Rheological Properties of Polystyrene-*b*-poly(sodium methacrylate) Diblock Ionomers

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ABSTRACT: The rheological properties of diblock ionomers based on polystyrene-*b*-poly(sodium methacrylate) (PS-*b*-PMANa) were studied. Comparing the melt rheology of the block ionomer with that of the star-shaped polymer, it was seen that the viscoelastic properties of the diblock ionomer could be attributed to the same molecular motion as those of star polymers, since the PS-*b*-PMANa forms micelles that persist even in the melt because of the strong association of the ionic blocks. The dynamic viscoelastic functions of the block ionomer suggested the existence of an additional relaxation at low frequencies. The additional relaxation was thought to be due to the thermal rotational diffusion of the micelles, restricted by the retraction process of polystyrene block chains. The estimated relaxation time was in good agreement with that found experimentally. An alternative explanation of the additional relaxation was based on the possible action of the micelles as a filler, since the rheological behavior of the diblock ionomer at low frequencies was similar to that of a suspension.

I. Introduction

Block copolymers have been the subject of extensive investigation during the past three decades, and many studies have been devoted to their morphology and physical properties. A large number of books and review articles have appeared on the subject,[1−14] so only a brief summary of the features most relevant to the present investigation will be presented here.

It has been shown that diblock copolymers form micellar structures at relatively low concentrations when dissolved in a selective solvent, i.e., a solvent that is good for one block but poor for the other.[9−14] The block copolymer micelles consist of aggregates of the insoluble blocks in the core, with chains of the soluble blocks forming the brush or corona. The stability of the micelles depends on the chemical nature of both the blocks and the solvent. It has also been reported that the properties of block copolymer micelles are in some respects similar to those of low molecular weight surfactants; for example, critical micelle concentrations have been observed.

Other physical properties of block copolymers have also been studied in relation to their morphology, but since this work deals with melt rheology, we mention only viscoelastic studies. Block copolymers tend to form ordered structures, and these can have an important effect on rheological behavior. Watanabe and Kotaka[8] investigated the dynamic viscoelasticity of polystyrene-*b*-polybutadiene diblock copolymers and polystyrene-*b*-polybutadiene-*b*-polystyrene triblock copolymers in concentrated solutions in a selective solvent. In such systems, micelle formation is observed; i.e., the polystyrene blocks associate to form cores surrounded by the polybutadiene block "brush". It is worth noting that a micellar structure was also observed by these authors in blends of polystyrene-*b*-polybutadiene diblocks with low molecular weight polybutadiene. Most importantly, they have reported that the micellar structure is associated with a slow relaxation mode that appears as an inflection or a shoulder at low frequencies in plots of the shear storage and shear loss moduli as functions of frequency. From an analysis using a tube model, they suggest the possible cooperative motion of the polybutadiene block corona.

Micellar structures resemble multiarm stars,[13] which suggests that we should compare their viscoelastic properties with those of star-shaped polymers in the melt. The melt rheology of star-shaped polymers has been studied since the late 1970s.[15−24] One of the characteristic features is an anomalous molecular weight dependence of the melt viscosity. The value of η_0 increases exponentially with molecular weight; i.e., the materials are subject to a strong viscosity enhancement. A tube model has been used to explain the linear viscoelasticity of star polymers.[25−29]

In block ionomers, i.e., block copolymers in which one of the blocks is ionic, the driving force for the phase separation is much greater than in nonionic systems.[11] Therefore, the enhancement of the numerical values of the properties (modulus, viscosity, etc.) that depend on phase separation should be higher than in their nonionic counterparts. Recently, several teams have investigated the structure and physical properties of block ionomers.[11,30−48] Most of these studies have been performed in a composition region in which the ionic domains are spherical. It has been reported that the properties of these materials are dominated by the large driving force for phase separation and by the fact that the glass transition temperature of the ionic blocks is, in general, much higher than that of the nonionic materials.

In this laboratory, the triblock ionomers of poly(4-vinylpyridine)-*b*-polystyrene-*b*-poly(4-vinylpyridine) quaternized with methyl iodide (P(4VP MeI)-*b*-PS-*b*-P(4VP MeI)) have been investigated with regard to their physical properties and phase structure. Gauthier and Eisenberg[33] showed that the block ionomers form a much more distinctly phase-separated structure than random ionomers of the same chemical species and that the block ionomers exhibit rubber elasticity behavior

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characteristic of a network. Gouin et al. have studied the structure of the block ionomer by small-angle X-ray scattering (SAXS)[34] and small-angle neutron scattering (SANS).[41] A peak corresponding to the ion aggregate lattice and structure factor features due to spheres were observed by SAXS. The distance between the centers of the ion aggregates increased with increasing ionomer block length. They also reported that the radius of gyration for the mid-block PS measured by SANS is comparable to that of homopolymer PS of the same molecular weight.

Recently, Desjardins et al.[37,42] prepared diblock ionomers of polystyrene-*b*-poly(sodium methacrylate) (PS-*b*-PMANa) and polystyrene-*b*-poly(cesium methacrylate) (PS-*b*-PMACs) and investigated their physical properties. In a selective solvent (good for PS), the diblock ionomers form reverse micelles with ionic cores. These reverse micelles are extremely stable, so that their size can be determined by size exclusion chromatography (SEC), intrinsic viscosity, or dynamic light scattering (DLS). The sizes estimated by these various methods agree with each other. The sizes of the micelles, e.g., the aggregation numbers, increase with the ionomer block length. Gao et al.[40] have also shown by means of nuclear magnetic resonance (NMR) that water in a solution of these micelles is in dynamic equilibrium between the ion core and the solvent. The partition of the water between the different environments is determined by the physicochemical properties of the solvent. Measurements of the aggregation numbres in the solid state, i.e., by SAXS or electron microscopy, generally tend to give values that are higher than those obtained by solution experiments, i.e., SEC or DLS. Desjardins and Eisenberg[44] also have prepared poly(sodium methacrylate)-*b*-polystyrene-*b*-poly(sodium methacrylate) (PMANa-*b*-PS-*b*-PMANa) triblock ionomers and have measured their mechanical properties. They found that the glass transition temperature of the ionic domains is extremely high, i.e., that the ionic core is very stable even at high temperatures.

For the diblock ionomers, no melt rheological study has been performed as yet. The PS-*b*-PMANa system has been found to form very stable reverse micelles,[37,42,44] which are expected to retain their structure in the melt. Thus, it is of interest to compare the melt rheology of the block ionomers with that of other block copolymers, on the one hand, and with that of star-shaped polymers on the other. This is the purpose of the present investigation. It will be shown that the melt rheology of the diblock ionomers is similar to that of star polymers. It will also be shown that the micelles of the diblock ionomers produce an additional relaxation at very low frequencies, as has been found in other block copolymer systems, and a molecular interpretation of this relaxation process will be offered.

