

Investigation of the Structure and Properties of Polyisobutylene-Based Telechelic Ionomers of Narrow Molecular Weight Distribution. II. Mechanical

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SYNOPSIS

Sulfonated polyisobutylene (PIB) telechelic ionomers with narrow molecular weight distribution (MWD) have been recently developed, providing additional control over the structure and properties of these novel polymers. A small angle X-ray scattering (SAXS) peak often associated with the aggregation of the ionic species in the bulk, and a secondary peak, were recently observed in the narrow MWD sulfonated PIB telechelics for the first time. SAXS evidence, given earlier as part I of this two-part series, suggests that compression-molded sulfonated PIB telechelic ionomers with a narrow MWD ($\bar{M}_w/\bar{M}_n \approx 1.15$) may have a local secondary structure of ionic lamellae or cylinders, and no such structure is found in similar broad MWD ($\bar{M}_w/\bar{M}_n \approx 1.8$) telechelics. It is shown that narrowing the MWD, which acts to promote locally continuous structure in the tri-arms, alters the character of the network, in that the modulus of the tri-arm telechelic systems increases and the elongation at break is lowered by narrowing the MWD or decreasing the \bar{M}_n . The tri-arms of the highest \bar{M}_n (49.5 kg/mol) exhibit strain hardening and the lowest modulus, highest-breaking stress, and highest elongation at break in the ionomers studied. The presence of local ionic structure is also indicated by stress relaxation experiments in which the long-term or near-equilibrium stress is seen to decrease when the MWD is broadened or \bar{M}_n increases. It is believed that the difunctional materials do not form extensive ionic networks at all, but principally chain-extend, as has also been found before. It is observed that the properties of a solution "blend" of narrow MWD ionomers that has the same counterion, \bar{M}_n , and polydispersity as a broad MWD system exhibits lower elongation to break, lower breaking stress, and modulus of narrow MWD systems relative to the broader MWD material. Dynamic mechanical data indicate that narrowing the MWD or decreasing \bar{M}_n increases the flow transition temperature and rubbery plateau modulus. The "blend" exhibits dynamic mechanical properties between the narrow and broad, having a higher flow transition temperature than the broad MWD, but lower than the narrow MWD, and a rubbery plateau modulus between the other two. © 1997 John Wiley & Sons, Inc.

INTRODUCTION

Ionomers are macromolecules which contain less than ca. 15 mol % ionic functionality as an inte-

gral part of the chain in an otherwise low dielectric constant polymer. Most commonly, the ionic moieties are randomly attached and models have been developed to describe their structure-property relationships.¹⁻⁹ By use of specific architectures such as segmented¹⁰⁻¹³ and block¹⁴⁻²³ ionomers one may control the placement of the ionic moieties along the chain. Similarly, telechelic ionomers offer a unique perspective from which to consider the structure-property relationships in

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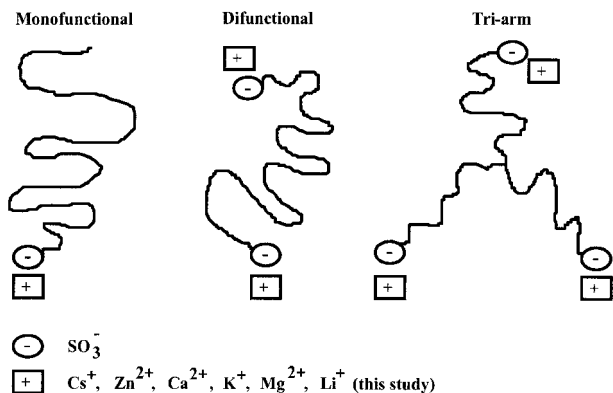


Figure 1 Schematic of the architecture of some types of sulfonated telechelic ionomers.

ionomers since the ion pair interaction is confined to the terminal points of the macromolecule. Examples of some of the most common telechelic ionomer architectures found in the literature are shown in Figure 1. With telechelic ionomers which are amorphous and elastomeric in nature, the effect of the ionic aggregates on the properties can be considered without the uncertainty of ionic group placement inherent in the use of random elastomeric ionomers. Specifically, in tri-arm sulfonated polyisobutylene (PIB) telechelic ionomers, the aggregation of the ionic species in the bulk results in the formation of a thermally reversible rubbery network structure.^{24–31} This structure may then be used to examine in detail the network properties of ionomer systems. In tri-arm PIB sulfonate telechelics *all* chain segments are network chains, in theory at least. Thus, there are no “dangling ends” to contend with, as are found in conventional, covalently crosslinked, elastomers.

The structure and properties of telechelic ionomers based on sulfonated PIB have been studied in detail by Wilkes, Kennedy, and coworkers.^{24–31} These ionomers exhibited good elastomeric properties such as low modulus, high elongation at break, and good recovery, and compare very favorably with a random elastomeric ionomer like sulfo-EPDM. Yet, no characteristic “ionomer peak” was observed in the SAXS profiles of these early PIB sulfonate ionomers, except for one very diffuse, weak peak observed in a single sulfonated tri-arm PIB telechelic ionomer of 8.3 kg/mol \bar{M}_n and K^+ counterion.³¹ The lack of the characteristic “ionomer peak” which is associated with the aggregation of the ionic species in the bulk was puzzling. The original investigation attributed the lack of a SAXS peak to the very small amount

(ca. 2–4 vol %) of ionic material present.³¹ These SAXS results and the mechanical properties suggested that for such small amounts of ionic material, no appreciable aggregation above that of the “multiplet,” e.g., to form a “cluster,” would occur and little scattering would result. As addressed in part I of this series,³² it is likely that the broad MWD ($\bar{M}_w/\bar{M}_n \approx 1.7$) of these early ionomers was actually the principal reason behind the lack of a consistent “ionic” scattering peak. In part I of this two-part series we have addressed the multiple peaks observed in the SAXS profiles of sulfonated PIB telechelics of narrow MWD ($\bar{M}_w/\bar{M}_n \approx 1.15$).³² In part I, we attribute the scattering behavior to local ordering in the ionic regions. As we pointed out, this is the first time primary and secondary peaks have been observed in sulfonated telechelic PIB ionomers. The morphological feature responsible for this scattering was determined from SAXS to be local ordering of the ionic domains into either cylinders or lamellae. The properties of specimens of these new, narrow MWD PIB telechelic ionomers and analogous broad MWD ($\bar{M}_w/\bar{M}_n \approx 1.8$) ionomers which exhibited no SAXS peak when compression-molded (like those studied by Bagrodia, Wilkes, and Kennedy³¹) are the subject of this paper. It is shown that altering the polydispersity of the network chains not only affects the structural order, as noted in part I, but also affects the mechanical, stress-relaxation, and dynamic mechanical properties of the ionomer.

