Melt Rheology of a Class of Polyester Ionomers

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ABSTRACT: The rheological response of a class of random polyester ionomers was investigated over a wide range of compositions and temperatures. The ionomers are derived from poly(ethylene terephthalate) (PET) modified through copolycondensation with a fully neutralized sulfonate moiety, (sodiosulfo)isophthalate (SIP). Isothermal and isochronous measurements, over a temperature range spanning from the glass-transition to the terminal zone, were conducted using oscillatory and steady-state techniques. Significant and systematic increases in melt viscosity and flow activation on addition of SIP to the PET backbone were observed, indicating strong association and a high degree of aggregation of the ionic species. At SIP levels >10 mol %, the time–temperature superposition rule was found to break down, suggesting the presence of phase-separated, large ionic domains (clusters) within the organic matrix, although no evidence for a second (cluster) glass transition was noted. Increase in SIP concentration also led to a significant increase in the plateau modulus and to substantial broadening of the glass-transition range of the host polymer. The experimental data are discussed in the context of the restricted mobility model of Eisenberg and co-workers.[25]

Introduction

The presence of a small amount of covalently bonded ionic moieties in organic polymers is known to exert a profound effect on their physical and rheological properties.[1–5] Indeed, ionomers (polymers containing <20 mol % of ionic groups) have been shown to exhibit considerably higher stiffness, higher glass-transition temperature and higher melt viscosity than their nonionic homologues. The increase in melt viscosity and modulus at the rubbery plateau is generally attributed to the formation of ionic aggregates within the organic matrix which act as thermoreversible cross-links[1] and effectively retard the translational mobility of the chains. The exact form and size of these aggregates is still open to debate but their existence, as evidenced from small angle X-ray scattering (SAXS), neutron scattering, and other techniques, is firmly established, at least for some materials.[4] In this paper we report on the rheological response of a class of polyester ionomers (PEI's) derived from poly(ethylene terephthalate) (PET) modified at random by a fully neutralized sulfonate moiety, (sodiosulfo)isophthalate (SIP). More complete morphological and thermal characterization of these materials is described elsewhere.[6]

Although melt rheology is not ideally suited to probe the structure and organization of the ionic aggregates, it is very sensitive to the size and number of aggregates and it can effectively complement other, more direct, characterization techniques and provide useful insights.[2–5] Any factor affecting the ionic associations and their interaction with the surrounding organic matrix, e.g., the structure of the ionic moiety, the counterion type, the degree of neutralization, the flexibility of the backbone polymer, and the presence of plasticizers, should also influence the melt rheology of the ionomer. Indeed, these effects have been corroborated in many studies on a wide variety of ionomeric systems.[1–5] In one of the earliest studies, Otocka et al.[7] demonstrated the strong effect of the neutralization level and counterion type on the viscosity of carboxy-terminated polybutadiene telechelics. Similar observation on the effect of the counterion were made by Weiss and co-workers,[8–10] among others.[11] The effect of the structure of the ionic moiety (e.g., sulfonate vs carboxylate) in polystyrene-based ionomers was reported by Lundberg and Makowski,[12] demonstrating very dramatic changes in melt viscosity due to variations in the type and concentration of the ionic species. Bagrodia et al.[13,14] and Bazuin and co-workers[15,16] have studied the effect of plasticizers and excess neutralizing agent, again showing substantial changes in melt rheology of various ionomers due to changes in plasticizer type and concentration.

In addition to a large increase in melt viscosity, several anomalous effects have been reported in studies on the melt rheology of ionomers. Sakamoto et al.,[17] Eisenberg and co-workers,[18,19] and Jerome and co-workers[20,21] among others[22,23] report on the breakdown of the time–temperature superposition rule for some ionomers at high levels of neutralization, i.e., unlike conventional organic polymers, some ionomers do not display a thermorheologically simple character. Sakamoto et al. have also shown that the Cox–Merz rule,[24] which expresses the equivalence of dynamic and steady-shear rheological properties, is not obeyed by some ionomers at high levels of neutralization and ion content, again in contrast to conventional, homogeneous polymer melts. These anomalies were attributed to the formation of large ionic aggregates ("clusters"), which presumably constitute a separate microphase within the hydrocarbon matrix, with a distinct relaxation spectrum and glass-transition temperature. At ion concentrations below the "onset" of clustering, the ionomer network is expected to behave like a conventional physical polymer network, obeying time–temperature superposition and the Cox–Merz rule. However, above some critical concentration, the aggregates are presumed to form a distinct microphase, giving rise to a nonideal rheological behavior. We note here that the idea of a critical concentration for cluster formation follows the general line of the restricted mobility (RM) model of Eisenberg and co-workers[25] but is not universally accepted. This model provides, nonetheless, a useful framework for discussing the structure and organization of random ionomers, and it will be described in more detail in the Discussion.

Most of the studies on ionomers to date have been limited to addition-type polymers, e.g., polyethylene, polystyrene, and polyisobutylene, with only a few cases in which the ionic functionalities are introduced via a condensation process. The melt rheology of polyester ionomers, with structures different from those considered

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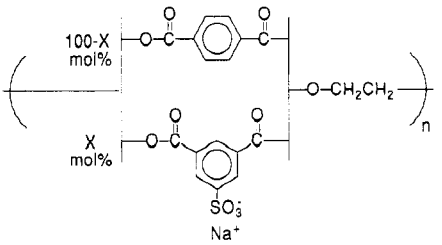

Figure 1. Molecular structure of PEI's.

in this study, was investigated by Connelly et al.[26] They report strong dependence of viscosity and relaxation time on the concentration of the ionic species but their materials appear to exhibit an *ideal* rheological response which implies, based on the RM model, that they have not passed the threshold for cluster formation. More recently, Gorda and Peiffer[27] have studied the morphology and physical properties of sulfonated poly(butylene terephthalate), but no consideration was given to the type and extent of ionic aggregation in this polymer class. The formation of clusters and the nature of ionic aggregation in the polyester ionomers (PEI's) of this study will be evaluated on the basis of the rheological data presented below. Other physical characterization data on the modified PET's are presented in a companion publication.[6]

Experimental Section

Materials. All the PEI's of this study are poly(ethylene terephthalate)s modified at random through copolycondensation by 5-(sodiosulfo)isophthalate (SIP)—a fully neutralized sulfonate moiety (see Figure 1). These polymers are designated PET-S*X* with *X* = mol % SIP of total diacid moieties. Thus, in accordance with this convention, the unmodified polyester (PET) would be designated PET-S0 or simply PET, while a resin containing 10 mol % SIP is PET-S10. It should be noted that the total molar concentration of SIP is half the value represented by *X* if the polyester is viewed as an AB-type copolymer. In this study *X* was varied in the range 0–20 mol %.

