Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Polymer 48 (2007) 7558–7566
polymer
www.elsevier.com/locate/polymer

Viscoelastic properties of poly(styrene-*co*-vinylphosphonate) ionomers

Qi Wu, R.A. Weiss*

Department of Chemical Engineering and Polymer Program, University of Connecticut, 97 N. Eagleville Road, Storrs, CT 06269-3136, USA

Received 7 August 2007; accepted 8 November 2007
Available online 12 November 2007

Abstract

Viscoelastic properties of neat and glycerol plasticized poly(styrene-*co*-diethyl vinylphosphonate) ionomers were investigated. Nanophase separation of a polar phase occurred due to hydrogen bonding or ionic interactions in the acid derivatives and the metal salts, respectively. Metal–phosphonate ion–dipole interactions were much stronger and more temperature persistent than the hydrogen bonding in the phosphonic acid derivatives, which were manifested by a much broader rubbery region in their viscoelastic behavior. The phosphonate interactions were thermally stable up to >250 °C, and the physically crosslinked network produced suppressed viscous flow of the ionomers to very high temperatures. Time–temperature superposition was not applicable for the SVP ionomers even at an ion content as low as 2.4 mol%. The addition of a polar plasticizer, e.g., glycerol, preferentially solvated the ionic associations and diminished the extent of the rubbery plateau of the ionomer and substantially decreased the terminal relaxation time.

Keywords: Ionomer; Phosphonate; Viscoelasticity

1. Introduction

Physical and mechanical properties of hydrocarbon polymers can be considerably modified by introducing a small amount of ionic functional groups. Much research has been conducted on ionomers, and several reviews and monographs [1–3] provide a comprehensive review of the general structure–property relationships of ionomers. Most of the studies indicate that the ionic interactions act as physical crosslinks, which can significantly modify the viscoelastic properties of the polymer. An extended rubbery plateau is observed in the viscoelastic behavior, and a transition at higher temperatures due to an ion-rich minor phase is usually observed. Ionomers have high melt viscosities and improved mechanical properties compared to the un-ionized polymer.

The literature is rich with papers concerning ionomers with considerable research on carboxylic acid and sulfonic acid groups [1–3]. Relatively few studies have considered phosphonate ionomers [4–7]. The strength of the ionic interactions in ionomers, and hence their physical and mechanical properties, depends on the acidity of the pendent anion. Polymers modified with the stronger acid, such as sulfonic acid ($pK_a \sim 1$), exhibit more dramatic changes in thermal, viscoelastic, rheological and solution properties than those modified with the weaker carboxylic acid ($pK_a \sim 4-5$). In a previous paper [4], we reported on the synthesis of poly(styrene-*r*-vinylphosphonic acid) (SVP) ionomers. Phosphonic acid possesses two ionizable groups ($pK_{a1} \sim 2-3$; $pK_{a2} \sim 7$), and although neither is as strong acid as sulfonic acid, the elastic modulus of the SVP ionomers at high temperature (>150 °C) was comparable or even higher than that of a comparable sulfonated polystyrene ionomer.

Low molecular weight additives, *plasticizers*, are often added to polymers to improve their melt flow characteristics. However, since ionomers are nanophase-separated materials, there is an opportunity to selectively add plasticizers to the two different phases, which can produce materials with completely different viscoelastic behavior. That is, relatively non-polar plasticizers partition into the neutral polymer phase and polar plasticizers partition into the ion-rich aggregates that compose the nanophase separation in ionomers. This was first demonstrated by Lundberg et al. [8] for sulfonated polystyrene

---

* Corresponding author. Tel.: +1 860 486 4698; fax: +1 860 486 6048.
E-mail address: rweiss@mail.ims.uconn.edu (R.A. Weiss).

0032-3861/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2007.11.015

ionomers. Non-polar plasticizers, such as dioctyl phthalate (DOP) or dibutyl phthalate (DBP), preferentially plasticized the polystyrene backbone, lowered the matrix glass transition, but had little effect on the ionic associations, while polar plasticizers, such as glycerol, were effective at solvating the ionic aggregations and greatly lowered the melt viscosity of the polymer. Other studies on the viscoelastic properties of plasticized polystyrene-based ionomers have been reported by Eisenberg et al. [9,10] and Weiss et al. [11–13]. Eisenberg and Kim [3] and Bazuin [14] have reviewed the subject.