EXPERIMENTAL

The telechelic PIB hydrocarbon precursors with narrow MWDs were produced using living carbocationic polymerization, according to published methods.^{33,34} Briefly, the initiation system for isobutylene polymerization consisted of either a di or trifunctional cumyl chloride-type initiator, along with the cointiator TiCl_4 and the electron donor pyridine, in a 60/40 (v/v) hexane/methyl chloride solvent mixture at -80°C . The resulting PIBs, possessing two or three *tert*-alkyl chloride end groups, were reacted directly with acetyl sulfate (4-fold molar excess, relative to PIB end groups) in a 90/10 (v/v) methylene chloride/hexane mixture (higher molecular weight PIBs required slightly higher proportions of hexane for solubility considerations) at room temperature for 3 h. It is important to note that this method represents the direct sulfonation of the *tert*-alkyl chloride termini, in contrast to the earlier method of Kennedy

Table I Molecular Characteristics of the Telechelic Ionomers Studied

\bar{M}_n (kg/mol)	Architecture	Counterions	\bar{M}_w/\bar{M}_n
10.3	Difunctional	Cs ⁺ , Zn ²⁺ , Ca ²⁺ , K ⁺ , Mg ²⁺ , Li ⁺	1.15
19.3	Difunctional	Same	1.15
11.6	Tri-arm	Cs ⁺ , Zn ²⁺ , K ⁺ , Mg ²⁺	1.8
11.8	Tri-arm	Cs ⁺ , Zn ²⁺ , Ca ²⁺ , K ⁺ , Mg ²⁺ , Li ⁺	1.15
20.4	Tri-arm	Same	1.15
20.6	Tri-arm	Cs ⁺ , Zn ²⁺ , K ⁺ , Mg ²⁺	1.8
21.4 ^a	Tri-arm	K ⁺	1.8 (blend) ^a
27	Tri-arm	Cs ⁺ , Zn ²⁺ , Ca ²⁺ , K ⁺ , Mg ²⁺ , Li ⁺	1.15
49.5	Tri-arm	Same	1.15

^a This ionomer is made by blending together four other ionomers, as noted in the text.

et al.,^{24–31} which involved first dehydrochlorination and then the sulfonation of the resulting olefinic end groups.

Purification of the crude sulfonated polymers was achieved either by ion-exchange column chromatography³³ or conventional flash-precipitation into hot water. Neutralization with each desired counterion (Cs⁺, Zn²⁺, Ca²⁺, K⁺, Mg²⁺, or Li⁺) was carried out to stoichiometric equivalence by dissolving the moist sulfonated polymer into THF (50 mg/mL) and titrating the solution at 50°C (Phloxine B indicator) with an ethanolic solution of the desired metal hydroxide or acetate. The ionomer was isolated by pouring the neutralized solution into a 1 L Teflon resin kettle and evaporating the solvents in an oven at 50°C for 2 days, then drying *in vacuo* for another 3 days at 60°C.

In contrast to part I of this series, all films utilized in this study were prepared by compression-molding the solvent-free polymer crumb between two Teflon sheets separated by steel shims for ca. 20 min at 130°C. All films were stored in a desiccator until the time of testing to avoid any moisture uptake. Past studies in our laboratory show that these PIB sulfonate telechelics do not sorb significant amounts of water, even in long-term exposure, because of the very small amount of ionic material present in these systems.³¹ A “blend” broad MWD ($\bar{M}_w/\bar{M}_n \approx 1.8$) K⁺ ionomer with an \bar{M}_n of 21.4 kg/mol was made by mixing four narrow MWD ionomers of different \bar{M}_n in solution: 30 wt % 11.8; 18 wt % 20.4; 11 wt % 27, and 41 wt % 49.5 kg/mol. The blended solution was mixed, cast, dried, and compression-molded, as before. As in part I, the sample nomenclature used here is given by the following example: 3-20.4-K refers to a tri-arm telechelic with an \bar{M}_n of 20.4 kg/mol and K⁺ counterion. Table I summa-

rizes the characteristics of the telechelic ionomers addressed in this study.

The stress–strain experiments were carried out using an Instron 1122 at a crosshead speed of 10 mm/min on small dogbones, 10 mm gage length by 3 mm wide, at ambient condition; $T \approx 25^\circ\text{C}$. Several samples were tested to ensure accuracy and the standard deviation of each property was calculated. The stress relaxation data were obtained using a Toyo-Sokki UTM-II tensile tester over the course of 3 h at ambient condition ($T \approx 25^\circ\text{C}$) at an extension ratio of 1.25. Dynamic mechanical analysis (DMA) was performed on a Seiko DMS-210 at a heating rate of 2°C/min in a nitrogen environment.

RESULTS AND DISCUSSION

Mechanical Properties of the Compression Molded Telechelics

Difunctional Telechelics

The ambient temperature mechanical properties of the difunctional telechelic ionomers are summarized in Tables II and III and example profiles are shown in Figure 2. In Table II, one can see that the 2-10.3 difunctional materials have moduli of ca. 2 MPa. The elongation to break is ca. 30% in all cases, which is low for elastomers. Note that the Ca²⁺ and Zn²⁺ ionomers exhibit the highest moduli at both \bar{M}_n s (see Tables II and III). The low elongation to break observed in the stress–strain profiles, shown in Figure 2, suggests that little three dimensional network character is present in either the 2-10.3 or 2-19.3 materials. The low elongation to break of both 2-10.3 and the 2-19.3 ionomers along with the decrease

Table II Properties of 10.3 kg/mol \bar{M}_n PIB Difunctional Telechelic Ionomers^a

Counterion	\bar{M}_w/\bar{M}_n	E, MPa ^b	Breaking Stress, MPa ^b	Breaking Strain, % ^b
Cs ⁺	1.15	1.7	0.49	33
K ⁺	1.15	1.7	0.59	38
Li ⁺	1.15	1.7	0.62	42
Zn ²⁺	1.15	1.9	0.54	37
Ca ²⁺	1.15	2.2	0.67	32
Mg ²⁺	1.15	1.7	0.45	28

^a Tested at ambient condition and 100%/min.