All the resins were synthesized by a batch condensation process in a 250-mL polymerization flask, yielding typically 50–150 g of resin. The flask was charged with 92 g (0.475 mol) of dimethyl terephthalate and a stoichiometric amount (depending on the desired SIP concentration) of dimethyl 5-(sodiosulfo)isophthalate, while ethylene glycol was added in large excess, typically 50 g. Zinc acetate dihydrate (Baker), a transesterification catalyst, was added as 5 mL of a 1% solution in ethylene glycol, and the polycondensation catalyst, antimony trioxide (M. C. B. Manufacturing), was added as 4 mL of 1% solution in ethylene glycol. Finally, a stabilizer package consisting of 0.15 g of Ultranox 626 (GE Specialty Chemicals), 0.15 g of Irganox 1010 (Ciba-Geigy), and 0.2 g of sodium acetate (Eastman) was added.

The single-necked polymerization flask was fitted with a 14-in. Vigreux distillation head and a nitrogen inlet tube. The sidearm was stoppered and the flask was placed in a 200 °C salt bath. Within 5 min the reactants had formed a clear melt and methanol had begun to reflux up the column. A Dean-Stark trap was fitted to the distillation head for measured collection of the methanol. After 90 min the theoretical volume of methanol had been collected and the temperature was raised gradually over the next 30 min to 250 °C. The distillation head and inlet tube were then removed and replaced with a mechanical stirring system, and the sidearm was unstoppered and attached to a vacuum manifold. Stirring commenced at 200 rpm, and the flask was opened and attached to a 50-mmHg vacuum. After degassing and methanol distillation, the flask was connected to a 0.1-mmHg vacuum and the temperature of the salt bath was raised to 280 °C. An ammeter was used to measure the power needed to stir at the required rate and thereby monitor the buildup in viscosity (molecular weight). The reaction was terminated by breaking vacuum and by removing the flask from the hot salt bath.

After allowing the flask to cool, liquid nitrogen was added to the flask to embrittle the polymer. Finally, the flask was broken and polymer chunks were removed and ground in a Wiley mill through a 1/8-in. screen. The PEI's prepared by this procedure are listed in Table I together with their respective zero-shear viscosities and inherent viscosities (IV's, see below). The compositions of the PEI's listed in Table I represent nominal values as determined from the reaction stoichiometry, rather than actual concentrations. However, recent analytical data (based mainly on X-ray fluorescence quantitation of atomic sulfur) indicate that these values are reasonable approximations.[6]

Table I. List of Materials

sample	composition	IV[a] (dL/g)	η_o[b] (10^2 Pa s)
1	PET-S2	0.345	1.78
2	PET-S4	0.326	4.5
3	PET-S5	0.292	3.75
4	PET-S5	0.317	7.47
5	PET-S5	0.275	2.93
6	PET-S5	0.383	23.8
7	PET-S5	0.270	1.87
8	PET-S5	0.291	3.90
9	PET-S6	0.264	3.61
10	PET-S8	0.278	15.0
11	PET-S10	0.362	61.5
12	PET-S12	0.216	9.4
13	PET-S14	0.179	7.32
14	PET-S16	0.162	4.0
15	PET-S16	0.191	12.6
16	PET-S16	0.231	49.8
17	PET-S16	0.127	15.6
18	PET-S16	0.170	5.3
19	PET-S20	0.107	2.66
20	PET-S20	0.119	2.88

[a] Inherent viscosity; see Experimental Section for details. [b] Complex zero-shear viscosity at 265 °C.

Drying Procedure. Because of the acute sensitivity of the PEI's to moisture (equilibrium water uptake ≈ 0.75 wt %/mol % SIP), all the samples in this study were thoroughly dried prior to rheological testing. Typically, the samples were stored in vacuo at 120 °C for 1 week and then transferred under a nitrogen blanket into a vacuum desiccator for further drying and storage prior to testing. Whenever this protocol was not strictly adhered to, the sample would undergo substantial hydrolysis, leading to a sharp drop in molecular weight and viscosity.

Dynamic-Mechanical Measurements. The Rheometrics System IV rheometer, operated in the oscillatory shear mode, was used to obtain the linear viscoelastic properties of the PEI's. Oscillatory measurements in the terminal zone were performed with a parallel plate (25-mm diameter) set up under constant temperature and by sweeping over a range of frequencies, typically 1–100 Hz. The dynamic tests were always conducted under a dry air purge with thoroughly dried samples. In a typical test dry sample, in coarse powder form, is loaded under nitrogen purge directly onto the 25-mm platens in the rheometer. The resin is then brought up to temperature under a dry air purge inside the rheometer's cell and formed without going through a separate molding step which could introduce undesired moisture into the sample. To minimize moisture pickup during loading, a special front cover was designed for the System IV for use with these resins to allow loading the samples under a nitrogen atmosphere.

The dynamic mechanical properties of several samples in the vicinity of the glass transition and the rubbery plateau were obtained by sweeping over a range of temperatures under a fixed frequency. In these runs a thoroughly dried sample was loaded onto 8-mm-diameter platens under a nitrogen purge and then melted and formed at 265 °C in a dry air atmosphere. The oven was then opened, and the sample was quenched to room temperature by spraying with dichlorodifluoromethane. A temperature sweep program then commenced at a rate of 2 °C/min, covering the range of ca. 30–140 °C. The isochronous dynamic measurements were performed at a frequency of 1 rad/s and a strain of 0.5%. To achieve better torque resolution at high temperatures, the isochronous measurements for some samples were repeated with the 25-mm platens over a temperature range of ca. 130–250 °C, at a strain of 0.1% and a scan rate of 2 °C/min. These data were then merged with the low-temperature data generated with the 8-mm platens to obtain the dynamic response of the sample over the widest possible temperature interval. To

