Macromolecules **1993,** *26,* 4919–4927

Statistical *n*-Butyl Acrylate–(Sulfopropyl)ammonium Betaine Copolymers. 5. Plasticization Studies

Monique Galin, André Mathis, and Jean-Claude Galin*

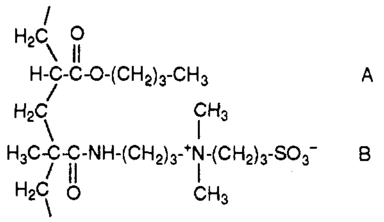
Institut Charles Sadron (CRM–EAHP), CNRS–ULP, 6 rue Boussingault, 67083 Strasbourg Cedex, France

Received February 18, 1993; Revised Manuscript Received May 17, 1993

ABSTRACT: The influence of additives of strongly different polarities such as dibutyl phthalate (DBP), ethylammonium nitrate (EAN), or water on the morphology of zwitterionomers of *n*-butyl acrylate (A) and 1,1-dimethyl-1-(3-methacrylamidopropyl)-1-(3-sulfopropyl)ammonium betaine (B) has been studied by differential scanning calorimetry (DSC) and small-angle X-ray scattering (SAXS). In the case of a clustered copolymer (F_B (molar fraction) = 0.11), addition of DBP as a selective solvent of A units (W_{DBP} (weight fraction) < 0.7) results in simultaneous plasticization of the soft matrix ($T_g^{S,p} \sim 237$–183 K) and of the hard zwitterionic domains ($T_g^{H,p} \sim 330$–260 K) without significant redistribution of A and B units: the DBP partition coefficient *K*, which measures the plasticizer fraction located in the matrix, is always in favor of a weakly preferential sorption of the additive by the matrix and slightly increases with the overall DBP content ($K \sim 0.84$–0.96). According to SAXS analysis (Bragg spacings corresponding to the "ionic" peak in the range 6–10 nm), the plasticization process differs only slightly from an isotropic homogeneous swelling of the system. Addition of EAN or water as a selective solvent of B units (number of polar additive molecules per zwitterionic unit <2.2) results in a fairly similar and nearly selective plasticization of the zwitterionic domains ($T_g^{S,p} \sim 237$–232 K, $T_g^{H,p} \sim 330$–250 K) with simultaneous reorganization of the B units: the rather strong increase of the Bragg spacings ($d \sim 6$–10 nm) suggests a reduction of the number of zwitterionic multiplets and an increase of their size and of their aggregation number.

Introduction

In the first two parts of this series, we reported the synthesis[1] and structural characterization[2] of statistical amorphous copolymers of *n*-butyl acrylate (A) and 1,1-dimethyl-1-(3-methacrylamidopropyl)-1-(3-sulfopropyl)ammonium betaine (B):



F_i = molar fraction of *i* units

Bulk copolymers of low and moderate B content ($0.04 < F_B < 0.35$) display a very typical biphasic structure which has been characterized by differential scanning calorimetry (DSC), solid-state wide-line ^{1}H NMR analysis, and small-angle X-ray scattering (SAXS): the copolymer morphology may be described in terms of a nearly pure A soft matrix, S ($227 < T_g^S$ (K) < 253, $F_B^S < 0.07$), and dispersed zwitterionic hard domains, H, still containing rather high amounts of A units ($303 < T_g^H$ (K) < 393, $0.45 < F_A^H < 0.75$). The presence of a single SAXS peak relatively insensitive to temperature and the variations of the corresponding Bragg spacings *d* (4–7 nm) according to a power law $d \propto \Phi_B^{-0.27}$ (Φ_B = volume fraction of B units) suggest a quasi-random distribution of the dipolar scattering entities within the apolar matrix. Moreover, ^{13}CP/DD/MAS NMR analysis[3] has confirmed the presence of zwitterionic rigid aggregates (spin diffusion over microdomains of about 2 nm at room temperature), still stable at very high temperatures such as $T_g^H + 100$. Finally, the dynamic mechanical properties in the glass transition, rubbery, and flow zones are consistent with a heterogeneous structure where zwitterion-rich microdomains behave as thermally reversible physical cross-links showing a broad spectrum of relaxation times.[4] All these morphological features and specific mechanical properties are of course highly reminiscent of those of the well-known ionomers[5–9] and are in good agreement with the new multiplet-cluster model recently introduced by Eisenberg et al.[10] The strong dipolar interactions between the B units arising from their unusually high dipole moment (μ = 20.7 and 27.7 D calculated for the curled and extended conformations, respectively,[11] versus 23 D as derived from dielectric measurements in aqueous solution[12]) and the low polarity and high mobility of the *n*-butyl acrylate matrix (T_g(An) = 227 K) are obviously the driving forces of the microphase separation actually observed.

The huge polarity difference between the zwitterionic hard domains and the apolar soft matrix clearly provides unique possibilities of preferential or selective plasticization of each phase, as first recognized by Lundberg et al.[13,14] in the case of ionomers (see especially ref 15 for a recent review article on plasticization in ionomers). The present work was thus devoted to the analysis of the influence of strongly different plasticizers on the heterogeneous structure of two copolymers previously studied in the pure state[2] and representative of unclustered (F_B = 0.04, one T_g) and clustered (F_B = 0.113, two T_g's) materials: (a) dibutyl phthalate (DBP) as a selective solvent of A units and *as a potential preferential plasticizer of the apolar matrix*; (b) water and ethylammonium nitrate ($C_2H_5NH_3^+$, NO_3^-, EAN), a liquid salt of very high polarity[16] in terms of ion–dipole and hydrogen-bonding interactions, as selective and good solvents of B units[17] and *as potential selective plasticizers of the dipolar zwitterionic domains.*

As in our previous work,[2] differential scanning calorimetry (DSC) and small-angle X-ray scattering (SAXS) were used as complementary techniques for characterization of the system heterogeneity at rather large and small scales, respectively.

Experimental Section

Materials. The copolymers AB-4.0 and AB-11.3 (F_B = 0.04 and 0.113, respectively) were the same as previously studied,[2] and their compositional and glass transition data are given in

0024-9297/93/2226-4919$04.00/0

Table I. Compositional Data and Glass Transitions (T_g and ΔT in K, ΔC_p in $J \cdot g^{-1} \cdot K^{-1}$) of the AB-4.0 and AB-11.3 Copolymers

		soft matrix					hard domains			
sample	W_B	W_B^S	W^S	T_g^S	ΔT^S	$\Delta C_p^{S\ b}$	W_B^H	T_g^H	ΔT^H	$\Delta C_p^{H\ b}$
AB-4.0[a]	0.087	0.087	1	233	16	0.280				
AB-11.3	0.225	0.072	0.670	237	21	0.275	0.536	331	35	0.203

[a] Monophasic copolymer without hard domains. [b] The ΔC_p values are normalized to 1 g of the corresponding phase.

