Macromolecules **1995**, *28*, 1567–1574

Plasticization of Biphasic Ionomers by Chemically Identical, Short, Monofunctional Oligomers

Michel Plante,[†] C. Geraldine Bazuin,[*,†] and Robert Jérôme[‡]

Centre de Recherche en Sciences et Ingénierie des Macromolécules (CERSIM), Département de Chimie, Université Laval, Québec, Canada G1K 7P4, and Centre d'Etude et de Recherche sur les Macromolécules (CERM), Université de Liège, Institut de Chimie, B6, Sart-Tilman, 4000 Liège, Belgium

Received September 12, 1994; Revised Manuscript Received November 22, 1994[®]

ABSTRACT: Blends of carboxylated polystyrene ionomers containing 7 mol % of ionic units and carboxylate-terminated, monofunctional, monodisperse styrene oligomers of MW 800 were investigated by dynamic mechanical analysis and small angle X-ray scattering (SAXS). Both Cs and Ba carboxylate salts were studied, as well as blends of the Cs oligomer with homopolystyrene. The cluster phase is preferentially plasticized by the oligomers for both salts. However, whereas the nonclustered phase of the Cs system is only a little more plasticized than that of the Ba system, the cluster phase in the Cs system undergoes dramatic plasticization, the cluster transition disappearing at 5 wt % oligomer content. Simultaneously, the SAXS "ionomer peak" disappears. A peak reappears at 20 wt % oligomer content, suggesting the development of a new morphology, proposed to be micelles or "inverted multiplets". The difference between the two systems is attributed to the much stronger electrostatic interactions in the Ba system; this is analyzed in terms of elementary ion units. It is concluded that, whereas the nature of the nonpolar tail is relatively unimportant, the nature and strength of the electrostatic interactions involved can be of critical importance to the plasticization effects in blends of ionomers with short, monofunctional oligomers.

Introduction

Biphasic ionomers owe their morphology to the huge difference in polarity between their major component, the matrix, and their minor component, the ionic counits.[1] According to the latest model describing ionomer morphology,[2] the ionic groups tend to aggregate into rigid entities called multiplets, whose rigidity reduces the mobility of the matrix segments in their vicinity; overlap of the regions of reduced mobility gives rise to larger regions called clusters, which have their own glass transition temperature (T_g), higher than that of the matrix, and which are clearly detectable as a distinct phase by dynamic mechanical analysis.

This dual nature of biphasic ionomers lends itself to "selective plasticization"[3] of the phases. Indeed, a large number of investigations of ionomer plasticization have been undertaken to date.[4–14] In general, it is observed that polar plasticizers affect primarily the cluster T_g, to the point where it even disappears;[4,8,9,14] nonpolar plasticizers usually affect both T_g's,[4–14] depending in part on the molecular weight of the plasticizer.[4,5,13] Plasticizers with both a polar and a nonpolar component, in particular end-functionalized oligomers or halatotelechelic polymers, may be expected to show behavior reminiscent of both polar and nonpolar plasticizers, depending on various molecular parameters.[4,6,7,12–14]

In this context, we have been investigating several ionomer/functionalized oligomer systems with specified molecular characteristics.[4,6,7,13] Of particular interest is one where the nonpolar and polar moieties of the ionomer and a monofunctional oligomer are identical, and, furthermore, where the length of the nonpolar part of the oligomer is comparable to the persistence length of the nonpolar component of the ionomer. This persistence length is thought to represent the approximate distance along the chain to which the reduced mobility in the ionomer is propagated from the point of attachment at the ionic moiety in the multiplet.[2] One report of such a system, but where the nonpolar part of the oligomer, sodium dodecyl benzene sulfonate, is *not* identical to that of the ionomer, a sodium sulfonated polystyrene, has appeared in the literature recently.[12] Preferential plasticization of the cluster phase was observed.

We have studied a system, presented in this paper, where both the ionomer and the oligomer are based on styrene; the ionic group, in both cases, is a carboxylate moiety. The oligomer, functionalized at one end, has a length of 8 styrene units, which is roughly twice the persistence length estimated for polystyrene.[2,15] The ion content chosen for the ionomer is 7 mol %, which means that the average segmental length between ionic groups in the ionomer (about 14 styrene units) is greater than that of the oligomer chain; this factor may have some importance in ensuring the miscibility of the system.[13] Two series of these ionomer/oligomer blends were investigated, one with Cs^+ as a counterion and the other with Ba^{2+}. These counterions were chosen in view of performing small angle X-ray scattering studies in addition to dynamic mechanical thermal analysis. It will be observed that the plasticization effects for the singly charged and the doubly charged counterions are very different.

Experimental Section

The styrene oligomer was synthesized via classical anionic techniques[16,17] in Liège, using THF as a solvent and butyllithium as a monofunctional initiator. The living chains were terminated with carboxylic acid by bubbling dry CO_2 through the reaction mixture and acidifying. The molar mass of the oligomers, determined by size exclusion chromatography, was 800 with a polydispersity (M_w/M_n) of 1.15. The functionality was determined to be 97% by titration with NaOH using phenolphthalein as the indicator. Neutralization of the acid groups into Cs and Ba salts was accomplished in benzene/methanol (90/10 v/v) solutions to which calculated amounts (to a 10% excess) of standardized solutions of the respective

---

[*] To whom correspondence should be addressed.

[†] CERSIM.

[‡] CERM.

[®] Abstract published in *Advance ACS Abstracts,* February 1, 1995.

hydroxide in methanol were added. The neutralized oligomers were then recovered by precipitation in methanol and were dried at 60 °C under reduced pressure for 2 weeks. The glass transition temperatures of the Cs and Ba oligomers, determined by differential scanning calorimetry (Perkin-Elmer DSC-4) at 20 °C/min, were 60 and 62 °C, respectively.

The copolymer was obtained through chemical modification of polystyrene, following the recipe of Hird and Eisenberg.[18] The polystyrene used was synthesized in the laboratory by classical free radical techniques and determined to have a molecular weight (M_w) of 100 000 and a polydispersity of 2.0. Following the carboxylation procedure and purification,[18] the copolymer was dried at 60 °C under reduced pressure for 1 week. The carboxylation was verified by proton NMR.[18] Size exclusion chromatography of the final product indicated that the molar mass was unaffected by the reaction. The acid content was determined to be 6.9 mol % by titration using phenolphthalein. Neutralization, recuperation, and drying of the Cs and Ba ionomers were accomplished in the same way as for the oligomers.