II. Experimental Section

Materials. Polystyrene-*b*-poly(methacrylic acid) diblock copolymers were synthesized by ionic polymerization and hydrolyzed as described previously.[37] The block copolymers in the acid form were neutralized in benzene/methanol (90/10) by adding methanolic sodium hydroxide. The solutions were freeze-dried and further dried under vacuum at about 160 °C for 1 day. The compositions of the block ionomers are given in Table 1.

It was observed previously that, in solution, the blocks containing very short ionic segments are leached out of the reverse micelles.[37] In order to separate out this dissolved material, i.e., the single chains containing very short ionic segments, from the micelle fraction, a solution fractionation technique was employed. This technique involved the dissolution of the total polymer, i.e., the micelle and the single chains, in benzene/methanol (65/35) at about 80 °C and then cooling to room temperature. The precipitated material that was obtained by this procedure consisted of micelles with only a negligible amount of single chains. The relative amount of micelles (f_m) in the whole polymer is also listed in Table 1.

Table 1. Molecular Architecture and Micelle Fraction of the Diblock Ionomers

	PS unit	PMANa unit	f_m (wt %)	N_{agg}[a]	r_{sc}/d_{Bragg}[a]
PS(1100)	1085				
PS(1100)PMANa(6)	1085	6	20		
PS(1100)PMANa(21)	1085	21	45	44	0.173
PS(1100)PMANa(42)	1085	42	48	112	0.220
PS(1100)PMANa(59)	1085	59	54	205	0.244
PS(1100)PMANa(6)P	1085	6	100	N/A	N/A
PS(1100)PMANa(21)P	1085	21	100	N/A	N/A
PS(1100)PMANa(59)P	1085	59	100	N/A	N/A
PS(170)	166				
PS(170)PMANa(9)	166	9	72	26	0.215
PS(170)PMANa(25)	166	25	89	50	0.333

[a] Data were measured by small-angle X-ray scattering.[37]

The sample designation PS(x)PMANa(y) indicates that the diblock ionomer is composed of a block of x units of polystyrene and a block of y units of poly(sodium methacrylate). PS(x)-PMANa(y)P designates the solution-fractionated (purified) diblock ionomer, and PS(x) means pure polystyrene of x units.

Rheological Measurements. For rheological measurements, the samples were compression molded at temperatures between 160 and 260 °C (depending on the fraction of the ionic block) into disks 25 mm in diameter and about 0.7 mm in thickness. A Rheometrics Dynamic Analyzer RDA-II was used to measure the dynamic viscoelastic properties of the block ionomers with parallel disk fixtures.

Measurements were performed in the frequency range from 0.1 to 100 rad/s at temperatures between 130 and 300 °C. At temperatures above 150 °C, the measurements were done in a nitrogen atmosphere to avoid the thermal oxidation of the samples. Strain values were kept within the linear region.

III. Results

For most polymers, viscoelastic functions measured at various temperatures can be superposed onto a master curve, employing time−temperature superposition. For some ionomers, the inapplicability of this method has been reported, especially for high ion contents.[49−57] However, since these systems contain ionic groups only inside the core, and not in the parts of polymer chain that are subject to deformation during dynamic flow, it is reasonable to expect time−temperature superposition to be applicable. Therefore, time−temperature superposition is used to analyze the results for the diblock ionomers.

Parts a and b of Figure 1 show the storage modulus $G'(\omega)$ and loss modulus $G''(\omega)$ for the PS(1100)PMANa(59) block ionomer at various temperatures. These curves show the transition, rubbery plateau, and terminal regions, just as in the case of linear polystyrene. However, in the terminal region, there is an additional inflection or shoulder, suggesting the existence of an additional relaxation mechanism. The time−temperature superposition applies very well to this block ionomer as well as to the other samples of the present study. The master curves of $G'(\omega)$ and $G''(\omega)$ are shown in parts a and b of Figure 1, respectively. The reference temperature is 160 °C.

Parts a and b of Figure 2 show master curves for $G'(\omega)$ and $G''(\omega)$, respectively, of the unfractionated family of

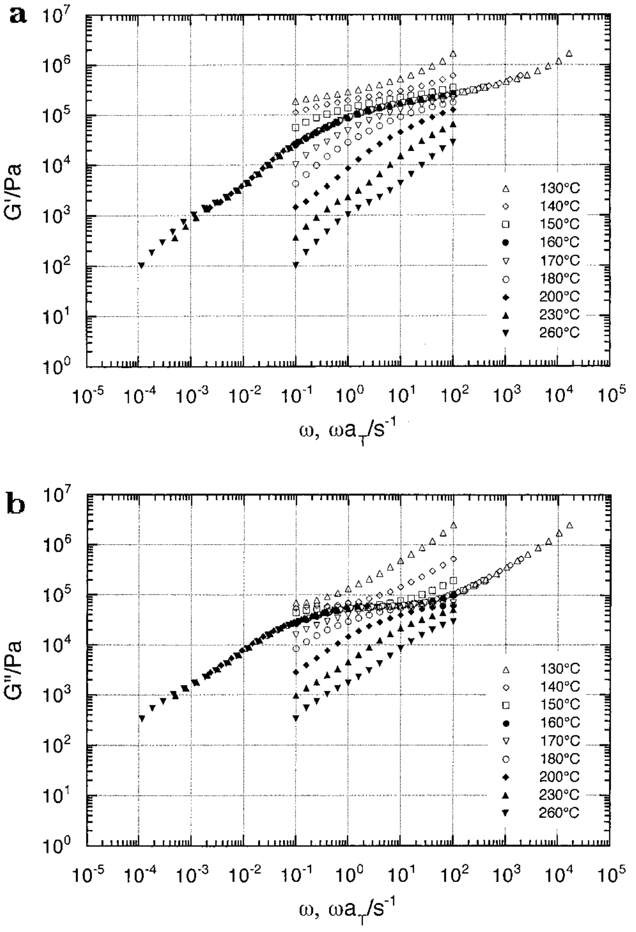

Figure 1. (a) Shear storage modulus $G'(\omega)$ for the PS(1100)-PMANa(59) block ionomer at various temperatures. The master curve of $G'(\omega)$ is also given. (b) Shear loss modulus $G''(\omega)$ for the PS(1100)PMANa(59) block ionomer at various temperatures. The master curve of $G''(\omega)$ is also given. The reference temperature is 160 °C.

the block ionomers with 1100 unit PS blocks, i.e., the PS(1100)PMANa(y) series, which contains both ionic micelles and single chains. $G'(\omega)$ and $G''(\omega)$ of the parent PS(1100) are also shown for comparison. The rubbery plateau region of the block ionomers extends to lower frequencies, and the plateau modulus, $G_N°$ is slightly higher than that of PS(1100). At low frequencies, the additional relaxation mentioned above is clearly seen as a shoulder in both the $G'(\omega)$ and $G''(\omega)$ plots for block ionomers with ionic blocks longer than 6 units. Except for this additional relaxation, the viscoelastic behaviors of these systems are almost the same. Since the $G_N°$ is comparable to that of polystyrene, the viscoelasticity of the block ionomers at these frequencies corresponds to the entanglement relaxation of the polystyrene chain. The values of $G'(\omega)$ and $G''(\omega)$ at low frequencies, specifically the heights of the shoulders, increase with the poly(sodium methacrylate) (PMANa) block length.