Table I. Dibutyl phthalate (DBP) of the best reagent grade available (purity ≥99%) was used without further purification. Ethylammonium nitrate (EAN) was prepared according to the literature:[18] the liquid salt dried at 70 °C under 10^{-2} Torr (1.3 Pa) had a residual water content of about 500 ppm (Karl Fischer titration) and was stored in a desiccator over P_2O_5. The various DBP or EAN plasticized samples were prepared from homogeneous 10% solutions in trifluoroethanol (TFE), a very good solvent for A and B units,[1] where calculated amounts of the copolymer and of the additive in the desired ratio were accurately weighed. TFE was exhaustively stripped off by an overnight evaporation at 40 °C followed by vacuum drying to constant weight at 70 °C under 10^{-2} Torr for at least 24 h. The final plasticizer content in the system was determined gravimetrically and further checked by nitrogen elemental analysis: only samples leading to an agreement between the two methods better than 5% were considered for DSC and SAXS measurements. For water plasticized samples, the copolymers were equilibrated to constant weight at 23 ± 0.5 °C in aluminum pans placed in desiccators where relative humidity was monitored between 22 and 90% using various saturated salt solutions, as described elsewhere.[19] The water uptake was measured after sealing the pan.

Whenever necessary, all the weight fractions W were converted into volume fractions Φ assuming additivity of the specific volumes of the various components whatever the system is: at 25 °C, v = 0.944, 0.721, 0.959, and 0.830 mL g^{-1} for An,[20] Bn,[2] DBP, and EAN,[18] respectively.

Differential Scanning Calorimetry (DSC). The glass transition temperatures and the corresponding specific heat capacity increments of the plasticized copolymers were determined on Perkin-Elmer DSC-2 and DSC-7 devices interfaced with a computer data station, after previous calibration with *n*-decane, gallium, and indium. Samples of 10–20 mg were hermetically sealed in the usual aluminum pans, and the following heating–cooling sequences were systematically repeated until reproducible scans were obtained (most often the second one): heating to 373 K at a rate of 20 K·min^{-1}, annealing for 5 min at this temperature, cooling to 150 K at a rate of 40 K·min^{-1}, and annealing for 5 min. The invariance of the pan weight after the DSC scans was systematically checked. In the case of water as plasticizer, its actual amount was derived after DSC scanning from the weight difference between the wet and dried copolymer, after exhaustive drying of the sample in its previously pierced pan at 80 °C under 10^{-2} Torr for at least 24 h: only pans showing good agreement between this water content and the previously measured water uptake were considered for a reliable analysis of the DSC data.

The T_g temperatures were taken at the midpoint of the baseline shift ($\Delta C_p/2$), and the transition width was estimated by $\Delta T = T_2 - T_1$, where T_1 and T_2 are the intersections of the extrapolated glassy and liquid baselines with the tangent to the thermogram inflection point. The glass transition T_g and ΔC_p values of DBP and water were taken from the literature: T_g = 178 K, ΔC_p = 0.540 J·g^{-1}·K^{-1} for DBP[21] and T_g = 134 K and ΔC_p = 1.94 J·g^{-1}·K^{-1} for water.[22] The corresponding values for EAN were measured in the following way. EAN (5–10 mg) was placed in hermetically sealed aluminum pans and then quenched at about 90–100 K by inserting the pan into an aluminum block previously cooled by immersing in liquid nitrogen. After 3 min, the sample was transferred to the measurement head of the DSC-7 calorimeter previously cooled at 100 K, and after equilibrating the system for 5 min, the DSC scan was performed at a rate of 10 K·min^{-1}. Several independent runs on supercooled EAN samples showing crystallinity degrees in the range 5–20% (T_m = 285 ± 2 K and ΔH_m = 115 ± 5 J·g^{-1} versus T_m = 287 K and ΔH_m = 116 J·g^{-1} according to the literature[18]) yielded the following data: T_g = 180 ± 2 K, ΔC_p = 0.86 ± 0.08 J·g^{-1}·K^{-1}.

Small-Angle X-ray Scattering (SAXS). SAXS experiments were carried out at room temperature with the usual experimental device[23] operating with a linear collimation (infinite height slit conditions) of a monochromatic X-ray beam of λ = 0.154 nm and fitted with a linear detector for quantitative analysis. The previously plasticized samples were directly transferred to the sample holder for X-ray measurements. Scattering patterns were recorded for scattering vectors q in the range 0.2–3 nm^{-1} ($q = (4\pi/\lambda) \sin \theta$), where 2θ is the scattering angle).

Results and Discussion

Nomenclature and General Framework of the DSC and SAXS Analysis. Because the systems under study involve three different components (monomeric units A and B and plasticizer P) distributed in a biphasic structure (soft matrix S and hard domains H), the following rather complex but logical symbols were adopted throughout the text. F_i, W_i, and Φ_i are related to the molar, weight, and volume fractions of component i (i = A, B, or P) normalized to the total system or to a given homogeneous phase; the indices S and H are ascribed to the soft and hard phases, respectively, followed by p when dealing with plasticized systems. For instance, F_A^S is the molar fraction of A units in the soft phase of the pure copolymer ($F_A^S + F_B^S = 1$), W_P is the weight fraction of plasticizer in the total plasticized system, $W_P^{H,p}$ is the weight fraction of plasticizer in the plasticized hard phase of the copolymer ($\sum_i W_i^{H,p} = \sum_i W_i^{S,p} = 1$), and $\Phi^{S,p}$ is the volume fraction of the plasticized soft phase in the system ($\Phi^{S,p} + \Phi^{H,p} = 1$).

In all the following discussion, the glass transition temperature and the corresponding heat capacity increment ΔC_p of a given homogeneous phase were correlated with its composition through the two complementary equations

$$\ln T_g = \sum_i W_i \Delta C_{p,i} \ln T_{g,i} / \sum_i W_i \Delta C_{p,i} \qquad (1)$$

$$\Delta C_p = \sum_i W_i \Delta C_{p,i} \qquad (2)$$

The general Couchman[24] equation (1) appears more reliable than the Fox–Flory relation ($T_g^{-1} = \sum_i W_i T_{g,i}^{-1}$) previously used[2] since it does not require any correlation between the $T_{g,i}$ and $\Delta C_{p,i}$ values of the pure components. Moreover, its efficiency for the analysis of the T_g variations of homogeneous polymer–diluent systems has been reemphasized recently.[25]

For monophasic systems (one T_g) obtained in some cases, composition is obviously known a priori, and eqs 1 and 2 are used only for comparison of the observed and calculated DSC data. For biphasic systems, the compositional data of each phase, $W_P^{S,p}$ and $W_P^{H,p}$, were derived from the observed corresponding T_g by straightforward calculations using eq 1, and their relative amounts $W^{S,p}$ and $W^{H,p}$ were derived from simple material balance (see Appendix I). A partition coefficient of the plasticizer K may be then defined as its fraction dissolved in the soft matrix:

$$K = W^{S,p} W_P^{S,p} / W_P$$

All this structural analysis requires that *no redistribution of A and B units between the soft and hard phases occurs on plasticization with respect to the original pure*

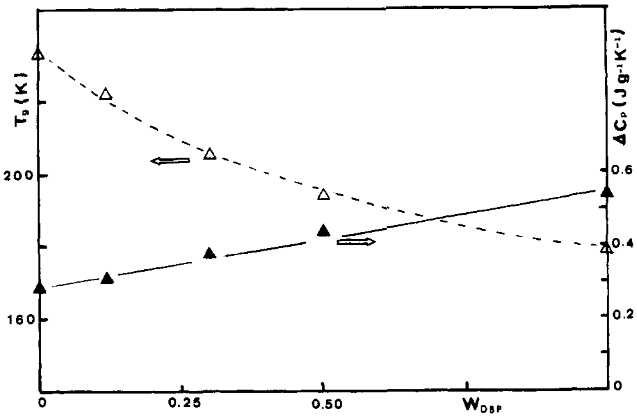


Figure 1. Glass transition temperatures (△) and specific heat increments at T_g (▲) of copolymer AB-4.0 plasticized by DBP. The lines are calculated according to eqs 1 and 2.

copolymer. The self-consistency of the thus derived compositional data with the DSC measurements was checked for every phase by comparison of the observed ΔC_p values (after renormalization) with those calculated through eq 2 (see Appendix II). It has to be stressed that eqs 1 and 2 assume that the various $\Delta C_{p,i}$ values are independent of temperature.