The blends were prepared by dissolving calculated amounts of the components in benzene/methanol (90/10 v/v) to give about 1% (w/v) solutions, which were stirred for about 12 h, then freeze-dried, and further dried at 60 °C under reduced pressure for 2 weeks. They were subsequently compression-molded into the desired form at about 100 °C above their estimated T_g, under a maximum pressure of 10 MPa for about 20 min. Following molding, the samples were kept in a desiccator containing P_2O_5 until used.

Dynamic mechanical thermal analysis was performed using the Polymer Laboratories DMTA, Mk II, in both dual cantilever bending mode and shear mode. The measurements were made at five frequencies (0.3, 1, 3, 10, and 30 Hz) and a deflection of 64 μm, at a heating rate of 1 °C/min. The sample chamber was constantly flushed with a light flow of dry nitrogen. For the bending mode, rectangular bars of dimensions 35 × 10 × 2 mm, giving a free length of 5 mm when clamped, were used. For the shear mode, twin disks of 12-mm diameter and 2.5-mm thickness were used; these were obtained by remolding the rectangular bars after the bending mode measurements.

Small angle X-ray scattering measurements at ambient temperature were taken with a Rigaku 12-kW rotating anode, using Ni-filtered Cu Kα radiation (λ = 0.154 nm), a Rigaku-Denki small angle camera under vacuum, and a Rigaku scintillation counter detector. The beam was collimated by two slits of widths 0.16 and 0.12 mm. The sample-to-detector distance was 200 mm. The samples were in the form of disks of 12-mm diameter and 1-mm thickness, obtained by further molding of the samples used for DMTA analysis. The time of exposure of the samples was about 3 h, identical for all samples. Since the X-ray analyses were for qualitative purposes, the only correction made to the profiles obtained was a subtraction of the data obtained for pure polystyrene.

Results

Dynamic Mechanical Analysis. The dynamic mechanical data obtained for the ionomer/oligomer blends at 1 Hz in the bending mode are shown in Figures 1 and 2 for the Cs and Ba series, respectively. First, in comparing the two ionomers without added oligomer, it is noted that the primary or matrix T_g (131 and 133 °C for the Cs and Ba ionomers, respectively, according to the loss tangent maximum at 1 Hz) is relatively insensitive to the type of counterion. The cluster transition is clearly visible for the Cs salt, identified by the higher temperature maximum at about 170 °C in the loss tangent curve (Figure 1). That for the Ba salt takes place at a higher temperature, as shown both by the considerably more extended rubbery plateau and by the much greater delay in upturn of the loss tangent above the matrix T_g for the Ba salt (Figure 2) compared to the Cs salt.

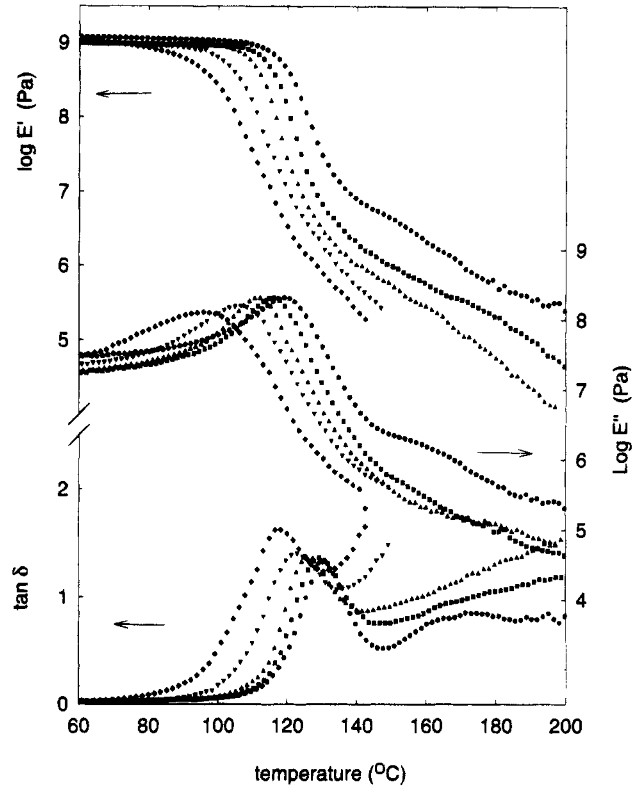


Figure 1. Dynamic Young's modulus and loss tangent as a function of temperature at 1 Hz for the Cs ionomer/oligomer blends. Ionomer/oligomer weight ratios: (●) 100/0, (■) 95/5, (▲) 90/10, (▼) 80/20, (◆) 60/40.

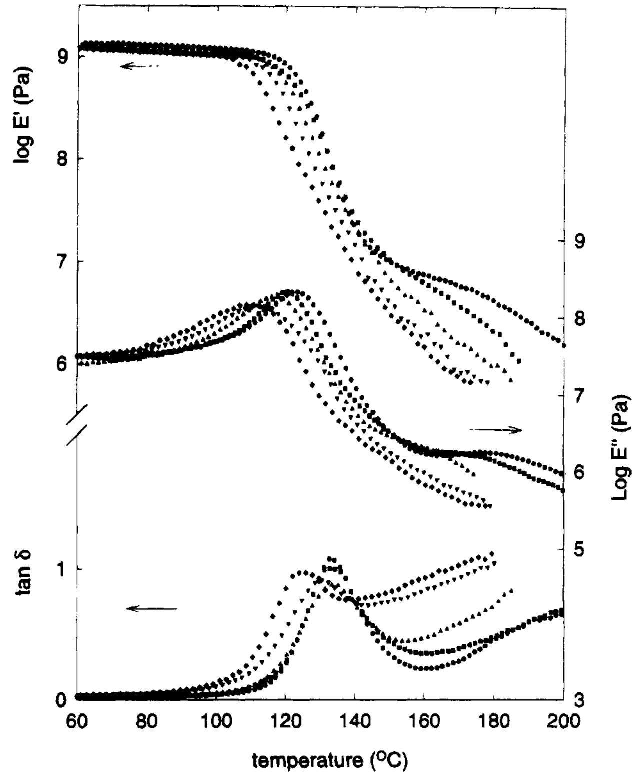


Figure 2. Dynamic Young's modulus and loss tangent as a function of temperature at 1 Hz for the Ba ionomer/oligomer blends. Ionomer/oligomer weight ratios: (●) 100/0, (■) 95/5, (▲) 90/10, (▼) 80/20, (◆) 60/40.

