Blends of an Amorphous Ionomer with Crystalline Small Molecules Bearing a Similar Functional Group

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As part of a series of investigations of different families of blends of ionomers with functionalized small molecules and oligomers, the study reported here focuses on a poly(ethyl acrylate-*co*-sodium acrylate) ionomer blended with sodium hexadecanoate (C16Na) and hexadecanoic acid (C16H). The main techniques used are dynamic mechanical thermal analysis (DMTA) and differential scanning calorimetry (DSC). Whether in the ionomer or in the parent polymer, the crystalline component remains crystalline, and hence phase-separated, in the blend. It reinforces the rubbery regions of both polymers but has no significant effect on the glass transition temperature. C16Na also does not affect the cluster transition of the ionomer. It is concluded that there is minor interaction between the ionic groups in the ionomer and in C16Na, although interfacial polar interactions between the two components may occur. On the other hand, C16H drastically decreases the cluster transition temperature and is itself significantly affected by the ionomer. Through infrared spectroscopy, these effects are shown to be due to ion exchange having occurred between the ionomer and C16H during sample preparation.

Introduction

In preceding contributions,[1,2] results were presented of plasticization of a microphase-separated poly(ethyl acrylate) ionomer (PEA-i), containing carboxylate groups, by an amine-functionalized linear molecule, namely, 4-decylaniline. With the carboxylate groups of the ionomer already neutralized with Na ions, there is little or no interaction between the carboxylate groups of the ionomer and the amine groups of the small molecule. On the other hand, the amine groups interact preferentially with ester groups in the ethyl acrylate side chains. This causes 4-decylaniline, despite its polar head group, to behave like a typical nonpolar ionomer plasticizer in that it decreases the matrix and cluster glass transitions of the ionomer equally.

In this contribution, we examine the same ionomer when it is blended with crystalline small molecules possessing an alkyl chain as in the above contribution, but with a functional group that is identical or similar to that of the ionomer. In these blends, there would be no preferential interactions between the ionic or functional groups of the ionomer and that of the small molecule, since the groups are of the same type. However, there is the possibility of dipolar-type association among the ionic groups of the two components in the blend, particularly since, as is well-known, the ionic groups in the ionomer itself associate via dipole–dipole interactions that result in multiplets and clusters and thereby form the basis of a unique microstructure in these materials.[3,4] The extent to which such an association is realized in the ionomer/small molecule blends, and the resulting properties, is thus the focus of this contribution. To this end, sodium hexadecanoate (C16Na) was chosen as the small molecule functionalized by ionic groups identical to those of the ionomer. Hexadecanoic acid (C16H), which can be considered to have functional groups similar to those of the ionomer, is also examined. Poly(ethyl acrylate)-based ionomers were chosen for their low glass transition temperature, thus allowing easy access to the higher temperature, or cluster, *transition associated with microphase-separated ionomers.* At the same time, the effect of a higher polarity matrix on the interactions in the ionomer/small molecule blends can be investigated.

Studies of the effects of the interactions in blends of ionomers and functionalized small molecules or oligomers have a special bearing on investigations of blends of two ionomers. It is now established that compatibility in ionomer blends based on immiscible parent polymers can be achieved through specifically interacting functional groups.[5] On the other hand, brief attention given to a blend of two ionomers possessing *similar* ionic groups indicated that general Coulombic interactions, in contrast to specific interactions, are not sufficient to significantly increase the degree of compatibility relative to the parent homopolymer blends.[6] The ionomer/small molecule blends investigated in this paper can be considered, from the point of view of the enthalpic interactions, to be a model system for blends of an amorphous ionomer and a semicrystalline ionomer with identical or similar ionic groups.

Only a few investigations of ionomer/small molecule blends, where the small molecule possesses one or more linear alkyl chains or is oligomeric, have been reported.[7] Those which are most closely related to the present investigation and which have been the most studied involve sulfonated EPDM (SEPDM) ionomers and metal stearates, especially Zn-neutralized SEPDM and Zn stearate ($ZnSt_2$).[8-13] The ionomer possesses sulfonate ionic groups,

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[1] Tong, X.; Bazuin, C. G. *J. Polym. Sci., Polym. Phys. Ed.*, in press.

[2] Neagu-Plesu, R.; Bazuin, C. G. *J. Polym. Sci., Polym. Phys. Ed.* 1991, *29*, 1305.

[3] Eisenberg, A.; King, M. *Ion-Containing Polymers, Physical Properties and Structure*; Academic Press: New York, 1977.

[4] Eisenberg, A.; Hird, B.; Moore, R. B. *Macromolecules* 1990, *23*, 4098.

[5] Smith, P.; Hara, M.; Eisenberg, A. In *Current Topics in Polymer Science*; Ottenbrite, R. M., Utracki, L. A., Inoue, S., Eds.; Hanser Publishers: New York, 1987; Vol. II, p 255.

[6] Smith, P.; Eisenberg, A. *J. Polym. Sci., Polym. Lett. Ed.* 1983, *21*, 223.

[7] The reader may refer to the following review article on plasticization in ionomers: Bazuin, C. G. ACS Symp. Ser. 1989, *395*, 476.

[8] Makowski, H. S.; Lundberg, R. D. *Adv. Chem. Ser.* 1980, *187*, 37.

[9] Makowski, H. S.; Agarwal, P. K.; Weiss, R. A.; Lundberg, R. D. *ACS Polym. Prepr.* 1979, *20*, 281.

[10] Agarwal, P. K.; Makowski, H. S.; Lundberg, R. D. *Macromolecules* 1980, *13*, 1679.

[11] Weiss, R. A. *J. Appl. Polym. Sci.* 1983, *28*, 3321.

[12] Duvdevani, I.; Lundberg, R. D.; Wood-Cordova, C.; Wilkes, G. L. *ACS Symp. Ser.* 1986, *302*, 184.

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the small molecule a carboxylate ionic group. It was observed that the mechanical properties of SEPDM are enhanced by the presence of ZnSt$_2$, which is crystalline at ambient temperature. It has been inferred from differential scanning calorimetry and X-ray data that interactions are present between the ionic groups in SEPDM and the crystalline ZnSt$_2$.[11-13] Furthermore, the melt rheological properties of the ionomer are improved due to presumed solvation of the ionic groups by the ZnSt$_2$ which is above its melting point in the melt region of the blend.[8-10] In contrast to the SEPDM/ZnSt$_2$ system, the ionic groups of the ionomer and the small molecule in the PEA-i/C16Na system reported here are identical. Moreover, C16Na remains unmelted throughout the temperature range investigated. The small molecule in the PEA-i/C16H system, however, does melt in the accessible temperature range. The relatively high polarity of the PEA matrix compared to the EPDM matrix may also have some significance. With the distinctions between the three systems in mind, it will be of interest to compare the results obtained in each case.