In this paper, the viscoelastic and rheological properties of the SVP ionomers are discussed in more detail. Results on 2.4Na-SVP plasticized with an ionic-domain plasticizer, glycerol, are reported. Physical properties of 2.4Na-SVP ionomer containing about 10 wt% of glycerol were characterized by TGA, DSC, DMA and SAXS. The effect of the polar plasticizer on the ionic associations in the SVP ionomer was investigated.

2. Experimental

2.1. Materials

The synthesis of poly(styrene-*r*-vinylphosphonate) ionomers was described in a previous paper [4]. This was achieved by a free-radical polymerization of styrene and diethyl vinyl phosphonate (DEVP) in toluene at 100 °C, followed by hydrolysis of the diethyl phosphonate groups with a concentrated HCl/dioxane solution. The resulting phosphonic acid derivatives were neutralized with an appropriate metal hydroxide or acetate to produce the ionomers. The sample notation used for the ionomers is *x.y*M-SVP, where *x.y* is the degree of phosphonation expressed as mol% of the DEVP monomer in the copolymer and M denotes the cation (i.e., M = H, Li, Na, K, Cs or Zn for the free acid (H^+), lithium (Li^+), sodium (Na^+), potassium (K^+), cesium (Cs^+) and zinc salts (Zn^{2+}), respectively). The neutral, styrene-DEVP copolymers are denoted as *x.y*E-SVP. It is assumed here that the composition and backbone molecular weight of the E-SVP copolymer did not change during the hydrolysis and neutralization reactions. Table 1 describes the poly(styrene-DEVP) copolymers synthesized for this study. Sulfonated polystyrene (SPS) was prepared by sulfonating a preformed polystyrene ($M_w \sim 280$ kg/mol) with acetyl sulfate. The synthesis and preparation of the Na- and Zn-salt were described in a previous paper [4]. The sample notation used for the sulfonate ionomers is *x.y*M-SPS, where *x.y* represents the sulfonation level (mol%) of the ionomer.

Table 1
Properties of styrene-DEVP copolymers

	S:DEVP in feed	Copolymer composition from ^{1}H NMR (mol% DEVP)	M_w (kDa) from GPC	M_w/M_n	T_g (°C) from DSC
2.4E-SVP	9:1	2.4	70	1.4	104.5
4.3E-SVP	5:1	4.3	70	1.5	103.3
6.4E-SVP	3:1	6.4	82	1.3	99.6
12.8E-SVP	3:2	12.8	61	1.5	88.0
15.4E-SVP	1:1	15.4	57	1.5	86.0

The Na-SVP ionomer with ion content of 2.4 mol% was plasticized with glycerol (dielectric constant, $\varepsilon = 42.5$; b.p. = 180 °C/20 mmHg). Glycerol (0.15 g) was added to a vigorously stirred solution of 1.5 g 2.4Na-SVP in 50 mL THF in a poly(tetrafluoroethylene) dish. A clear mixture was obtained and stirred for 2 days in a fume hood to allow THF to evaporate. The mixture was further dried under vacuum at room temperature for 1 day, 45 °C for 3 h and 70–80 °C for 2 days. The plasticizer content was determined gravimetrically by thermogravimetric analysis (TGA).

Powders of the E-SVP copolymers and M-SVP ionomers were dried in vacuum before molding into specimens for dynamic mechanical analysis (DMA). Samples were molded at $T_g + 40$ °C with a Wabash hydraulic press; samples with very high melt viscosity were molded in a vacuum oven at ca. $T_g + 80$ °C using two steel plates (10 cm × 10 cm) connected with springs at each corner to provide the compression.

2.2. Polymer characterization

Thermogravimetric analysis (TGA) was performed with a TGA 2950 thermogravimetric analyzer (TA Instruments). Thermal degradation of the polymers was examined in a nitrogen atmosphere using a heating rate of 20 °C/min from 60 to 800 °C. The glass transition temperatures (T_gs) were measured with a TA Instruments DSC 2929 using a nitrogen atmosphere using indium and tin standards to calibrate temperature. The samples were first heated to above the transition temperature, cooled at 20 °C/min and reheated at 20 °C/min. The T_g was defined as the midpoint of the change in heat capacity at the transition in the 2nd heating curve.