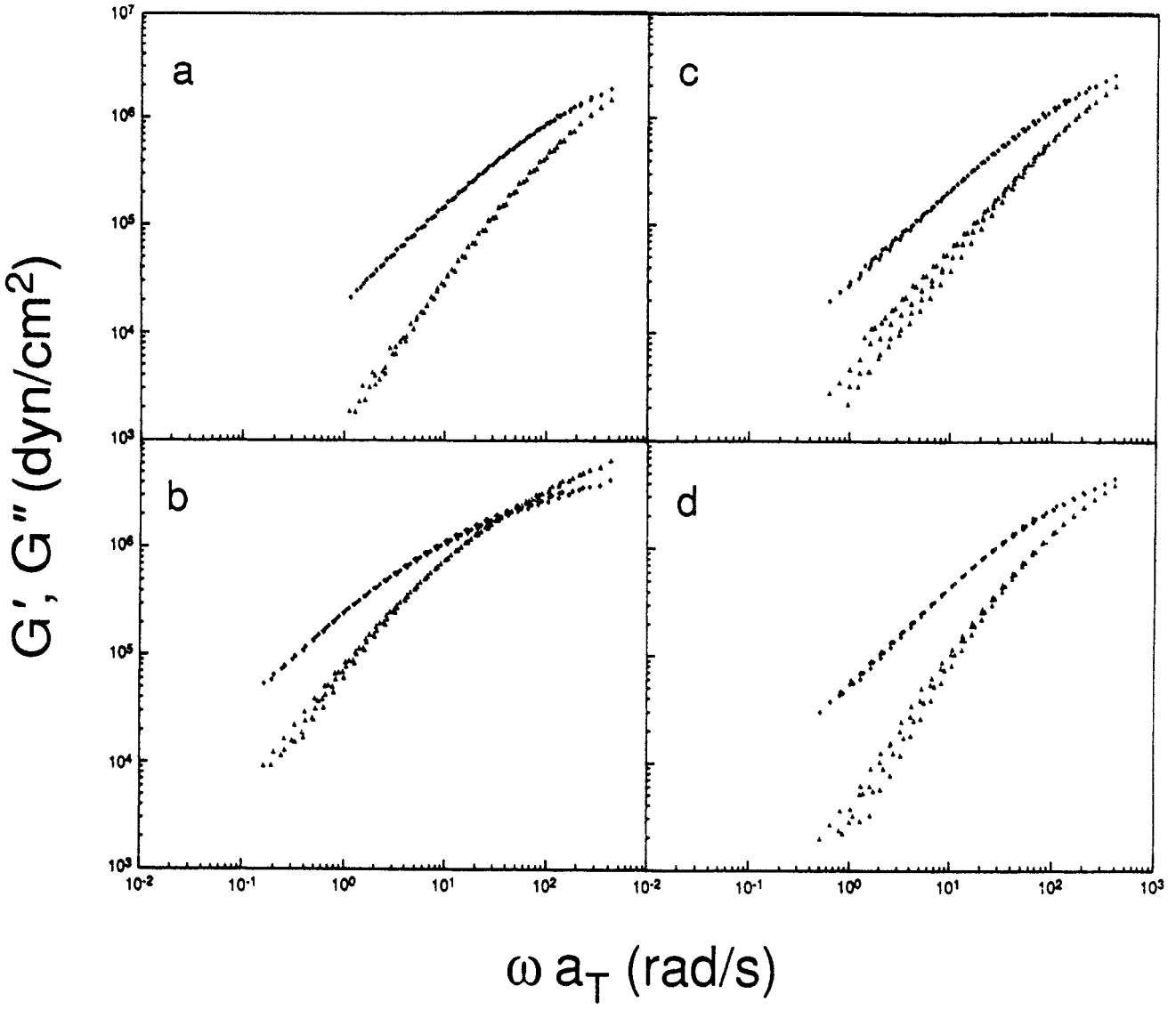

Figure 2. Mastercurves and pseudomastercurves of dynamic moduli vs frequency for modified PET's: (a) PET-S8 at *245*, 255, 265, and 275 °C; (b) PET-S10 at *235*, 245, 255, 265, and 275 °C; (c) PET-S12 at *245*, 255, 265, and 275 °C; (d) PET-S14 at *235*, 245, 255, and 265 °C. Reference temperatures italicized. G' (▲), G'' (♦).

achieve good overlap between the two data sets, some upward shift in the low-temperature data was needed to compensate for slight changes in gap opening with temperature in the 8-mm fixture.

Capillary Measurements. Steady-shear measurements at high shear rates were performed for some resins using the Instron capillary rheometer. A capillary with a diameter of 1.277 mm and L/D ratio of 40 was used in all runs. The Weissenberg–Rabinowitsch correction was applied in the data analysis, but no attempt was made to correct for end effects. The melt temperature in the rheometer was calibrated with standard polymers and corrected as needed. To minimize moisture pickup during loading, the opening of the barrel of the rheometer was purged with dry nitrogen as the solid sample was packed inside the barrel.

Inherent Viscosity. The inherent viscosity (IV) was used to characterize the molecular size of the PEI's. This property was measured at 25 °C with a solvent mixture of phenol/chlorobenzyl (60/40 by wt) at a concentration of 0.25 g/dL. All the *ionomer* solutions were screened with a large excess (0.05 M) of tetrabutylammonium bromide salt in order to effectively neutralize all the ionic sites in the test polymers. At the given concentration, the measured IV is a close approximation of the *intrinsic* viscosity of the polymer which is more directly associated with its molecular weight.

Results

A variety of rheological measurements were performed on a homologous series of the modified PET's, PET-S*X*, with *X* varying in the range 0–20 mol % (see Table I). We first examine the dynamic-mechanical response of the test samples in the terminal zone. Curves of loss and storage moduli as a function of frequency were generated for all the samples at four temperatures (at least), well above the glass-transition range. The data were then reduced, following the standard procedure of time–temperature superposition,[28] by shifting the experimental curves horizontally (along the frequency axis) and trying to superimpose the loss and storage moduli for three temperatures onto the corresponding reference curves. The data are considered superposable only if both, the loss and storage, moduli are fully overlapping. For some samples, however, the storage moduli could not be superimposed although the loss moduli were found to fully overlap for all temperatures. Reduced plots for these samples were generated by forcing the loss moduli to superimpose while allowing the storage moduli to "float" (the corresponding curve is referred to as a *pseudomastercurve*). Reduced plots of storage and loss moduli for several representative samples are shown in Figure 2.

Inspection of the data reveals that time–temperature superposition breaks down at SIP concentrations ≥10 mol %, as manifested by the inability to superimpose the curves for the storage moduli at the terminal zone. In accordance with the restricted mobility model,[25] this concentration represents the onset of phase inveserion in the molten

