in the form of a tight ion-pair within a non-polar medium (maximum electrostatic interaction between the two charged sites) or in the form of a more separated ion-pair in a medium of high dielectric permittivity, the dipole moment of the sulphopropylbetaine may be roughly estimated to be between 6 and >20 D (27.5 D for δ-aminobutyric acid in its carboxybetaine form in water solution, for instance[14]).

All the poly(sulphopropylbetaines) are able to dissolve salts of widely different lattice energies, such as NaCl or $LiClO_4$, up to stoichiometric amounts ([salt]/[zwitterion] = 1) to yield amorphous blends. For the system B-5/$LiClO_4$, for instance, crystallization of the salt in segregated domains is actually observed only for a ratio [$LiClO_4$]/[zwitterion] > 1.25 according to WAXS patterns (presence of the characteristic diffraction peaks of the salt crystalline lattice). Salt solvation by polar polymers is generally restricted to low amounts of ionic species[15], and this very unusual ability to complex salts up to a stoichiometric ratio has only been observed in two cases: $LiCF_3SO_3$ or $LiClO_4$ with polymethacrylates carrying pendant oligo(oxyethylene) amorphous chains[16]; $LiClO_4$ with a poly(electrolyte) complex derived from poly(lithium acrylate) or poly(sodium 2-acrylamino-2-methylpropanesulphonate) and a polycation of the ionene type (obtained from 1,6-dibromohexane and *N,N* tetramethyl-1,3-propanediamine)[43]. Moreover, for [$LiClO_4$]/[zwitterion] > 0.25, SAXS patterns of the $LiClO_4$/B-5 blends show a well-defined peak at about 19 Å, almost independent of salt content and temperature either in the glassy or liquid state (at $T > T_g \sim 144$°C, see *Figure 1*). This typical scattering, which is not observed with the other betaine polymers, results from microphase separation which may arise from the conjugate contributions of the two favourable factors: high contrast of polarity between the zwitterion domains and the other segments of the chain, and the presence of a flexible spacer between the dipolar heads of the lateral groups and the backbone. Such structural characteristics are indeed similar to those of polysoaps such as poly(sodium styrylundecanoate)[18] or poly(sodium undecenoate)[19]. This may suggest for $LiClO_4$/B-5 blends a lamellar structure of thickness of about 19 Å, with alternate location of the lateral groups on both sides of the backbone; this optimizes the possibilities of ion–dipole and dipole–dipole interactions between the zwitterions and the added salt and minimizes steric hindrance between vicinal lateral groups. Such a tentative lamellar structure, already observed for long chain poly(alkylmethacrylates)[20], obviously requires further examination.

Glass transition temperatures of the poly(sulphopropylbetaines) and of their amorphous blends with $LiClO_4$

In d.s.c. experiments all the samples show irreversible yellowish discoloration and possible structural modifications at temperatures >250°C (decomposition of B-4 is reported to start at about 300°C, as detected by thermal gravimetry[21]), and a well-defined T_g is observed only for B-5 polymer: $T_g = 133$°C, $\Delta C_p = 0.255\ \text{J K}^{-1}\ \text{g}^{-1}$, the value of $\Delta C_p \times T_g = 103.6\ \text{J g}^{-1}$, which is in fairly good agreement with the empirical constant value proposed by Boyer[22], $115\ \text{J g}^{-1}$. This very high T_g may be correlated with the high chain rigidity derived from the analysis of the dilute aqueous solution properties[2] (steric factor $\sigma = 3.3$); however, it remains lower than that predicted by the empirical T_g–σ correlation suggested by Lipatov *et al.*[23] (calculated $T_g > 227$°C). The dramatic increase in the T_g values of the betaine polymers with respect to those of their tertiary amino precursors[24] (see *Table 1*) probably results from strong intra- and intermolecular dipolar interactions between the zwitterionic units.