2.3. Viscoelastic property measurements

Dynamic mechanical analysis (DMA) was carried out with a TA instruments DMA 2980 using a nitrogen atmosphere. All measurements were made within the linear viscoelastic region, which was determined from strain sweeps. Isochronal temperature scans were made at a frequency of 1 Hz in tensile mode using a heating rate of 2 °C/min. Isothermal frequency sweeps from 0.04 to 30 Hz were carried out at different temperatures using a shear sandwich fixture. For the ionomers, experiments were run at temperatures between $T_g + 40$ °C and $T_g + 140$ °C, while for E-SVP copolymers, a narrower temperature range, $T_g + 30$ °C to $T_g + 60$ °C, was used due to very low forces at the higher temperatures. Time–temperature superposition was attempted by shifting the isothermal modulus–frequency curves along the frequency axis with $T_{ref} = T_g + 50$ °C. Vertical corrections were made by a factor of T_{ref}/T to compensate for the temperature dependence of the modulus.

3. Results and discussion

3.1. Effect of phosphonation

Fig. 1(a) and (b) shows the tensile storage modulus and tan δ vs. temperature curves for 6.4E-, H-, Na- and Zn-SVP and 6.4Na- and Zn-SPS. The unmodified 6.4E-SVP copolymer shows the typical viscoelastic behavior of an amorphous polymer with no specific interactions. Although the number average molecular weight (M_n) of the copolymer was 63,000 g/mol, which was well above the entanglement molecular weight of PS ($M_e = 16{,}600$ g/mol [15]), no plateau region in E' was observed above T_g. tan δ of the 6.4E-SVP showed a single, rather sharp peak, typical of the glass transition region of a homogeneous amorphous polymer.

In contrast with the phosphonate ester copolymer, a hint of a rubbery plateau was observed for the SVP-acid derivative and the Na- and Zn-ionomers clearly exhibited a plateau region. The rubbery modulus increased in the order H < Na ~ Zn. For the acid derivative (H-SVP), the rubbery region, due to intermolecular hydrogen bonding between the vinylphosphonic acid groups, persisted for only ~10 to 20 °C and was immediately followed by viscous flow of the ionomer. Although hydrogen bonding did provide some physical crosslinking of the polymer, the hydrogen bond interaction severely weakened as the temperature increased above 150 °C. Two peaks were observed in the tan δ curve of 6.4H-SVP, at ca. 150 and 180 °C, which suggests that phase separation of aggregates of vinylphosphonic acid groups occurred. That phenomenon was also observed for H-SVP with acid concentrations from 2.4 to 15.4 mol%.

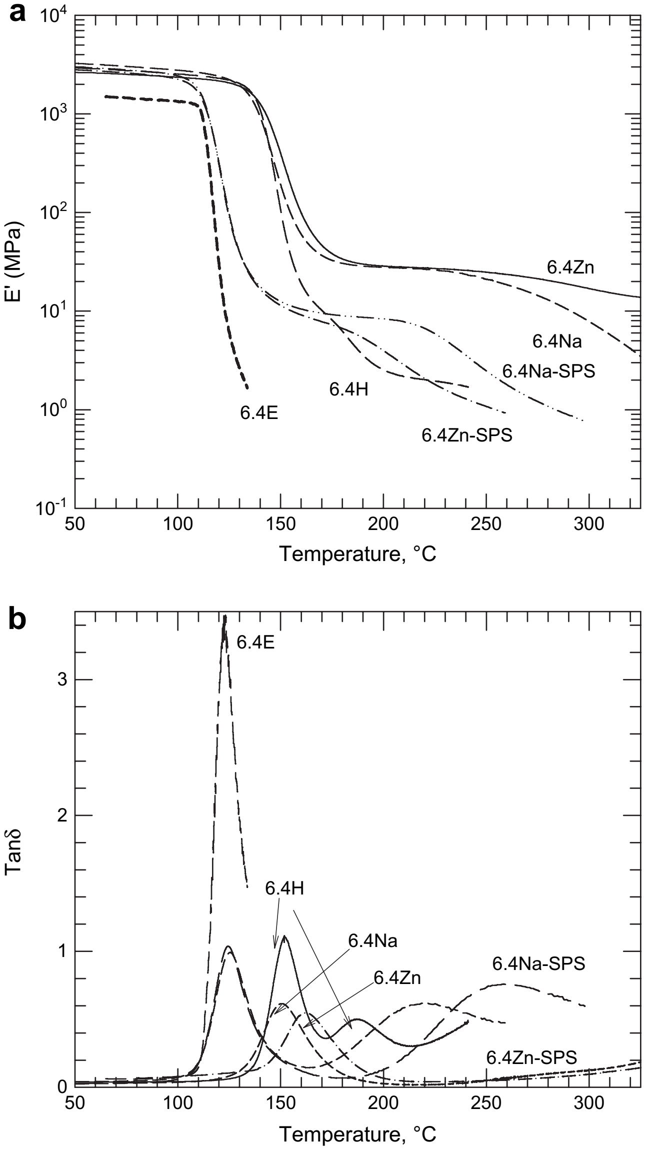

Fig. 1. Dynamic mechanical behavior of 6.4E-, H-, Na- and Zn-SVP and 6.4Na- and Zn-SPS ($f = 1$ Hz, 2 °C/min): (a) E'; (b) tan δ.