Quantitative analysis of the entire SAXS patterns according to the various and still controversial structural models of ionomers[26–28] is beyond the scope of the present work, and discussion is restricted to the analysis of the variations of the Bragg spacings d ($d = 2\pi/q$) derived from the position of the typical so-called "ionic peak" as a function of the plasticizer concentration in the systems. Because of increasing experimental evidence in favor of interparticle interference models (liquid-like hard-sphere model[29,30]), the d values are considered as proportional to, but not as a precise measure of, interzwitterionic aggregate distances. This interpretation is obviously compatible with the most recent views of Eisenberg et al.,[10] since they assume that d values reflect only intermultiplet distances which are not characterized by a uniform distribution but by a most prevalent spacing within the clusters.

Plasticization of the Unclustered Zwitterionomer AB-4.0 by DBP. All the plasticized samples are clear and transparent except for the highest DBP concentration, $W_P = 0.50$, where the material is slightly hazy. DSC shows only one well-defined glass transition of nearly constant width, $\Delta T = 15 \pm 2$ K, and the corresponding temperature T_g is a monotonous decreasing function of W_P. Figure 1 shows that the observed values of T_g and of the related heat capacity increment ΔC_p are in very good agreement with the calculated ones (see previous eqs 1 and 2). As expected, the system behaves as a homogeneous phase because of the miscibility of DBP and acrylate units and of the low zwitterion content ($0.03 < \Phi_B < 0.07$).

The SAXS patterns of the plasticized copolymers show a characteristic broadening and a progressive shift of the "ionic" peak toward lower scattering vectors when the DBP concentration increases. Dilution occurs with a simultaneous broadening of the distribution of the correlation distances between the zwitterionic aggregates, and the persistence of a correlation for the more dilute system ($\Phi_P \sim 0.70$, $\Phi_B \sim 0.02$) implies a long-range interaction potential between multiplets. The "microscopic" swelling measured by the ratio of the Bragg distances d/d_0, where d_0 refers to the pure copolymer, may be compared with the macroscopic isotropic swelling of the system $(1 - \Phi_P)^{-1/3}$. Figure 2 shows that plasticization results in an affine deformation over the whole concentration range: the size and the number of the zwitterionic aggregates are not significantly changed. In a similar way, the experimental power law d (nm) $= 3.02\Phi_B^{-0.316}$ (regression coefficient over five data points = −0.991) is in good agreement with such an isotropic homogeneous swelling process: a theoretical exponent of $-{}^1/_3$ is expected for a random distribution of scattering entities.[6,8,10] In the oversimplified space-filling model which assumes quantitative and homogeneous aggregation of all the B units, the multiplets would correspond to spherical domains of radius of about 1.75 nm containing about 64 zwitterions.

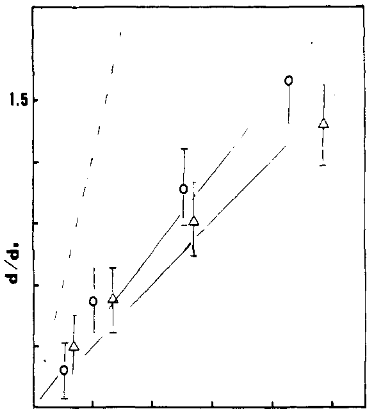


Figure 2. Comparison of the microscopic d/d_0 and macroscopic swelling $(1 - \Phi_P)^{-1/3}$ of copolymers AB-4.0 (△) and AB-11.3 (○) plasticized by DBP; dashed line, carboxylated poly(ethyl acrylate) ionomers, $F_B \sim 0.05$–0.10, plasticized by 4-decylaniline.[33]

Table II. Experimental Characteristic Parameters of the Glass Transitions (T_g and ΔT in K, ΔC_p in J·g^{-1}·K^{-1}) of the DBP-Plasticized Copolymer AB-11.3

	W_P					
	0.10	0.24	0.47	0.64	0.71[c]	0.89[c]
$T_g^{S,p}$	223	208	192	187	185	183
$\Delta T^{S,p}$	21	17	14	9	7	5
$\Delta C_p^{S,p}$ [a]	0.21	0.25	0.33	0.38	0.42	0.50
$T_g^{H,p}$	306	288	275	260		
$\Delta T^{H,p}$	30	22	b	b		
$\Delta C_p^{H,p}$ [a]	0.09	0.08	0.05	0.03		

[a] The ΔC_p values are the primary DSC data normalized to 1 g of total plasticized sample (see Appendix II). [b] Not measurable. [c] The calculated T_g and ΔC_p values for these monophasic systems are T_g = 191 and 186 K and ΔC_p = 0.474 and 0.515 J·g^{-1}·K^{-1} for W_P = 0.71 and 0.89, respectively.

Plasticization of the Clustered Zwitterionomer AB-11.3 by DBP. All the plasticized samples are transparent over the whole DBP concentration range in these systems.

DSC Analysis. For $W_P < 0.7$, increasing the plasticizer concentration results in a narrowing of the glass transition widths and in a nearly parallel decrease of the corresponding temperatures T_g *both* for the soft and hard phases: see Table II. DBP has a fairly negligible affinity for the zwitterionic units (addition of ca. 0.04 weight fraction of DBP in pure poly(zwitterion) Bn yields, however, a homogeneous plasticized system with a characteristic T_g depression of about 50 K), and the observed behavior may be thus ascribed to its partition between the soft and hard phases, which mainly reflects their relative A content.

In a first approach (model I), the amount of DBP in a given phase may be assumed directly proportional to its A content ("homogeneous distribution"): this probably oversimplified model allows the derivation of a partition coefficient of the plasticizer which has a constant value over the whole concentration range, $K = (W^S W_A^S)/W_A =$

Table III. DBP Partition Coefficient, Compositional Data, and Characteristic Parameters of the Glass Transitions (T_g in K, ΔC_p in J·g^{-1}·K^{-1}) of the DBP-Plasticized Copolymer AB-11.3 Calculated According to Models I and II (See Text)

	model I				model II			
	$W_P = 0.10$	$W_P = 0.24$	$W_P = 0.47$	$W_P = 0.64$	$W_P = 0.10$	$W_P = 0.24$	$W_P = 0.47$	$W_P = 0.64$
K	0.80	0.80	0.80	0.80	0.845	0.880	0.924	0.959
$W_P^{S,p}$	0.117	0.274	0.515	0.680	0.121	0.299	0.586	0.709
$W^{S,p}$	0.691	0.704	0.732	0.756	0.699	0.707	0.741	0.865
$T_g^{S,p}$	223	210	195	188	*a*	*a*	*a*	*a*
$\Delta C_p^{S,p}$ [b]								
calc	0.306	0.347	0.411	0.455	0.307	0.354	0.430	0.463
obs	0.302	0.356	0.458	0.504	0.300	0.355	0.451	0.440
$W_P^{H,p}$	0.062	0.159	0.347	0.516	0.052	0.098	0.138	0.193
$T_g^{H,p}$	302	269	238	209	*a*	*a*	*a*	*a*
$\Delta C_p^{H,p}$ [b]								
calc	0.224	0.257	0.320	0.377	0.220	0.236	0.250	0.268
obs	0.353	0.284	0.172	0.139	0.299	0.286	0.178	0.248

[a] No calculated T_g in model II. [b] The ΔC_p values are normalized to 1 g of the corresponding plasticized phase (see Appendix II).