The d.s.c. thermograms of the $LiClO_4$/B-5 blends show no trace of crystallinity (no melting endotherm at $T_m(LiClO_4) = 236$°C) in good agreement with the previous WAXS data, and a well-defined glass transition temperature which is a linear increasing function of the ratio $r = [LiClO_4]/[\text{zwitterion}]$ $T_g(°C) = 133 + 9.27r$, $R(6) = 0.9945$ (*Table 2*). The presence of low molecular weight salts dissolved in a polymeric matrix may induce two opposite trends: a T_g decrease by a plasticizing effect due to an increase of free volume, and a T_g increase in the case of strong enough interactions between the ions and the chain, which leads to a lowering of the average segmental mobility[15]. The slight increase of about 10°C

Table 2 Glass transition temperatures (T, °C) and increments in heat capacity at $T_g(\Delta C_p)$ of polymer B-5 and of its amorphous blends with $LiClO_4$

$\frac{[LiClO_4]}{[B]}$	T_b	T_e	T_1	T_2	T_g	ΔC_p ($\text{J g}^{-1}\ \text{K}^{-1}$)
0	115	145	126	142	133	0.255
0.2	94	150	121	144	135	0.275
0.4	86	159	122	150	137	0.276
0.6	89	158	123	149	138	0.268
0.8	87	160	128	150	140	0.268
1	89	163	130	156	143	0.279

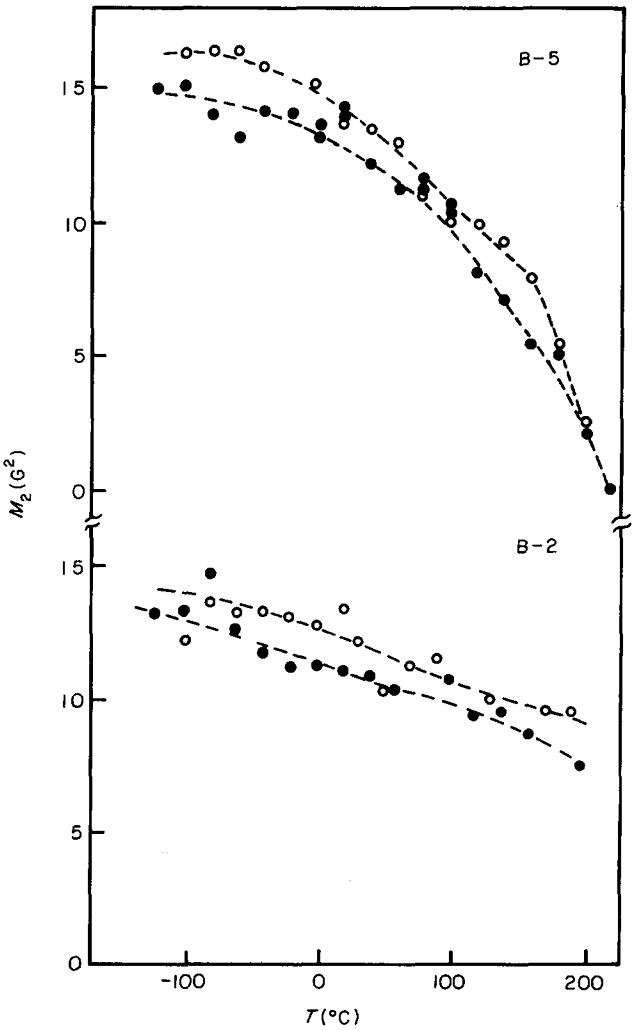


Figure 2 Broad line n.m.r. spectra of polymers B-2 and B-5: ○, without $LiClO_4$; ●, with stoichiometric amount of $LiClO_4$

within the whole composition range suggests that specific interactions between the zwitterion and the salt are actually weak, in good agreement with the quasi insensitivity of the ^{13}C n.m.r. spectrum of B-5 polymer with respect to added $LiClO_4$ (Ref. 25). This characteristic behaviour is in sharp contrast to that of a number of lithium salt–polyether systems for instance, where coordination of the cation by the ether oxygens drastically increases the T_g values[16,26,27]. The glass transition width is a slightly increasing function of the salt content (see $\Delta T = T_2 - T_1$ in *Table 2*) and this broadening may be ascribed to less genuine homogeneity of the blends as the salt concentration is progressively increased[29]. Microphase separation is actually observed for $r > 0.25$, as detected by SAXS experiments (see previous X-ray discussion). Finally, the increments in heat capacity at T_g (ΔC_p) were calculated with respect to the total weight of the blends, which have to be considered as new chemical species (see *Table 2*). The ΔC_p variations with composition are quite negligible: $\Delta C_p \simeq 0.27 \pm 0.01$ J g^{-1} K^{-1}. This type of behaviour, already observed for $ZnCl_1$/poly(oxypropylene) amorphous blends, has been interpreted in terms of the formation of a true salt–polymer complex in which both components are involved in the T_g process[29]. It is more probably quite fortuitous and with no real physical meaning (ΔC_p values are not measured at the same temperature and there is no reason *a priori* to expect identical calorimetric properties for the pure polymer and its complexes with salt).