It is of interest to see the effect of fractionation on the viscoelastic behavior of the diblock ionomers. Parts a and b of Figure 3 show $G'(\omega)$ and $G''(\omega)$ for the solution-fractionated block ionomers PS(1100)PMA-Na(y)P. The $G'(\omega)$ and $G''(\omega)$ plots look qualitatively similar to those for the unfractionated materials. However, the solution fractionation shifts the terminal region to lower frequencies and makes the plateau region wider and the shoulder higher.

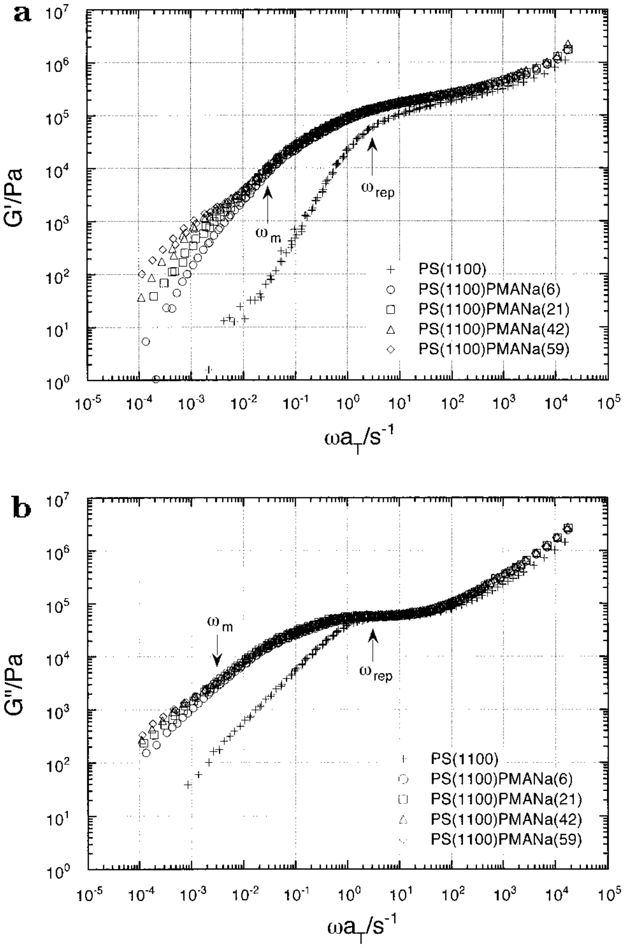

Figure 2. (a) Master curves of $G'(\omega)$ for the unfractionated family of the block ionomers: the PS(1100)PMANa(y) series. The master curve of the parent PS(1100) is also shown. The reference temperature is 160 °C. The characteristic time, $\tau_{rep} = 3.26 \times 10^{-1}$ s for PS(1100) and $\tau_m = 3.36 \times 10^1$ s, for PS-(1100)PMANa(y), are represented by arrows as reciprocal values ω_{rep} ($=1/\tau_{rep}$) and ω_m ($=1/\tau_m$), respectively. (b) Master curves of $G''(\omega)$ for the unfractionated family of the block ionomers: the PS(1100)PMANa(y) series. The master curve of the parent PS(1100) is also shown. The reference temperature is 160 °C. The arrows represent ω_{rep} and ω_m, as in (a).

The samples discussed above have a PS block length of 1100 units, far in excess of the entanglement spacing of PS. By contrast, the 170 unit chain of polystyrene is shorter than the critical length for entanglements. It is of interest to see how the PS(170)PMANa(y) block ionomers behave. Parts a and b of Figure 4 show $G'(\omega)$ and $G''(\omega)$ for the PS(170)PMANa(y) systems. These diblock ionomers show an inflection and a plateau region at about 3×10^5 and 5×10^4 Pa, respectively. The PS(170)PMANa(25) sample does not flow in the experimental range.

It is known that the shift factor, a_T, for time–temperature superposition at temperatures between the glass transition temperature, T_g, and $T_g + 100$ °C follows the WLF relation,[58] i.e.,

$$\log a_T = \frac{-c_1(T - T_r)}{c_2 + (T - T_r)} \qquad (1)$$

where T_r is the reference temperature, and c_1 and c_2 are the WLF parameters. c_1 and c_2 become material constants when $T_r - T_g$ is fixed. In this study, T_r is taken at 160 °C as mentioned before. Figure 5 shows WLF plots: a_T against $T - 160$ for PS(1100)PMA-