0.80, and it can completely define the morphology of the system in terms of internal composition and relative importance of the soft and hard phases. Comparison of the observed and calculated T_g and ΔC_p values for the two glass transitions (Table III) shows that the agreement is good for the soft matrix (differences less than 4 K and 11% for the T_g and ΔC_p values, respectively), but quite unsatisfactory for the hard domains (differences greater than 15 K and 40% for the T_g and ΔC_p values, respectively).

In a second approach (model II), the composition and the relative importance of the two phases may be directly derived from the experimental T_g values and from the overall composition of the system (see Appendix I): this procedure allows the calculation of the ΔC_p values for both transitions and the definition of a DBP partition coefficient for each system. The data given in Table III show that, compared to the previous model, the agreement between the ΔC_p values is still better for the soft matrix (differences less than 5%) and significantly improved for the hard domains (differences less than 30%). Better self-consistency of all the DSC data and DSC-derived compositional data cannot be expected for a number of reasons. The primary experimental $\Delta C_p^{H,p}$ values, normalized to 1 g of total plasticized system as given directly by the DSC measurements, always remain lower than 0.10 J·g^{-1}·K^{-1} and their accuracy is thus rather poor, of about 15%. The unavoidable misuse of the experimental ΔC_p^{P} value, determined at $T_g^P = 178$ K, in a much higher temperature range ($250 < T_g^{H,p}$ (K) < 310) may or may not[25] bias the calculations. Finally, the Couchman equation may fail for the higher DBP concentrations in the case of the hard phase, which shows the stronger difference between the T_g of its components[31] (T_g^P and T_g^H). The major feature of the improved model II is that the DBP partition coefficient K is always higher than for a "homogeneous" distribution and that it is a slightly and quasi-linear increasing function of the DBP concentration in the system (Figure 3). Such a trend suggests a kind of saturation phenomenon in the hard domains: this appears more clearly from the variations of the ratio r_H of the number of DBP molecules per A unit in the hard phase, as shown in Figure 3. For model II, r_H tends to an asymptotic value of about 0.2 in the range $W_{DBP} \sim 0.5$–0.65, in sharp contrast with the higher r_H values which increase continuously from 0.7 to 1.3 within the same DBP concentration range for model I. Differences between the two structural models are obviously considerably attenuated for the corresponding ratio r_S of the number of DBP molecules per A unit in the soft matrix (note that $r_H = r_S$ for the "homogeneous" distribution).

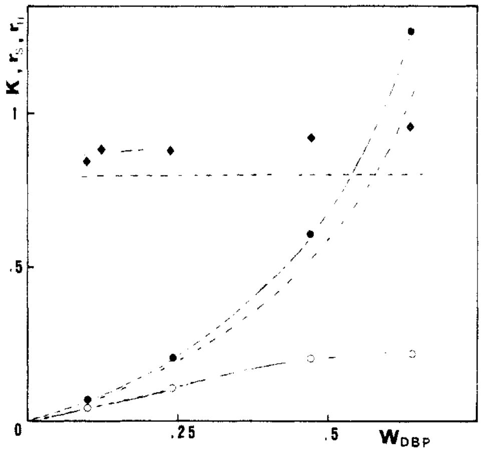


Figure 3. Variations of the DBP partition coefficient K and ratios r_S and r_H with the DBP concentration for plasticized copolymer AB-11.3 according to model I (dashed lines for $K = 0.80$ and $r_S = r_H$) and model II (full lines K (◆); r_s (●) and r_H (○)).

Comparison of these data with some recent and closely related results on ionomers plasticized by nonpolar species[15] reveals both analogies and differences depending on the systems under study. In carboxylated polystyrene and poly(ethyl acrylate) ionomers plasticized by diethylbenzene[32] and *n*-decylaniline,[33] respectively, only negligible deviations from a "uniform" distribution of the plasticizer in the material are considered. In contrast, dioctyl phthalate is assumed to be quantitatively excluded from the ionic clusters in sulfonated polystyrene.[34,35] Finally, in the case of a carboxylated polystyrene ionomer plasticized by a styrene oligomer ($M = 800$), preferential distribution in the matrix would shift to a more "uniform" distribution when the plasticizer concentration increases.[36] Clearly, if the exclusion of the nonpolar plasticizer from the dipolar multiplets is well ascertained, a comprehensive analysis of its partition between the matrix and the clusters obviously needs more quantitative data on a broader variety of systems.

For the highest DBP concentrations in the plasticized systems, $W_P > 0.7$, only one sharp ($\Delta T = 6 \pm 1$ K) glass transition may be identified in the DSC thermograms, and the observed and calculated T_g and ΔC_p values for these monophasic systems are in good agreement: see Table II. This characteristic behavior cannot be ascribed to a too small ΔT_g difference between hypothetical soft and hard phases: extrapolated ΔT_g values would remain higher than 60 K; it merely arises from the relative amount of hard domains which would show extrapolated weight fractions $W^{H,p}$ lower than 0.10, too low to be detected.

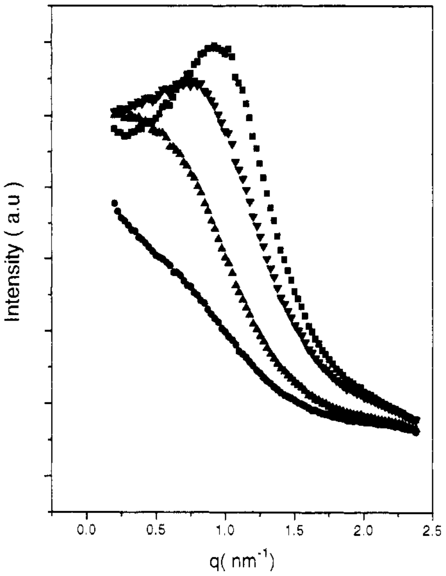


Figure 4. SAXS patterns of copolymer AB-11.3 plasticized by DBP to various extents: W_{DBP} = 0 (■), 0.24 (▼), 0.47 (▲), and 0.84 (●).

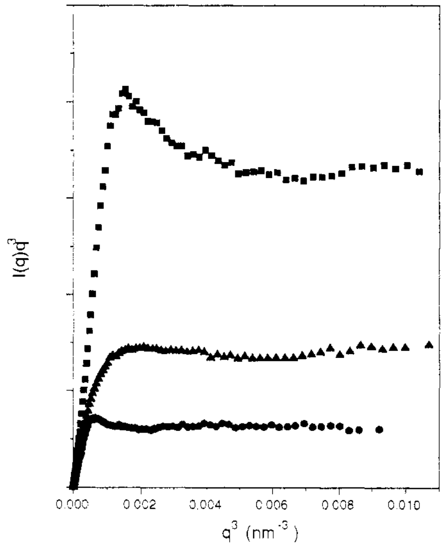


Figure 5. Porod's analysis of the SAXS patterns at high *q* values for copolymer AB-11.3 plasticized by various additives: W_{DBP} = 0.47 (▲); W_{EAN} = 0.101 (■); W_{H_2O} = 0.057 (●).