The experimental data of broad line n.m.r. spectroscopy (*Figure 2*) for two representative spectra are in good agreement with the previous conclusions. Samples B-1 to B-4 show second moment values characteristic of a rigid lattice up to 210°C.

For polymer B-5 and its stoichiometric blend with $LiClO_4$, T_g values, conventionally measured at the mid-point of the nearly linear strong decrease of the second moment in the high temperature range (157 and 187°C, respectively), are compatible with those derived from d.s.c. (133 and 143°C).

The variations of rigidity induced by $LiClO_4$–zwitterion interactions in the amorphous blends are systematically very weak, and the slight increase observed in, for example, sample B-5 is in good agreement with the d.s.c. measurements.

Finally, no clear sub-T_g relaxation giving a well-defined and sharp decrease of the second moment value is observed, whatever the polymer.

Water–poly(sulphopropylbetaine) interactions

The poly(sulphopropylbetaines) are very hygroscopic[1], and the water–poly(zwitterion) interactions were studied by d.s.c. for polymer B-5 (see *Figure 3*). Three behaviours may clearly be seen when the weight fraction of water W_H in the sample increases.

(*a*) $W_H < 0.25$, *non-freezing bound water.* This water, in very strong specific interaction with the organic matrix, does not show any melting endotherm on heating above −123°C, and the glass transition temperature of the polymer is a strongly decreasing function of W_H.

(*b*) $0.25 < W_H < 0.40$, *freezable bound water.* This water, still in strong interaction with the matrix probably through the previous first solvation layer, shows no exotherm on cooling (10°C min^{-1}), but a crystallization exotherm at −38 to −33°C and a melting endotherm at

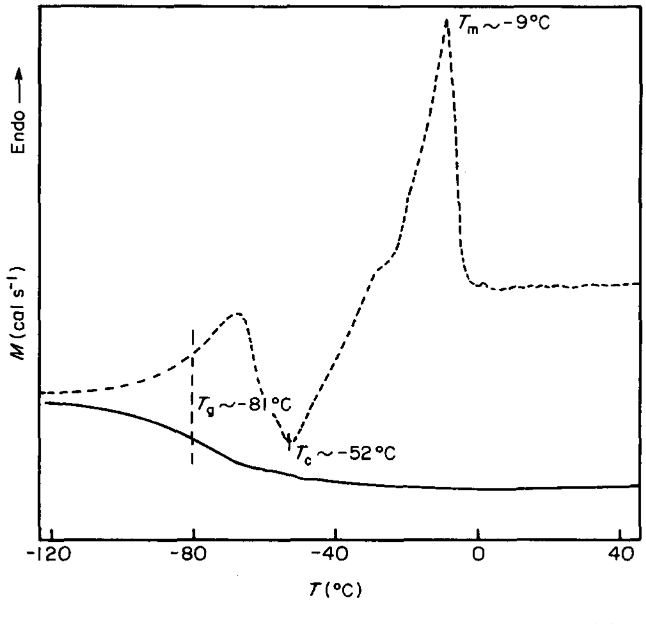


Figure 3 D.s.c. thermogram of hydrated polymer B-5 ($W_H = 0.28$). ——, Freezing curve (10 K min^{-1}); - - - -, melting curve (20 K min^{-1})