When oligomer is added, the primary glass transition region in the Cs series is clearly plasticized (Figure 1). The storage modulus curves are essentially displaced to lower temperatures, and the additional inflection

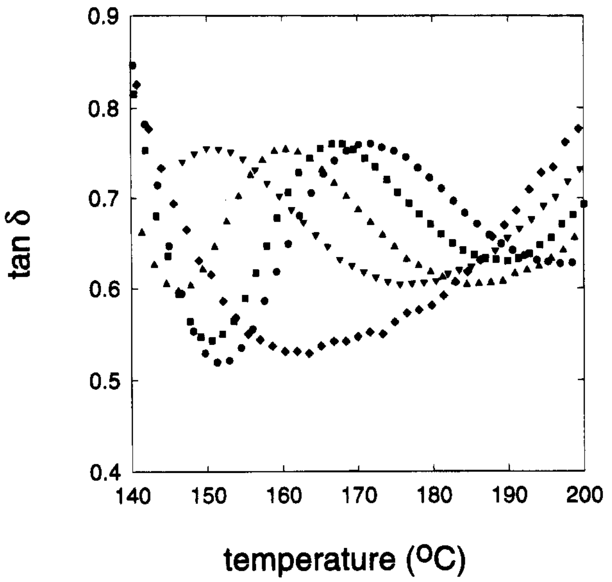


Figure 3. Loss tangent in the shear mode as a function of temperature at 1 Hz for the Cs ionomer/oligomer blends. Ionomer/oligomer weight ratios: (●) 100/0, (■) 99/1, (▲) 98/2, (▼) 97.5/2.5, (◆) 95/5.

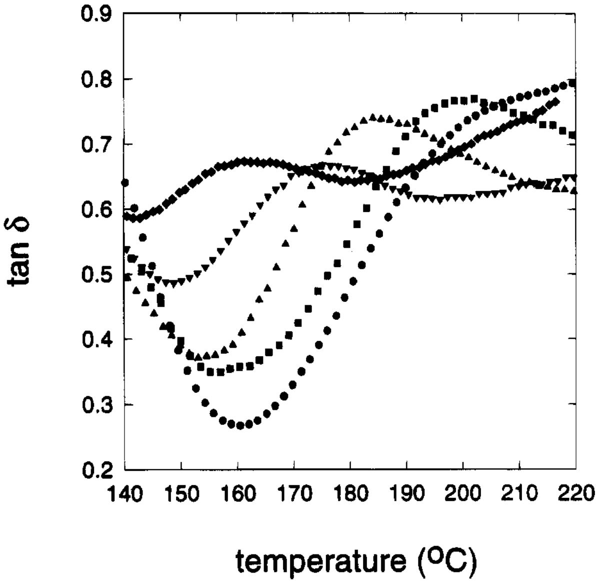


Figure 4. Loss tangent in the shear mode as a function of temperature at 1 Hz for the Ba ionomer/oligomer blends. Ionomer/oligomer weight ratios: (●) 100/0, (■) 95/5, (▲) 90/10, (▼) 80/20, (◆) 60/40.

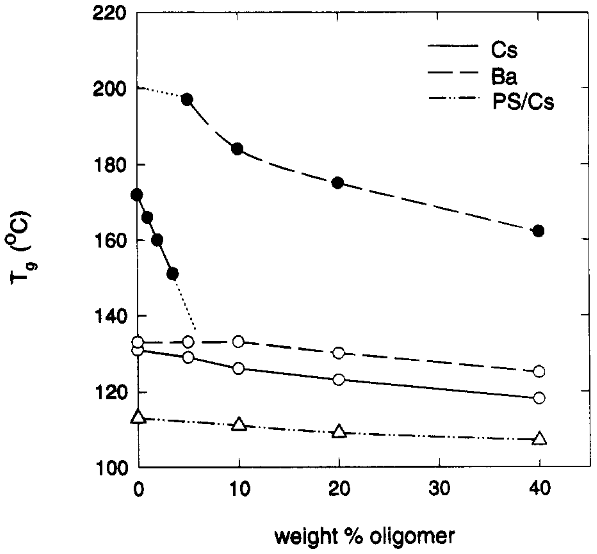


Figure 5. Glass transition temperatures, determined by the loss tangent maxima at 1 Hz, of the Cs and Ba ionomers as a function of oligomer concentration: (O) matrix T_g; (●) cluster T_g. The open triangles give the T_g's of the polystyrene/(Cs oligomer) blends.

point due to the clustered regions of the ionomer apparently disappears as oligomer is added. In the loss curves, the higher temperature relaxation in the ionomer similarly seems to disappear, and the intensity and the width of the primary glass transition tend to increase with oligomer content. The decrease in T_g, at a rate of about 0.3 °C/wt % oligomer, is significantly less than that predicted by the Fox equation,[19] an equation which is frequently applicable to conventionally plasticized polymers.[14] For example, at the 60/40 ionomer/oligomer composition, the experimental T_g is about 10 °C higher than the predicted T_g [in these calculations, 15 °C was added to the DSC-determined T_g's of the oligomers, which corresponds approximately to the difference we usually observe between the DSC and DMTA T_g's[5,6]].

In the Ba system (Figure 2), the oligomer is less effective in overall plasticization of the ionomer. The primary loss tangent maximum of the ionomer is decreased by less than 10 °C when 40 wt % oligomer is present. The width of the transition increases somewhat, but its intensity tends first to decrease with addition of oligomer, followed by a slight increase at higher oligomer concentrations. In both the Cs and Ba systems, the apparent Arrhenius activation energies of the glass transition are little affected by the oligomer, remaining approximately constant at 530 ± 30 kJ/mol. Most significantly, the cluster transition region appears to be less affected by the oligomer in the Ba system than in the Cs system.