^b All mechanical property data reflect 10% SD or less.

in modulus noted upon increasing \bar{M}_n indicates that the continuity of the ionic structure influences the mechanical properties. By increasing \bar{M}_n , the local ionic continuity is disrupted and diluted and the modulus decreases. Our earlier small-angle X-ray scattering (SAXS) results suggested that some *local* continuity in the morphology existed in the form of ionic cylinders or lamellae.³² This local ionic domain structure acts to decrease the local chain mobility in telechelic ionomers, and thus increase the modulus. For example, Vanhoorne et al. have recently shown by solid state ¹³C nmr that there is local restriction of motion in difunctional carboxylated polystyrene telechelics of narrow MWD ($\bar{M}_w/\bar{M}_n \approx 1.15$) and \bar{M}_n ca. 10 kg/mol.³⁵ In this study, the authors showed that the onset of motion in the chain segment nearest the ionic groups at the chain ends was approximately 30 K higher in temperature than similar, nontelechelic polystyrene. The authors did not present SAXS evidence that might have indicated local structure like that found for the PIB sulfonate telechelics studied here. However, another recent paper gives evidence that such complex morphology might be present in telechelic ionomers.³⁶ Specifically, Fontaine et al.

found that difunctional carboxylated poly(*t*-butyl acrylate) Ba²⁺ and Mg²⁺ telechelic ionomers of 22 kg/mol \bar{M}_n and $\bar{M}_w/\bar{M}_n \approx 1.2$ exhibited several orders of weak scattering. The authors did not indicate the precise structural feature that might cause such scattering behavior in this glassy system, although it was speculated that hexagonally packed cylinders could be the source. Therefore, the local restriction of motion in our difunctional narrow MWD PIB sulfonate ionomers may be substantial due to the local ionic ordering and such ordering would certainly affect the mechanical properties. Upon increasing the \bar{M}_n to 19.3 kg/mol, one notes from Figure 2 that the modulus decreases for the ionomers and that the elongation at break increases. The local ordering associated with the ionic domains strongly affects the properties of these difunctional materials. Reducing the amount of ionic material in the system improves elongation to break and lowers the modulus.

Tri-Arm Telechelic Ionomers

The mechanical behavior of the narrow MWD K⁺ tri-arm telechelic ionomers is illustrated in Figure

Table III Properties of \bar{M}_n 19.3 kg/mol PIB Difunctional Telechelic Ionomers^a

Counterion	\bar{M}_w/\bar{M}_n	E, MPa ^b	Breaking Stress, MPa ^b	Breaking Strain, % ^b
Cs ⁺	1.15	1.1	0.44	55
K ⁺	1.15	1.5	0.60	60
Li ⁺	1.15	0.89	0.37	61
Zn ²⁺	1.15	1.6	0.73	74
Ca ²⁺	1.15	1.5	0.62	74
Mg ²⁺	1.15	1.1	0.43	62

^a Tested at ambient condition and 100%/min.

^b All mechanical property data reflect 10% SD or less.

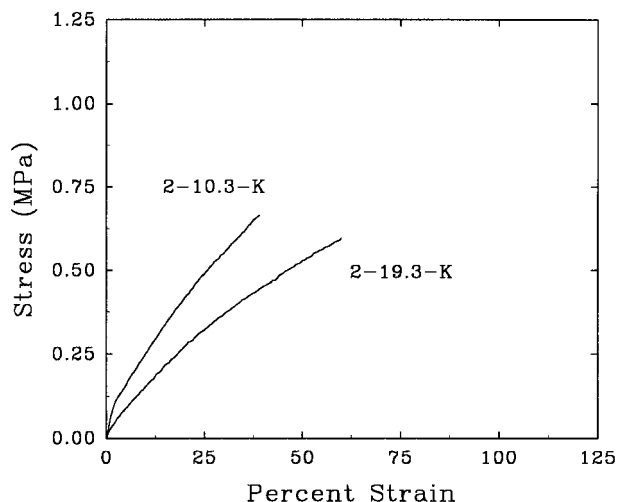


Figure 2 Tensile behavior of difunctional PIB K^+ telechelic ionomers.

3. The mechanical properties of all the PIB sulfonate tri-arm telechelic ionomers are summarized in Tables IV–VII. Observing Figure 3, which addresses the K^+ tri-arm materials, it is again noted that these become more elastomeric, exhibiting lower Young's moduli and higher elongations to break as the \bar{M}_n of the tri-arm increases. The change in the nature of the ionomers' response with increasing \bar{M}_n is related to several factors. First, the increase in \bar{M}_n "dilutes" the effect of the ionic aggregates on the system, just by lowering the ionic volume fraction. Secondly, the increase in volume fraction of nonionic material reduces and very likely eliminates any ionic phase continuity, even on a local scale. It was shown in part I that the SAXS peak intensity and sharpness decreased as \bar{M}_n increased (samples 3-11.8 to 3-20.4). Primary and secondary SAXS peaks were observed in only the Zn^{2+} and Cs^+ 3-27 materials but neither peak was found in the 3-49.5 materials.³² Thirdly, the critical molecular weight for entanglements ('sliplinks') in linear PIB is reported at 9 to 17 kg/mol³⁷ (although the materials addressed here are tri-arm telechelics). The narrow MWD tri-arm materials reach the range of critical molecular weight for entanglement, i.e., the mass of two arms, for the 20.4 kg/mol materials and the 27 kg/mol materials are also within this range. Note that 3-27-K is the first material to exhibit a near-linear stress–strain region (from ca. 75% strain up to break) which can be attributed to the presence of an entangled network, where the network chains are the PIB arms. Thus, the decrease in both the ionic content and ionic

phase continuity and the increased presence of entanglements are all being exhibited as one moves from the 11,800 \bar{M}_n narrow MWD tri-arms, 3-11.8, to the 49.5 kg/mol \bar{M}_n narrow MWD tri-arms, 3-49.5 (Fig. 3, Table VII). The 3-49.5 materials have high elongations to break and low moduli, and except for 3-49.5-Ca, these tri-arm telechelics (especially K^+ , Li^+ , Zn^{2+}) tended to have the lowest moduli and highest elongations to break of all the narrow MWD tri-arm ionomers.

Strain hardening was also observed in some of the 3-49.5 ionomers (K^+ , Li^+ , Zn^{2+}), as illustrated by 3-49.5-K in Figure 3. This figure also serves to indicate the excellent properties often displayed by the 3-49.5 materials, with low moduli (ca. 0.5 MPa), relatively high stress at break (ca. 3 MPa) and very high strain at break (ca. 1000%). The 3-49.5 K^+ , Li^+ and Zn^{2+} materials exhibit properties similar to those of the broad MWD ($\bar{M}_w/\bar{M}_n \approx 1.7$) 34 kg/mol \bar{M}_n ionomers studied earlier by Bagrodia, Wilkes, and Kennedy.³¹ The similarity of the material properties reported here to those of Bagrodia's earlier work extends to the fact that these 3-49.5 telechelics also exhibit no SAXS peak. That is, in Bagrodia's earlier work none of the ionomers exhibited SAXS peaks at any \bar{M}_n except for the single 8.3 kg/mol \bar{M}_n K^+ ionomer. Again, this lack of local ionic connectivity would seem to enhance the elastomeric qualities of the network in the PIB sulfonate ionomers.