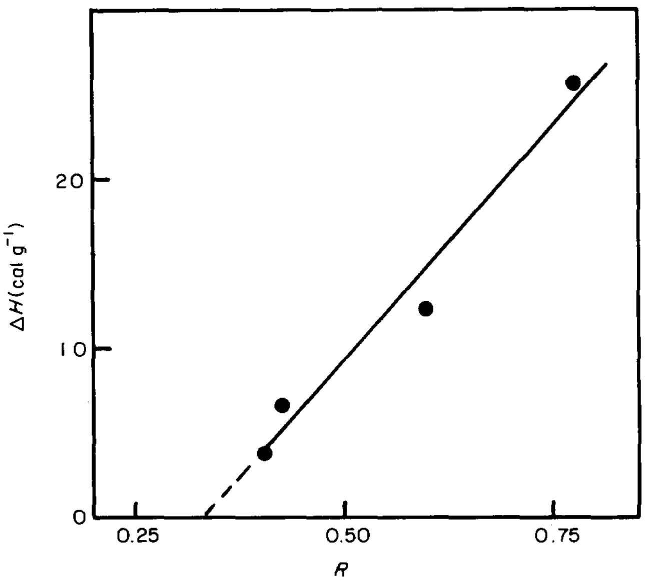


Figure 4 Variations of the total enthalpy of melting of bound water per g of polymer, ΔH, *versus* the ratio R = weight of water/weight of polymer for polymer B-5

−13°C on heating (20°C min^{-1}), quite different from those of pure water. The T_g of the polymer remains almost constant at about −73°C.

(*c*) $W_H > 0.40$, *free water.* The d.s.c. trace shows a complex crystallization exotherm at −43°C and a melting endotherm at −3°C as well as the previous transitions.

The number of non-freezing bound water molecules per monomeric unit, derived from the intercept of the linear variations of the experimental total enthalpy of melting ΔH versus the ratio weight of water/weight of dry polymer, as shown in *Figure 4*, is rather high, about 6.5, similar to that (6.0) found for poly(styrenesulphonic acid)[30]: it is definitely greater than those measured for various water soluble polymers such as poly(ethylene oxide) (0.3)[30], poly(vinyl alcohol) (0.7–1.5)[31], poly(methacrylic acid) (3.1)[31] or poly(*N*-vinylpyrrolidone) (4.2)[31]. The standard enthalpy of melting of freezable bound water, directly given by the slope of the same linear plot, is about 231 J g^{-1}, drastically lower than that of pure water, 334 J g^{-1}. Such a strong decrease has already been observed in a number of hydrated polymers, and it has been tentatively ascribed to a partial deformation of the ice structure of bound water in interaction with the organic matrix[30]. The maximum number of freezable bound water molecules per zwitterionic unit, estimated from the difference between the total amount of water and the sum of non-freezing bound water and free water (assuming ΔH melting of free water = ΔH melting of pure water = 334 J g^{-1}), is about 4.0, still higher than those observed for the water-soluble polymers previously considered[30].

The depression of T_g induced by non-freezing bound water may be analysed according either to the Gordon–Taylor–Wood (GTW) equation[32,33] (1) or to the Couchman equation[34,35] (2), which has a very similar form and involves the heat capacity increments of the components at T_g, ΔC_p, without requiring any adjustable parameter:

$$T_g = \frac{W_B T_g(\text{B}) + K W_H T_g(\text{H}_2\text{O})}{W_B + K W_H} \qquad (1)$$

with $T_g(\text{H}_2\text{O}) = -139°\text{C}$ (Ref. 36)

$$T_g = \frac{W_B \Delta C_p(\text{B}) T_g(\text{B}) + W_H \Delta C_p(\text{H}_2\text{O}) T_g(\text{H}_2\text{O})}{W_B \Delta C_p(\text{B}) + W_H \Delta C_p(\text{H}_2\text{O})} \qquad (2)$$

with $\Delta C_p(\text{H}_2\text{O}) = 1.94\ \text{J K}^{-1}\ \text{g}^{-1}$ (Ref. 36)

where W_B is the weight fraction of polymer B in the sample.