Because of the very weak concentration in zwitterionic units in such highly diluted systems, $W_B < 0.07$, the situation becomes similar to that previously observed for the unclustered copolymer AB-4.0.

SAXS Analysis. As in the previous case of the unclustered copolymer, the SAXS "ionic" peak broadens and shifts toward smaller values of the scattering vector when the DBP concentration increases in the systems (Figure 4). Porod's analysis of the scattering profile at high *q* values ($q > 1.5$ nm^{-1}) shown in Figure 5 is consistent with a well-defined and rather sharp interface between the scattering entities and their environment. For the more dilute system ($\Phi_P = 0.72$), which appears monophasic in DSC experiments, a well-defined "ionic" peak can no longer be accurately located (flat "maximum" in the range $d \sim$ 10–11 nm) in spite of a volume fraction of zwitterionic units $\Phi_B = 0.05$ higher than for the unclustered copolymer AB-4.0, which does show a better defined "ionic" peak under similar conditions ($\Phi_B = 0.02$ for $\Phi_P = 0.70$). This feature does not obviously imply the lack of the "ionic" peak in the AB-11.3 plasticized system. The "microscopic" swelling ratio d/d_0 is slightly but significantly higher than expected for an isotropic homogeneous swelling processes, in particular for high "macroscopic" swelling ratios: see Figure 3. Analogously, the power law d (nm) = $3.31\,\Phi_B^{-0.395}$ (regression coefficient over five data points of −0.990) with a characteristic exponent significantly lower than $-^1/_3$ reveals the same deviation. However, it remains quite weak compared, for instance, to that recently observed on a poly(ethyl acrylate-*co*-sodium acrylate) ionomer (molar fraction of ionic units ~0.05–0.10) plasticized by 4-decylaniline:[33] see Figure 3. No definite explanation can be proposed for the observed behavior, which appears difficult to reconcile with a preferential swelling process of the matrix, as suggested by DSC. It may arise from partial reorganization of the B units in the multiplets (less aggregates of increasing size for instance?). The actual shape and size of the multiplets cannot be derived obviously from our limited SAXS analysis. In any case, a lamellar structure of the material, similar to that already observed in polysiloxane zwitterionomers[37] (side group $(CH_2)_3NH^+((CH_2)_3SO_3^-)((CH_2)_2NH_2^+(CH_2)_3SO_3^-))$, may be safely ruled out: swelling would result in a power law of the type $d \propto \Phi_B^{-1}$, incompatible with our experimental data. Assuming a simple space-filling model as in the previous case of the unclustered copolymer, the multiplets would correspond in the unplasticized copolymer to spherical domains of radius of about 2.25 nm and containing up to 140 zwitterions: these very crude figures have to be considered with great caution.

Plasticization of the Clustered Copolymer AB-11.3 by EAN and H₂O. DSC Analysis. EAN is not miscible with poly(butyl acrylate). DSC measurements on an An–EAN blend of moderate salt content, W_{EAN} = 0.11, show two well-separated glass transitions arising from quantitative phase separation: $T_g \sim 184$ K corresponding to the dispersed salt (T_g(EAN) = 180 K), and $T_g \sim 227$ K with $\Delta C_p \sim 0.337$ J·g^{-1}·K^{-1} corresponding to the homopolymer (T_g(An) = 227 K, ΔC_p(An) = 0.335 J·g^{-1}·K^{-1} according to ref 2).

Addition of small amounts of EAN to the clustered copolymer ($W_{EAN} < 0.16$) results in opposite behaviors for the two glass transitions of the plasticized systems: see Table IV. The quasi-invariance of the transition of the soft matrix (constant width 20 ± 2 K and $T_g^{S,P}$ values included in the very narrow range 237–231 K) is in sharp contrast with the narrowing of the transition of the hard domains ($\Delta T_g^{H,P}$ decreases from 35 to 17 K), suggesting greater homogeneity of this phase, and with the strong decrease of the corresponding temperature $T_g^{H,P}$ ($T_g^{H,P} \sim$ 310–250 K). Addition of water ($W_P < 0.03$) yields fairly similar trends. The nearly identical efficiency of EAN and H_2O as quasi-selective plasticizers of the hard domains is stressed in Figure 6, where the $T_g^{H,P}$ and the $T_g^{S,P}$ variations may be described by a single curve emphasizing the critical role of the number of polar additive molecules per zwitterionic unit n_P/n_B over the entire concentration range $n_P/n_B < 2.2$.

Since EAN and H_2O are selective solvents of the B units, their distribution between the soft and hard phases may be assumed to reflect their relative B content. As in the previous case of DBP, this probably oversimplified model allows the calculation of a partition coefficient of the plasticizer showing a constant value $K = W_B^S W^S / W_B$ = 0.214 as well as the derivation of the composition and the relative importance of the two phases. Comparison of the observed and calculated T_g and ΔC_p values for the two glass transitions given in Table V points out that the agreement is fairly good for the soft matrix (differences less than 3 K and 15% for the $T_g^{S,P}$ and $\Delta C_p^{S,P}$ values,

Table IV. Experimental Characteristic Parameters of the Glass Transitions (T_g and ΔT in K, ΔC_p in $J \cdot g^{-1} \cdot K^{-1}$) of the Copolymer AB-11.3 Plasticized by Water and EAN

	H_2O plasticizer			EAN plasticizer					
	$W_P = 0.019$	$W_P = 0.025$	$W_P = 0.057^b$	$W_P = 0.011$	$W_P = 0.022$	$W_P = 0.053$	$W_P = 0.101$	$W_P = 0.148$	$W_P = 0.225^c$
$T_g^{S,p}$	231	231	230	234	233	233	232	231	231
ΔT	25	22	27	22	18	21	19	*d*	25
$\Delta C_p^{S,p\,a}$	0.22	0.20	0.45	0.21	0.18	0.18	0.18	0.18	0.44
$T_g^{H,p}$	276	265		302	299	291	265	253	
ΔT	23	22		28	28	22	18	*d*	
$\Delta C_p^{H,p\,a}$	0.11	0.13		0.08	0.12	0.12	0.17	0.20	

[a] Same comments as in note *a* of Table II. [b] Calculated for the equivalent monophasic system: $T_g = 218$ K, $\Delta C_p = 0.406\ J \cdot g^{-1} \cdot K^{-1}$. [c] Calculated values for the equivalent monophasic system: $T_g = 222$ K, $\Delta C_p = 0.436\ J \cdot g^{-1} \cdot K^{-1}$. [d] Not measurable because of partial overlapping of the two transitions.