Fig. 2 shows the dynamic mechanical behavior of H-SVP vinylphosphonic acid derivatives with various acid concentrations. For acid contents of 2.4–6.4 mol%, two distinct loss peaks were observed in tan δ. As the phosphonic acid content increased, the lower temperature loss peak decreased in intensity and broadened, while the intensity of the higher temperature peak increased. For the higher acid concentrations, 12.8 and 15.4 mol%, the lower temperature loss process occurred at 210–220 °C and was considerably broader than that for the lower acid contents. For those two samples, a very broad higher temperature relaxation also occurred between 250 and 300 °C, which indicates a rather broad distribution of relaxation times for the higher temperature relaxation process.

The observation of a second transition above the matrix T_g has been widely reported for other ionomers, and the higher temperature transition has been attributed to a relaxation of a nanophase-separated ion-rich phase. In the case of the H-SVP ionomers, nanophase separation of the phosphonic acid groups occurs as a result of hydrogen bonding interactions. Nanophase separation is usually observed with metal neutralized ionomers, but it has also been reported for the sulfonic acid derivative of styrene-based ionomers [16,17]. It is not usually observed in the weaker hydrogen bonded carboxylic acid containing polystyrene-based ionomers [18].

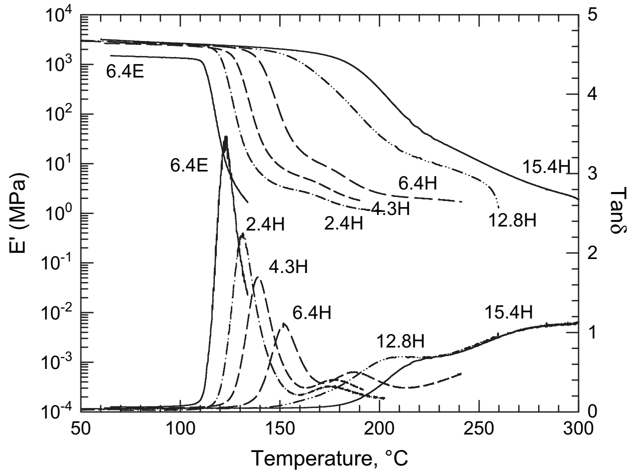

Fig. 2. Dynamic mechanical tensile properties of 6.4E-SVP and H-SVP ionomers ($f = 1$ Hz, 2 °C/min).

No rubbery plateau was observed for a 2.0H-SPS sample with higher molecular weight ($M_n = 100{,}000$ g/mol) using the same experimental conditions as for the H-SVP ionomers, which suggests that the physical network formed by hydrogen bonding of the vinylphosphonic acid groups is stronger than that formed by aromatic sulfonic acid groups. The strong hydrogen bonding interaction between phosphonic acid group (attached either to a phenyl ring or to a vinyl group) was previously observed by Zhuang et al. [19,20] in an investigation of miscibility of blends of poly(styrene-*co*-4-vinylbenzenephosphonic acid) or poly(styrene-*co*-vinylphosphonic acid) with poly(*n*-butyl methacrylate) and with poly(vinyl methyl ether).

Surprisingly, the 6.4Na- and Zn-SVP ionomers exhibited only a single tan δ peak at high temperature, which corresponded to the glass transition of the physically crosslinked matrix, see Fig. 1(b). The absence of a high temperature peak in tan δ might indicate the absence of nanophase-separated ionic aggregates in these materials. The E' data, however, clearly indicate that the physically crosslinked network formed by the ionic group interactions persists to very high temperature, higher than that formed by the SPS ionomers. The DMA results for the 6.4Na- and Zn-SPS ionomers (see Fig. 1) show a narrower rubbery plateau and a lower T_g than the SVP ionomers, but they exhibit a distinct high temperature tan δ peak. These results indicate that the physically crosslinked network formed by the phosphonates seems to have a higher crosslink density than the comparable sulfonated one, as judged by the higher T_g and rubbery modulus for the phosphonates.