Experimental Section

Sample Preparation. The synthesis of the PEA homopolymer and subsequent treatment of the homopolymer, via partial saponification, to obtain the sodium-neutralized carboxylated ionomer of various ion contents have been described elsewhere.[1,14,15] In the study reported here, results are given exclusively for the ionomer containing 10 mol % sodium carboxylate (to be referred to simply as PEA-i) and compared with those for the homopolymer (PEA).

Sodium hexadecanoate, C16Na, and hexadecanoic acid, C16H, were purchased from Aldrich and used as received. They were reported to have the following purities: C16Na, 98%; C16H, 99%.

The blends were prepared by dissolving dried polymer and small molecule, in the desired weight ratio, in a 1% benzene/methanol (50/50 v/v) solution, stirred for about 15 h, and freeze-dried. Blends of ionomer and C16Na were also prepared in a solution of ethanol/water (95/5), and the solvent was removed through evaporation. All blends were ultimately dried under reduced pressure for 4–5 days at 55 °C for C16H and 70 °C for C16Na. The solutions, in all cases, were completely clear.

Samples were molded to the required form under 2 metric tons of compression at T_g + 100 °C for 20 min, followed by free cooling to room temperature before removal of the sample from the mold. Prior to measurements, the prepared samples were stored under reduced pressure in a desiccator containing CaCl$_2$. *All molded blends were turbid at room temperature, becoming increasingly so as C16Na or C16H content increased. Above about 30% C16Na blended with PEA-i, the blends were essentially opaque. It was noted that blends of C16H with PEA and PEA-i are generally transparent at molding temperatures and become turbid on cooling.*

Analysis Techniques. Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer DSC-4, calibrated with indium. Scanning rates were 20 °C/min. Glass transition temperatures were identified with the midpoint of the transition in the heating curves, as determined by means of extrapolated baselines below and above the transition. First-order transition temperatures were defined as the maxima of endothermic or exothermic peaks.

Dynamic mechanical thermal analysis (DMTA) was performed using a Polymer Laboratories dynamic mechanical thermal analyzer. Measurements were performed at five frequencies (0.3, 1, 3, 10, and 30 Hz) with a deflection of 64 μm and a heating rate of 1 °C/min. The sample chamber was constantly flushed with a light flow of dry nitrogen. All samples were analyzed in the dual cantilever bending mode, for which rectangular bars of dimensions 35 × 10 × 2 mm were molded and a free length of 5 mm was used. Although the bending mode data are generally valid for the entire range of modulus values investigated in this study, certain samples were also analyzed in shear mode, for which twin disks of 12-mm diameter and 2.5-mm thickness were prepared. The shear mode data (valid for moduli of less than about $10^{7.5}$ N/m^2) qualitatively confirmed the bending mode data. However, features above the glass transition, especially in the loss curves, are often better observed and more noise-free in shear mode than in bending mode, according to our experience with the instrument used. When this was true for the DMTA results presented in this paper, the shear mode data was chosen for presentation over the bending mode data in the regions where the former were more satisfactory.

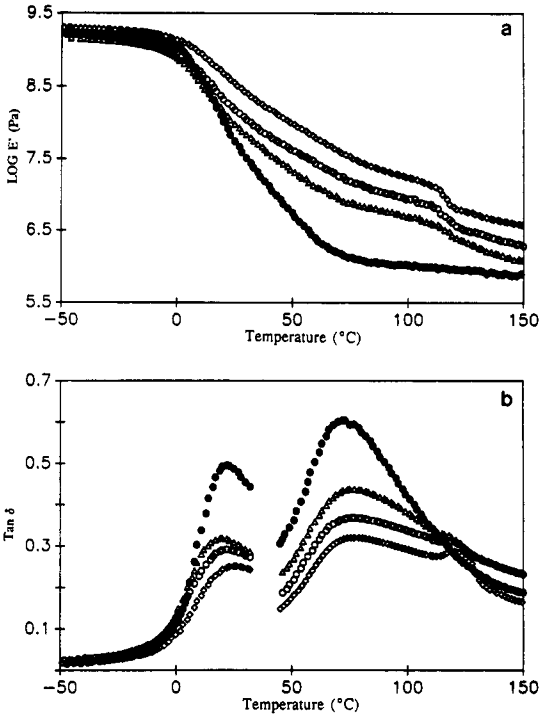

Figure 1. Dynamic storage modulus (a) and loss tangent (b) at 1 Hz versus temperature for PEA-i/C16Na blends. Wt % C16Na content: ●, 0; △, 12; ○, 22; ◇, 36.

Infrared spectra were obtained with a Mattson FTIR spectrometer from 200 interferograms at a resolution of 2 cm^{-1}. Films of ca. 30-μm thickness were prepared by solvent casting 50/50 (v/v) benzene/methanol solutions of 2% solute onto a KBr window, with subsequent drying under reduced pressure at 50 °C for 1–2 days.

Results and Discussion

Blends with Sodium Hexadecanoate. Dynamic Mechanical Thermal Analysis. Young's storage moduli and loss tangent curves as a function of temperature at 1 Hz are shown in Figure 1 for PEA-i blended with various percentages of C16Na. In the case of the loss tangent curves shown, for reasons explained in the Experimental Section, the data in the lower temperature region were obtained in bending mode, those in the higher temperature region in shear mode. In fact, all of these blends were measured in both bending and shear mode for samples prepared in two different solvent systems: the four sets of curves were qualitatively identical.

There are several observations to be made. First, the rubbery region (Figure 1a) of the ionomer is increasingly reinforced as the percentage of C16Na in the blend is increased, approximately by 1.10 Pa/wt % C16Na as estimated at 100 °C. Second, a small decrease in the modulus occurs at ca. 120 °C, becoming more significant as C16Na concentration increases; above this transition, the

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(13) Weiss, R. A.; Sen, A.; Galambos, A. F.; Koberstein, J. T.; Russell, T. P. *Polym. Mater. Sci. Eng.* **1988**, *59*, 176.