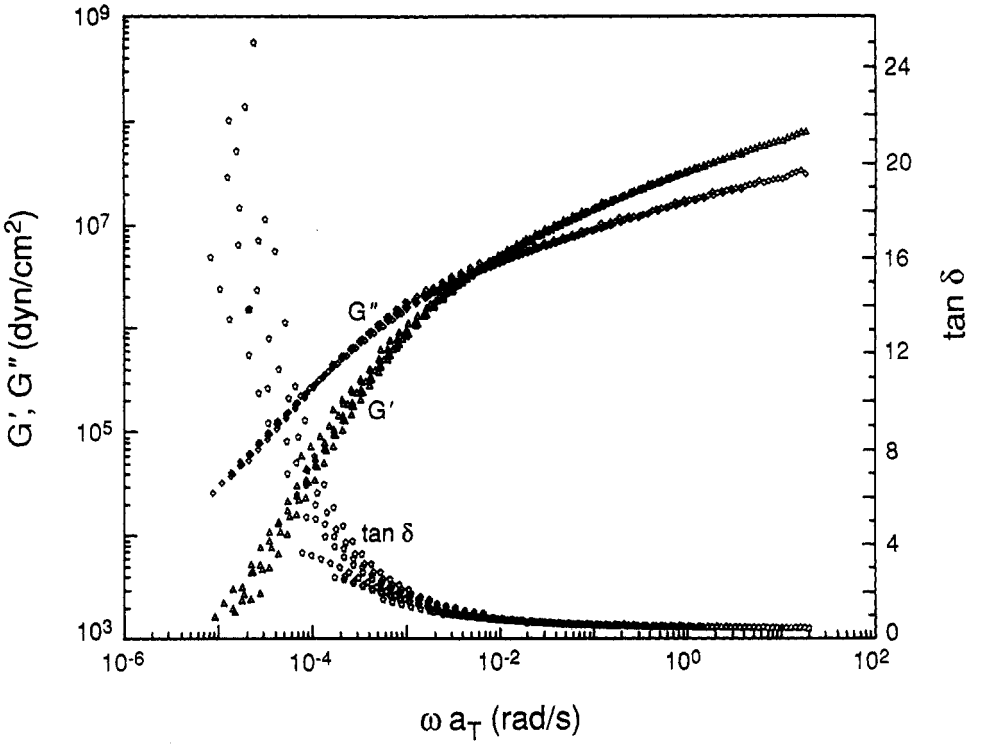

Figure 3. Pseudomastercurve of loss tangent and dynamic moduli vs frequency for PET-S14. Data at 160, 170, 180, 190, 210, 220, 235, 245, 255, and 265 °C shifted to a reference temperature of 160 °C.

PEI's and will be referred to, somewhat loosely, as the *clustering point*. It is noteworthy that in most cases the data cover mostly the terminal zone, and for samples that fail time–temperature superposition the departure from the terminal slope (slope of the double-logarithmic G'–ω curve <2) is more pronounced at lower temperatures. By extending the dynamic measurements to lower temperatures, it is possible to probe the response of the polymer well into the rubbery regime, as illustrated in Figure 3 for PET-S14. This pseudomastercurve clearly shows that the failure of time–temperature superposition is confined to the terminal (low-frequency) zone and is manifested mainly by a mismatch in G'. A qualitatively similar response was observed by Earnest and MacKnight[22] in a study on partially neutralized ethylene–methacrylic acid copolymers.

To further augment the dynamic-mechanical data and cover a wider temperature range, isochronous dynamic moduli of several materials were measured over a range of temperatures closer to the glass transition region. This test was performed on samples that lie both above and below the clustering point, based on the superposability criterion (Figure 2). Since the unclustered samples are also crystallizable,[6] dynamic-mechanical data in the vicinity of T_g can be obscured by the onset of crystallization. In order to inhibit crystallization, all the materials were first heated to a high temperature (>265 °C), then quenched to below T_g, and finally heated again at a controlled rate during the measurement itself (see Experimental Section). This procedure was quite effective in suppressing crystallinity in the unclustered samples although some indication of limited crystallization at high temperatures (ca. 140 °C) was noted for PET-S5 and PET-S10. This was manifested by an anomalous and abrupt increase in modulus (G') with temperature and the appearance of haze in the sample (cf. Figures 4 and 5). Isochronous storage moduli for selected samples of the PEI series are shown in Figure 4. The data illustrate the significant effect of SIP level on the modulus at the rubbery regime; a systematic increase in the plateau modulus with increase in SIP level is observed up to a SIP concentration

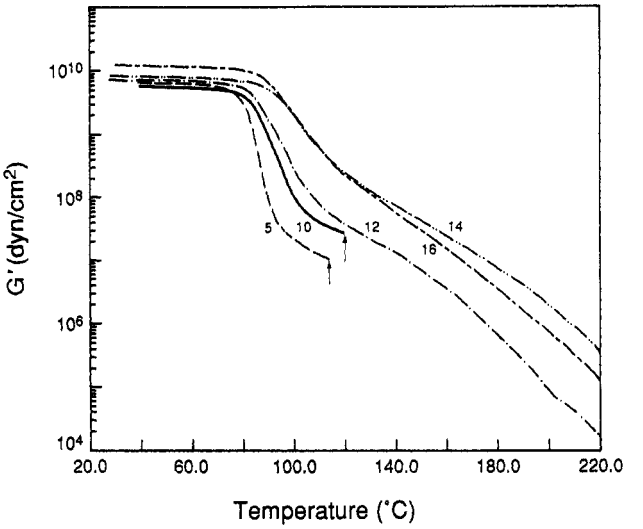

Figure 4. Isochronous storage modulus vs temperature for several modified PET's. SIP concentration (X, in mol %) is indicated. Frequency: 1 rad/s. Arrows mark onset of crystallization. (PET-S16 is sample 15 and PET-S5 is sample 8 in Table I.)

of 14 mol % where the effect appears to level off. The narrow plateau, which for some samples is hardly discernable, is a result of the low molecular weights of the PEI's especially those with high ionic contents (see Table I). In any case, this result underlies the networking capacity of the ionic species and its strong dependence on ionic content.

It is also evident from the data in Figure 4 that the addition of SIP leads to an increase in the glass-transition temperature (cf. Figure 11) and to a substantial broadening of the glass-transition range. This is more clearly demonstrated by the data in Figure 5 where the corresponding loss tangents are plotted vs temperature. The prominent loss peaks in this figure are clearly associated with the primary (α) transition of the unclustered phase but their height (intensity) and position are dependent on ion content: The α peak is broadened, its position is shifted to higher temperatures and its height is substantially

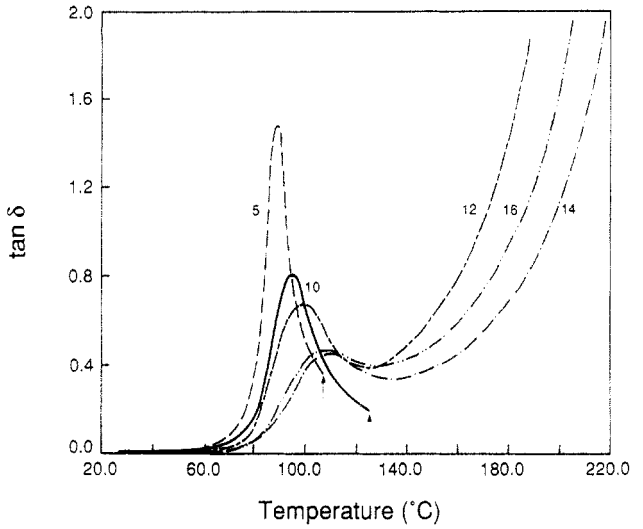

Figure 5. Isochronous loss tangent vs temperature for several modified PET's. SIP concentration (X, in mol %) is indicated. Frequency: 1 rad/s. Arrows mark onset of crystallization. (PET-S16 is sample 15 and PET-S5 is sample 8 in Table I.)