In order to observe more clearly the effect of the oligomer on the cluster transition region, DMTA measurements were performed also in the shear mode at temperatures above the primary T_g. The results for the Cs system at oligomer contents of up to 5 wt % are shown in Figure 3. It is observed that the cluster T_g, whose loss tangent maximum is at *ca.* 170 °C in the ionomer alone, decreases rapidly with the addition of a small amount of oligomer, at a rate of about 6 °C/wt % oligomer; at 5 wt % oligomer, it has apparently merged with the primary glass transition. In contrast, the cluster transition of the Ba system, for which the loss tangent maximum of the pure ionomer is indistinct, but clearly at a much higher temperature than that for the Cs ionomer (we estimate it to be at about 200 °C), remains visible for all the blends studied (Figure 4); its maximum decreases at an average rate of about 1 °C/wt % oligomer. The apparent Arrhenius activation energy for the cluster transition of the Ba system increases somewhat from about 200 kJ/mol in the 95/5 blend to 270 kJ/mol in the 60/40 blend. That for the Cs system, at the composition where the transition is visible, is constant at about 220 kJ/mol. These activation energies are typical of those generally found for the cluster transition in polystyrene ionomers.[5,20]

The effects of the two oligomers on the matrix and cluster T_g's are summarized in Figure 5. This figure highlights two points. One, the cluster phase is more plasticized than the matrix phase by the short, monofunctional oligomers. Two, whereas the matrix phase is subject to only a little more plasticization in the Cs

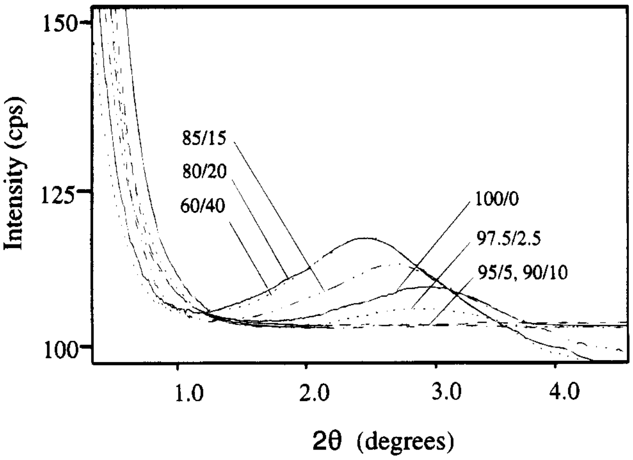


Figure 6. Small angle X-ray scattering profiles of the Cs ionomer/oligomer blends at the weight ratios indicated.

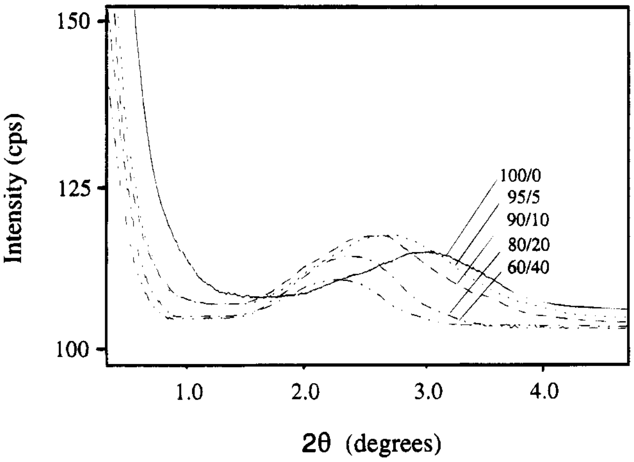


Figure 7. Small angle X-ray scattering profiles of the Ba ionomer/oligomer blends at the weight ratios indicated.

system than in the Ba system, the cluster phase in the Cs system undergoes dramatic plasticization compared to that of the Ba system.

Small Angle X-ray Scattering. The scattering profiles that were obtained for the Cs and Ba series are shown in Figures 6 and 7. The unblended ionomers show the typical diffuse "ionomer peak", whose maximum appears at $2\theta = 3.0°$ for both salts. This maximum corresponds to a Bragg spacing of 2.9 nm and compares well with that measured for Na– and Zn–carboxylated polystyrene.[21,22]

As oligomer is added to the Ba ionomer (Figure 7), the ionomer peak maximum is increasingly displaced toward smaller angles, and its intensity decreases. At the 60/40 composition, the peak maximum corresponds to a Bragg spacing of 4.2 nm.

The Cs system behaves quite differently (Figure 6). In the composition range corresponding to the rapid decrease in temperature and then disappearance of the cluster peak in DMTA analysis, the SAXS ionomer peak also decreases in intensity and is no longer visible at 5% oligomer content, nor at 10%. However, a peak appears again beyond 10% oligomer content, increasing in intensity and decreasing in scattering angle until 20% oligomer content. There is no further change on increasing the oligomer content to 40 wt %. At these compositions, the corresponding Bragg spacing of the maximum is 3.5 nm.

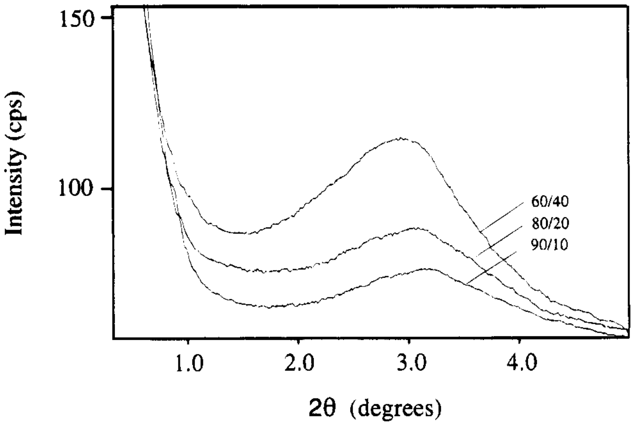


Figure 8. Small angle X-ray scattering profiles of the polystyrene/(Cs oligomer) blends at the weight ratios indicated.

This behavior was compared with that observed for blends of the Cs oligomer with the styrene homopolymer. As shown in Figure 8, a diffuse small angle peak at about $2\theta = 3°$ is also observed for these blends; it increases in intensity with addition of oligomer and undergoes only a slight displacement toward smaller diffraction angles, from an equivalent Bragg spacing of 2.7 nm at 10 % oligomer content to 2.9 nm at 40% oligomer content. Dynamic mechanical measurements of this system indicate a single T_g, which decreases moderately, with increasing oligomer content (Figure 5). The rate of decrease is much less than that predicted by the Fox equation, having decreased by only 5 °C at the 60/40 (w/w) PS/oligomer composition.