In Figure 4, the effect of \bar{M}_w/\bar{M}_n is illustrated for the case of the 3-11.6-K (broad) and 3-11.8-K (narrow) ionomers. In the figure and Table IV, it

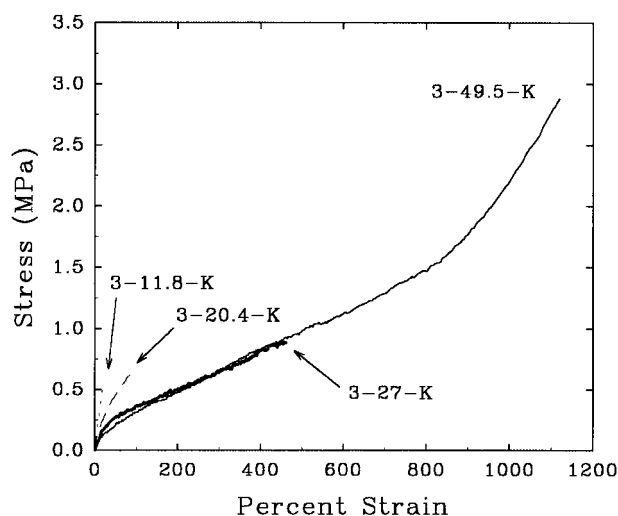


Figure 3 Effect of \bar{M}_n on the mechanical behavior of the narrow MWD PIB K^+ tri-arm telechelics.

Table IV Properties of 12 kg/mol \bar{M}_n PIB Tri-Arm Telechelic Ionomers^a

Counterion	\bar{M}_w/\bar{M}_n	E, MPa ^b	Breaking Stress, MPa ^b	Breaking Strain, % ^b
Cs ⁺	1.15	1.6	0.23	14
Cs ⁺	1.8	0.20	0.13 ^a	250 ^a
K ⁺	1.15	2.8	0.52	21
K ⁺	1.8	0.20	0.28 ^a	215 ^a
Zn ²⁺	1.15	2.7	0.56	22
Zn ²⁺	1.8	0.40	0.35	227
Ca ²⁺	1.15	5.7	1.2	21
Mg ²⁺	1.15	2.6	0.43	17
Mg ²⁺	1.8	0.65	0.65	263

^a Tested at ambient condition and 100%/min. Narrow MWD (\bar{M}_w/\bar{M}_n ca. 1.15) $\bar{M}_n = 11.8$ kg/mol; broad MWD (\bar{M}_w/\bar{M}_n ca. 1.8) $\bar{M}_n = 11.6$ kg/mol.

^b All mechanical property data reflect 10% SD or less. In the broad MWD (\bar{M}_w/\bar{M}_n ca. 1.8) Cs⁺ and K⁺ ionomers, the *peak* stress and strain are taken as the ultimate values.

is clear that the broadening of the MWD distinctly lowers the modulus and provides a higher elongation at break, versus the narrow MWD. The moduli of the narrow MWD ionomers is always larger than that of the broad MWD ionomers, though the difference is smaller in the Cs⁺ than in the K⁺ ionomers. However, the breaking strain of the broad MWD ionomers is always larger than that of the narrow MWD ionomers and the Cs⁺ ionomers exhibit a larger difference in breaking strain than the K⁺ ionomers. In the divalent ionomers, the moduli of the narrow MWD ionomers are larger for Zn²⁺ than for Mg²⁺. Again, the breaking strain of the Zn²⁺ ionomers is larger than that for the Mg²⁺ ionomers. Thus, it appears that there is generally an increase in the modulus which is accompanied by a decrease in the breaking strain

upon narrowing the MWD. Furthermore, this observation holds true for comparison between the pairs of divalent (Zn²⁺ versus Mg²⁺) or monovalent (Cs⁺ versus K⁺) counterions. There is little difference in the shape of the 3-11.8-K and 2-10.3-K profile (Fig. 2), both having a strongly linear response.

The broad MWD tri-arm materials have higher elongation at break and lower stress at break relative to the narrow MWD materials. Even though the mechanical properties indicate that the broad MWD materials of monovalent salts form networks, the very poor recovery (only ca. 50%) indicates that these materials (Cs⁺ or K⁺) may not be fully neutralized or that the functionality of the tri-arms is lower than three. On the other hand, all the narrow MWD and the divalent cat-

Table V Mechanical Properties of 20 kg/mol \bar{M}_n PIB Tri-Arm Telechelics^a

Counterion	\bar{M}_w/\bar{M}_n	E, MPa ^b	Breaking Stress, MPa ^b	Breaking Strain, % ^b
Cs ⁺	1.15	1.2	0.4	62
Cs ⁺	1.8	0.80	0.5 ^a	266 ^a
K ⁺	1.15	2.5	0.67	87
K ⁺	1.8	0.60	0.46 ^a	364 ^a
K ⁺	1.8 (blend)	1.0	0.25	65
Li ⁺	1.15	0.90	0.43	75
Zn ²⁺	1.15	2.2	0.51	99
Zn ²⁺	1.8	1.1	1.9	570
Ca ²⁺	1.15	1.5	0.57	41
Mg ²⁺	1.15	2.3	0.47	75
Mg ²⁺	1.8	1.1	1.1	240

^a Tested at ambient condition and 100%/min. Narrow MWD (\bar{M}_w/\bar{M}_n ca. 1.15) $\bar{M}_n = 20.4$ kg/mol; broad MWD (\bar{M}_w/\bar{M}_n ca. 1.8) $\bar{M}_n = 20.6$ kg/mol.

^b All mechanical property data reflect 10% SD or less except for the broad MWD (\bar{M}_w/\bar{M}_n ca. 1.8) Cs⁺ and K⁺ ionomers, where the *peak* stress and strain are taken as the ultimate values.

Table VI Properties of 27 kg/mol \bar{M}_n PIB Tri-Arm Telechelic Ionomers^a

Counterion	\bar{M}_w/\bar{M}_n	E, MPa ^b	Breaking Stress, MPa ^b	Breaking Strain, % ^b
Cs ⁺	1.15	1.1	0.95	445
K ⁺	1.15	1.0	1.0	500
Li ⁺	1.15	1.0	0.62	380
Zn ²⁺	1.15	1.0	0.75	350
Ca ²⁺	1.15	2.1	3.2	690
Mg ²⁺	1.15	1.0	1.3	450

^a Tested at ambient condition and 100%/min.