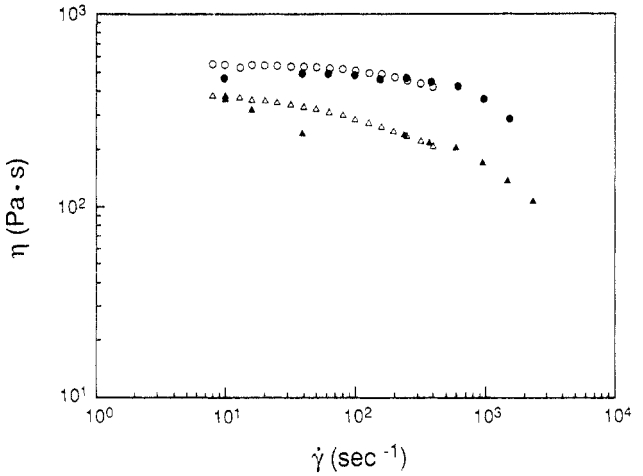

Figure 6. Flow curves for PET-S5 (S8) (△) and PET-S16 (S18) (○) at 265 °C; (open symbols) dynamic viscosity; (solid symbols) steady shear viscosity (by capillary viscometer).

reduced with an increase in SIP concentration. It is also noted that, for the clustered samples—PET-S16, PET-S14, and PET-S12—a large dispersion appears at high temperatures (>120 °C) which may simply represent the onset of the terminal zone. The increase in tan δ at this temperature range for the *unclustered* samples is possibly masked by the onset of crystallization so that the two sets of samples cannot be properly distinguished under these conditions.

Complete viscosity curves for two resins, PET-S5 and PET-S16, were generated by combining dynamic-mechanical and steady-shear data obtained with parallel-plate and capillary rheometers (see Experimental Section). Composite flow curves for both materials, covering a wide range of shear rates, are shown in Figure 6. Both PEI's exhibit a characteristic but mild shear-thinning response and reasonably good overlap between the dynamic and steady-shear data. This indicates that the Cox–Merz rule[24] is obeyed over the range of shear rates (frequencies) covered by both, the clustered and unclustered, polymers. The Cox–Merz rule expresses the analogy between the complex and steady-shear viscosities through

$$|\eta^*(\omega)| = \frac{1}{\omega}\sqrt{(G' + G'')} = \eta(\dot{\gamma})|_{\dot{\gamma}=\omega} \qquad (1)$$

where $\dot{\gamma}$ is the shear rate, ω is the radian frequency, G' and G'' are the storage and loss moduli, and η and η^* are the

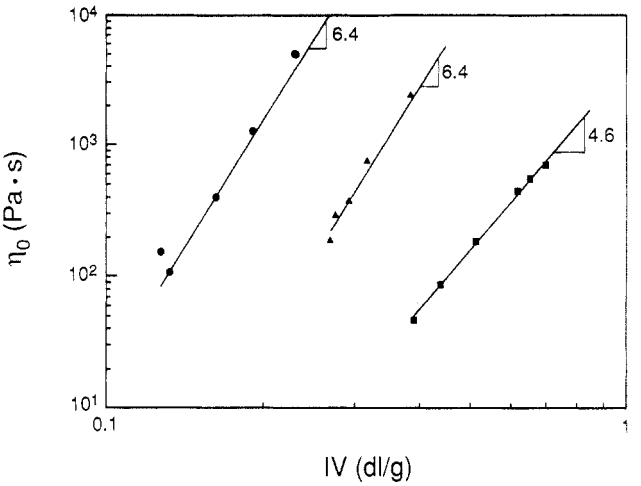

Figure 7. Zero-shear viscosity at 265 °C vs inherent viscosity for PET (■), PET-S5 (▲), and PET-S16 (●).

steady-shear and complex viscosities, respectively. The small difference in the shape of the flow curves between PET-S5 and PET-S16 may possibly be due to differences in molecular weight and the modes of ionic aggregation in these materials (cf. Figure 8 and Table I), but the close correspondence between the steady-shear and dynamic viscosities for both resins is evident.

In order to evaluate the intrinsic effect of the ionic moiety on melt viscosity, it is necessary to somehow account for the differences in molecular weight among the various samples which vary over a fairly wide range (cf. Table I). Since the molecular weights of the PEI's could not be determined directly (e.g., via gel permeation chromatography) due to their limited solubility, we will use the given inherent viscosities (IV's) to represent their molecular size. This quantity is a close approximation of the *intrinsic* viscosity and, hence, it should be intimately related to the hydrodynamic volume of a single PEI chain in the test solvent. Logarithmic melt viscosity–IV curves for PET, PET-S5, and PET-S16 are given in Figure 7. The relative scatter in the data for the PEI's is likely due to some fluctuations in SIP level and some noise in the IV data. It is, however, apparent that at any given IV the PEI's are considerably more viscous than the unmodified PET and their viscosity has a much stronger dependence on IV. It is also noted that while the viscosity of the PEI's is strongly dependent on SIP concentration, the slope of the double logarithmic viscosity–IV curve is quite insensitive to the concentration of the ionic species within the range covered. The dependence of viscosity on IV can be expressed by a power-law relationship of the form

$$\eta_0 = K''(\mathrm{IV})^b \qquad (2)$$

where the exponent b is the slope of the linearized curves in Figure 7. Linear regression of the data gives $b \approx 4.6$ for PET and $b \approx 6.4$ for the PEI's. These large exponents can be rationalized in terms of the Mark–Houwink (MH) equation[29] for the intrinsic viscosity,

$$[\eta] = K'M^a \qquad (3)$$

and the well-known 3.4th power dependence of viscosity on molecular weight M (assuming that all the polymers in question are above the critical "entanglement" molecular weight[30]). The parameter a in the MH equation is closely associated with the degree of hydrodynamic expansion of a single molecular coil in solution, and it usually varies in the range 0.5–0.8 for synthetic, random-coil polymers. From the given b's and assuming that IV $\approx [\eta]$, it can be shown that the values of the MH parameter a are 0.74 and 0.53, respectively, for an unmodified PET and for the

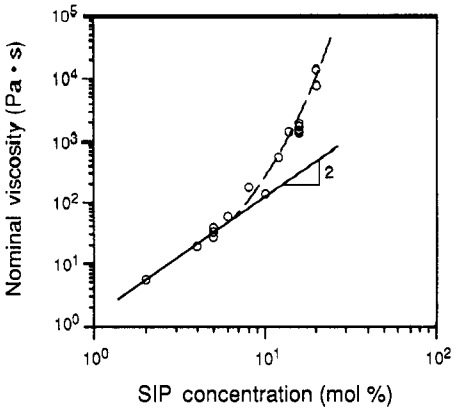

Figure 8. Nominal viscosity (see eq 5) vs SIP concentration.