The fits of both equations to the experimental points is shown in *Figure 5*. The adjustable parameter K of the GTW relation, $K = 0.12$, is often assumed to reflect specific interactions between the two components of the binary system; its value is significantly lower than those derived from literature data for wet poly(*N*-vinyl pyrrolidone)[37], $K = 0.26$, or poly(hydroxyethyl methacrylate)[38], $K = 0.32$. This suggests stronger specific interactions in the case of polymer B-5, in good agreement with the higher dipole moment of the zwitterionic structure. On the other hand, the fairly good fit observed with the Couchman equation, as for instance for the water–epoxy resin systems[36], tends to show that the large T_g depression may also result from an overall plasticization effect and not exclusively from very specific zwitterion solvation, since this relation was established according to a thermodynamic approach of the transition of miscible blends with perfect mixing of the two components. The oxyethylene spacer and the ester carbonyl functions of the structure of B-5 are actually hydrogen bond acceptors. The width of the transition range, as measured by $\Delta T = T_2 - T_1$, is about 20°C and almost independent of the water content of the sample. Once again the lack of any significant broadening may be interpreted as an argument in favour of perfect mixing of the two components.

Dielectric relaxation processes as studied by thermally stimulated depolarization currents

In order to analyse the influence of non-freezing bound water, t.s.d.c. were first recorded once the samples were clamped between the electrodes and then, in a second set of experiments, after drying the samples in the t.s.d.c. device at >110°C for more than 6 h under 10^{-2} torr.

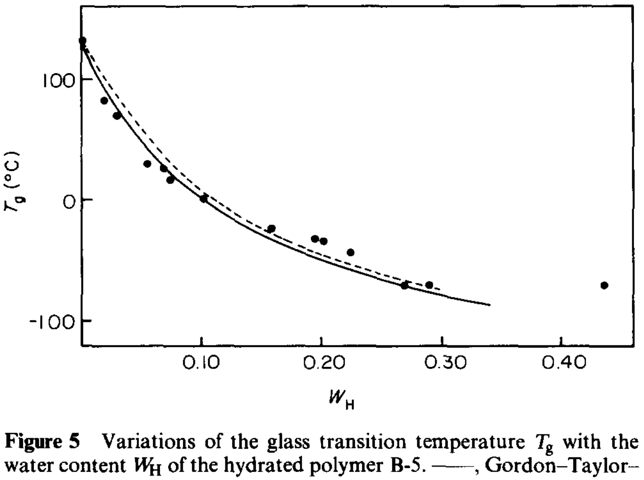


Figure 5 Variations of the glass transition temperature T_g with the water content W_H of the hydrated polymer B-5. ——, Gordon–Taylor–Wood equation ($K = 0.12$). ----, Couchman equation

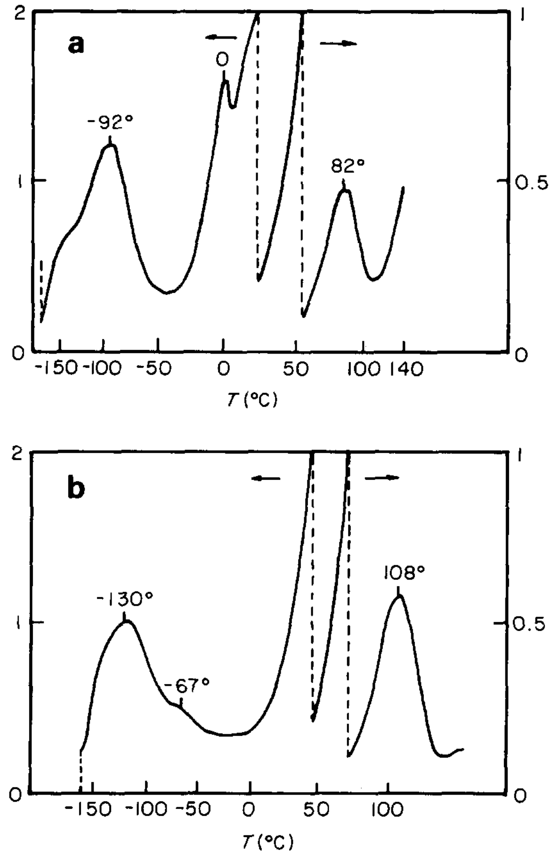


Figure 6 T.s.d.c. thermograms of polymer B-1: (a) undried; (b) dry sample. Poling: 500 V, 15 min at 140°C. Sample: diameter, 12 mm; thickness, 1.61 mm

Typical examples of t.s.d.c. plots are shown in *Figures 6* and *7* for polymers B-1 and B-5 respectively.