(14) Simmons, A. M.Sc. Thesis, McGill University, Montreal, 1986.

(15) Simmons, A.; Natansohn, A.; Eisenberg, A. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 2221.

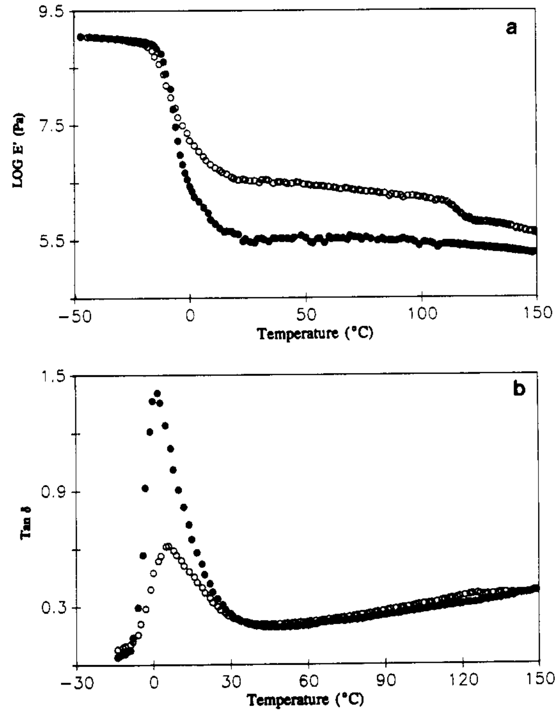

Figure 2. Dynamic storage modulus (a) and loss tangent (b) at 1 Hz versus temperature for PEA (●) and for PEA blended with 21 wt % C16Na (○).

modulus continues to show reinforcement proportional to the C16Na concentration in the blend. Third, the loss tangent curves (Figure 1b) show that the two transitions characteristic of the (microphase-separated) ionomer—the lower one to be called the T_g (matrix glass transition) and the higher one the T_i (ionic or cluster transition)—both diminish progressively in intensity but remain approximately constant in temperature as C16Na concentration in the blend increases. All T_g values measured from the loss tangent maxima shown are in the range of 21 ± 4 °C and the T_i values in the range of 75 ± 3 °C. Finally, the small relaxation observed at ca. 120 °C in the storage moduli curves of the blends is also evident as a transition in the loss tangent curves at about the same temperature. For all samples studied, the apparent Arrhenius activation energies calculated from the loss tangent maxima at five different frequencies were constant as a function of C16Na concentration, in the range 260 ± 30 and 125 ± 10 kJ mol^{-1}, respectively, for the T_g and T_i.

For comparison, the effect of one concentration of C16Na blended with the PEA homopolymer is shown in Figure 2. As observed in the case of the ionomer, the rubbery region is reinforced by ca. 1.1 Pa/wt % C16Na (Figure 2a), a small transition which partly diminishes the reinforcing effect of C16Na is apparent at ca. 120 °C, and the glass transition maximum at 4 °C remains constant in temperature but diminishes in intensity in the presence of C16Na (Figure 2b). Thus, the effect of C16Na on the dynamic mechanical properties of the ionomer and of the parent homopolymer are the same.

Differential Scanning Calorimetry. The heating and cooling curves obtained for the ionomer alone, the C16Na alone and three blends of PEA-i/C16Na are shown in Figure 3. Except for the C16Na alone, which was a powder, the endotherms are first heating scans of samples molded under the same conditions as those used for DMTA and stored for several days; the exotherms were recorded following maintenance of these samples at 155 °C for 10 min.

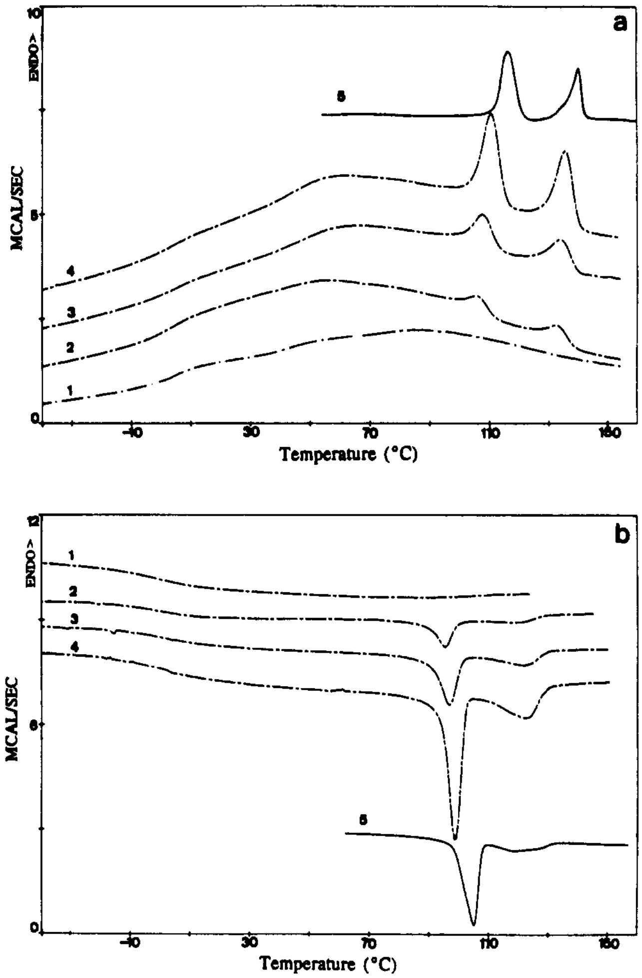

Figure 3. DSC thermograms of molded PEA-i/C16Na blends: (a) first heating scans, (b) first cooling scans. Wt % C16Na content: 1, 0; 2, 12; 3, 22; 4, 36; 5, 100.

The most prominent features in the endotherms are two first-order transitions, due to the C16Na, whose maxima are located at 116 and 139 °C, respectively, in pure C16Na. In the cooling curves, the exotherm at 105 °C for pure C16Na is the dominant feature, with a transition centered at ca. 120 °C also present. These transitions are the first two in a rich series of transitions between the fully crystalline and fully melted state.[16-18] The two observed here have been identified with structural changes as follows: upon heating, the lamellar crystalline structure at lower temperatures[16,17] changes to a highly ordered tilted orthorhombic smectic mesophase (also called subwaxy phase) at the first transition and to a similar but orthogonal mesophase (also called waxy phase) at the second transition.[18] The melting point of C16Na is approximately 300 °C.