Fig. 3 shows the tan δ curves of Na-SVP ionomers with ion concentration from 2.4 to 15.4 mol%. No clear high temperature relaxation above T_g was observed for any of these ionomers, which suggests the absence of nanophase separation of ionic aggregates. However, room-temperature SAXS data, Fig. 4, show a peak for samples with greater than 6.4 mol% phosphonation, indicating nano-sized ionic aggregates (characteristic spacing, $d \sim 2.1-2.5$ nm) similar to what is observed for other ionomers, though a bit smaller than what is observed for similar SPS ionomers ($d \sim 3-5$ nm) [21]. The intensity of the ionic peak in the neat ionomers increased with increasing ion content, and the peak shifted to higher q, corresponding to smaller d, as the ion concentration increased.

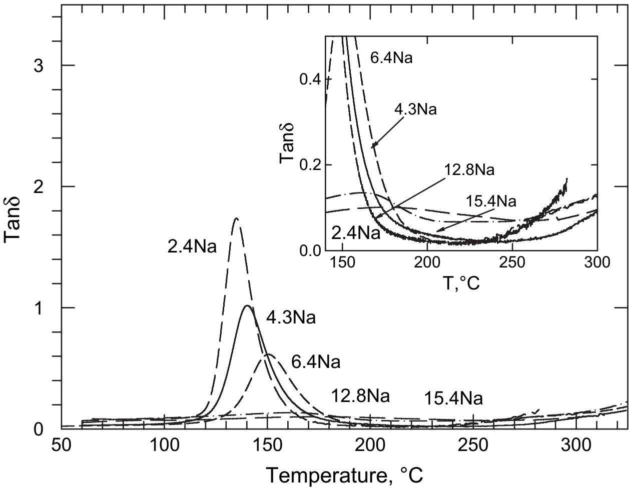

Fig. 3. Dynamic mechanical tan δ curves of Na-SVP ionomers with various phosphonate concentrations ($f = 1$ Hz, 2 °C/min).

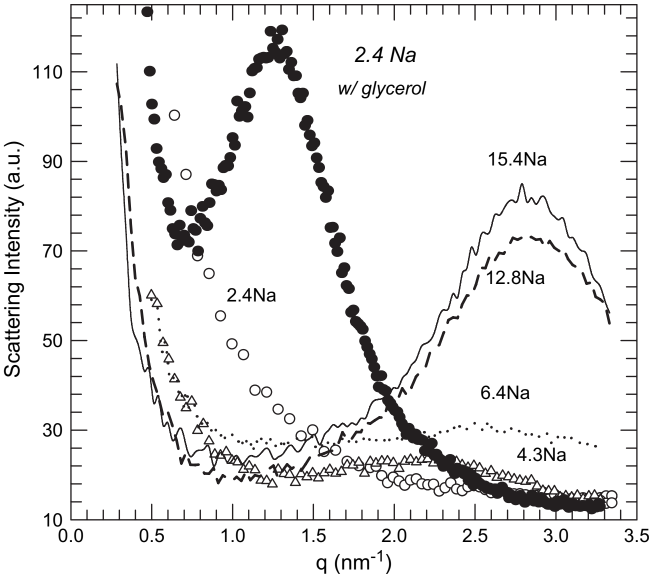

Fig. 4. Small-angle X-ray scattering data for Na-SVP ionomers and 2.4Na-SVP/10% glycerol blend.

The absence of a high temperature relaxation in the SVP ionomers, but the clear presence of nanophase separation at room temperature shown by the SAXS data in Fig. 4 may indicate that either the temperature stability of that nanophase is poor above T_g, but that simple crosslinks formed from ion–dipole interactions of phosphonate groups effectively provide a physically crosslinked network at elevated temperatures, or that the nanophase separation of the phosphonate species is much stronger than that of the sulfonates, so that a relaxation of the phosphonate nanophase is not observed over the temperatures probed in this study. The latter scenario is supported by data that are discussed in the next section of this paper. The E' data show that viscous flow of the Na-salt started at 225 °C, but relatively little flow was observed in the Zn-salt up to 300 °C. At these high temperatures, however, some degradation of the polymers is likely, which complicates the structure analyses.