In the temperature range below 0°C, the withdrawal of water changes the shape of the spectrum but not the total relaxation strengths of the movements involved (main chain motions of a few carbon–carbon linkages and secondary relaxation of side-chain dipoles). For the aromatic polymers B-1 to B-3, the strongest peak is shifted to lower temperatures. The peak appears at -130 to -145°C in moisture-free samples. The release of water–polymer hydrogen bonds would increase the mobility of the disorienting units, thereby decreasing the activation energy involved and thus the temperature of the peak. For the two dry aliphatic polymers B-4 and B-5 the spectrum is more complex, and the main peak is located at higher temperature than that of the aromatic ones. In all cases, the dielectric increment $\Delta\varepsilon$, derived from the area underneath the t.s.d.c. curve, is of the same order for the betaines and their tertiary amino precursors; it never exceeds a value of 3.8 ($\Delta\varepsilon \simeq 3.3$ for A-1 and B-1) and no peak common to all five polyzwitterions is observed. All these features, especially the low $\Delta\varepsilon$ value, show that there is no rapid side-chain motion involving the doubly charged highly polar groups in the low temperature range.

In the 5–30°C range a very strong peak occurs for undried poly(zwitterions). For sample B-5, for instance, the temperature variation of the relaxation time, τ, obeys an Arrhenius law with an activation energy of about 1.4 eV; the value of τ at the temperature of peak maximum, $T_m = 12$°C, is 74 s. The peak is also present when the current is recorded while the field is maintained during the heating stage, but it does not occur on cooling, field on. It is no longer observed for dried samples in both types of experiments. All these features rule out events due to relaxation of dipole moments for this peak.

Above 80°C, a peak or a shoulder is observed for all samples, and it is shifted to higher temperatures without an appreciable change in its strength as moisture is removed. For polymer B-5 it may be assigned to the α relaxation related to the occurrence of the glass transition, as evidenced by the d.s.c. signal at nearly the same temperature (see *Table 1*), water being an efficient plasticizer (see previous discussion); the assignment of the high temperature t.s.d.c. peak differs for the other polyzwitterions and will be discussed in a forthcoming paper. The $\Delta\varepsilon$ values in *Table 1* (poorly reproducible when the peak appears as a shoulder) are the lower limits found. The remarkable feature is the very high $\Delta\varepsilon$ value for the α process in the case of polymers B-5, $\Delta\varepsilon > 1 \times 10^2$. Clearly, the highly polar zwitterionic groups are involved in this relaxation, thereby showing that side chains participate in the micro-Brownian motion of main chain segments related to the glass transition of polymers. This supports Johari's argument that a low temperature process, lower than the relaxation one, is not necessarily characteristic of a specific dipolar group of the molecule without consideration of its local environment[39].

The addition of $LiClO_4$ does not yield any appreciable change in the low temperature range, while a strong rising current is recorded above 0°C due to an unavoidable

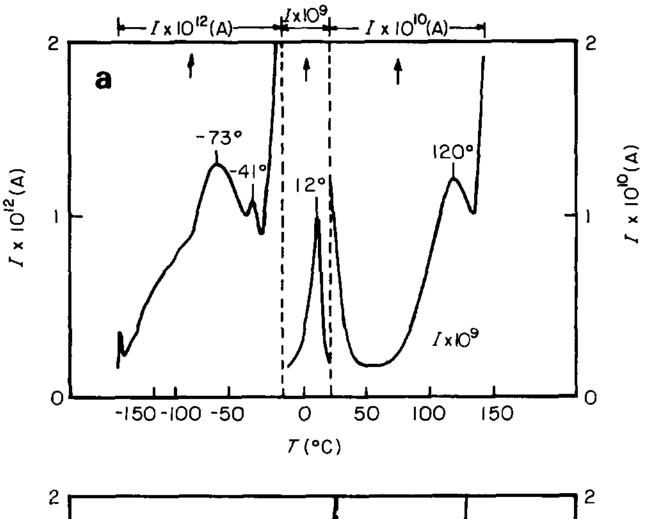


Figure 7 T.s.d.c. thermograms of polymer B-5: (a) undried (W_H 0.005); (b) dry sample. Poling: 300 V, 15 min at 160°C. Sample: diameter, 12 mm; thickness, 0.97 mm