Discussion

General Features. Because of the presence of the ionic end groups in the short, monofunctional oligomers, identical to the ionic groups in the ionomers, it is expected that the oligomer molecules will participate strongly in the formation of the ionic aggregates and have less influence on the matrix T_g. The above data, showing the mild decrease in the matrix T_g (much less than that predicted by the Fox equation) and the much stronger influence on the cluster T_g, entirely support this supposition. The general trends are similar to those observed by Kim *et al.*[12] for the (sodium–sulfonated polystyrene)/(sodium dodecylbenzenesulfonate) blends. From this point of view, the nature of the nonpolar portion of the oligomers, *whether identical or not* to that of the ionomer, appears unimportant—at least for these relatively short oligomers. In both cases, association of the ionic groups of the oligomer with those of the ionomer necessarily involves placement of the nonpolar portion of the oligomer in the region of restricted mobility surrounding each ionic aggregate.[12] This increases their mobility by addition of free volume; and, since most (although not all) of the multiplets are found in the clusters, it is principally the cluster phase that is affected.[4,6,12] The presence of a minor amount of isolated multiplets or even lone ion pairs can account for the modest decrease in the matrix T_g with added oligomer.[12] It is noteworthy that the surfactant system of Kim *et al.* resembles the behavior of the Ba system more than that of the Cs system.

The general effect of the monofunctional oligomer on the ionomer contrasts sharply with that of a nonfunctionalized styrene octamer, S8, which partitions preferably into the matrix phase where there are fewer ionic groups to inhibit its solubility; the matrix T_g is thus reduced much more than the cluster T_g.[5] The above effect also contrasts with that in the ionomer/surfactant

Table 1. Nature of the Effective Cross-Link Provided by a Single, Neutralized Ion Unit and a Pair of Ion Units in the Cs and Ba Systems

cation	elementary ion unit	nature of effective cross-link
Cs^+	$Cs^{+-}OOC$---	none
Ba^{2+}	---$COO^{-+}Ba^{+-}OOC$---	ionic

cation	ion unit pair	nature of effective cross-link
Cs^+	$Cs^{+-}OOC$--- ---$COO^{-+}Cs$	dipolar
Ba^{2+}	---$COO^{-+}Ba^{+-}OOC$--- ---$COO^{-+}Ba^{+-}OOC$---	ionic and dipolar

mixture poly(ethyl acrylate-*co*-sodium acrylate)/(sodium hexadecanoate), where the surfactant remains crystalline to well above the cluster transition, and therefore virtually affects neither T_g in the ionomer.[7]

Although the general trends are similar for the Cs and the Ba systems, the effect in the Cs system is much more dramatic, in that the cluster T_g is actually lost with the addition of 5% oligomer. At first sight, one might think that the cluster T_g for the Cs system simply merges with that of the matrix T_g as oligomer is added, without necessarily perturbing significantly the ionic aggregate structure. However, the SAXS data tell us that something more fundamental occurs, since the ionic peak arising from the most prevalent spacings between multiplets[2] also disappears at 5 wt % oligomer content. The reappearance of a peak at higher oligomer contents suggests, furthermore, that a reorganization of the ionic aggregate structure has taken place. However, before we conjecture about possible morphologies in the Cs ionomer/oligomer system, the striking difference in the behavior of the Cs and Ba systems should be addressed.

Electrostatic Interaction Strengths and Their Consequences. The source of the differences in behavior between the Cs and Ba systems is necessarily related to the size and valence of the counterions. First, the ionic radius of the Ba cation (0.135 nm) is smaller than that of the Cs cation (0.169 nm), which already results in stronger electrostatic interactions in the Ba system than in the Cs system. However, by itself this is probably not enough to explain the difference in behavior of the two systems. For example, it was noted in halatotelechelic poly(butadienedicarboxylates) that, even when the ionic radius is taken into account, the alkaline earth carboxylates have a much more elastic behavior than the alkali carboxylates.[23,24] Now, the monovalent Cs^+ cations form ion pairs with the carboxylate anions (COO^-Cs^+), which at this level do not introduce any effective cross-links, whereas the divalent Ba^{2+} cations form ion triplets ($COO^+Ba^{+-}OOC$) that in themselves can already act as ionic cross-links. Furthermore, interactions between carboxylate groups in the former case are dipolar in nature, whereas in the latter case they are both dipolar and ionic. This means that the cross-linking effects of the ionic aggregates are based on dipolar interactions in the Cs system and on both dipolar and ionic interactions in the Ba system. The situation is summarized in Table 1, where the simplest and the next simplest ion units are shown.

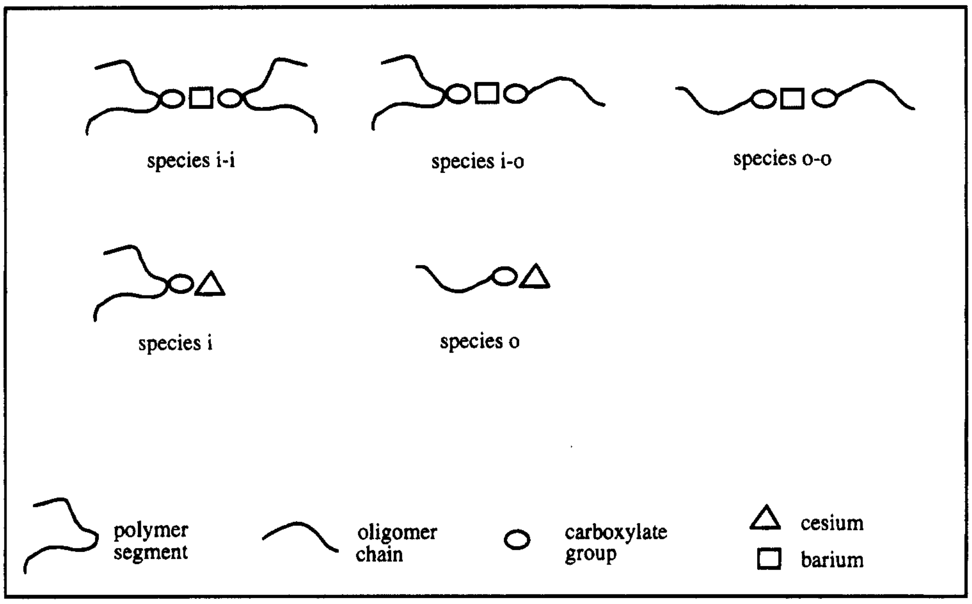
When ionic interaction strengths (which fall off as 1/distance) are significantly greater than dipolar interaction strengths (which fall off as 1/distance^3), the distinctions made in Table 1 can have important consequences. In particular, *the nature and strength of the effective cross-links necessarily affect the cluster phase*, whose characteristics depend on the strength and stability of the ionic aggregates. The DMTA data for the pure ionomers and, as noted above, the data for the halatotelechelic polymers show that, in the pure ionomer, the effective cross-links provided by Ba give rise to multiplets which are much more thermally stable than those of Cs. Clearly, then, the ionic (plus dipolar) interactions in the Ba system are much stronger than the dipolar interactions in the Cs system. By contrast, for the Na sulfonate ion pairs in the system studied by Kim *et al.*,[12] the dipolar interactions alone are much stronger than those for the Cs carboxylates, and they are probably comparable in strength to the ionic forces in Ba carboxylates, thus also giving rise to stable multiplets; this would account for the similarity in behavior of the Ba carboxylate and the Na sulfonate systems noted above.