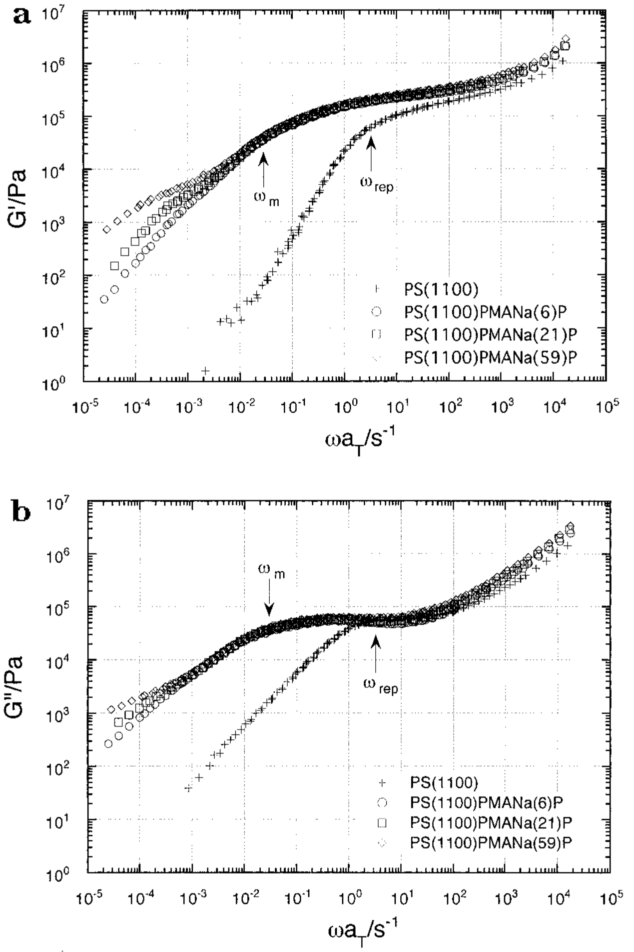

Figure 3. (a) Master curves of $G'(\omega)$ for the solution-fractionated block ionomers: the PS(1100)PMANa(y)P series. The master curve of the parent PS(1100) is also shown. The reference temperature is 160 °C. The characteristic times, $\tau_{\mathrm{rep}} = 3.26 \times 10^{-1}$ s for PS(1100) and $\tau_{\mathrm{m}} = 3.36 \times 10^{1}$ s for PS-(1100)PMANa(y)P, are represented by arrows as reciprocal values ω_{rep} ($=1/\tau_{\mathrm{rep}}$) and ω_{m} ($=1/\tau_{\mathrm{m}}$), respectively. (b) Master curves of $G''(\omega)$ for the solution-fractionated block ionomers: the PS(1100)PMANa(y)P series. The master curve of the parent PS(1100) is also shown. The reference temperature is 160 °C. The arrows represent ω_{rep} and ω_{m}, as in (a).

Na(y), PS(1100)PMANa(y)P, and PS(170)PMANa(y). Each family also includes the plot for the parent polystyrene of length identical to that of the block ionomer for comparison. The temperature dependence of a_T of the block ionomers is the same as that of the parent polystyrene; i.e., a_T is independent of the PMANa block length (ionomer content). This behavior is quite different from that of the poly(styrene-*co*-sodium methacrylate) random ionomers.[49] In the case of the random ionomers, the temperature dependence of a_T changes dramatically as the ionomer content increases. This independence of a_T on the ionomer content for the diblock ionomer implies that the temperature shift of the rheological functions of the diblock ionomer is dominated by the polystyrene phase and that the ion core is rigid at least up to 300 °C, as is also the case for the selective solvents at room temperature. The WLF parameters c_1 and c_2 calculated from these plots are listed in Table 2. The values of c_1 and c_2 for the block ionomers are almost the same as the values for a star polystyrene: $c_1 = 6.40$ and $c_2 = 111$.[16]

The elasticity of polymer melt can be characterized by $G_N°$, which is related to the molecular weight between entanglements M_e by[58]

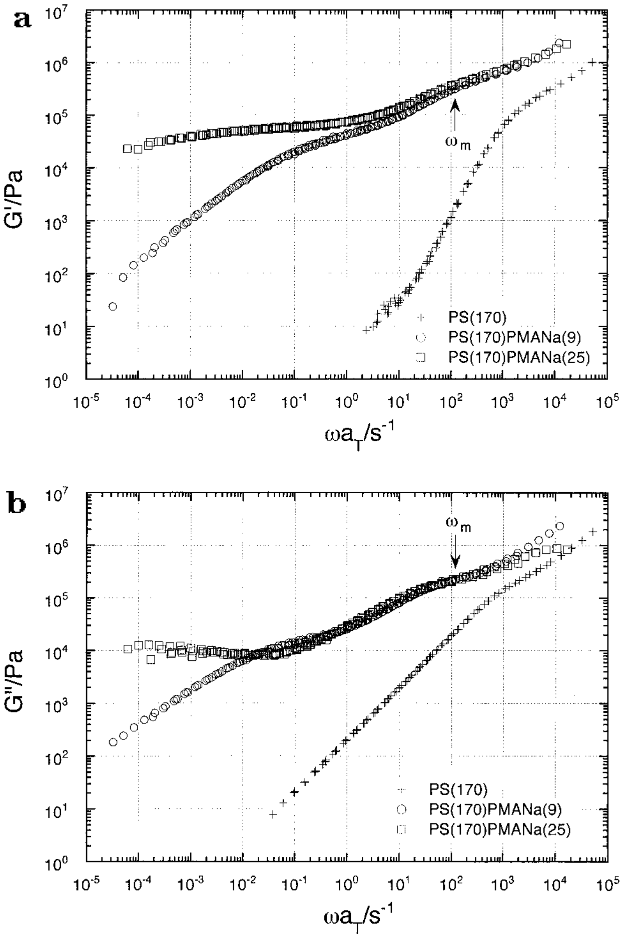

Figure 4. (a) Master curves of $G'(\omega)$ for the PS(170)PMA-Na(y) series. The master curve of the parent PS(170) is also shown. The reference temperature is 160 °C. The characteristic time, $\tau_{\mathrm{m}} = 8.10 \times 10^{-3}$ s for PS(1100)PMANa(y), is represented by the arrow as a reciprocal value ω_{m} ($=1/\tau_{\mathrm{m}}$). (b) Master curves of $G''(\omega)$ for the PS(170)PMANa(y) series. The master curve of the parent PS(170) is also shown. The reference temperature is 160 °C. The arrow represents ω_{m} ($=1/\tau_{\mathrm{m}}$), as in (a).

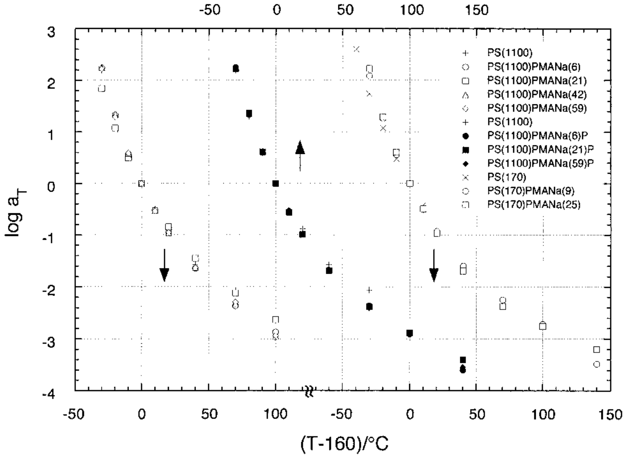

Figure 5. WLF plots of a_T for PS(1100)PMANa(y), PS(1100)-PMANa(y)P, and PS(170)PMANa(y).

$$G_N° = \frac{\rho R T}{M_e} \tag{2}$$

The value of $G_N°$ is estimated from the frequency dependence of $G''(\omega)$:[58]