For the other ion concentrations investigated in this study (2.4–15.4 mol%), a higher temperature transition peak in tan δ was also not clearly identified. Similar to numerous other studies [1–3] of metal salts of sulfonated and carboxylated polystyrene ionomers, a higher temperature transition characteristic of an ion-rich phase was observed for the 6.4Na- and Zn-SPS ionomers, Fig. 1(b). The temperature difference (ΔT) between the relaxation processes of the ion-rich phase and the matrix is related to the strength of the ionic interactions. At comparable ion concentration, ionomers containing a sulfonic acid exhibit higher ΔTs than those containing weaker acids, carboxylic acid. For example, $\Delta T \sim 114$ °C for a 6.2Na-SPS ionomer, while ΔT was only about 44 °C for a 5.8Na-CPS ionomer [22]. Although a high temperature relaxation peak in tan δ was not observed in the isochronal DMA data for the 6.4 M-SVP ionomers, the high value of modulus that persisted at elevated temperatures for those ionomers suggests that the ΔT values for the 6.4 M-SVP ionomers are comparable with or even higher than that of the Na-SPS ionomers. Fig. 1(a) also shows that the plateau moduli of the 6.4 M-SVP ionomers were considerably higher than those of 6.4 M-SPS ionomers, which indicates that ionic interactions were actually stronger in the SVP ionomers. This seems contradictory to the assumption that ionomers containing the stronger sulfonic acid would possess stronger ionic associations than those in the ionomers with the weaker vinylphosphonic acid. But, vinylphosphonic acid contains two acid groups, while sulfonic acid is a monovalent acid. At the same acid concentration, the ion exchange capacity of vinylphosphonic acid is higher than that of the sulfonic acid, which appears to have a significant influence on the intermolecular interactions and properties of these ionomers.

At comparable ionic group concentrations, the modulus of the rubbery plateau was similar for the Na- and Zn-salt of the SVP ionomers. But in all cases, the Zn-salt was much more resistant to flow at high temperature than the Na salts. Hara et al. [23] reported similar results for the Na- and Ca-salt of SPS ionomers, where the divalent salt exhibited a more extended rubbery plateau than the monovalent salt. Lefelar and Weiss [24] reported a broader rubbery plateau for Zn-SPS compared with Na-SPS, but a higher storage modulus for the Na-salt, which is the opposite result to that shown in Fig. 1 for similar ionomers. Weiss et al. [17] also reported that the relaxation time of the ionic aggregates was shorter for Zn-SPS than for the Na-SPS. Tomita and Register [24] observed that the ionic associations in Zn-CPS were weaker than in Na-CPS.

3.2. Effect of counter-ion

The dynamic mechanical properties of 2.4 M-SVP ionomers where M = alkali metal salts (Li^+, Na^+, K^+ and Cs^+) are shown in Fig. 5. The cations in the alkali metal group have the same valency (1), but the charge/radius (q/a) ratio decreases in the order of $Li^+ > Na^+ > K^+ > Cs^+$. q/a is a measure of the ionization potential, or strength, of the ion-pair. The ion–dipole interactions and properties dependent on them, e.g., T_g, often scale in the same order as q/a for carboxylate ionomers [25]. The T_gs of the 2.4 mol% alkali metal-SVP ionomers, however, were independent of q/a, ~116 °C, and no difference in the T_gs was previously observed for SPS ionomers with various alkali metal salts [26].

The choice of the alkali metal cation did, however, have a significant effect on the magnitude of the rubbery modulus and the onset of viscous flow, see Fig. 5(a). The plateau modulus decreased in the order of $Li^+ > Na^+ \sim K^+ > Cs^+$, and the Cs-salt clearly exhibited viscous flow at lower temperature than the other salts. Those results are consistent with the relative values of q/a, i.e., the ion–dipole interactions weakened as q/a decreased (note that for a constant cation valency, decreasing q/a corresponds to increasing size of the cation). The 2.4Na- and Li-salt did not exhibit a relaxation peak in tan δ above T_g, and there was no clear evidence of viscous flow in the E' data for those two ionomers to $T > 250$ °C. The K- and Cs-salt, however, exhibited a high temperature tan δ peak at 230 and 265 °C, respectively, which also corresponded to the onset of viscous flow in the E' curves. If the "ionic relaxation" in tan δ scales with q/a, one would expect that the nanophase relaxation in the Na- and Li-salt would occur at higher temperatures, though such temperatures were too high to access in these experiment, because of concerns about polymer degradation. This observation is consistent with the speculation discussed above that the nanophase separation in the SVP ionomers persisted to much higher temperatures than those for the SPS ionomers.