When blended with the ionomer, it is clear from the DSC curves that the C16Na transitions are not significantly perturbed. There seems to be only a dilution effect as the ionomer percentage in the blend increases, resulting in decreasing intensities as the ratio of C16Na to PEA-i decreases, along with a modest decrease in the temperatures of the maxima. The blend of 22% C16Na with the PEA homopolymer shows behavior identical to that with the ionomer (Figure 4), except that the temperatures of

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(16) Vold, M. J.; Macomber, M.; Vold, R. D. *J. Am. Chem. Soc.* **1941**, *63*, 168.

(17) Stosick, A. J. *J. Chem. Phys.* **1950**, *18*, 1035.

(18) Skoulios, A. E.; Luzzati, V. *Acta Crystallogr.* **1961**, *14*, 278.

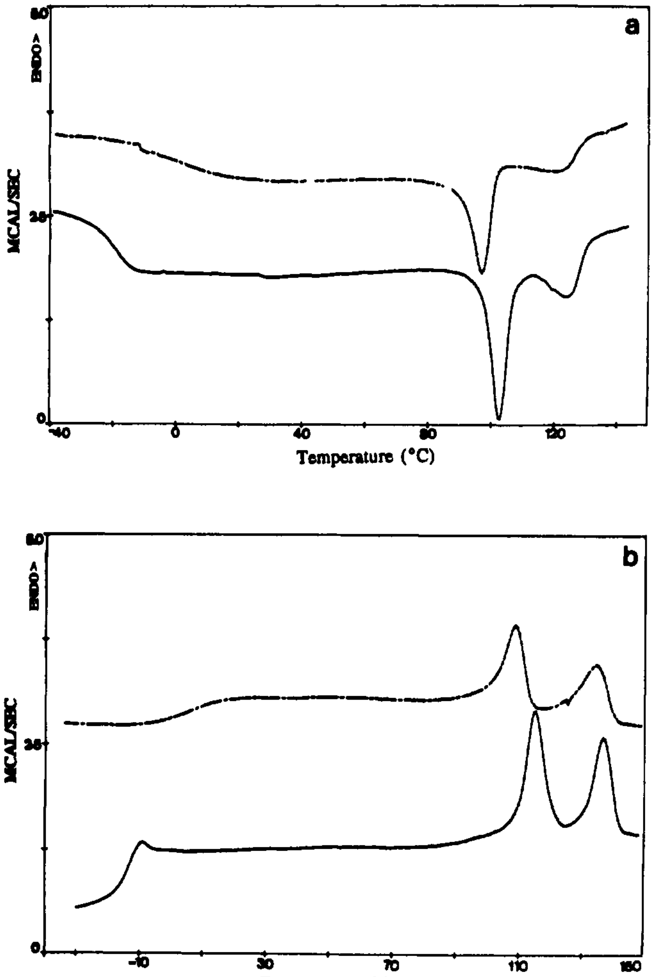

Figure 4. DSC thermograms of freeze-dried blends of 22 wt % C16Na with PEA-i (broken line) and PEA (solid line): (a) first cooling scans; (b) second heating scans.

the maxima are less reduced by the dilution effect; for example, the lower temperature exothermic peak in the cooling curve of the PEA blend is located at 103 °C compared to 97 °C for the equivalent PEA-i blend (and 105 °C for pure C16Na). This may indicate some slight effect of the ionic groups in the ionomer on the crystalline domains of C16Na.

As for the ionomer-related features in the curves, the T_g is clearly visible at 5 °C in the heating curves and is observed to remain constant. The T_g of PEA remains constant at −13 °C. Interestingly, another Tg-like transition appears to be present at ca. 45 °C for the ionomer blends, particularly evident in the pure ionomer (Figure 3). The two transitions are shown in expanded form in Figure 5. This may well be an example of the seldom reported appearance of the cluster T_g in DSC curves of ionomers[19-21] remembering that the endothermic curves presented in Figure 3 are first heating scans of molded samples that have been stored for some time.

Discussion. It is clear from the above data, as well as the observation that the molded blends are turbid, that there is phase separation between the ionomer and C16Na in the blend, just as there is between the parent homopolymer and the C16Na. On the other hand, C16Na acts as a reinforcing filler in both the homopolymer and the ionomer, as indicated by the progressive rise in the rubbery modulus as a function of C16Na concentration. The transition from the crystalline to the subwaxy phase for C16Na at ca. 115 °C in the DSC curves can be identified with the small relaxation observed at ca. 120 °C in the DMTA curves. Although maintaining its ability to act as a reinforcing filler, C16Na is somewhat less effective in this role in the subwaxy phase than it is in the crystalline phase.

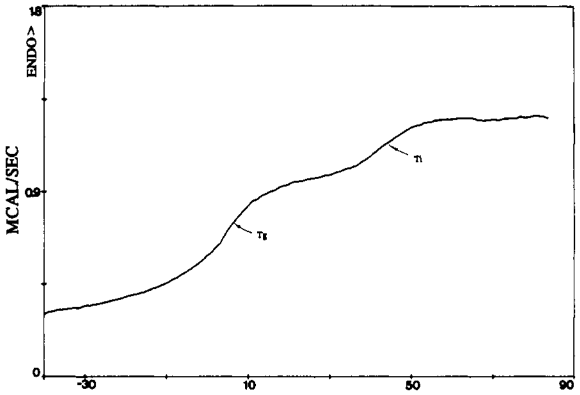

Figure 5. Enlarged DSC heating scan of PEA-i (see text for details).