^b All mechanical property data reflect 10% SD or less.

ion (Zn²⁺, Mg²⁺) broad MWD materials exhibited full recovery after rupture. For comparison, note in Figure 4 that the low elongation at break (ca. 215%) in 3-11.6-K is much lower than that for the tri-arm K⁺ ionomers (ca. 800%, with strain hardening) of 11 kg/mol \bar{M}_n ($\bar{M}_w/\bar{M}_n \approx 1.7$) studied earlier by Bagrodia, Wilkes, and Kennedy.³¹ This discrepancy between the mono and divalent broad MWD materials and the earlier work of Bagrodia et al. is not fully understood at this point. Still, the broadening of the MWD enhances the elastomeric nature of these ionomers, in terms of increasing the breaking strain and lowering the modulus. These broad MWD 3-11.6 ionomers do not exhibit SAXS peaks, suggesting there is little or no local ionic phase periodicity and continuity to promote a relatively high modulus and low elongation to break, like that seen in the narrow MWD materials. The ordering in the 3-11.6 materials is likely that of randomly located multiplets, which provide network character in the system, but do not act to enhance the modulus as much as in the narrow MWD ionomers, due to the lack of local ionic phase continuity. Thus, the broad MWD yields a system where the packing of the ionic ends of the telechelic is more spatially random in the bulk material versus the narrow MWD

ionomers due to the larger variation in arm length.

The effect of MWD on the properties of the three tri-arms which have \bar{M}_n s of ca. 20 kg/mol is illustrated in Figure 5, and their properties are summarized in Table V. Figure 5 also contains a typical profile for the “blend” ionomer, 3-21.4-K. The \bar{M}_w/\bar{M}_n of 3-21.4-K (“blend”) is ca. 1.8 and it is composed of four narrow MWD tri-arm materials, as described in the Experimental section. The broadening of the MWD has the same effect on the 3-20 tri-arm ionomers that it had in the 3-12 materials, increasing the elongation at break and lowering the modulus. However, the difference between the moduli of the two MWDs at 20 kg/mol \bar{M}_n is not as large as in the 12 kg/mol \bar{M}_n tri-arms. Figure 5 shows that increasing the \bar{M}_n of the system tends to enhance the elastomeric nature of the response by lowering the modulus and increasing the elongation to break. A notable exception to this trend is 3-20.4-Ca, which has a lower breaking stress than the 3-11.8-Ca material, though a higher breaking strain. It is not certain what the cause of this discrepancy might be. The “blend” ionomer (3-21.4-K) exhibits the properties of a narrow MWD material, having a higher modulus and lower breaking strain than the

Table VII Properties of 49.5 kg/mol \bar{M}_n PIB Tri-Arm Telechelic Ionomers^a

Counterion	\bar{M}_w/\bar{M}_n	E, MPa ^b	Breaking Stress, MPa ^b	Breaking Strain, % ^b
Cs ⁺	1.15	0.57	1.8	520
K ⁺	1.15	0.56	2.2 (2.9 max)	820 (1120 max)
Li ⁺	1.15	0.56	2.1 (2.2 max)	530 (1040 max)
Zn ²⁺	1.15	0.64	2.2 (3.3 max)	570 (920 max)
Ca ²⁺	1.15	1.0	3.5	425
Mg ²⁺	1.15	0.56	2.6	720

^a Tested at ambient condition and 100%/min.

^b All mechanical property data reflect 10% SD or less.

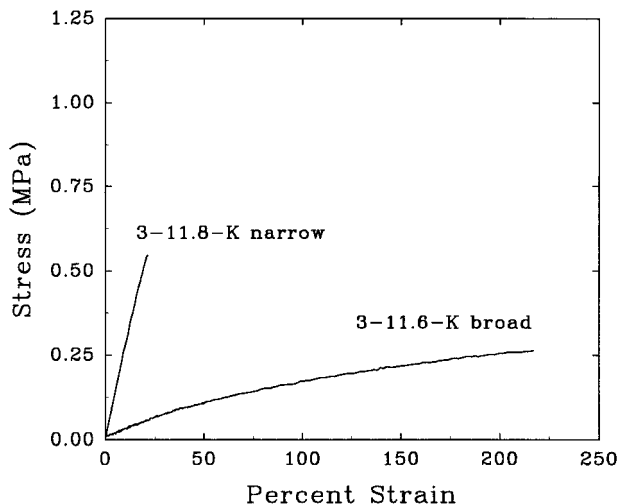


Figure 4 Comparison of narrow (3-11.8-K) and broad (3-11.6-K) MWD K^+ tri-arm ionomers of 12 kg/mol \bar{M}_n .

broad MWD ionomer of similar \bar{M}_n (3-20.6-K). Our structural studies, given as part I of this series, show a single SAXS peak in the 3-21.4-K ionomer like that in the narrow MWD ionomer (3-20.4-K), although the narrow MWD ionomer also shows a secondary peak.³² Still, the properties of the blend ionomer are clearly not the same as those of 3-20.4-K, which is thought to be due to the multimodal MWD of the blended material. Thus, by blending together four narrow MWD ionomers, one obtains a material whose properties

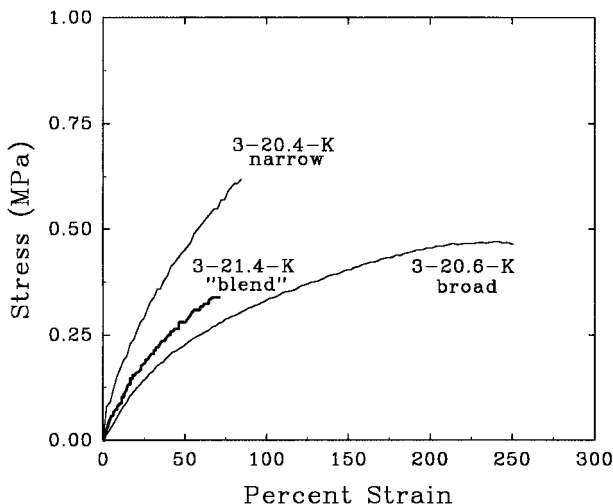


Figure 5 Effect of MWD polydispersity and modality on the properties of narrow (3-20.4-K), broad (3-20.6-K), and "blend" (3-21.4-K), K^+ PIB tri-arm ionomers of \bar{M}_n ca. 20,000. Note that 3-20.4-K is the narrow MWD ionomer, 3-20.6-K is the broad MWD ionomer, and 3-21.4-K is the blend ionomer.