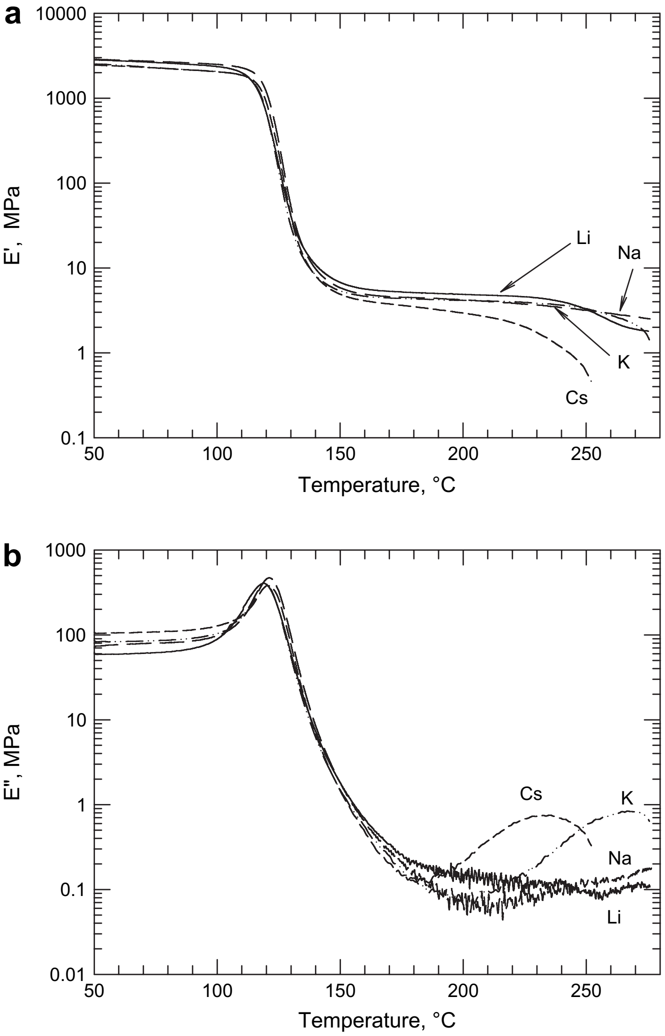

Fig. 5. Dynamic mechanical tensile properties of alkali metal salts of 2.4-MSVP ($f = 1$ Hz, 2 °C/min): (a) E'; (b) E''.

G'' results for dynamic shear tests at multiple frequencies are shown for the 2.4Cs-SVP ionomers in Fig. 6. The high temperature ionic transition peak shifted to higher temperatures as the frequency increased from 0.2 to 20 Hz, and an activation energy of $E_a = 206$ kJ/mol of that relaxation process was calculated from an Arrhenius equation:

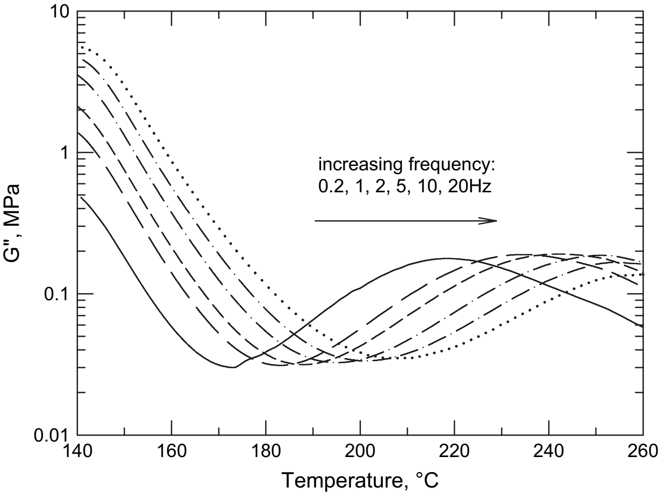

Fig. 6. Dynamic mechanical shear loss moduli of 2.4Cs-SVP ionomers at multiple frequencies: 0.2, 1, 2, 5, 10, 20 Hz (heating rate: 2 °C/min).

$$f_{\max} \propto A_1 \exp[-(E_a/RT)] \tag{1}$$

That value compares favorably with the activation energy reported for 1.82Na- and Zn-SPS ionomers (230 and 220 kJ/mol, respectively) [17]. Unfortunately, the tan δ peak was resolved at sufficient frequencies to get a reasonable calculation of E_a only for the Cs-salt, which had the weakest ion–dipole interactions.