Table 2. WLF Parameters and Rheological Characteristics of the Diblock Ionomers

	c_1	c_2	$G_N°$ (Pa)	η_0 (Pa s)	$J_s°$ (Pa^{-1})	$\eta_0 J_s°$ (s)
PS(1100)	5.8	110	2.10×10^5	5.37×10^4	2.00×10^{-5}	1.07×10^0
PS(1100)PMANa(6)	6.4	119	2.59×10^5	1.02×10^6	1.82×10^{-4}	1.86×10^2
PS(1100)PMANa(21)	6.2	112	2.87×10^5	1.82×10^6	2.69×10^{-4}	4.90×10^2
PS(1100)PMANa(42)	6.2	112	2.89×10^5	2.50×10^6	6.92×10^{-4}	1.73×10^3
PS(1100)PMANa(59)	6.2	113	2.79×10^5	2.82×10^6	1.07×10^{-3}	3.02×10^3
PS(1100)PMANa(6)P	6.6	118	2.62×10^5	8.76×10^6	3.17×10^{-4}	2.78×10^3
PS(1100)PMANa(21)P	6.6	118	2.76×10^5	1.46×10^7	4.61×10^{-4}	6.73×10^3
PS(1100)PMANa(59)P	7.3	126	3.09×10^5			
PS(170)	6.0	130		1.84×10^2	3.40×10^{-6}	6.26×10^{-4}
PS(170)PMANa(9)	6.1	114	3.63×10^5 4.56×10^4 [a]	4.72×10^6	1.24×10^{-3}	5.85×10^3
PS(170)PMANa(25)	6.6	107	2.81×10^5 7.98×10^4 [a]			

[a] Plateau modulus at low frequencies.

$$G_N° = \frac{2}{\pi}\int_{-\infty}^{\infty}\{G''(\omega) - G''_g(\omega)\}\,d\ln\omega \tag{3}$$

where $G''_g(\omega)$ is the loss modulus contribution from the glass transition. The viscoelastic flow of the molten polymer is characterized by the limiting viscosity at zero shear rate (η_0) and the steady-state shear compliance ($J_s°$). η_0 is a measure of the fluidity of the polymer and is proportional to the longest relaxation time. $J_s°$ corresponds to the permanent elasticity. These are estimated from the frequency dependence of $G'(\omega)$ and $G''(\omega)$ as follows:[58]

$$\eta_0 = \lim_{\omega\to 0}\left[\frac{G''(\omega)}{\omega}\right] \tag{4}$$

$$J_s° = \lim_{\omega\to 0}\left[\frac{G'(\omega)}{(\eta_0\omega)^2}\right] \tag{5}$$

The estimated values are summarized in Table 2. The $G_N°$ values for the block ionomers are almost constant but are slightly larger than that of the parent polystyrene. The values of η_0 and $J_s°$ increase with PMANa block length, corresponding to the increase of the shoulder height. Comparing these values for fractionated and unfractionated diblock ionomers, the $G_N°$ value for the fractionated block ionomers is the same as that for the unfractionated materials, since it depends mainly on M_e of the polystyrene. However, the η_0 and $J_s°$ values for the solution-fractionated block ionomers are much larger than those for the unfractionated block ionomers.

The PS(170)PMANa(*y*) samples show an inflection and a plateau region, and the value of $G_N°$ for the high-frequency inflection is the same as that of the pure polystyrene plateau, as mentioned above. The rubbery plateau at low frequencies is broad, and the $G_N°$ value is relatively high when compared with that from the shoulder of the PS(1100)PMANa(*y*).

IV. Discussion

A spherical micellar structure of PS(*x*)PMANa(*y*) block ionomers has been suggested on the basis of results of SEC and DLS experiments with a selective solvent, such as dimethylformamide (DMF) or tetrahydrofuran (THF), as well as SAXS experiments on the solid state at room temperature.[37,42] A micelle structure involves an ionic core, i.e., an aggregate of PMANa blocks. Since the chains in the ion core are subjected to strong ionic interactions, it is expected that the core will remain stable up to relatively high temperatures.

For the diblock ionomers with PS blocks of 1100 units, $G'(\omega)$ shows a rubbery plateau at high frequencies and an inflection at low frequencies, as was shown in Figures 2 and 3. Except for this inflection, the viscoelastic behaviors of the various block copolymers in this system are almost identical. Since the plateau modulus is comparable to that of polystyrene, the viscoelasticity of the block ionomers in this frequency region is dominated by the entanglement relaxation of the PS chains, i.e., the “brush” of the micelles. The appearance of an inflection at low frequencies suggests the existence of an additional relaxation. Furthermore, the values of $G'(\omega)$ and $G''(\omega)$ at low frequencies (the widths of the shoulders) increase with the PMANa block length. Since with increasing PMANa block length the ionic cores of the diblock ionomer micelles become larger,[37] it appears that the additional relaxation is related to the size of the ion core and to the aggregation number.

Fractionated diblock ionomers, PS(1100)PMANa(*y*)P, show larger inflections, which appear at lower frequencies than those in the unfractionated diblock ionomers. The removal of single PS chains is the reason for this difference.

In the case of the diblock ionomers with PS blocks of 170 units, $G'(\omega)$ shows an inflection at high frequencies and a plateau region at low frequencies, as mentioned before. Since the inflection at high frequencies has the same value as the rubbery modulus of PS, this feature is most likely due to entanglements of the PS chains. Entanglements occur because of the micelle structure of the diblock ionomer, which effectively raises the molecular weight. The plateau at low frequencies is probably attributable to a slower relaxation process than that of the entanglement relaxation. Its modulus and width are larger than those of the shoulder of $G'(\omega)$ for PS(1100)PMANa(*y*) diblocks. Furthermore, PS(170)-PMANa(25) does not flow in the experimental range. Thus the viscoelastic behavior of the PS(170)PMANa(*y*) series is slightly different from that of the PS(1100)PMANa(*y*) series. This is possibly associated with a morphological change of the core, e.g. to rods.

The micelle structure observed here makes the polymers similar to a star-shaped polystyrene with many arms.[13] Pearson and Helfand[28] calculated the viscoelastic properties of star polymers using the tube model. In the case of a linear polymer in which the molecular weight M is larger than $2M_e$ (M_e is the molecular weight between entanglements; for polystyrene $M_e = 18\,100$[59]), the diffusion of an entangled polymer chain can be modeled by reptation in a tube.[28] The characteristic time of reptation τ_{rep} is

$$\tau_{\mathrm{rep}} = \frac{n\zeta {L_{\mathrm{eq}}}^{2}}{2k_{\mathrm{B}}T} \tag{6}$$

where L_{eq} is the contour length of the chain at equilibrium

$$L_{\mathrm{eq}} = \left(\frac{M}{M_{\mathrm{e}}}\right)a \tag{7}$$

n is the number of monomer units per chain, ζ is the friction coefficient of a monomer, k_{B} is Boltzmann's constant, and a is the radius of the tube. τ_{rep} can be related to $G_{\mathrm{N}}{}^{\circ}$ and η_0:

$$\tau_{\mathrm{rep}} = \left(\frac{12}{\pi}\right)\frac{\eta_0}{G_{\mathrm{N}}{}^{\circ}} \tag{8}$$