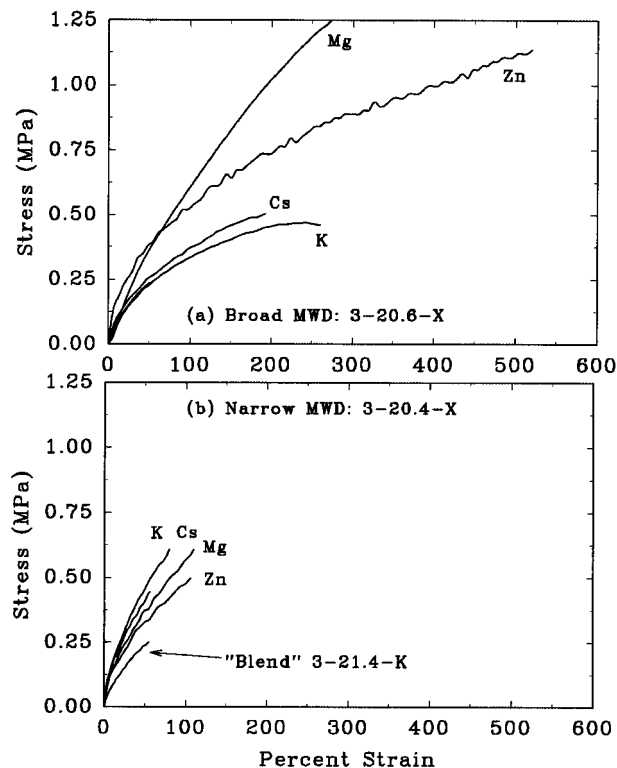


Figure 6 Mechanical behavior of PIB tri-arm telechelic ionomers of 20 kg/mol \bar{M}_n as a function of ion type.

are more similar to those of narrow MWD ionomers. The modulus of 3-21.4-K is like that of 3-49.5-K or 3-27-K, and the strain at break is like that of 3-11.8-K. The 3-11.8-K and 3-49.5-K materials are the principal components of the blend, so it appears, at least in this case, that the blend exhibits the poorest properties of its components.

The effect of counterion identity on the mechanical properties of the 3-20.6 (broad MWD) and 3-20.4 (narrow MWD) tri-arm telechelics is shown in Figure 6. Note that the response curves again indicate that the narrow MWD materials exhibit much lower elongation to break and higher moduli (Table V). In the broad MWD materials, however, it is apparent that the divalent cation materials are generally of higher modulus and have higher elongation to break. In the case of both the 3-20.4 and 3-20.6 materials, the best performing counterion appears to be Zn^{2+} , leading to a higher modulus and elongation to break.

Recovery is an extremely important property in elastomers, for such a material should be able to return to its original shape after deformation. The mode of fracture in these ionomers was generally to tear with almost total recovery. The range

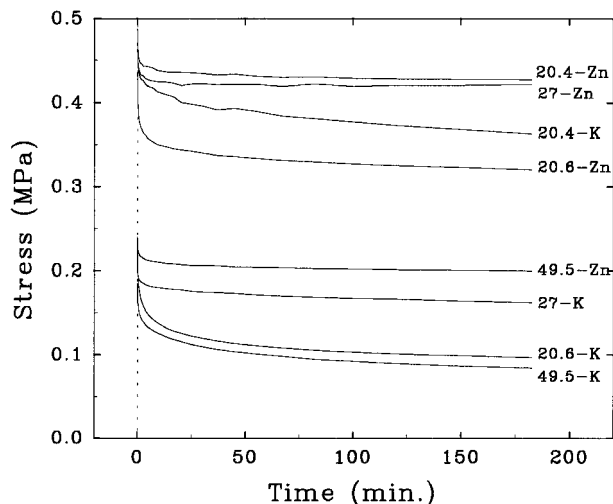


Figure 7 Stress relaxation behavior of K^+ and Zn^{2+} tri-arm PIB telechelic ionomers.

of recovery times varied, but the lower \bar{M}_n and narrow MWD materials generally recovered their original length faster than the higher \bar{M}_n and broad MWD materials, as might be expected. However, in the case of the monovalent (Cs^+ , K^+) tri-arms of broad MWD, the mode of failure was to break over the course of ca. 20-40% strain with little or no recovery after break. As noted before, this could be due to under-neutralization in the 3-11.6 and 3-20.6 Cs^+ and K^+ broad MWD tri-arms. The “blend” ionomer, 3-21.4-K, exhibited the rapid, full recovery of a narrow MWD ionomer. Thus, the MWD distribution and \bar{M}_n also play a role in determining the recovery characteristics of these ionomers.

Clearly, the mechanical properties of the tri-arm ionomers indicate that narrowing the MWD or decreasing the \bar{M}_n tends to alter the character of the network. As the \bar{M}_n decreases or the MWD becomes more narrow, the network tends to have increased modulus and lower elongation to break. Due to the reversible nature of ionic crosslinks and the presence of entanglements, it is also important to consider how the properties of these ionic, elastomeric networks vary with time and temperature. Therefore, the stress relaxation and dynamic mechanical properties of these systems were determined and are discussed next.

Stress Relaxation in Tri-arm Telechelics

The stress relaxation profiles of selected Zn^{2+} and K^+ tri-arm telechelics are shown in Figure 7, where the specimens were rapidly extended to a

draw ratio (λ) of 1.25 (temperature ca. 25°C). To the right of each curve is the designation of the \bar{M}_n and the counterion. Note that the phenomenon of “ion hopping” most certainly plays a role in the response of the ionomers in general, since the terminal region of the curve shows the stress to be slowly decaying over time. This mechanism was first noted by Hara et al. in tri-arm PIB sulfonates,³⁸ where ion pairs are pulled out of one ionic domain and “hop” to another in the stressed network, thus decreasing the stress in the network. Therefore, the stress reported as “equilibrium” stress (observed at 180 min) is actually influenced to an extent by this slow “ion hopping.” In Figure 7, for the same counterion, the “equilibrium” stress decreases as the \bar{M}_n of the tri-arm increases. This would seem to be a direct consequence of the decrease in the amount of ionic phase and ionic phase continuity when going from a the 3-20.4 to the 3-49.5 narrow MWD systems. This effect is also partly due to a simple decrease in equilibrium stress predicted from the Gaussian theory of rubber elasticity which has been applied with reasonable success to sulfonated PIB tri-arms before.³¹ Specifically, the first-order Gaussian theory predicts that the equilibrium engineering stress, σ_{eq} , is given by:

$$\sigma_{\text{eq}} = \rho RT / \bar{M}_c (\lambda - 1/\lambda^2) \quad (1)$$

Where: ρ is the polymer density, R is the gas constant, T is temperature, \bar{M}_c is the average molecular weight between crosslinks, and λ is the draw ratio. Thus, as the molecular weight between ionic crosslinks (\bar{M}_c) increases (e.g., with increasing \bar{M}_n) the equilibrium stress (σ_{eq}) decreases. In fact, Bagrodia, Wilkes, and Kennedy³¹ found a similar result in the earlier, broad MWD ionomers they studied. Broadening the MWD also decreases the “equilibrium” stress, though the effect is much greater in the K^+ ionomers than in the Zn^{2+} ionomers. This effect, like the effect of MWD on tensile modulus, is also indicative of the level of structural ordering in the system. Here, the data clearly indicate that the narrow MWD imparts higher long-term stress in the network and is not simply a short-term effect. In addition, it is again apparent that lowering the \bar{M}_n and narrowing the MWD have similar effects. It can then be speculated that the higher modulus and higher “equilibrium” stress of the narrow MWD systems is due largely to the decrease in local chain mobility near the ionic aggregates. Restriction of motion

in the nonionic chain segments nearest the ionic aggregate is central to Eisenberg's recent treatment of ionomer structure-property relationships⁹ and is found plausible for telechelic ionomers in the ¹³C nmr work of Vanhoorne et al.,³⁵ mentioned earlier. Thus, it is possible that such restriction of motion could play a role in increasing the modulus, increasing "equilibrium" stress, and decreasing the elongation at break of these ionomers. For each \bar{M}_n , the Zn²⁺ ionomers possess higher near "equilibrium" stress values than the K⁺ ionomers. This effect has also been observed^{31,39} in the PIB telechelics of broad MWD studied earlier by Bagrodia. The reason for the higher stress in the Zn²⁺ ionomers is believed to be the larger extent of covalent character in the Zn²⁺ ion, versus the K⁺ ion.³⁹ The unfilled *d* orbitals of the Zn²⁺ ion allow stronger bonding with the sulfonate group than in the case of an alkaline earth metal such as K⁺. It should be noted that other factors, such as neutralization level and the reinforcing effect noted in systems with excess neutralizing agent³¹ may also play a role in these systems.

Dynamic Mechanical Analysis of the Tri-arms

The dynamic mechanical analysis (DMA) profiles of the narrow MWD K⁺ tri-arm ionomers of $\bar{M}_n \geq 20$ kg/mol are shown in Figure 8. In Figure 8, note that the general shape of either the E' or $\tan \delta$ profiles is unaffected by \bar{M}_n , except in the flow transition region. (The unusual peak with a shoulder in the $\tan \delta$ curves will be addressed in detail later.) The 3-20.4-K ionomer has a higher rubbery plateau modulus than either the 3-27-K or 3-49.5-K ionomers, which is in agreement with the tensile data presented earlier. Note that the transition to flow occurs at lower temperature in the 3-27-K (ca. 150°C) material than for the 3-20.4-K (ca. 180°C) material and that the 3-49.5-K material has the lowest flow transition temperature (ca. 120°C). This observation derives from two things. There is more ionic phase continuity in 3-20.4-K than the other materials, based on the stress-strain behavior noted here and the earlier SAXS results given as part I of this series.³² Such ionic phase continuity would also tend to enhance the thermomechanical stability of the network and provide the higher DMA rubbery plateau modulus. The second reason is that a lower fraction of ionic material is present at higher \bar{M}_n and so the system acts more like the PIB homopolymer in terms of flow behavior. Again, the process of

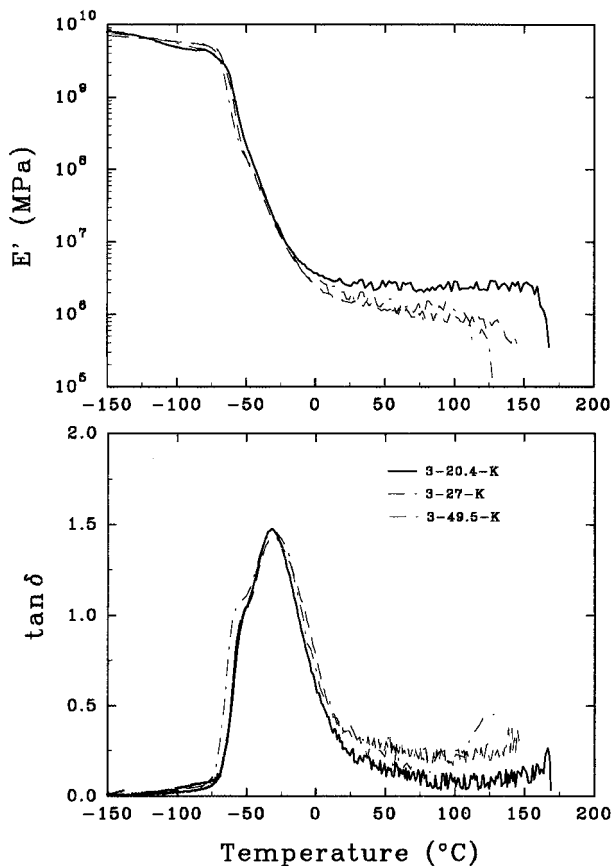


Figure 8 Dynamic mechanical analysis of the narrow MWD K⁺ tri-arm ionomers and the effect of \bar{M}_n .

"ion hopping" is evident in the DMA spectra. The material which has the least amount of ionic crosslinks, 3-49.5-K, has the lowest transition to flow. There are fewer ionic domains in the materials as \bar{M}_n increases, in addition to the noted effect of decreasing local ionic domain continuity. The $\tan \delta$ curves in the flow transition region also give some indication of the extent of ionic phase continuity. These curves clearly show that the loss behavior increases significantly in each of the ionomers near the flow transition. The 3-27-K and 3-49.5-K E' curves decrease in magnitude, while $\tan \delta$ remains nearly constant up to ca. 100°C. At the flow transition, the 3-20.4-K material rapidly begins to flow, whereas the other two ionomers exhibit increasing loss behavior across the whole rubbery plateau. This suggests that the extensive local ordering indicated by SAXS and mechanical testing in the 3-20.4-K material is the reason for the sudden transition to flow. Likewise, the lack of extensive local order (indicated by our earlier SAXS studies, part I) may be the reason for the