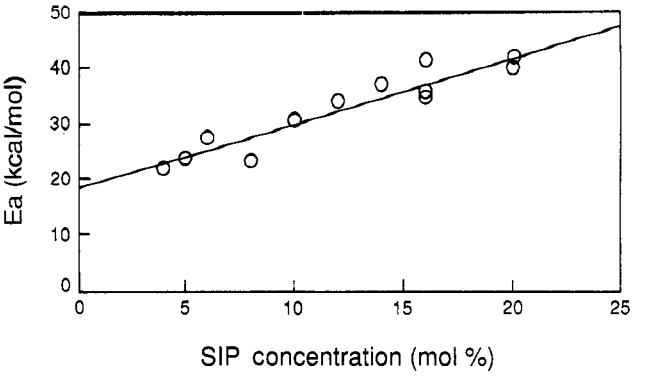

Figure 9. Flow activation energy vs SIP concentration.

PEI's. This implies that the PEI coil is nearly collapsed to the Θ solution limit ($a = 0.5$) in the IV test, while the PET coil is fairly expanded. This result is plausible given the electrostatic nature of the PEI's and the nonpolar character of the solvent used in the IV test.

To compensate for the large disparity in molecular weight, the viscosities of the various resins must be shifted to a nominal value corresponding to a standard IV and temperature. For an IV of 0.2 dL/g and a temperature of 265 °C and by assuming $b \approx 6.4$ (cf. eq 2) for all the resins (except PET), the *nominal* viscosity is given by

$$\eta_{nom} \approx \eta_0(@265\ °C)(0.2/IV)^{6.4} \quad (4)$$

The selected value of b is based on the reasonable supposition that all the PEI's have a similar MH exponent and they all form entanglements in the melt state. With this arbitrary but reasonable normalization, the *nominal* viscosity is expected to express the intrinsic effect of molecular structure on the extent of thickening of the bulk polymer. The effect of SIP level on the nominal viscosity of the SIP-modified PET's is shown in Figure 8. Despite some scatter in the data, the strong, nearly exponential effect of SIP on viscosity is evident. For the range of SIP concentrations the viscosity is increased over nearly four decades, and there is some indication, although it is quite uncertain, that the logarithmic viscosity–SIP concentration curve exhibits a change in slope in the vicinity of 10 mol % SIP, coincident with the clustering point for this series. The slope of the curve below 10 mol % is ca. 2 and it increases monotonically to >5 at the highest concentrations, indicating strong molecular associations above the clustering point.

Although some of the materials tested fail time–temperature superposition, the apparent viscosities of all the polymers appear to follow Arrhenius activation at the temperatures used in the melt rheology runs (230–275 °C). This apparent contradiction can be reconciled by recalling that the departure from thermorheological simplicity in Figures 2 and 3 is manifested mainly by differences in G' in the terminal zone, which has normally little effect on the dynamic viscosity (cf. eq 1), while G'', the dominant component of η^*, appears to obey time–temperature superposition for all the materials tested. The activation energy for viscous flow (E_a) is nominally temperature independent within the temperature range covered, but it is strongly dependent on the molecular structure of the PEI. The effect of SIP on E_a is illustrated in Figure 9: Within the scatter of the data, E_a appears to increase linearly with SIP level and its value is nearly doubled over the range of concentrations studied (0–20 mol %). This result is in qualitative agreement with observations on other ionomeric systems,[2] and it suggests that the volume of the flow unit is increased and its translational mobility is restricted on addition of ionic groups to the polyester backbone.

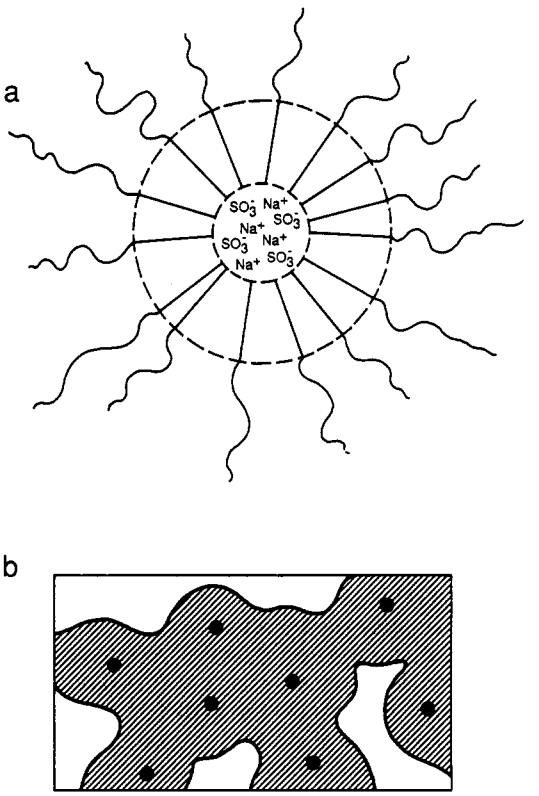

Figure 10. Restricted mobility model of Eisenberg et al.:[25] (a) a schematic of a multiplet and its restricted mobility shell; (b) a schematic two-dimensional representation of a cluster. Solid spheres are the ionic multiplets, the hatched area is the restricted mobility domain, and the unmarked area is the unclustered hydrocarbon matrix.

Discussion

The experimental results presented above can be interpreted in the context of the restricted mobility (RM) model of Eisenberg and co-workers.[25] This model, developed recently for random ionomers, is conceptually quite simple, yet it can account for many experimental observations not fully explained by some earlier models. The basic premise of the RM model is that at low ionic concentrations the ionic moieties aggregate into loosely defined *multiplets* consisting typically of 2–8 ion pairs (cf. Figure 10a). The formation of these aggregates is induced by electrostatic forces applied by the ionic moieties which must overcome the entropic and elastic forces exerted by the hydrocarbon chains to which they are attached. The constraint imposed on the chains by the

multiplet restricts their segmental mobility over a distance of the order of the persistence length of the bulk polymer from the multiplet interface. This restricted mobility "corona" surrounding the multiplet core is distinct from the bulk polymer matrix, and its size is dependent on the aggregation number of the multiplet and the stiffness of the polymer backbone. Typially, the size of this corona/core entity is too small (<50 Å) to form a distinct phase and its effect is limited to that of a physical cross-link. As the ion content is increased, the number of multiplets grows and the restricted mobility "coronas" of neighboring multiplets start to overlap and coalesce until a point is reached where a contiguous region of restricted mobility is formed whose size is sufficiently large to be considered a distinct phase (Figure 10b). This aggregate of neighboring multiplets is called a *cluster* and the ionic concentration at which clusters first appear is the *clustering point*. It is argued, in fact, that the restricted mobility domains become the dominant (continuous) phase at the onset of clustering so that the clustering point actually marks the onset of *phase inversion*, rather than phase separation. In any case, clusters, according to the RM model, are relatively large (>50 Å) domains of polymer with restricted mobility that may contain several multiplets. These domains are nominally *phase-separated* from the polymer bulk (matrix) and should have a distinct glass-transition and relaxation spectrum.