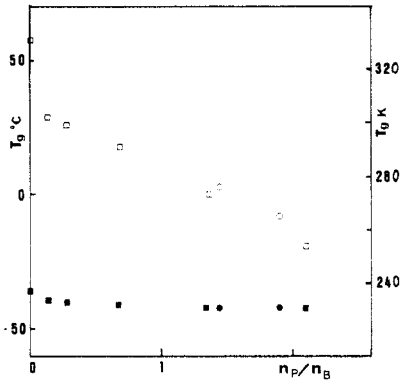


Figure 6. Variations of the glass transition temperatures of copolymer AB-11.3 plasticized by EAN and H_2O versus the molar ratio n_P/n_B. EAN: $T_g^{S,p}$ (■); $T_g^{H,p}$ (□). H_2O: $T_g^{S,p}$ (●); $T_g^{H,p}$ (○).

respectively) but definitely worse for the hard domains (differences greater than 20 K and 15% for the $T_g^{H,p}$ and $\Delta C_p^{H,p}$ values, respectively). Moreover, the derivation of the internal composition and of the relative importance of the two phases from the observed T_g values and from a simple material balance, as in the analysis of DBP (model II), leads to physically meaningless results, such as a strong predominance of the hard domains and a partition coefficient of the salt in favor of the soft matrix. Two different reasons may be tentatively proposed to account for these discrepancies. First, strong and very localized specific interactions between the polar additives and the zwitterionic multiplets probably result in nonrandom mixing and may thus induce plasticization of the hard domains according to a process which does not necessarily obey the Couchman equation derived for a perfectly homogeneous phase.[24] Second, the assumption of the lack of any redistribution of the A and B units in the sample is probably incorrect: the strong increase of the hard phase mobility and the strong incompatibility between the polar additives and the A units may result in the transfer of some isolated B units or multiplets from the matrix to the hard domains and vice versa for some A units. This reorganization of the zwitterionic units in the plasticized material is strongly supported by the results of the SAXS analysis, as will be discussed shortly. However, quantitative phase separation of solvated B units in a pure A matrix is unrealistic because of the statistical distribution of the B units along the chain; moreover, it would lead to calculated T_g^H values higher by at least 100 K than the observed ones for low EAN contents ($W_{EAN} < 0.025$).

The disappearance of the characteristic high-temperature transition on the DSC thermograms for higher plasticizer concentrations, $n_P/n_B > 2.2$ ($W_{EAN} > 0.16$ and $W_{H_2O} > 0.03$), cannot be ascribed, as for DBP, to a too low volume fraction of hard domains, since the total volume fraction of the polar additive in all of the systems is too small ($\Phi_{EAN} < 0.22$, $\Phi_{H_2O} < 0.07$) to change drastically the relative amounts of the two phases whatever its distribution is. Moreover, the slight but significant increase of the primary $\Delta C_p^{H,p}$ values with the plasticizer concentration (see Table IV) is incompatible with a strong decrease of the volume fraction of the corresponding phase. Extrapolation of the T_g values for these higher plasticizer concentrations suggests that the $\Delta T_g = T_g^{H,p} - T_g^{S,p}$ differences have become less than 20 K and thus are too weak to allow a reliable discrimination of the two T_g's in DSC experiments. It has to be stressed that the identification of only one glass transition with T_g and ΔC_p values in fairly good agreement with those calculated for an ideal homogeneous system of identical composition (see notes *b* and *c* in Table IV) does not imply true homogeneity for the plasticized zwitterionomers: coexistence of two phases of different compositions, respectively B and P rich and B and P poor, but of similar glass transitions, is highly probable in spite of the lack of any significant broadening of the observed transition, as would be normally expected (incidental perfect superposition of the two transitions?).

Finally, for the highest water concentration, $n_{H_2O}/n_B = 10.6$, phase separation of the dipolar additive occurs during DSC scanning, as typified by the emergence of its melting endotherm at 260 K. It may be noted that the maximum content of unfreezable bound water (the only form showing a plasticizing effect) measured on the homopolymer Bn[38] corresponds to a critical value $n_{H_2O}/n_B = 8.4$. For the highest EAN concentration, $n_{EAN}/n_B = 3.5$, no crystallization or melting of the salt may be observed during the cooling or heating DSC cycles: the plasticizer is tightly bound to the macromolecular chain through very strong specific ion–dipole interactions.

All these characteristic features of the transitions of the clustered zwitterionomer plasticized by strongly polar additives are very similar to those generally observed on homologous ionomer systems mostly studied by dynamic mechanical spectroscopy:[15] see, for instance, the quasi-selective plasticization of the ionic domains by glycerol in the case of carboxylated[32] and sulfonated[34,35] polystyrenes. However, for increasing diluent concentrations, our experimental data are more in favor of a trend toward a coincidence of the transitions of the two phases without any drastic change in their relative amounts[35] rather than toward a contribution of a strongly increased fraction of the material to the glass transition of the matrix.[32]

SAXS Analysis. Addition of moderate amounts of EAN or H_2O ($\Phi_P < 0.25$) to the copolymer yields a characteristic narrowing and a progressive shift of the "ionic" peak toward smaller scattering vectors: see Figure 7 for the representative case of water. Moreover, the Porod analysis of the scattering profile for high q values ($q > 1.5$ nm^{-1}) given in Figure 5 is consistent in all cases with a rather sharp interface between the scattering dipolar

Table V. Compositional Data and Characteristic Parameters of the Glass Transitions (T_g in K, ΔC_p in J·g^{-1}·K^{-1}) of the Copolymer AB-11.3 Plasticized by Water or EAN Calculated for a Constant Partition Coefficient K = 0.214 ("Homogeneous" Distribution)

	H_2O plasticizer		EAN plasticizer				
	W_P = 0.019	W_P = 0.025	W_P = 0.011	W_P = 0.022	W_P = 0.053	W_P = 0.101	W_P = 0.148
$W_P^{S,P}$	0.006	0.008	0.003	0.007	0.018	0.034	0.053
$W^{S,P}$	0.663	0.659	0.665	0.660	0.646	0.619	0.603
$T_g^{S,P}$	231	230	236	235	234	231	227
$\Delta C_p^{S,P}$ [a]							
calc	0.285	0.288	0.277	0.279	0.285	0.295	0.306
obs	0.332	0.288	0.314	0.273	0.279	0.295	0.298
$W_P^{H,P}$	0.045	0.058	0.026	0.051	0.118	0.209	0.293
$T_g^{H,P}$	250	236	311	296	265	240	224
$\Delta C_p^{H,P}$ [a]							
calc	0.281	0.304	0.220	0.237	0.281	0.341	0.397
obs	0.327	0.381	0.251	0.344	0.341	0.469	0.503

[a] The ΔC_p values are normalized to 1 g of the corresponding plasticized phase (see Appendix II).

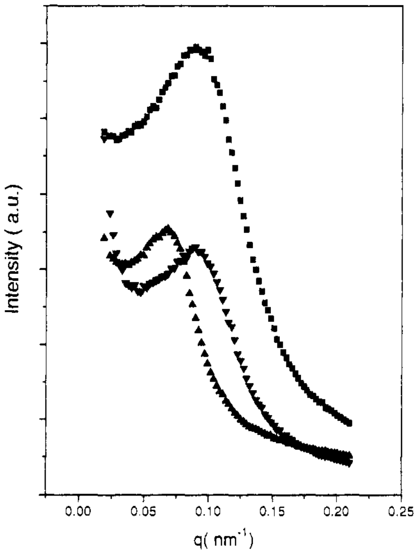


Figure 7. SAXS patterns of copolymer AB-11.3 plasticized by water to various extents: W_{H_2O} = 0 (■), 0.06 (▼), and 0.13 (▲).

aggregates and their environment. These features suggest a narrowing of the distribution of the correlation distances between the scattering dipolar aggregates and some kind of a dilution effect. However, the "apparent microscopic swelling" estimated by the d/d_0 ratio of the corresponding Bragg spacings ($d/d_0 < 1.55$) is much higher than the "macroscopic" one, which should remain very low in the plasticizer concentration range under investigation ($(1 - \Phi_P)^{-1/3} < 1.10$).