Since the stability of the cluster phase is related to *the ease of ion-hopping*, we can examine specifically the consequences of the valency on this aspect. If ion-hopping of one carboxylate group from one multiplet to another is considered, then in the Cs ionomer this involves a neutral ion pair and breakage of dipolar attractive forces, whereas in the Ba ionomer, this involves not only breakage of both ionic and dipolar attractive forces but also migration of a charged ion or ion pair, which is still less energetically favorable. If electroneutrality is respected, then ion-hopping must involve the elementary ion unit. In the Ba ionomer, this means ion triplets, and hence the cooperative motion of two chain segments, whereas the neutral Cs ion pair involves only one chain segment: this, too, is energetically expensive for the Ba case.

Let us go to a step further with the concept of the elementary ion unit. When the two ionomers are blended with their respective oligomers, the molecular consequences, illustrated in Table 2, are the following. In the first place, each Cs carboxylate ion pair involves either an ionomer segment or an oligomer molecule, and it interacts with other ionomer segments or oligomer molecules via dipolar interactions only. With Ba as the counterion, the interactions involving ion triplets are both ionic and dipolar, which, as argued above, implies much more stable or stronger interactions between ionomer segments and oligomer molecules. The triplets themselves can be divided into three species (see Table 2): one involving two ionomer segments (species i–i), one involving one ionomer segment and one oligomer chain (species i–o), and a third one involving two oligomer chains (species o–o). Let us suppose, to a first approximation, that the elementary ion units form undissociable entities. Then, clearly, the last species must have more mobility than the first two. Similarly, the Cs ion pair at the end of an oligomer chain (species o) must have considerably more mobility, and hence ion-hopping ability, than that attached to the polymer segment (species i). Species o–o in the Ba system and species o in the Cs system can thus be considered as the most active species in weakening the multiplets, and therefore in affecting the thermal stability of the cluster phase.

This sets the stage for considering the effect of the oligomer on the cluster phase of the ionomer in each system as a function of oligomer concentration. We will examine the Ba system first, assuming that, when the ionomer and oligomer are blended in solution, *the three species of ion triplets form randomly* and are a function only of the relative concentrations of ionomer and oligomer carboxylate anions. When the oligomer concentration is low, species i–i is the predominant species.

Table 2. Types of Single Ion Unit Species Present in the Cs and the Ba Ionomer/Oligomer Blends, Where i and o Represent Ionomer and Oligomer Chains, Respectively



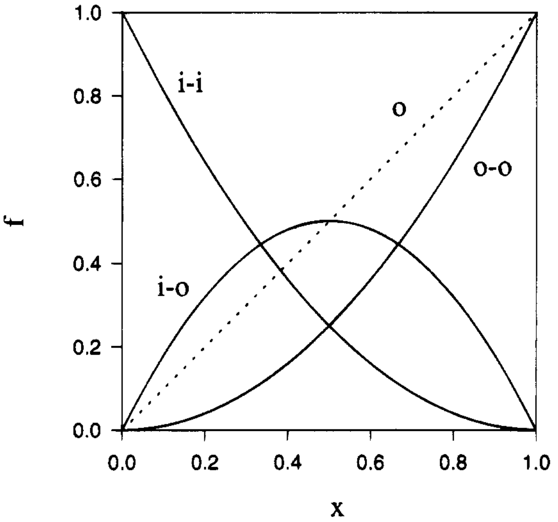


Figure 9. Schematic diagram of the molar fraction, *f*, of ion unit species as a function of the molar fraction, *x*, of oligomer chains in the ionomer/oligomer blends. The solid lines indicate the three species (Table 2) in the Ba system, and the broken line indicates species o in the Cs system.

Upon addition of more oligomer, species i–o and then species o–o become important. The relative proportions of the three species, described by Bernouillian probabilities, are shown in Figure 9 as a function of the molar fraction of oligomer molecules.

It is instructive to examine the situation at a molar fraction of 0.5, which corresponds to approximately 40 wt % oligomer content. At this composition, 75% of the ion triplets are composed of species i–i and i–o and only 25% of species o–o. By contrast, in the Cs system, the molar fraction of species o corresponds exactly to the molar fraction of oligomer carboxylate groups present (as indicated by the dotted line in Figure 9). At all molar fractions between 0 and 0.5, there are thus more than twice as many species o in the Cs system than there are species o–o in the Ba system at the same molar fraction. (Moreover, with just one rather than two oligomer chains attached to the ion unit, species o can be considered to be even more mobile than species o–o.) From this point of view, and combined with the fact that the ionic aggregates in the Cs ionomer are already much less thermally stable than those in the Ba ionomer, it is understandable that the cluster phase in the Cs system is apparently destabilized, even destroyed, by small amounts of added oligomer, whereas the Ba system simply undergoes gradual plasticization without destruction of the cluster phase up to the oligomer concentrations studied, according to both the DMTA and SAXS results. Furthermore, with the electrostatic interactions being weaker for the Cs carboxylates than for the Ba carboxylates, it apparently does not take much to essentially dissolve the Cs ion pairs in the polystyrene matrix at low oligomer concentrations. This paves the way for the development of a new morphology at higher oligomer concentrations.

Morphologies. First of all, it is useful to consider the morphology in the homopolystyrene/(Cs oligomer) blend, where a SAXS peak is also present. In this system, it is difficult to envisage anything other than the formation of inverted micelles of oligomer molecules within a polystyrene matrix; in other words, the ionic end groups of the oligomer chains aggregate to form the core, and the styrene chains are pointed outward where they can mix with the polystyrene matrix. This is the same structure as is observed with multiplets, except that the styrene segments attached to the ionic groups are not covalently linked to polystyrene chains. The free tails of the inverted micelles likely introduce sufficient additional free volume to decrease moderately the T_g of the matrix.