Given that the reinforcing filler effect is approximately equal in PEA-i and PEA, it seems reasonable to relate it to polar interactions between the crystalline domain surfaces of C16Na (presuming that they contain carboxylate groups) and the ester groups in the ethyl acrylate side chains of the homopolymer and the ionomer. These interactions are sufficiently weak that both the bulk crystalline domains of C16Na and the T_g of PEA-i and PEA are practically unaffected. The presence of carboxylate groups in PEA-i apparently adds very little to the overall interactions between the crystalline domains and the polymer matrix. On the other hand, that some of the ionomer carboxylate groups may be involved in interfacial polar interactions is indicated by the somewhat greater dilution effect on the C16Na transitions in the ionomer blend compared to those in the homopolymer blend. However, such interactions are sufficiently minor that the role of the ionomer carboxylate groups in forming the PEA-i microdomain structure is unperturbed: this is clear from the persistence and thermal constancy of the cluster transition in the dynamic mechanical measurements and is confirmed by the persistence of the ionic peak in preliminary small-angle X-ray scattering measurements.[22] To further explore the interaction between the two components in these blends, a solid-state NMR study was undertaken and will be published elsewhere.[23]

Blends with Hexadecanoic Acid. Dynamic Mechanical Thermal Analysis. Young's storage moduli and loss tangents at 1 Hz as a function of temperature for PEA-i blended with 21 and 34% C16H are shown in Figure 6 and compared with the bulk ionomer. The same curves for bulk PEA and for PEA blended with 21% C16H are compared in Figure 7. In the latter case, the principal features are not very different from those observed in

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(19) Maurer, J. J. In *Thermal Analysis*; Miller, B., Ed.; Wiley: New York, 1982; Vol. 2, p 1040.

(20) Weiss, R. A.; Lundberg, R. D.; Turner, S. R. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 549.

(21) Ehrmann, M.; Mathis, A.; Meurer, B.; Scheer, M.; Galin, J. C., submitted for publication.

(22) Small-angle X-ray scattering scans of molded blends, using a 12-kW Rigaku rotating anode generator and scintillation counter detector, indicate that the typical ionomer peak in PEA-i, as published in ref 1, remains present at the same position in the blends with C16Na. These studies were not pursued because complicated by scattering features due to the C16Na.

(23) Natansohn, A.; Tong, X.; Bazuin, C. G. *Can. J. Chem.*, submitted.

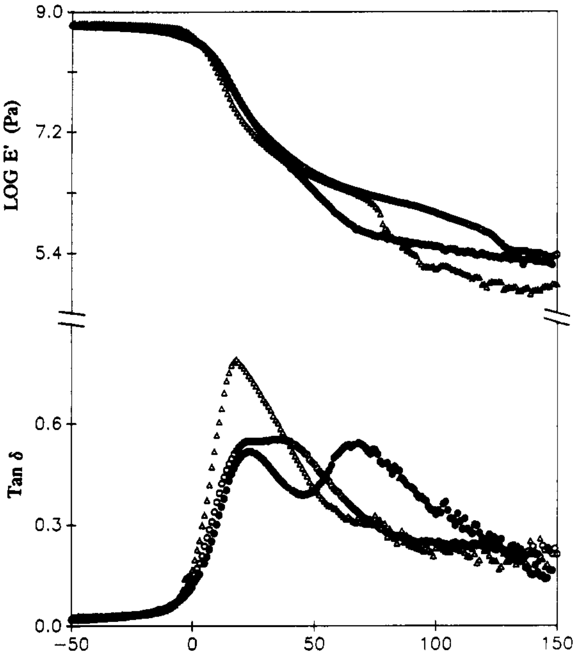

Figure 6. Dynamic storage modulus and loss tangent at 1 Hz versus temperature for PEA-i/C16H blends. Wt % C16H content: ●, 0; ○, 21; △, 34.

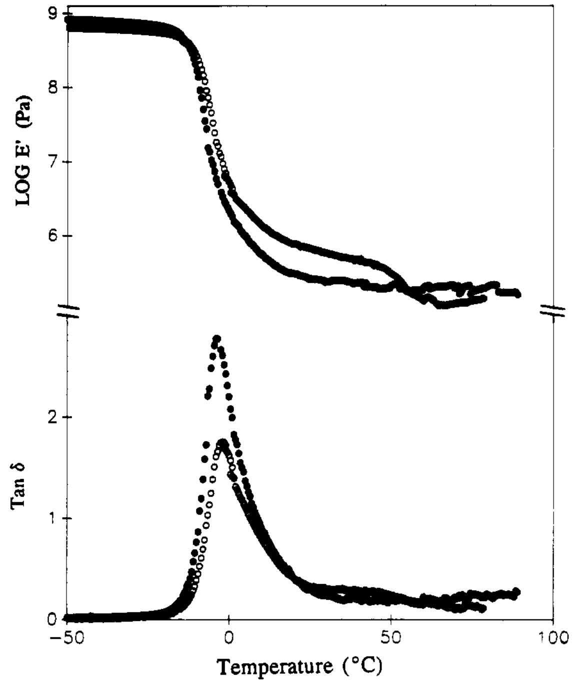

Figure 7. Dynamic storage modulus and loss tangent at 1 Hz versus temperature for PEA (●) and for PEA blended with 21 wt % C16H (○).

blends of PEA and C16Na. First, the rubbery region is reinforced in modulus by the crystalline C16H (by approximately 1.03 Pa/wt % C16Na), followed by a relaxation at ca. 55 °C; at temperatures above this relaxation, on the other hand, the modulus appears to be lower than that for bulk PEA, contrasting with what was observed in PEA/C16Na blends. Second, the glass transition temperature of PEA is unaffected by the C16H, although the intensity of the transition is reduced, as by C16Na, due to the reduction of total PEA content in the blend.

In contrast, the blending of C16H with the ionomer gives very different results from PEA-i/C16Na blends. In the storage moduli curves, the reinforcing effect of C16H in the rubbery region is evident, but the moduli relax to values similar to those of the bulk PEA-i at ca. 120 °C for the blend with 21% C16H and at ca. 80 °C for the blend with 34% C16H. Furthermore, the extent of reinforcement is similar at both concentrations, in contrast to the blends with C16Na where it was observed to increase with C16Na concentration. In the loss tangent curves, the cluster transition is clearly very much affected by the presence of C16H. In fact, it is drastically reduced in temperature with increasing C16H. At 21% C16H, the two transitions are poorly resolved, appearing to be separated by ca. 15 °C. Neither the glass transition temperature nor the relative intensities of the two transitions are significantly altered. At 34% C16H, there is just one intense peak, with a shoulder on the higher temperature side. The maximum is reduced in temperature by ca. 5 °C compared to the T_g of pure PEA-i, whereas the intensity of the T_g is increased considerably at the expense of the T_i. The curves for 11% C16H blended with the ionomer, not shown, are similar to those for the 21% C16H blend.