The entangled star polymer cannot simply reptate in its star-shaped tube because of the branch point. According to the model of Pearson and Helfand, the branch point of the star polymer can diffuse only when one of the arm chains comes back to the branch point and creates another arm tube. This mechanism is called retraction of the arm chain. Thus, the characteristic time of star polymer, τ_{m}, depends only on the length of the arm chains and is much larger than τ_{rep} for a linear polymer of the same total molecular weight as the star polymer. Pearson and Helfand calculated τ_{m} assuming a Hookean potential for the retraction of the arm chain. The result is

$$\tau_{\mathrm{m}} = \left(\frac{na\zeta^{*}{L_{\mathrm{eq}}}^{2}}{2\alpha k_{\mathrm{B}}T}\right)\left(\frac{\pi}{\alpha}\right)^{1/2} \mathrm{e}^{\alpha} \tag{9}$$

where

$$\alpha = \nu'\left(\frac{M_{\mathrm{a}}}{M_{\mathrm{e}}}\right) \tag{10}$$

ζ^{*} is the friction coefficient for a monomer in the arm of the star polymer, ν' is a numerical factor obtained experimentally, and M_{a} is the molecular weight of one arm chain. Assuming $\zeta^{*} = \zeta$ and $\alpha \gg 1$, we obtain

$$\tau_{\mathrm{m}} = \left(\frac{\tau_{\mathrm{rep}}}{\alpha}\right)\left(\frac{\pi}{\alpha}\right)^{1/2} \mathrm{e}^{\alpha} \sim \left(\frac{M_{\mathrm{a}}}{M_{\mathrm{e}}}\right)^{3/2} \exp\left[\nu'\left(\frac{M_{\mathrm{a}}}{M_{\mathrm{e}}}\right)\right] \tag{11}$$

η_0 of a star polymer is then given by

$$\eta_0 = \frac{G_{\mathrm{N}}{}^{\circ}}{2\alpha}\tau_{\mathrm{m}} \sim \left(\frac{M_{\mathrm{a}}}{M_{\mathrm{e}}}\right)^{1/2} \exp\left[\nu'\left(\frac{M_{\mathrm{a}}}{M_{\mathrm{e}}}\right)\right] \tag{12}$$

This result shows again that τ_{m} and η_0 of a star polymer depend on the molecular weight of its arms (M_{a}) but not on the total molecular weight. The theory explains very well the experimental results for star-shaped polystyrene, polybutadiene, polyisoprene, etc.

The characteristic times, τ_{rep} for PS(1100) and τ_{m} for PS(1100)PMANa(y) and PS(1100)PMANa(y)P, were estimated using the above theory. The results are $\tau_{\mathrm{rep}} = 3.26 \times 10^{-1}$ s for PS(1100) and $\tau_{\mathrm{m}} = 3.36 \times 10^{1}$ s for PS(1100)PMANa(y) and PS(1100)PMANa(y)P. These numbers are represented by arrows in Figures 2a,b and 3a,b as reciprocal values ω_{rep} ($=1/\tau_{\mathrm{rep}}$) and ω_{m} ($=1/\tau_{\mathrm{m}}$). These values agree well with the terminal frequency of the rubbery plateau for PS(1100), PS(1100)PMANa(y), and PS(1100)PMANa(y)P. For PS(1100)PMANa(y), ω_{m} is slightly lower than the expected terminal frequency, while for PS(1100)PMANa(y)P, it is close to the expected terminal frequency. Since the $G'(\omega)$ and $G''(\omega)$ plots are independent of the PMANa block length except for the shoulder arising from the additional relaxation, these deviations between τ_{m} and the expected terminal frequencies for the unfractionated block ionomers may be due to the existence of a small amount of unmicellized chains. It is noteworthy that a single τ_{m} value can explain the terminal frequency zone for all the block ionomers with polystyrene blocks of 1100 units. This also implies that the block ionomers maintain their micellar structure even in the molten state at high temperatures, with the polystyrene blocks behaving like the arms of a star polymer.

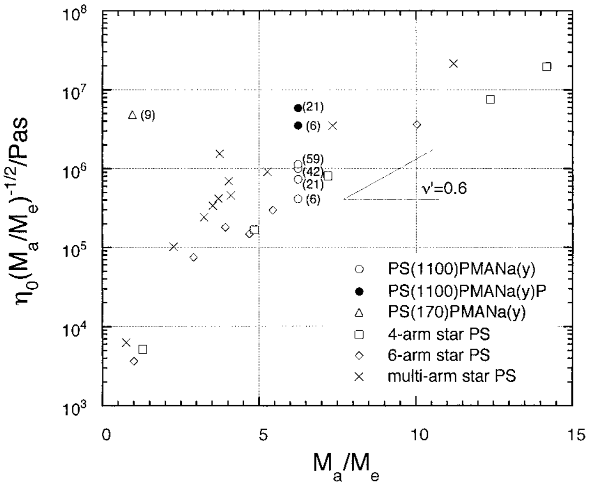

Figure 6. $\eta_0(M_{\mathrm{a}}/M_{\mathrm{a}})^{-1/2}$ vs $M_{\mathrm{a}}/M_{\mathrm{e}}$ for the block ionomers. The experimental values for star polystyrenes[16,18,21,22] are also plotted for comparison. The slope corresponding to the value $\nu' = 0.6$ suggested by Pearson and Helfand[28] is depicted. The number in parentheses represents PMANa block length.

For PS(170)PMANa(y), a value of 8.10×10^{-3} s is estimated for τ_{m}. This value is represented by an arrow in Figure 4a,b as ω_{m} ($=1/\tau_{\mathrm{m}}$). Although the molecular weight of PS(170) is smaller than $2M_{\mathrm{e}}$, the value of τ_{m} is in good agreement with the terminal frequency zone of the inflection at high frequencies for the PS(170)-PMANa(y). This implies that the PS(170)PMANa(y) series also has the polystyrene brush behaving like an entangled star polymer.

A convenient way of presenting the viscosity data for star polymers is suggested when eq 12 is modified to

$$\log\left[\eta_0\left(\frac{M_{\mathrm{a}}}{M_{\mathrm{e}}}\right)^{-1/2}\right] \propto \frac{M_{\mathrm{a}}}{M_{\mathrm{e}}} \tag{12'}$$

Thus, a plot of $\log[\eta_0(M_{\mathrm{a}}/M_{\mathrm{e}})^{-1/2}]$ against $M_{\mathrm{a}}/M_{\mathrm{e}}$ should give a straight line for star polymers. This line should be independent of the number of the arms, but the slope should be related to the parameter ν'. The experimental data for the block ionomers are plotted in Figure 6 using the above relation, along with the experimental values for star polystyrenes with various numbers of arms reported by Graessley and Roovers[16] and by Masuda et al.[18,21,22] This plot shows good agreement with theory, and the value $\nu' = 0.6$ suggested by Pearson and Helfand appears to be appropriate. The points for the

PS(1100)PMANa(y) series fall near the curve defined by data for the star polystyrenes. This again is consistent with a micellar structure of the block ionomer in the melts. The value of $\eta_0(M_a/M_e)^{-1/2}$ for the block ionomers increases with increasing PMANa block length, corresponding to the increase of η_0, which involves a contribution from the additional relaxation. This increase must be due to the enlargement of the ionic core and the aggregation number with increasing ionic block length.