The variations of the ratios d/d_0 with respect to the plasticizer content expressed in terms of the number of diluent molecules per zwitterion n_P/n_B or of the ratio of the volume fractions of diluent and zwitterionic units Φ_P/Φ_B are given in Figure 8. In the case of water, the deviations of the d/d_0 values from a quasi-linear increasing function of the water content remain weak, and a higher number of more accurate data would be required to ascertain the apparent plateau value observed for n_{H_2O}/n_B between 2 and 5 (Figure 8A). The saturation of the binding sites of the first sorption monolayer corresponds precisely to two molecules of water per zwitterion, as derived from the analysis of sorption isotherms of the homopolymer Bn,[19] but this coincidence may be purely incidental. In the case of EAN, the d/d_0 variations also show two distinct regimes separated by a plateau value for n_{EAN}/n_B between 0.7 and 1.5 (Figure 8A), and, here again, this behavior may be tentatively related to a transition step in the solvation and the potential reorganization of the B units and multiplets (see below). In any case, there is no a priori reason that specific solvation of the zwitterionic units results in a structural change appearing as a strictly monotonous increasing function of the plasticizer concentration. Finally, if the molar volumes of the two solvents are taken into account as in the curve $d/d_0 = f(\Phi_P/\Phi_B)$ (Figure 8B), differences between EAN and water appear significant only for the lower solvent concentrations, $\Phi_P/\Phi_B < 0.6$, where the salt yields the stronger morphology rearrangement: this behavior may be physically sound, since greater differences may be expected for the stronger specific interactions between the zwitterions and the first tightly bound solvent molecules.

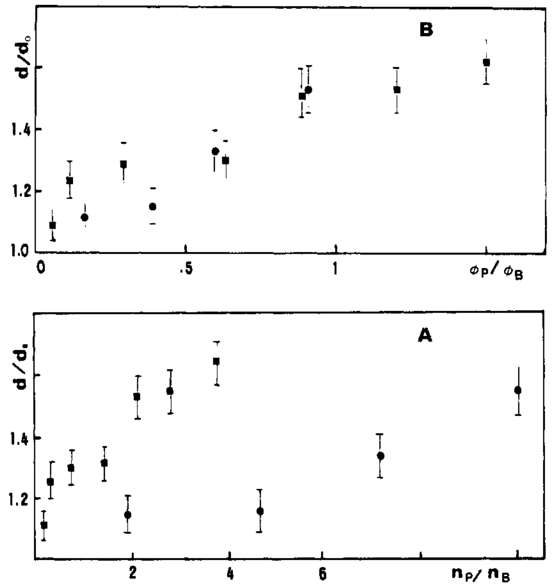


Figure 8. Variations of the microscopic swelling d/d_0 in AB-11.3 copolymer plasticized by EAN (■) and H_2O (●): (A) d/d_0 versus the molar ratio n_P/n_B; (B) d/d_0 versus the volume ratio Φ_P/Φ_B.

These general trends are very similar to those observed for a variety of ionomers plasticized by polar additives, such as methanol or glycerol[34,35] and more especially water.[26,28,39,40] The rather strong increase of the Bragg spacings has been ascribed to a reorganization of the selectively solvated ionic species in the plasticized materials: besides a possible change in the fraction of ions which are aggregated, it likely involves a decrease of the number of multiplets and a simultaneous increase of their size. This conclusion is obviously transposable to the zwitterionomer under study. In spite of the lack of a quantitative analysis of the SAXS patterns, beyond the scope of the present work, the oversimplified space-filling model, which assumes quantitative segregation of the solvated B units in uniform spherical domains, allows us to estimate that the number of zwitterionic units per aggregate is increased for both EAN and water by a factor of about 3 when going from the pure copolymer to the systems with a plasticizer constant $W_P = 0.2$. This picture must of course be considered with caution because of the crudeness of the assumed structural model; it is, however, fairly compatible with the corresponding increase of the aggregation number of the ionic "micelles" in perfluorinated ionomer membranes of similar ionic content and hydrated to a similar extent.[28]

Conclusion

Plasticization of a representative "clustered" butyl acrylate zwitterionomer by additives of strongly different polarities, such as dibutyl phthalate, ethylammonium nitrate, or water, occurs over a broad concentration range without destroying its characteristic two-phase morphology. Because of its good affinity for butyl acrylate units, DBP ($W_{DBP} < 0.70$) plasticizes simultaneously the soft matrix and the hard domains. Redistribution of A and B units appears negligible, and the partition coefficient of the plasticizer K is always in favor of the soft matrix with respect to a "homogeneous" distribution directly proportional to the A content of the two coexisting phases. According to SAXS analysis, the plasticization process differs only very slightly from a homogeneous isotropic swelling of the system. However, in spite of its definite interest since it allows a complete and quantitative analysis of the two-phase morphology of the plasticized zwitterionomer, such a structural model may still remain oversimplified and cannot be considered as fully ascertained. It relies upon the analysis of the T_g depressions only in terms of a "copolymer" effect which emphasizes the differences in chemical composition of the corresponding phases but which neglects the so-called "thermal stress effect" identified in the case of block copolymers[41,42] and sometimes advocated for plasticized ionomers:[34,35] the T_g^H depression may be partly ascribed to the mobility increase of the matrix because of the strong connectivity of the two phases (individual chains pervade both the hard and soft phases). Moreover, the interdependence of the relaxation processes in polymeric materials displaying microphase separation has been recently emphasized through new theoretical approaches of chain dynamics in reversible networks.[43]

Because of their strong and specific interactions with the dipolar B units, water and EAN plasticize hard domains in a fairly similar and nearly selective way, resulting in the coexistence of two phases of strongly different compositions but of converging and finally similar glass transition temperatures as far as the plasticizer content increases ($W_P < 0.25$). It is no longer possible to derive a simple structural model from the DSC results, and the lack of any correlation between the "apparent microscopic" swelling derived from SAXS analysis and the macroscopic swelling of the system suggests redistribution of the A and B units in the plasticized zwitterionomer: there is a possible change in the fraction of the aggregated B units and an increase in the aggregation number and in the size of the dipolar multiplets, along with a more homogeneous distribution in the system.

All these typical features, already observed in the case of the well-known ionomers,[15] are in good agreement with the recent multiplet-cluster concept proposed by Eisenberg et al.[10] Quantitative interpretation of SAXS data within the framework of the various structural models available[26-28] and solid-state NMR spectroscopy[2,3] (^{1}H broad line and ^{13}C CP/DD/MAS) should certainly contribute toward a comprehensive analysis of the dual mode of preferential or selective plasticization of the clustered zwitterionomers and, as a feedback consequence, toward a better knowledge of the typical two-phase morphology of the unplasticized systems.

Acknowledgment. The authors gratefully acknowledge Mrs. M. Scheer for her efficient contribution to the DSC measurements.

Appendix I. Derivation of Compositional Data from T_g Measurements

Straightforward calculations from the Couchman equation (1) yields

$$W_P^{S,p} = \frac{\Delta C_p^S(\ln T_g^{S,p} - \ln T_g^S)}{\Delta C_p^S(\ln T_g^{S,p} - \ln T_g^S) - \Delta C_p^P(\ln T_g^P - \ln T_g^S)}$$

$$W_P^{H,p} = \frac{\Delta C_p^H(\ln T_g^{H,p} - \ln T_g^H)}{\Delta C_p^H(\ln T_g^{H,p} - \ln T_g^H) - \Delta C_p^P(\ln T_g^P - \ln T_g^H)}$$

where the indexes S and H refer to the pure soft and hard phases in the original copolymer and the indexes S,p and H,p to the same phases plasticized; P refers to the plasticizer.