Insofar as cluster formation is equivalent to microphase separation, the breakdown of time–temperature superposition can be used as an effective marker for the onset of clustering. The departure from a thermorheologically simple behavior is typically observed in well-defined heterogeneous (multiphase) systems and is attributed to the presence of several distinct relaxation mechanisms associated with the various phases. Below the critical ion concentration the mutliplets act as simple physical cross-links which modify the topology of the polymeric matrix without affecting its fundamental relaxation behavior. Above the critical concentration two relaxation mechanisms appear, one associated with the unclustered hydrocarbon phase and the other representing the ion-rich cluster phase. Thus, according to our dynamic-mechanical data (Figures 2 and 3), the clustering point for the SIP-modified PET's is at ca. 10 mol % SIP (equivalent to 5 mol % overall concentration if the polyester is viewed as an alternating, AB-type, copolymer; see Experimental Section). This result is somewhat higher than a value quoted for polystyrene-based ionomers[1] although, given the significant difference in structure, a direct comparison between these two polymer classes is not warranted. It should be emphasized, in fact, that expressing the ion concentration in units of mol % is somewhat misleading, since it does not adequately represent the interionic spacing along the chain. Since the length of the repeat unit of PET is large (ca. 11 Å) compared to that of vinyl polymers (ca. 2.5 Å), the effective clustering point (expressed in mol %) should indeed be expected to occur at higher molar concentrations than for polystyrene if the persistence lengths and multiplet aggregation numbers for both polymers are assumed to be of the same order. It is also noted that the failure of time–temperature superposition is manifested only in the terminal zone (cf. Figure 3), thus suggesting that the relaxation spectra of the clustered and matrix phases differ mainly in their terminal relaxation times, i.e. the long range translational motions of the chains. The fact that only G' is not superposable indicates that only the tail end of the molecular weight distribution is modified by ionic aggregation as it is well-known that G' is far more sensitive than G'' (or viscosity) to changes in the high moments of the distribution (e.g., $\bar{M}_z$, $\bar{M}_{z+1}$).[31]

Further support for this qualitative picture is provided by the isochronous dynamic data in Figures 4 and 5. The large increase in the plateau modulus with the addition of SIP is indicative of an increase in cross-link density which is apparently enhanced by cluster formation. The average molecular weight between clusters (cross-links) can be estimated from[32]

$$M_c \approx \rho R T_i / G_i \tag{5}$$

where ρ is the bulk density of the material at the rubbery regime and G_i and T_i are the values of the storage modulus and temperature at the inflection point. M_c for the highly clustered samples, PET-S14 and PET-S16, is of the order of 500—a low value indicating fairly high cross-link densities at this ionic level. The fact that the rubbery plateau of PET-S14 is somewhat broader than that of PET-S16 may be due to its higher molecular weight (IV); see Table I. This result may also suggest that the effect of clustering levels off at ca. 14 mol % SIP; i.e., the volume fraction of the clustered phase saturates at this ionic concentration (cf. Figure 5).

Inspection of the corresponding loss tangent data, Figure 5, reveals additional interesting features of the modes of aggregation of the PEI's. Below the clustering point (particularly for PET-S5), the a dispersion, corresponding to the glass transition point of the matrix (unclustered) phae, is quite prominent. This peak is gradually decreased, broadened, and shifted to higher temperatures with an increase in SIP level. The onset of the glass transition as well as the area under the α peak appear to be quite insensitive to the SIP level, but the breadth of the transition is nearly proportional to the ionic concentration (see also Figure 4) up to SIP concentration of ca. 14 mol %. The general effect of SIP concentration on the dynamic response of the material in the transition and rubbery zones is qualitatively similar to results reported by Hird and Eisenberg[33] and by others[1-5] on polystyrene-based and other addition-type ionomers. In the context of the RM model, the gradual suppression of the a peak with addition of SIP represents the gradual depletion of the matrix phase and the corresponding buildup of the cluster phase which should be manifested by a second lossy dispersion at a higher temperature. However, the large upturn in tan δ observed at high temperatures, >120 °C, for the SIP-rich samples may simply mark the onset of the terminal zone, rather than a second lossy dispersion. Indeed, it is significant to note that tan δ does not exhibit a second peak over the temperature range covered, 120–230 °C, in variance with observations on other ionomer systems above the clustering point.[1,16,33] The apparent absence of a second lossy peak (the "cluster T_g", according to the RM model) may be a result of the low molecular weights and the corresponding "narrowness" of the rubbery plateaus of the clustered PEI's. Indeed, it has been recently observed that the height of the second peak is intimately dependent on the molecular weight of the host polymer, and for sufficiently low molecular weights, it may be fully suppressed or masked by the early onset of the lossy dispersion associated with the terminal zone.[34] Because of the formation of crystallinity in the unclustered samples it is not possible to probe the response of the low-SIP samples at high temperatures (>120 °C) but it is very likely that these samples would exhibit a similar upturn in tan δ.

Another feature of cluster formation, first reported by Sakamoto et al.,[17] is the breakdown of the Cox–Merz rule (see eq 2) which is also a manifestation of microphase separation. In contrast to the observations of Sakamoto et al., our data in Figure 6, for resins below and above the clustering point, show good overlap of dynamic and steady-

state viscosity data. However, due to the limited range of the shear-thinning region for both melts, these data should be considered inconclusive and the validity of the Cox–Merz rule may require more rigorous experimental testing.

The strong effect of SIP on the melt viscosity of the PEI's is shown in Figure 8 for a wide range of SIP concentrations. We recall that through the definition of η_{nom} (see eq 4), these results are adjusted to account for differences in molecular weight (IV) and are thus expected to express the intrinsic contributions of molecular structure to the apparent melt viscosity. Clearly, SIP exerts a profound effect on the viscosity of the modified polyesters which can be ascribed to the networking capacity (functionality) of the multiplets. Although the data are quite scattered, the slope of the double-logarithmic curve in Figure 8 appears to change at ca. 10 mol % SIP, coincident with the clustering point, as inferred from the oscillatory data. The slope of the logarithmic curve rises from ca. 2 below the transition to >5 above it. The diffuse nature of the transition can be explained by recalling that the melt viscosity measurements are performed at high temperatures, possibly above the glass transition of the clustered phase, so that the reduced mobility regions defining the cluster are, in fact, quite mobile and flexible under the test conditions and the contrast between the clustered and unclustered phases becomes relatively small. This may also explain the fact that the Cox–Merz rule is obeyed by the clustered polymer and that the breakdown of time–temperature superposition is manifested only by deviations in the shape of the *storage modulus* in the terminal zone. It is interesting to note that the proportionality of the viscosity to the square of SIP concentration below 10 mol % is in line with predictions of a recent theory by Leibler et al.[35] on the relaxation behavior of linear entangled chains containing a small number of "stickers", i.e., sites capable of forming temporary cross-links.