We must then consider if the SAXS peak arises from intra- or interparticle scattering. If intraparticle scattering, the increase in intensity of the peak as oligomer concentration is increased, along with the modest displacement to smaller angles, can be easily explained as an increase in the number of inverted micelles, with only a minor effect on their size. However, given the similarity in structure of these blends to traditional ionomers, it seems more satisfactory to interpret the data as arising from interparticle scattering, as is generally accepted now for ionomers.[2] It is necessary, in this case, to postulate that inverted micelles of an optimal size aggregate to an optimal average distance of closest approach. Then, the increase in intensity of the SAXS peak with added oligomer can again be attributed to an increasing number of the inverted micelles, with a minor effect on their size. This postulate is supported by data obtained by Shull *et al.*[25,26] for block copolymer micelles in high molecular weight homopolymer matrices, for which it is argued that the observed segregation of the micelles is in part due to "attractive interactions between polymer brushes". One of the contributions mentioned is related to the interface between the homopolymer and micellar corona which reduces the number of available polymer conformations in the vicinity of the micelle, and hence increases the (entropic) free energy of the system; this creates a driving force toward micellar segregation (shown for the block copolymer micelles to be near the surface) in order to minimize the number of sharp interfaces.[25]

Now, inverted micelles of oligomer may also form in the blends with the ionomer, in this case with ionic groups from the ionomer incorporated in the core. When this happens, there is no clear distinction between multiplets (involving covalent bonds with the matrix) and inverted micelles (without covalent attachments to the matrix); rather, as oligomer content is increased, one can imagine that multiplets gradually evolve into inverted micelles. This explanation seems consistent with the data for the Ba system, where changes in both the SAXS ionic peak and the DMTA glass transition temperatures are gradual. The incorporation of oligomer molecules into the multiplets may be responsible for the increase in the apparent Bragg distance between multiplets, by virtue of the styrene tails swelling the styrene matrix between the ionic cores. As polar plasticizers, the oligomer molecules may also facilitate rearrangement of the ionic aggregates into a smaller number of larger multiplets. The latter explanation has been advanced to rationalize the SAXS data of other polar-plasticized ionomers, for which the ionic SAXS peak also decreases in scattering angle as plasticizer content is increased.[4,8,9] In our system, the intensity of the maximum decreases with added oligomer. A possible explanation for this is that the ionic cores gradually become less defined as the multiplets grow, due to a certain amount of styrene material being forced into the core to accommodate the ion-pair aggregation; it is also possible that some of the multiplets become destabilized and the ionic groups dispersed (or solubilized) in the styrene matrix as the number of participating oligomer molecules increases.

In the Cs system, apparent destabilization of the ionic aggregates occurs at low oligomer contents, for the reasons explained earlier. At higher oligomer contents, detectable morphological features reappear in the SAXS data. Although other explanations are not excluded, we propose that there is a new morphology at high oligomer contents. The good intensity compared to the pure ionomer indicates that the scattering centers are at least as well-defined as those in the pure ionomer. On the other hand, the Bragg distance for the blends of high oligomer content is significantly greater than for the pure ionomer; if the SAXS peak is due to interaggregate scattering (as proposed by the EHM model), the observed Bragg distance implies that there are fewer, and hence necessarily much larger, aggregates in the blends than in the pure ionomer. It seems difficult to reconcile large multiplet sizes with the good scattering contrast observed in the blends (and, in addition, go through a point in oligomer content where both the SAXS peak and DMTA T_{g_2} peak disappear) without evoking some morphological transformation where the oligomer chains are accommodated in such a way that the scattering centers are well-defined.

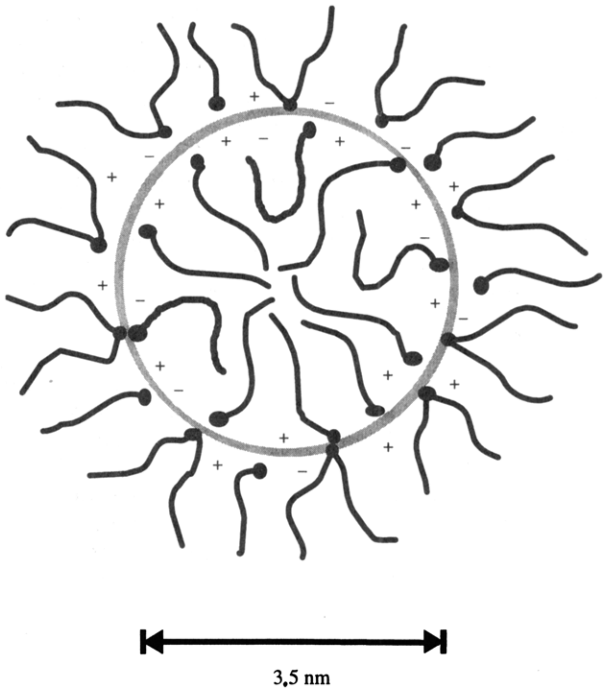


Figure 10. Schematic diagram of a micelle (or inverted multiplet) with oligomer chains at the core and ionomer segments and some oligomer chains radiating outward. The gray ring represents the ionic interface, and the diameter given is a translation of the SAXS maximum.

An intriguing possibility for a new morphology is the formation of micelles, or "inverse multiplets", as illustrated in Figure 10. The representation shows the styrene tails of the oligomer molecules forming the heart of the micelles, whereas the ionic head groups are located at the periphery where they can associate with the ionic groups of the ionomer. In this situation, there would be essentially no ionic groups in the core of the micelle and very few in the zone just outside the ionic shell, thus creating a good electron contrast between the ionic and nonionic regions. The small angle peak may then be considered to be due to intraparticle interference, and the corresponding Bragg spacing would be associated with the diameter of the micelles. This interpretation is similar to that proposed by MacKnight *et al.*,[1,27] a core–shell model to describe ionomer microstructure (although without the inner nonpolar core as in our case). It is reasonable that a diameter of 3.5 nm for the nonpolar core, according to the SAXS data, can accommodate disordered oligomer styrene chains of about 2.5 nm contour length. Furthermore, it is reasonable that, once the new morphology is well-developed, the spacing is little affected by the addition of still more oligomer, if it is more likely to influence the number of micelles rather than their size.