A simple material balance of the plasticizer distributed between the soft and hard plasticized phases of respective weight fractions $W^{S,p}$ and $W^{H,p}$ leads to

$$W_P = W_P^{S,p} W^{S,p} + W_P^{H,p} W^{H,p} \quad \text{with } W^{S,p} + W^{H,p} = 1$$

Hence

$$W^{S,p} = (W^P - W_P^{S,p})/(W_P^{S,p} - W_P^{H,p})$$

The partition coefficient of the plasticizer K, defined as its fraction located in the matrix, is directly given by

$$K = (W^{S,p} W_P^{S,p})/W_P$$

Appendix II. Calculation of the Specific Heat Increments ΔC_p

For every plasticized phase, S,p or H,p, the primary experimental ΔC_p* values given per gram of *total* system have to be normalized to 1 g of the corresponding phase according to

$$\Delta C_p^{S,p} = \Delta C_p^{*S,p}/W^{S,p}; \qquad \Delta C_p^{H,p} = \Delta C_p^{*H,p}/W^{H,p}$$

The corrected "experimental" values may be then compared with the "theoretical" ones calculated through eq 2, taking into account the previously normalized ΔC_p values of the soft and hard phases in the pure copolymer (ΔC_p^S and ΔC_p^H, respectively) and that of the plasticizer (ΔC_p^P) according to

$$\Delta C_p^{S,p} = \Delta C_p^P W_P^{S,p} + \Delta C_p^S(1 - W_P^{S,p});$$
$$\Delta C_p^{H,p} = \Delta C_p^P W_P^{H,p} + \Delta C_p^H(1 - W_P^{H,p})$$

References and Notes

(1) Ehrmann, M.; Galin, J. C. *Polymer* **1992**, *33*, 859.
(2) Ehrmann, M.; Mathis, A.; Meurer, B.; Scheer, M.; Galin, J. C. *Macromolecules* **1992**, *25*, 2253.
(3) Ehrmann, M.; Galin, J. C.; Meurer, B. *Macromolecules* **1993**, *26*, 988.
(4) Part 4: Ehrmann, M.; Galin, J. C.; Muller, R.; Bazuin, C. G. *Macromolecules*, previous paper in this issue.
(5) Eisenberg, A.; King, M. *Ion Containing Polymers*; Academic Press: New York, 1977.

(6) MacKnight, W. J.; Earnest, T. R. *J. Polym. Sci., Macromol. Rev.* **1981**, *16*, 41.

(7) Bazuin, C. G.; Eisenberg, A. *Ind. Eng. Chem. Prod. Res. Dev.* **1981**, *20*, 271.

(8) Mauritz, K. A. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1988**, *C28*, 65.

(9) Fitzgerald, J. J.; Weiss, R. A. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1988**, *C28*, 99.

(10) Eisenberg, A.; Hird, B.; Moore, B. *Macromolecules* **1990**, *23*, 4098.

(11) Bredas, J. L.; Chance, R. R.; Silbey, R. *Macromolecules* **1988**, *21*, 1633.

(12) Galin, M.; Chapoton, A.; Galin, J. C. *J. Chem. Soc., Perkin Trans. 2* **1993**, 545.

(13) Makowski, H. S.; Lundberg, R. D. *Adv. Chem. Ser.* **1980**, *No. 187*, 37.

(14) Lundberg, R. D.; Makowski, H. S.; Westerman, L. *Adv. Chem. Ser.* **1980**, *No. 187*, 67.

(15) Bazuin, C. G. *Adv. Chem. Ser.* **1989**, *No. 395*, 476.

(16) Harrod, W. B.; Pienta, N. J. *J. Phys. Org. Chem.* **1990**, *3*, 534.

(17) Knoesel, R.; Ehrmann, M.; Galin, J. C. *Polymer* **1993**, *34*, 1925.

(18) Evans, D. F.; Yamouchi, A.; Roman, R.; Casassa, E. F. *J. Colloid Interface Sci.* **1982**, *88*, 89.

(19) Galin, J. C.; Galin, M. *J. Polym. Sci., Part B: Polym. Phys.* **1992**, *30*, 1113.

(20) Anderson, G. R. *Ark. Kemi* **1963**, *20*, 513.

(21) Ceccorulli, G.; Pizzoli, M.; Scandola, M. *Polymer* **1987**, *28*, 2077.

(22) Couchman, P. R.; Karasz, F. E. *Macromolecules* **1978**, *11*, 117.

(23) Guillon, D.; Mathis, A.; Skoulios, A. *J. Phys.* (*Les Ullis, Fr.*) **1975**, *36*, 695.

(24) Couchman, P. R. *Macromolecules* **1978**, *11*, 1156.

(25) Righetti, M. C.; Ajroldi, G.; Pezzin, G. *Polymer* **1992**, *33*, 4779.

(26) Fujimara, M.; Hashimoto, T.; Kawai, H. *Macromolecules* **1982**, *15*, 136.

(27) Yarusso, D. J.; Cooper, S. L. *Macromolecules* **1983**, *16*, 1871.

(28) Dreyfus, B.; Gebel, G.; Aldebert, P.; Pineri, M.; Escoubes, M.; Thomas, M. *J. Phys. Fr.* **1990**, *51*, 1341.

(29) Visser, S. A.; Cooper, S. L. *Macromolecules* **1991**, *24*, 2584.

(30) Visser, S. A.; Cooper, S. L. *Macromolecules* **1992**, *25*, 2230.

(31) Righetti, M. C.; Ajroldi, G.; Pezzin, G. *Polymer* **1992**, *33*, 4787.

(32) Bazuin, C. G.; Eisenberg, A. *J. Polym. Sci., Part B: Polym. Phys.* **1986**, *24*, 1137.

(33) Tong, X.; Bazuin, C. G. *J. Polym. Sci., Part B: Polym. Phys.* **1992**, *30*, 389.

(34) Fitzgerald, J. J.; Weiss, R. A. *J. Polym. Sci., Part B: Polym. Phys.* **1990**, *28*, 1719.

(35) Weiss, R. A.; Fitzgerald, J. J.; Kim, D. *Macromolecules* **1991**, *24*, 1064.

(36) Villeneuve, S.; Bazuin, C. G. *Polymer* **1991**, *32*, 2811.

(37) Graiver, D.; Litt, M.; Baer, E. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 3573, 3625.

(38) Galin, J. C.; Galin, M. *J. Polym. Sci., Part B: Polym. Phys.* **1992**, *30*, 1103.

(39) Yarusso, D. J.; Cooper, S. L. *Polymer* **1985**, *26*, 371.

(40) Kumar, S.; Pineri, M. *J. Polym. Sci., Part B: Polym. Phys.* **1986**, *24*, 1767.

(41) Morese-Seguela, B.; St. Jacques, M.; Renaud, J. M.; Prud'homme, R. *Macromolecules* **1980**, *13*, 100.

(42) Granger, A. T.; Wang, B.; Krause, S.; Fetters, L. J. *Adv. Chem. Ser.* **1986**, *No. 211*, 127.

(43) Leibler, L.; Rubinstein, M.; Colby, R. H. *Macromolecules* **1991**, *24*, 4701.