For all the resins investigated the viscous flow process appears to be Arrhenius-activated over the temperature range covered (>230 °C), but the activation energy is strongly dependent on the level of SIP (see Figure 9). Over the full range of SIP concentration (0–20 mol %), the activation energy nearly doubles and it appears to be linearly dependent on concentration. Because of significant scatter in the data, it is not possible to determine whether a discontinuity or an inflection exists at the clustering point which, as in the case of η_{nom} above, may be too diffuse to detect by this method. A systematic increase in flow activation with an increase in cross-link density was also observed for chemically cross-linked polymers below their gel point,[36,37] thus suggesting that the flow activation process is intimately related to the structure of the evolving ionic network. The change in activation energy, which represents the size of the flow unit, is fully consistent with the qualitative picture of the RM model if one assumes that the flow unit comprises portions of the restricted mobility regions. The volume of the restricted mobility region, hence the activation energy of the melt, is expected to increase linearly with ion content.

The qualitative picture of ionic aggregation and clustering that emerges from the rheological data is corroborated by other characterization techniques.[6] Although interpretation of small angle X-ray scattering (SAXS) data is still not fully resolved, the appearance of the so-called *ionomer* (or *cluster*) *peak* at relatively low Bragg angles is considered a characteristic feature of the superstructure of the ionic aggregates in random ionomers and is usually associated with clustering. For the PEI's of this study a cluster peak appears at ca. 8 mol % SIP with a d_{Bragg} of 55–70 Å.[6] The apparent Bragg spacing is independent of ionic content at higher concentrations but the intensity of the peak is increased with ion concentration. This result is similar to that reported for polystyrene-based ionomers[1] and, according to the RM model, it expresses the average intermultiplet spacing within a cluster, which is closely related to the persistence length of the backbone ($d_{Bragg} \approx 2 \times$ persistence length + diameter of multiplet). Differential scanning calorimetry data also lend some credence to the proposed clustering mechanism. Although the PEI's are nominally semicrystalline, crystallinity is fully suppressed at SIP levels ≥10 mol %, i.e. above the clustering point.[6] This implies that crystallinity is excluded from the restricted mobility regions within the cluster, thus asserting the idea of phase dominance (or phase inversion) proposed in the RM model. The absence of crystallinity in the clustered polymers may be kinetic in origin, i.e., crystallization rate within the hydrocarbon phase of the cluster is retarded due to its restricted mobility. Indeed, under extensive annealing crystallinity can be induced even in samples containing high levels of SIP.[6] Strong suppression of crystallinity at high ionic content was noted also by Gorda and Peiffer[27] who studied a similar system of sulfonated poly(butylene terephthalate)s. Also, in complete agreement with the dynamic-mechanical data (see Figures 5 and 11), it is found that the glass transition temperature (of the matrix) increases linearly with ion content which is attributed to the increase in cross-link density, i.e., the number of multiplets in the system. Essentially, the strongly associated multiplets place restrictions on the backbone mobility within the matrix, thus raising its T_g. The general efficiency of the ionic aggregates to raise the T_g of the host polymer appears to be quite low ($dT_g/dC \approx 0.8$ °C/mol %) compared to other random ionomer systems.[1,38] However, as noted previously, this is partly due to the fact that expressing ion concentration in units of mol % does not adequately represent the interionic distance on the chain. Since the length of the repeat unit of PET is large compared to that of vinyl polymers (ca. 11 and 2.5 Å, respectively), the effective concentration dependence of T_g is much stronger than implied by the value given above. We also note that no discontinuity or inflection around the clustering point, 10 mol % SIP, is detected and it is difficult to discern a second T_g from the DSC traces.

Summary

The melt rheology of PET modified with SIP, a fully neutralized sulfonate moiety, was investigated over a wide range of compositions and temperatures. The addition of SIP is shown to substantially increase the zero-shear viscosity (Figure 8), the plateau modulus (Figure 4) and the glass transition temperature (Figure 11) of the host polymer, in line with observations on other random ionomers. (It is noted that the melt viscosity results are corrected for differences in molecular weight by shifting data for resins with various inherent viscosities (IV's) to a standard IV and temperature; see eq 4.)

The dramatic effect of SIP on melt viscosity and plateau modulus is attributed to the formation of stable ionic aggregates which act as simple thermoreversible cross-links; At low SIP concentration, these aggregates can be classified as multiplets, i.e., several associated ion pairs, which increase the effective molecular weight of the polymer without modifying the basic nature of its relaxation response. Above some critical ion concentration (ca. 10 mol % SIP) the multiplets appear to form a distinct microphase—a cluster. This is manifested mainly by the breakdown of the time–temperature superposition rule, the suppression of crystallinity, the appearance of a

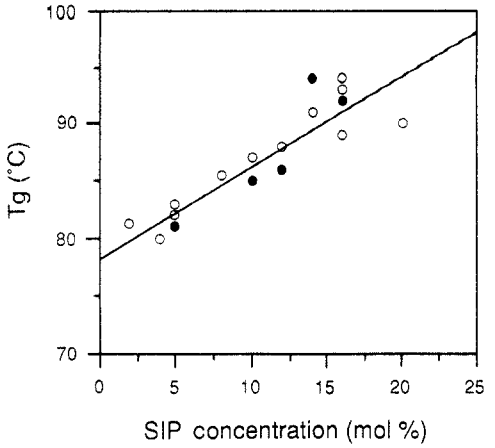

Figure 11. Glass-transition temperature vs SIP concentration for modified PET's: (○) by DSC,[6] (●) by DMA (based on G'' peak).

characteristic *cluster* peak at low Bragg angles in SAXS diffraction data and by a large increase in the slope of a double logarithmic curve of viscosity vs ion concentration. The multiplet-to-cluster transition and other related phenomena reported here are qualitatively similar to data on polystyrene-based and other random ionomers and are generally consistent with the restricted mobility model of Eisenberg et al.[25] In variance with the RM model, however, we do not observe "cluster T_g's" through either calorimetric or dynamic-mechanical measurements, and the so-called multiplet-to-cluster "transition" is a rather diffuse concentration range over which the ionic aggregates approach a critical size and appear to phase-separate from the polymer matrix. This phase heterogeneity is detectable only by dynamic-mechanical measurements in the terminal zone and by small angle X-ray diffraction on the solid polymer.

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