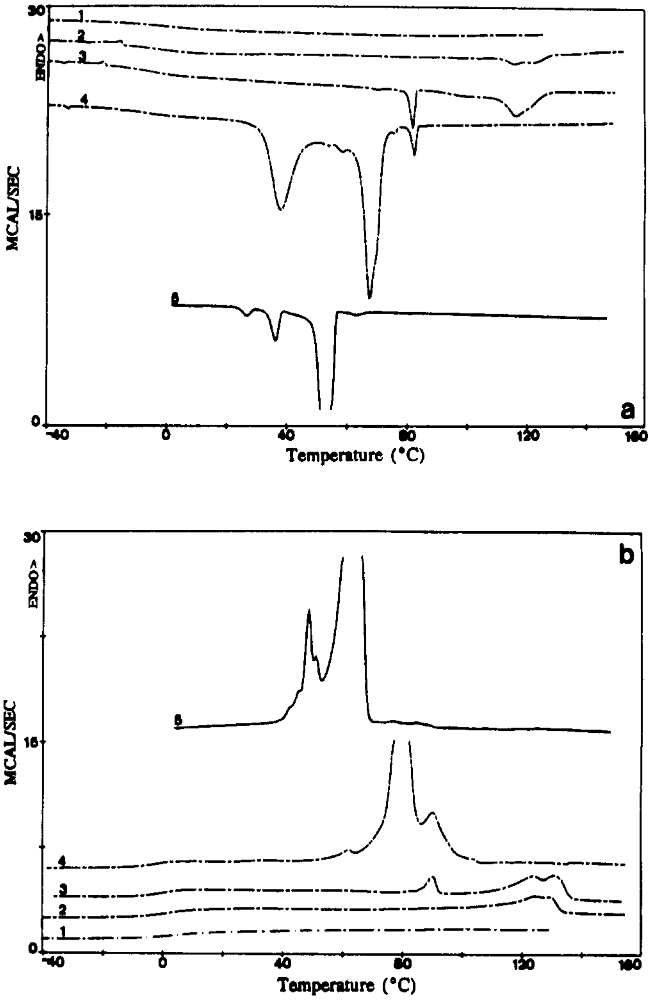

Figure 8. DSC thermograms of freeze-dried PEA-i/C16H blends: (a) first cooling scans; (b) second heating scans. C16H content: 1, 0; 2, 11; 3, 21; 4, 34; 5, 100.

Differential Scanning Calorimetry. First cooling and second heating scans of the ionomer alone, C16H alone, and three different blends of the two, are shown in Figure 8. For comparison, scans of a blend of C16H with PEA are shown in Figure 9. All blends were analyzed from freeze-dried form. As far as the ionomer is concerned, only the T_g is visible (most clearly in the heating curves): it decreases a little as C16H content in the blend increases,

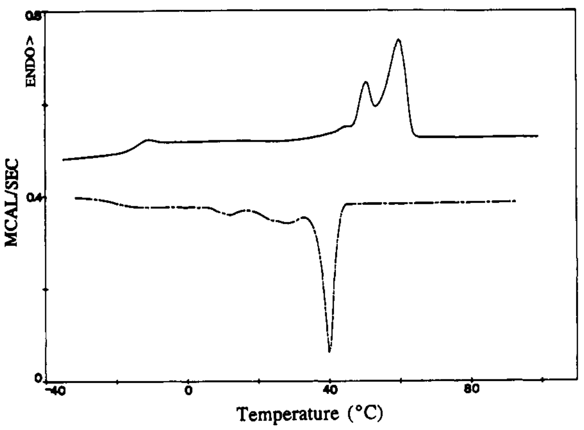

Figure 9. DSC first cooling scan (broken line) and second heating scan (solid line) of PEA blended with 21 wt % C16H.

by no more than 4 °C at 21% C16H and by ca. 8 °C at 34% C16H.

The changes in the crystallization behavior of C16H as its concentration in the blend varies is particularly striking. In pure form, it melts in the range 60–65 °C and crystallizes at ca. 10 °C lower, with a second transition 10–15 °C below the dominant transition. In the blend with the PEA homopolymer, the melting and crystallization behavior of C16H is not significantly perturbed. In fact, the complete melting of C16H correlates with the relaxation at ca. 55 °C observed in the DMTA curves of the PEA/C16H blend, following which the modulus decreases to values below that of bulk PEA (Figure 7). When blended with the ionomer to 34%, the melting and crystallization temperatures are increased notably, with the dominant transition ca. 15 °C higher than that in pure C16H, possibly indicating a different crystalline form from that of pure C16H. At 21% and 11% C16H, new transitions at still higher temperatures have appeared, in the latter case exclusively. Significantly, these new transitions appear in the same range as those for C16Na (Figure 3). These transitions can be compared with the decrease in the rubbery modulus (Figure 6), at ca. 80 and 120 °C for the ionomer blends with 34% and 21% C16H, respectively, and the obvious conclusions drawn.

Infrared Spectroscopy. To explain the above behavior, it can be supposed that ion exchange has occurred between the ionomer and the C16H during blending, such that some of the C16H has been converted to C16Na. The ionomer, in that case, is effectively partially neutralized in the blend. Infrared analysis indeed demonstrates that ion exchange has taken place in the PEA-i/C16H blends. Figure 10 compares the spectra in the 1500–1800-cm^{-1} region of PEA, of PEA-i and of the blends of each polymer with 21% C16H. This concentration represents a 1:1 stoichiometry between the carboxylic acid groups of C16H and the sodium carboxylate groups of the ionomer. In Figure 11, the spectra of pure C16Na and of blends of PEA-i with three different concentrations of C16Na are shown. The noteworthy features for the present analysis are the sharp, intense band at 1560 cm^{-1} attributed to deformation of the (crystalline) carboxylate group of C16Na, and the broad band centered at 1592 cm^{-1}, which is attributed to deformation of the carboxylate group in the ionomer. Neither PEA nor C16H absorb in this region. Thus, it is most significant that a sharp band at 1560 cm^{-1} appears in the spectrum of the PEA-i/C16H blend (Figure 10): the presence of C16Na in this blend is clearly indicated.