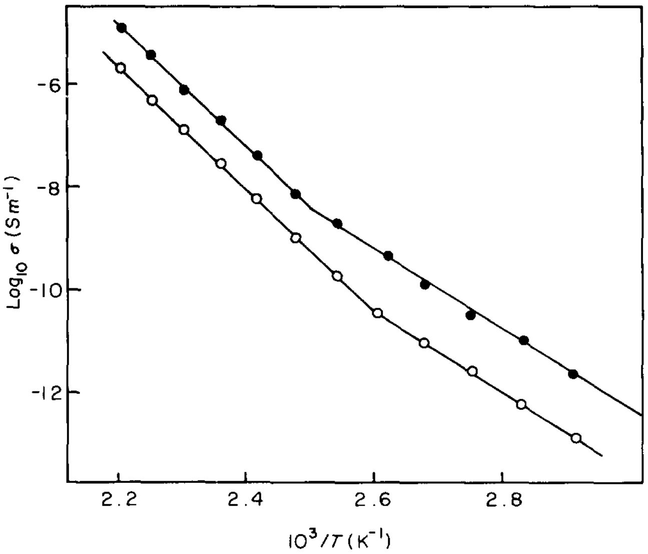


Figure 8 Arrhenius plot of the conductivity of amorphous $LiClO_4$/B-5 blends: ○, $[LiClO_4]/[B] = 0.4$; ●, $[LiClO_4]/[B] = 1$

voltage of electrochemical origin. This obscures the t.s.d.c. response and only a weak shoulder appears near 130°C for the α relaxation of, for example, B-5/$LiClO_4$ stoichiometric blends (see *Figure 7*). Conductivity measurements, performed in a narrow range around T_g (70–180°C) proved to be more sensitive in detecting the glass transition temperature as the break-point in the linear Arrhenius plots of the conductivity σ, as shown in *Figure 8*. The thermal activation energy of conductivity is increased from 1.6 eV in the glassy state to 2.4 eV in the liquid state, and is independent of the salt content for $[LiClO_4]/[B] \geq 0.4$. The glass transition temperature is raised by about 15°C when the molar ratio of $LiClO_4$ increases from 0.4 to 1, in qualitative agreement with the reported d.s.c. and n.m.r. results. Adding a stoichiometric amount of $LiClO_4$ enhances the conductivity of pure B-5 from about 1×10^{-10} to $2 \times 10^{-9}\,\mathrm{S\,m^{-1}}$ at 120°C, in sharp contrast to the behaviour of ionomers[40] or halato-telechelic polymers[41], where conductivity is a decreasing function of the degree of neutralization of the acidic groups. The $LiClO_4$–polyzwitterion systems also differ from poly(oxyethylene)–polyurethane networks containing sodium tetraphenylborate, whose apparent activation energies just above T_g depend on salt content and which are more conductive at moderate temperature[42]. However, the conductivity of the stoichiometric $LiClO_4$/B-5 blend is close to that of the networks containing up to 5% of sodium tetraphenylborate when compared at their respective T_g values[42]: $\sigma \simeq 2 \times 10^{-8}\,\mathrm{S\,m^{-1}}$ at about 20°C for the POE system and at about 130°C for the poly(sulphopropylbetaine) one.

CONCLUSIONS

The strongly dipolar character of the zwitterionic structure of their lateral groups and the specific interactions they can exchange with polar solutes afford to the atactic aliphatic or aromatic poly(sulphopropylbetaines) a number of unique bulk properties: local dipole moment > 5 D, a very high dielectric permittivity increment at T_g ($\Delta\varepsilon > 1 \times 10^2$), solvation of salts of widely different lattice energies in stoichiometric amounts to yield amorphous microphase separated blends, and the ability to bind as much as 6 mol unfreezable water per monomeric unit. Stable zwitterionic structures may thus appear as most promising functional groups towards new polymers of potential technological interest. The structural analogy (microphase separation)[17] we have recently pointed out between the well-known ionomers and some sulphopropylbetaine copolymers may be considered as one example of the many original properties which may be expected from such macromolecular materials.

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