One might think it unlikely that such micelles would be stable at oligomer contents higher than 40 wt %, given that the ratio of oligomer ionic groups to ionomer ionic groups begins to exceed 1 at this composition. However, some of the oligomer styrene tails may be oriented outward from the ionic shell. It may also be thought that the formation of such micelles would cause a new cluster transition to appear. However, the disordered alkyl tails at the core of the micelles, along with some perhaps directed into the ionomer matrix, probably render these aggregates insufficiently rigid to have a stiffening effect on the ionomer segments in their vicinity; they may even contribute to the mild plasticization observed for the matrix at the higher oligomer concentrations. It should be emphasized that the evolution from the normal cluster morphology to the new morphology with increasing oligomer content in the Cs system is progressive, with no abrupt transition evident in the dependence of the matrix T_g on oligomer content; this is also consistent with the continuing presence of alkyl chains directed into the ionomer matrix.

Conclusions

Preferential plasticization of the ionomer cluster phase is observed for blends of biphasic, carboxylated polystyrene ionomers with chemically identical, short monofunctional oligomers. This can be easily attributed to participation of the ionic head groups of the oligomer in the ionomer multiplets, which introduces free volume and thereby reduces the cluster transition temperature. This result is similar to that observed earlier for a blend in which the oligomer tail is dissimilar to the ionomer matrix,[12] suggesting that, for short, monofunctional oligomers, the nature of the tail is relatively unimportant to the plasticization behavior.

On the other hand, the nature and strength of the electrostatic interactions involved can be of critical importance. This was highlighted by a comparison of the behavior in Cs and Ba blends, the effective cross-links in the Cs blend being characterized by relatively weak, dipolar interactions and those in the Ba blend by both ionic and dipolar interactions. Whereas the cluster transition in the Ba blend is clearly plasticized but not destroyed, that in the Cs blend disappears at low oligomer concentrations. Furthermore, it seems that a new morphology forms at higher oligomer concentrations in the Cs system, proposed to be micelles or "inverted multiplets". This significant difference in behavior can be attributed to the greater stability of the multiplets in the Ba system compared to that in the Cs system.

Acknowledgment. C.G.B. and M.P. gratefully acknowledge the financial support of NSERC (Canada) and FCAR (Québec) for this research. R.J. is grateful to the "Services Fédéraux des Affaires Scientifiques, Techniques et Culturelles" (SSTC) for financial support in the framework of the "Pôles d'Attraction Interuniversitaires: Polymères". The "Ministère de l'Enseignement Supérieur et des Sciences du Québec" and the "Communauté Française de Belgique" are acknowledged for providing funds for a cooperative program. We also thank Dr. Bryn Hird for providing the recipe for the synthesis of the carboxylated polystyrene before its publication.

References and Notes

(1) Eisenberg, A.; King, M. *Ion-Containing Polymers, Physical Properties and Structure*; Academic Press: New York, 1977.
(2) Eisenberg, A.; Hird, B.; Moore, R. B. *Macromolecules* **1990**, *23*, 4098.
(3) Lundberg, R. D.; Makowski, H. S.; Westerman, L. *Adv. Chem. Ser.* **1980**, *187*, 67.
(4) Bazuin, C. G. In *Multiphase Polymers: Blends and Ionomers*; Utracki, L. A., Weiss, R. A., Eds.; ACS Symposium Series 395; American Chemical Society: Washington, DC, 1989; Chapter 21 (see also references therein). This article reviews plasticization studies of ionomers dating before 1989.
(5) Villeneuve, S.; Bazuin, C. G. *Polymer* **1991**, *32*, 2811.
(6) Tong, X.; Bazuin, C. G. *J. Polym. Sci., Part B: Polym. Phys.* **1992**, *30*, 389. Neagu-Plesu, R.; Bazuin, C. G. *J. Polym. Sci., Part B: Polym. Phys.* **1991**, *29*, 1305.
(7) Tong, X.; Bazuin, C. G. *Chem. Mater.* **1992**, *4*, 370. Natansohn, A.; Bazuin, C. G.; Tong, X. *Can. J. Chem.* **1992**, *70*, 2900.
(8) Galin, M.; Mathis, A.; Galin, J.-C. *Macromolecules* **1993**, *26*, 4919.
(9) Weiss, R. A.; Fitzgerald, J. J.; Kim, D. *Macromolecules* **1991**, *24*, 1064.
(10) Gauthier, M.; Eisenberg, A. *Macromolecules* **1989**, *22*, 3756.
(11) Wollmann, D.; Williams, C. E.; Eisenberg, A. *Macromolecules* **1992**, *25*, 6775.
(12) Kim, J.-S.; Roberts, S. B.; Eisenberg, A.; Moore, R. B. *Macromolecules* **1993**, *26*, 5256.
(13) Plante, M. Ph.D. Thesis, Chemistry Department, Laval University, Quebec, 1993.
(14) Bazuin, C. G.; Eisenberg, A. *J. Polym. Sci., Part B: Polym. Phys.* **1986**, *24*, 1137.
(15) Wignall, G. D.; Ballard, D. G. H.; Schelten, J. *Eur. Polym. J.* **1974**, *10*, 861.
(16) Broze, G.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1982**, *15*, 920.
(17) Vanhoorne, P.; Jérôme, R.; Teyssié, P.; Lauprêtre, F. *Macromolecules* **1994**, *27*, 2548.
(18) Hird, B.; Eisenberg, A. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 1377.
(19) Fox, T. G. *Bull. Am. Phys. Soc.* **1956**, *2*, 123.
(20) Hird, B.; Eisenberg, A. *J. Polym. Sci., Part B: Polym. Phys.* **1990**, *28*, 1665.
(21) Hird, B.; Eisenberg, A. *Macromolecules* **1992**, *25*, 6466.
(22) Tomita, H.; Register, R. A. *Macromolecules* **1993**, *26*, 2791.
(23) Broze, G.; Jérôme, R.; Teyssié, Ph. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 2205.
(24) Horrion, J., Jérôme, R.; Teyssié, Ph.; Marco, C.; Williams, C. E. *Polymer* **1988**, *29*, 1203.
(25) Shull, K. R.; Kramer, E. J.; Hadziioannou, G.; Tang, W. *Macromolecules* **1990**, *23*, 4780.
(26) Shull, K. R.; Winey, K. I.; Thomas, E. L.; Kramer, E. J. *Macromolecules* **1991**, *24*, 2748.
(27) MacKnight, W. J.; Taggart, W. P.; Stein, R. S. *J. Polym. Sci., Polym. Symp.* **1974**, *45*, 113.

MA941212H