In the case of PS(170)PMANa(9), the value of $\eta_0(M_a/M_e)^{-1/2}$ is much larger than that of PS stars. This deviation can probably be attributed to a morphology difference as mentioned above.

In the following discussion, two possible mechanisms of the additional relaxation at low frequencies for the PS(1100)PMANa(y) are presented. The first is based on the assumption that the micelle structure can be regarded as a spherical ionic core surrounded by polystyrene chains as a corona.[13] The number of polystyrene chains is equal to the aggregation number, N_{agg}, of the micelles. The values of N_{agg} determined by SAXS[37] are given in Table 1. The micelle, because of its size, moves more slowly than the PS chains. This slow motion of the micelle might be responsible for the additional relaxation via rotational diffusion due to thermal motion.[60,61] The equation for rotational diffusion in spherical coordinates is

$$\frac{\partial\Psi}{\partial t} = \left(\frac{D_r}{\sin^2\theta}\right)\left\{\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\varphi^2}\right\}\Psi \qquad (13)$$

where Ψ is the probability distribution function that a specific point on the surface of the sphere is found in the direction (θ,φ) at time t, and D_r is the rotational diffusion coefficient. Equilibrium thermal motion of the micelle will now be considered. The unit vector $\mathbf{u}(t)$, which points from the origin of the sphere to the specific point (θ,φ) on the spherical surface at time t, rotates randomly as a result of thermal motion. The rotational relaxation is expressed as

$$\langle\mathbf{u}(t)\mathbf{u}(0)\rangle = \exp[-2D_r t] \qquad (14)$$

where $\langle\ \rangle$ represent the correlation function. From this equation, the rotational relaxation time, τ_{rot}, can be defined as

$$\tau_{rot} = \frac{1}{2D_r} \qquad (15)$$

A polystyrene chain of the corona of the micelle retracts once during the time τ_m. Furthermore, the solid angle subtended by a polystyrene chain is $4\pi/N_{agg}$. This solid angle becomes free within a time span τ_m. Since the rotational diffusion coefficient, D_r, relates to this basic process,

$$D_r \sim \left(\frac{4\pi}{N_{agg}}\right)\frac{1}{\tau_m} \qquad (16)$$

Substituting eq 16 into eq 15, one obtains

$$\tau_{rot} \sim \left(\frac{N_{agg}}{8\pi}\right)\tau_m \qquad (17)$$

Thus, the rotational relaxation time is proportional to the aggregation number, N_{agg}, and the characteristic time, τ_m, which corresponds to the retraction process of the "brush" of the micelles.

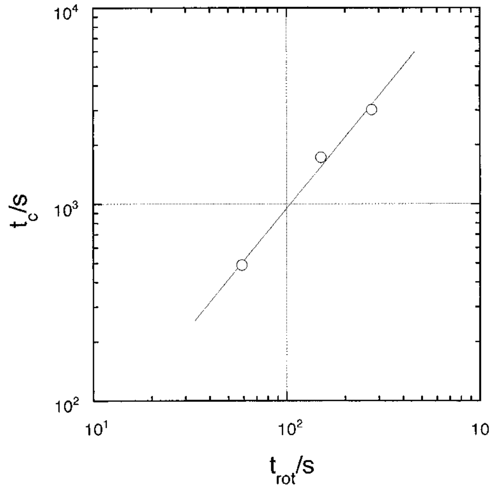

Figure 7. Correlation between the τ_{rot} and τ_c.

An attempt will now be made to relate this τ_{rot} to the additional relaxation at low frequencies. The product of η_0 and $J_s°$ is a characteristic time of viscoelastic flow, τ_c. According to the Rouse theory, τ_c is proportional to the longest relaxation time of the viscoelastic material. In this case, τ_c may correspond to the relaxation time for the thermal motion of the micelle, which appears as the additional relaxation at low frequencies. Figure 7 shows the correlation between the estimated value τ_{rot} and the experimental value τ_c. Although τ_{rot} is numerically 1 order of magnitude lower than τ_c, there appears to be a correlation with a slope of about 1. Thus, it can be concluded that the additional relaxation at low frequencies may be due to the rotational thermal motion of the micelle.

In the case of PS(170)PMANa(9), τ_c is much larger than τ_{rot} for a sphere. This also implies a morphological change of the core.

An alternative interpretation of the additional relaxation at low frequencies is based on the assumption that the ionic core acts as a filler particle. It seems reasonable that at low frequencies, polystyrene chain entanglements do not affect the viscoelastic properties of the block ionomer, because the relaxation time of the polystyrene chain entanglements is much shorter than the time corresponding to the additional relaxation. Thus the polystyrene matrix acts as a viscous fluid of viscosity η_m, and the ion core can be considered as a solid particle in the polystyrene matrix.

Suspensions consisting of a polymer melt filled with solid particles occasionally show higher viscosity at low frequencies than the pure polymer melt does. Figure 8 depicts the master curves of complex viscosity, $\eta^*(\omega)/a_T$ as a function of frequency for the PS(1100)PMANa(y) diblock ionomer system and the PS(1100) homopolystyrene. $\eta^*(\omega)/a_T$ of PS(1100) shows a typical viscoelastic behavior of a polymer melt: a constant viscosity (a Newtonian viscosity) region at low frequencies and a frequency-dependent viscosity region at high frequencies. At frequencies higher than 10^{-2} s^{-1}, the two diblock ionomers show the same behavior. The $\eta^*(\omega)/a_T$ curve implies a constant value at low frequencies corresponding to η_m for the matrix polystyrene. However, an extra upturn appears at lower frequencies and the height of $\eta^*(\omega)/a_T$ at low terminal frequency increases with PMANa block length. As in the case of suspensions, this upturn may be attributable to the ionic core.