From the series of spectra in Figure 11, a calibration curve of the intensity ratio of the 1560 cm^{-1} band to the reference band at 1733 cm^{-1} (attributed to the carbonyl stretching vibration in the ester side chain of the polymer) as a function of C16Na concentration in the blend can be constructed (Figure 12). (It should be noted that the contribution from the overlapping broad band was sub-

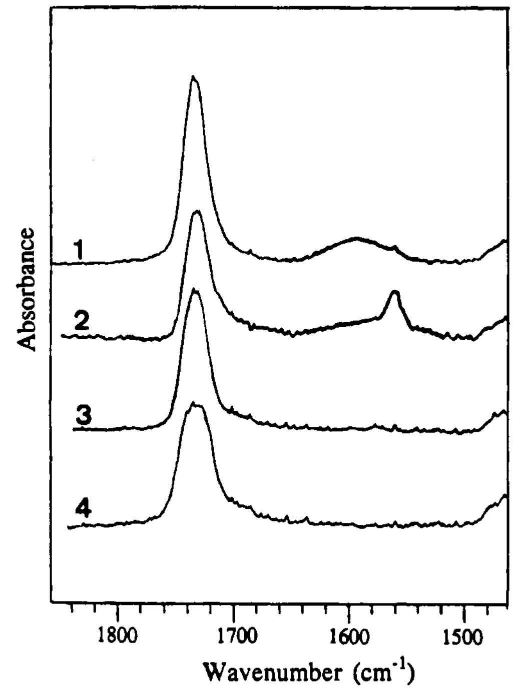

Figure 10. Infrared spectra of (1) PEA-i, (2) PEA-i/C16H blend, (3) PEA/C16H blend, (4) PEA. C16H content in the blends is 21 wt %.

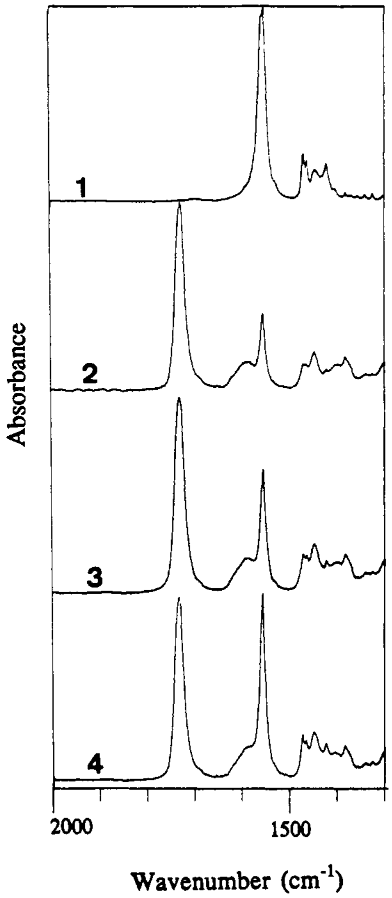

Figure 11. Infrared spectra of (1) C16Na and of PEA-i/C16Na blends containing (2) 12, (3) 22, (4) 36 wt % C16Na.

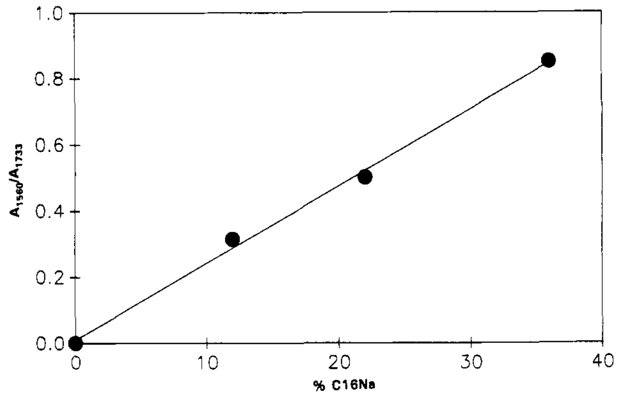

Figure 12. Intensity ratio of the infrared bands, 1560–1733 cm^{-1}, of the PEA-i/C16Na blends as a function of wt % C16Na content.

tracted out in determining the intensity ratio.) From this calibration curve, which is linear, it is observed that the intensity ratio for the PEA-i/C16H blend, which is 0.25, corresponds to a concentration of 10% C16Na. This result indicates a 50% ion exchange between the ionomer and C16H. Since the carboxylic acid groups and carboxylate groups in the blend are present in stoichiometric amounts, the extent of ion exchange suggests that the exchange occurred under equilibrium conditions, with no preference for either the ionomer or C16H.

Discussion. If it is assumed that ion exchange indeed took place under equilibrium conditions, with no preference for the ionomer or the small molecule, there would be more C16H than C16Na at 34% C16H concentration in the blend. There may well be cocrystallization of C16Na with C16H at that concentration, which could account for the apparently different crystalline form[24] and a melting transition above that of pure C16H. As the C16H concentration in the blend is decreased, the proportion of C16H converted to C16Na increases such that C16Na or C16Na-rich domains dominate; the DSC curves for the 22% C16H blend hints that these domains crystallize separately from what may be remaining C16H-rich domains. At 11% C16H concentration, there is no evidence in the DSC curves of any transition involving C16H or C16H-rich domains; only C16Na-type transitions remain.

As far as the ionomer is concerned, the change from complete neutralization to partial neutralization with the addition of C16H is no doubt at the root of the drastic changes in the mechanical properties observed, in particular in the cluster transition region. It is known that, for a given ionizable comonomer content, increasing degree of neutralization has similar (although not identical) effects to increasing degree of ionic group content. The T_g's increase[25,26] and the transition zone broadens.[27] At sufficiently high neutralization levels, depending on total comonomer content, mechanical property features associated with cluster formation develop.[26,27] Although studies of the effect of degree of neutralization on ionomer properties have been confined mainly to polystyrene-[25–27] and polyethylene-based[26,28] ionomers, the latter being complicated by the fact that the materials are semicrystalline, the observations are probably quite general. Certainly the behavior observed in the current study (Figure 6) is consistent with those observations—in particular, the decrease in temperature, and then effective disappearance, of the cluster transition. The consequences of partial neutralization on the modulus curves are masked by the presence of the small molecule. From the existing literature, it is not clear to what extent the minimal effect of the ion exchange on the T_g relative to that on the T_i observed in the PEA-i/C16H blends is due to the presence of the small molecule or if it may be related to the ionomer in question.

Finally, it can be speculated that, above the melting point of C16H in the blends with PEA and PEA-i, there may be specific interactions of the hydrogen-bonding type between the carboxylic acid group of C16H and the ester carbonyls of the polymer, just as was proposed for the amine group of 4-decylaniline and the same polymer.[1] Thus, the blends would be effectively miscible at the higher temperatures. This would account for the observed transparency of the blends at molding temperatures (see Experimental Section). This would also result in C16H being dispersed throughout the ionomer, with a consequential plasticizing effect in the rubbery region above the melting transition; such a plasticizing effect may account in part for the fact that the modulus values of the blend at higher temperatures are lower than those of the pure polymer (Figures 6 and 7). At lower C16H concentrations, where more is converted to C16Na, any plasticizing effect of C16H would be compensated for by the reinforcing filler effect of C16Na or C16Na-rich domains. The apparent transparency of the samples at the higher temperatures, despite the presence of those crystalline domains may be rationalized by supposing that those domains may be too small or too few in number to scatter light sufficiently to be easily visible.