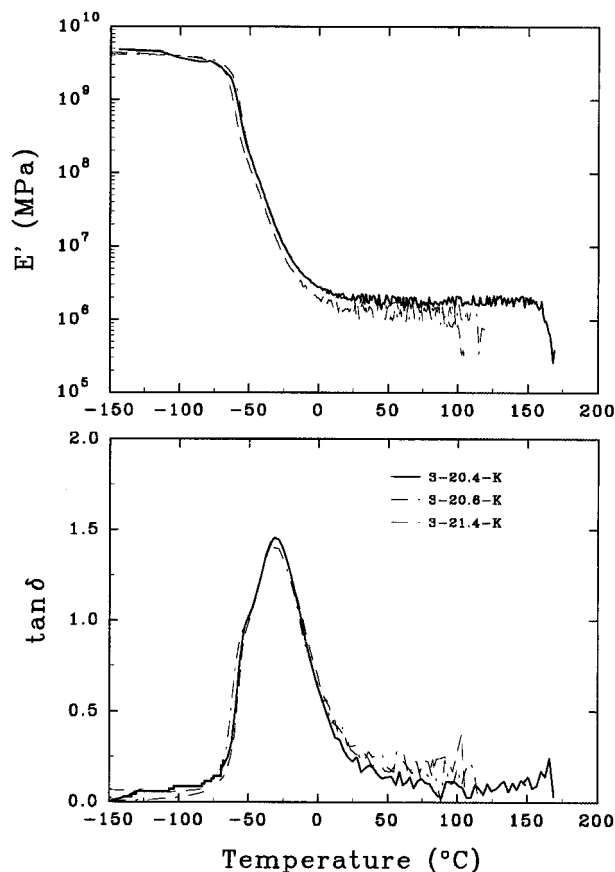


Figure 9 Dynamic mechanical analysis of the 20 kg/mol \bar{M}_n K^+ tri-arm ionomers and the effect of MWD; 3-20.4-K = narrow MWD. 3-20.6-K = broad MWD. 3-21.4-K = "blend" MWD.

gradually increasing loss behavior in the 3-27-K and 3-49.5-K materials.

The effect of molecular weight polydispersity and modality in the K^+ tri-arms of 20 kg/mol \bar{M}_n is shown in Figure 9. (Note in the $\tan \delta$ curves that there is again the peak with a shoulder, these will be discussed in the next paragraph). The E' curves again show that the 3-20.4-K (narrow MWD) material generally has the highest rubbery plateau modulus. However, note that the "blend" ionomer (3-21.4-K) exhibits a higher modulus like that of 3-20.4-K until ca. 25°C, where the modulus of 3-21.4-K drops considerably. The $\tan \delta$ of 3-21.4-K is always higher than that of 3-20.4-K, which implies that the damping effect is increased by including the higher \bar{M}_n chains in the MWD. There is also the question of whether this difference is in part due to the continuity and longer-range ordering of the ionic structure in the blend ionomer (3-21.4-K), owing to the lack of a secondary scattering peak in SAXS as well as a

lower tensile modulus, relative to the narrow, monomodal MWD ionomer, 3-20.4-K. The drop in E' for the blend (3-21.4-K) at room temperature is evidence that there is a change in the network relaxation behavior that is possibly correlated with its extremely multimodal MWD. The 3-20.6-K (broad MWD) material exhibits a lower rubbery plateau modulus than the other materials and broadening the MWD also enhances the loss tangent value (Fig. 9). Note that the broad MWD ionomer also exhibits the highest $\tan \delta$ values across the rubbery plateau. At the transition to flow, the narrow MWD monomodal 3-20.4-K material exhibits a higher transition temperature (ca. 180°C) than does the blend (ca. 120°C) as well as the broad MWD tri-arm (ca. 100°C). Interestingly, 3-20.6-K, the broad MWD ionomer which has no observed local ionic domain continuity and perhaps only "multiplets," exhibits the lowest transition temperature of all the K^+ tri-arms is observed (ca. 100°C). The blend ionomer exhibits a transition to flow that is above the broad MWD ionomer and below the narrow MWD ionomer.

The repeated observation of the peak with a shoulder in the glass transition region of the $\tan \delta$ of Figures 8 and 9 was puzzling at first. However, this effect was noted years ago by Fitzgerald, Grandine, and Ferry in their dielectric spectroscopy⁴⁰ and steady-flow viscometry⁴¹ studies of linear polyisobutylene of \bar{M}_v 1.35×10^6 g/mol. In the first study,⁴⁰ the authors noted that there was a dual peak phenomenon in the plot of $\tan \delta$ (as J''/J') versus $\log \omega a_T$, where the ordinate is the "shifted" frequency, according to the Williams-Landel-Ferry relationship. Two overlapping peaks were noted, a large, broad one and a smaller peak at a slightly higher thermally "shifted" frequency. This result corresponds to the peak and shoulder in Figures 8 and 9 by the principle of time temperature superposition, which dictates that frequency and temperature are inversely related to one another. Thus, the smaller, higher frequency peak of Fitzgerald, Grandine, and Ferry corresponds to the smaller, lower temperature shoulder in Figures 8 and 9. Likewise with the other part of the peak in Figures 8 and 9. In the second study,⁴¹ the authors show a plot of $\tan \delta$ (as G''/G') versus $\log \omega a_T$. Again, the same dual peak is seen, with a small high-frequency shoulder and a large, broad lower-frequency shoulder. The original authors gave no particular molecular explanation for this phenomenon, but this result does appear to account for the peak and shoulder observed in the DMA experiments here.

CONCLUSIONS

It has been shown that the properties of sulfonated PIB telechelic ionomers are strongly influenced by controlling the MWD. As the MWD becomes more narrow, modulus increases and there is lower elongation to break. As \bar{M}_n increases, the rubber-like nature of these ionomers improves, with the best properties (low modulus, highest breaking stress, highest elongation at break) exhibited by the 49.5 kg/mol \bar{M}_n narrow MWD tri-arms. The stress relaxation properties of these tri-arm ionomers also show that the narrow MWD materials can bear greater long-term stress than the broad MWD ionomers. Increasing the \bar{M}_n tends to disrupt the local continuity of the ionic domains and lower the volume fraction of them, thus lowering the near-equilibrium stress. DMA, in conjunction with the earlier reported SAXS results, indicates that a systematic variation in the continuity of the ionic structure is the basis of the properties observed in these ionomers. DMA further indicates that narrowing the MWD will increase the flow transition temperature and increase the rubbery plateau modulus. Also, the "blend" multimodal MWD ionomer exhibits DMA properties intermediate to those of the narrow and broad ionomers of similar \bar{M}_n , having a higher flow transition temperature than the broad MWD, but lower than the narrow MWD, and a rubbery plateau modulus between the other two. Lastly, the puzzling dual maxima in the $\tan\delta$ profile are attributed to the nature of the PIB relaxation spectrum.

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