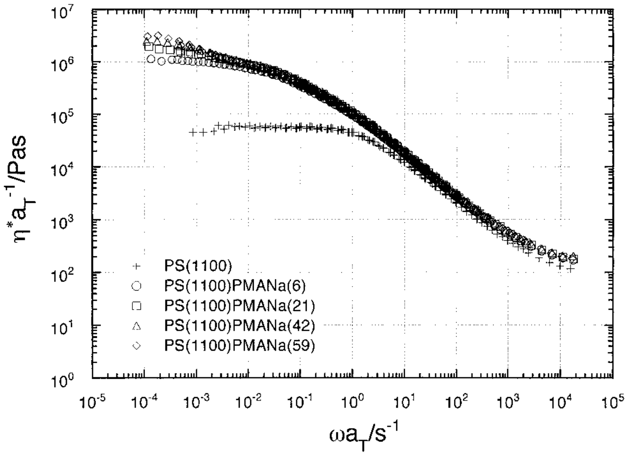

Figure 8. Master curves of complex viscosity for the PS(1100)-PMANa(y) diblock ionomer system. The reference temperature is 160 °C.

The viscous flow of suspensions has been discussed by many workers.[62−65] In this study, two of the most general suspension models are applied to the diblock ionomer. These are the Mooney model[66] and the Maron−Pierce model,[67] which are applicable over a relatively wide concentration range. The relationship between the viscosity of the suspended system (η_x), the volume fraction of the filler (ϕ), and the viscosity of the matrix (η_m) is different for each model. The Mooney equation is

$$\ln[\eta_x/\eta_m] = k_E\phi/\{1 - (\phi/\phi_m)\} \tag{18}$$

where k_E is the Einstein parameter; in the case of rigid spheres

$$k_E = 2.5$$

ϕ_m is the maximum packing fraction of the filler particles; for the case of a simple cubic array

$$\phi_m = 0.5236$$

The Maron−Pierce equation is

$$\eta_x/\eta_m = \{1 - (\phi/A)\}^{-2} \tag{19}$$

where A is a constant corresponding to ϕ_m of the Mooney equation. Kataoka et al.[68] and Kitano et al.[69] reported that a value of $A = 0.44$ fits data for various suspensions.

For the diblock ionomer, the polystyrene phase is considered to be the matrix with a viscosity η_m. η_m is assumed to have the same value as η_0 for a star polystyrene having a value of M_a equal to the molecular weight of the PS block; the ion core is taken to be the filler particle. If the radius of the filler particle is r and the distance between the particles is d, which corresponds to the lattice constant of the simple cubic array, the value of ϕ is

$$\phi = (4\pi/3)(r/d)^3 \tag{20}$$

Using eqs 18 and 19, the value of (r/d) can be estimated from the viscosity of the diblock ionomers. The calculated values of (r/d) are listed in Table 3. The value of η_0 for PS(1100)PMANa(6) is very close to the value of η_m for star polystyrene. The values for the sample PS(1100)PMANa(y)P system are much larger than those for the unfractionated PS(1100)PMANa(y), as is also the case for the viscosity. The (r/d) value of PS(170)-PMANa(9) is calculated using the data for a six-arm star polystyrene ($M_a = 1.72 \times 10^4$, $\eta_0 = 3.67 \times 10^3$ Pa s) of Graessley and Roovers[16] and is also listed in Table 3.

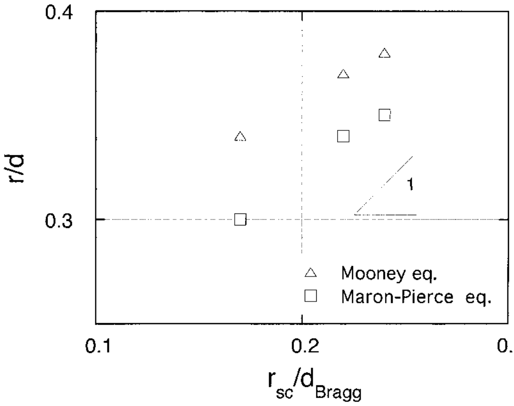

Figure 9. Correlation between (r/d) estimated by the Mooney and the Maron−Pierce equations and (r_{sc}/d_{Bragg}) from the SAXS experiment.

Table 3. Estimated Relaxation Time and Relative Core Radius of the Diblock Ionomers

	τ_{rot} (s)	$(r/d)_M$	$(r/d)_{MP}$
PS(1100)			
PS(1100)PMANa(6)			
PS(1100)PMANa(21)	5.88×10^1	0.337	0.298
PS(1100)PMANa(42)	1.50×10^2	0.370	0.336
PS(1100)PMANa(59)	2.74×10^2	0.380	0.347
PS(1100)PMANa(6)P		0.427	0.410
PS(1100)PMANa(21)P		0.437	0.426
PS(1100)PMANa(59)P			
PS(170)			
PS(170)PMANa(9)	2.00×10^{-2}	0.473	0.467
PS(170)PMANa(25)	4.90×10^{-2}		

Table 1 lists the values of (r_{sc}/d_{Bragg}) determined by SAXS, where r_{sc} is the radius of the ion core assuming a simple cubic array of spherical cores, and d_{Bragg} is the distance between the ion cores estimated from the Bragg angle in SAXS data. In order to test the validity of this approach, the values of (r/d) for PS(1100)PMANa(y) estimated from the rheological data are plotted against the ratio (r_{sc}/d_{Bragg}) from SAXS in Figure 9. The values of (r/d) estimated from the Mooney and Maron−Pierce equations lie on lines of slope close to 1. This good correlation suggests that the diblock ionomer melt does behave like a suspension at low frequencies. However, the values of (r/d) by these equations are about 0.1 larger than the values of (r_{sc}/d_{Bragg}) by SAXS. It may be speculated that the ion core with surrounding polystyrene layer is probed in the rheological measurements, while the dense ion core alone is detected by the SAXS measurements. For PS(170)PMANa(9), (r/d) is much larger than (r_{sc}/d_{Bragg}). This again suggests the morphological change of the PS(170)PMANa(y) series.

V. Conclusions

The PS(x)PMANa(y) block ionomers form a micelle structure in the melt because of the strong association of the ionic blocks. This structure is quite stable, even at high temperatures, and affects the viscoelastic properties of the block ionomer by giving the material some of the properties of a star polystyrene. It is shown that viscoelastic properties of the diblock ionomer can be attributed to the same molecular motion as in star polymers, except for an additional relaxation at low frequencies.

One possible origin of the additional relaxation is that it is due to thermal motion of the micelles. Specifically, the additional relaxation is explained as being due to the thermal rotational diffusion of the micelles, restricted by the retraction process of polystyrene block chains. The estimated relaxation time shows a good correlation with the experimental results for the diblock ionomers with relatively long polystyrene blocks. In the case of relatively short polystyrene block ionomers, a possible morphological change is suggested.

An alternative explanation for the additional relaxation is that the micelles act as a filler. The relative radius of the ion core is estimated using empirical viscosity equations for the suspensions. Although the estimated values are somewhat larger than the corresponding values measured by SAXS, the slope of the correlation plot is approximately 1. This implies that the rheological behavior at low frequencies of the diblock ionomer is similar to that of a suspension.

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