General Discussion and Conclusions

In comparing the results for the above two systems and those in the published literature for the SEPDM/$ZnSt_2$ system, several aspects can be discussed. In all three systems, as pointed out in the Introduction, the type of ionic or functional group in the ionomer and in the small molecule additive is the same. Thus, there are no one-to-one interactions between the ionic groups of the ionomer and the functional group of the additive, as there would be if, say, the functional group in one component were acidic and that in the other, basic. Consequently, any interactions between the functional groups in the two components are nonspecific in nature.

Now, for all three blend systems, there is a temperature range to above the T_g of the ionomer in which the additive remains crystalline. In other words, whatever interactions do exist between the two components, they are not sufficiently strong to overcome the intermolecular forces among the small molecules that cause them to crystallize. Thus, the ionomer and the additive are phase-separated in the blend as long as the additive remains crystalline, and the majority of the functional groups in the additive are hence removed from interaction with the ionomer.

In the crystalline form, the additive in all three systems significantly reinforces the rubbery region of the ionomer. In the SEPDM/$ZnSt_2$ case, this was attributed to interfacial interactions between the ionic groups of the ionomer and those of $ZnSt_2$.[8–13] These interactions were further

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(24) Small-angle X-ray scattering scans of the PEA-i/C16H blends, obtained under the same conditions as those of ref 22, give little or no evidence of the ionomer peak when compared to PEA-i/C16Na blends at the same concentration. Scattering features due to the C16H also indicated some evolution in its crystalline form as its concentration in the blend with PEA-i varied, particularly at 34% C16H; the latter is consistent with the DSC endotherm for the same blend (Figure 8).

(25) Ogura, K.; Sobue, H.; Nakamura, S. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *11*, 2079.

(26) Connolly, J. M. Ph.D. Thesis, University of Massachusetts, Amherst, MA, 1990.

(27) Navratil, M.; Eisenberg, A. *Macromolecules* **1974**, *7*, 84.

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

indicated by the strong effects of the ionomer on $ZnSt_2$ crystallization and melting behavior, as observed through DSC, compared to blends of EPDM with $ZnSt_2$.[11] In the systems studied here, the reinforcement of the rubbery modulus, observed also for PEA, is attributed primarily to interfacial ion pair–dipole interactions between the functional group of the additive and the ester groups in PEA-i or PEA. Presumably, the higher polarity of the latter polymers, due to the presence of the ester group in the side chains of the ethyl acrylate repeating unit, allows for interfacial interactions that minimize the importance of ion pair–ion pair interactions between the two blend components. The lesser role of the latter interactions is supported by the constancy of the cluster transition temperature as observed through DMTA. Thus, although there may well be some interfacial interactions involving the carboxylate groups of both components in blends with PEA-i (as indicated by the greater dilution effect on the DSC transitions of C16Na, compared to blends with PEA), this occurs without disturbing the morphology of the ionomer; furthermore, the total reinforcing effect of the additive is essentially unmodified.

Specific interactions, notably hydrogen bonding, were also observed between the amine group of 4-decylaniline (4DA) and the ester groups in PEA-i or PEA.[1,2] In this case, these interactions were sufficiently strong to disrupt the crystallinity of the small molecule, and thus allow it to behave as a typical nonpolar ionomer plasticizer. On the basis of this result, hydrogen-bonding interactions between the small molecule functional group and the polymer ester groups are also postulated for the blends of C16H with PEA and PEA-i in order to explain the apparent miscibility at temperatures above the melting point of C16H. This may be further compared to the SEPDM/$ZnSt_2$ blend above the melting point of $ZnSt_2$, where it is presumed that the ionic associations between the two components solvate the ionic domains of the ionomer such that melt flow is improved dramatically.[10]

The extent to which the crystallinity of the additives is disrupted when blended with ionomers depends not only on the strength of the polymer–additive interactions but also on the strength of the intermolecular forces among the small molecules. The relative strengths are indicated by the melting points of the pure additives. For C16Na, with a melting point of ca. 300 °C, these forces are very strong. In fact, because C16Na in the blends is never fully melted in the thermal studies, the C16Na transitions observed are very little influenced by coexistence with the ionomer, in contrast to the SEPDM/$ZnSt_2$ blend. For 4DA, with a melting point at ca. 25 °C, the intermolecular forces among the 4DA molecules are relatively weak and thus fairly easy to overcome by hydrogen-bonding interactions with the polymer, as indicated by the fact that no crystallinity of 4DA was detected in the blends.[1] The interactions in neat $ZnSt_2$, which has a melting point of ca. 125 °C, are affected, but not eliminated, by the interactions between the Zn carboxylate groups in $ZnSt_2$ and the Zn sulfonate groups in the ionomer.[8–13] It is also noted that, in contrast to the univalent Na ion, the Zn ion is divalent and thus has the possibility of simultaneously bonding to an ionic group in SEPDM and an ionic group in $ZnSt_2$, thus strengthening the interactions between the ionic groups of the two blend components compared to the PEA-i/C16Na system.

Finally, the case of the PEA-i/C16H system is instructive. Clearly, the occurrence of ion exchange between the ionomer and C16H rules the properties of the resulting material, whose components are no longer those of the starting materials. Results reported for SEPDM neutralized by various cations and blended with various metal stearates[8] may also be affected by this process. In the present system, ion exchange took place between carboxylate groups, with no preference shown for either those in the ionomer or those in the small molecule. In the case of blends of SEPDM with metal stearates, by contrast, the occurrence and extent of ion exchange will likely be affected by the differing acid strengths of the sulfonate group in the former compared to the carboxylate group in the latter. Ion exchange in these systems may also be influenced by the metal ion being used. Nevertheless, the present study has clearly shown that ion exchange is possible in blend systems where two components have similar functional groups (such as an acid and a neutralized group, as in this study, or two neutralized groups with different counterions); this must be taken into account in analyzing properties of such systems.

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