3.3. Time–temperature superposition

Time (frequency)–temperature superposition (TTS) of the isothermal frequency sweep data for the E-SVP copolymers and the H-, Na- and Zn-SVP ionomers was attempted. Isothermal shear moduli (G' and G'')–frequency data at different temperatures were shifted horizontally along the frequency axes using a reference temperature of $T_{\mathrm{ref}} = T_g + 50\,°\mathrm{C}$. Vertical corrections were made using a factor of T/T_{ref} to compensate for the temperature dependence of the modulus. For the acid and salt derivatives, the data did not superpose, indicating the rheological complexity of those materials as a consequence of nanophase separation. Pseudo-master curves were constructed, e.g., Fig. 7, by overlapping the data at high frequency, in which case the low frequency data did not superimpose. This approach tries to superimpose the shorter time responses of the polymer (i.e., higher frequency), which are dominated by the short range elastic motions of the polymer chain. The longer time relaxations due to ionic interactions are characterized by the low frequency data, where TTS failed. The same shift factors calculated for the G' data, e.g., Fig. 7(a), were used to construct the pseudo-master curves for G'', such as in Fig. 7(b). The shift factors used to construct the pseudo-master curves were used to calculate activation energies for the viscous flow of the ionomers.

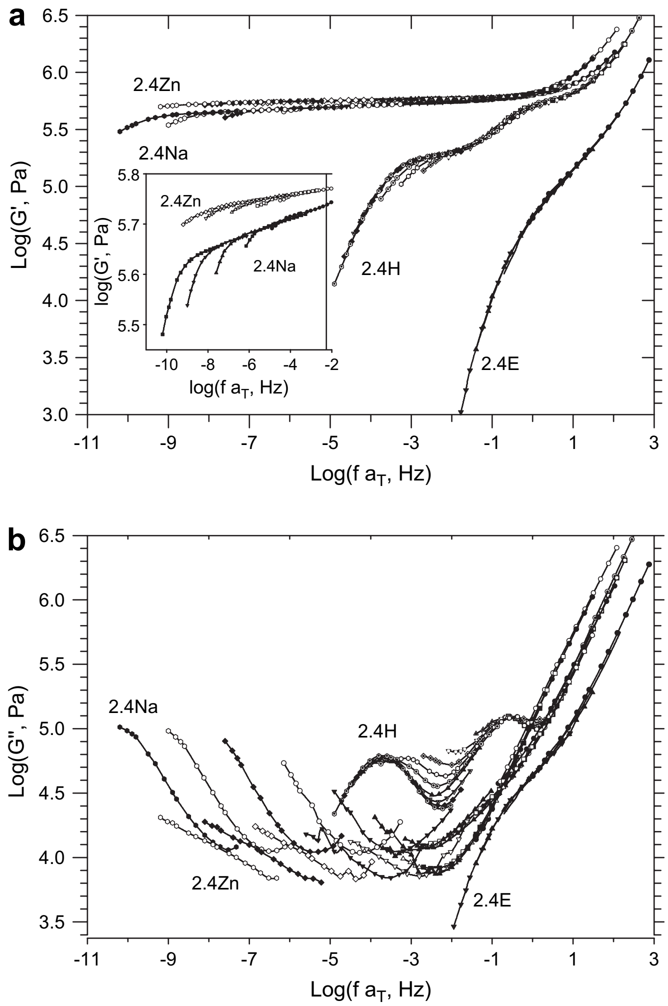

Fig. 7. Dynamic mechanical shear moduli master curves for 2.4E-SVP and pseudo-master curves for 2.4H-, Na- and Zn-SVP ionomers; $T_{\mathrm{ref}} = T_g + 50\,°\mathrm{C}$: (a) G'; (b) G''. Temperature range: 2.4E- (135–165 °C); 2.4H- (145–245 °C); 2.4Na- and Zn-SVP (155–255 °C).

The G' and G'' vs. reduced frequency master curves for 2.4E-SVP copolymer and pseudo-master curves for 2.4H-, Na- and Zn-SVP are shown in Fig. 7. For the ionomers, the pseudo-master curves covered up to 13 decades of reduced frequency. The G' and G'' data for the unmodified E-SVP copolymers superimposed successfully and the polymer exhibited terminal behavior at the lower frequencies – that is, slopes of 2 and 1 for log G' vs. log frequency and for log G'' vs. log frequency, respectively. The H-SVP derivatives did not exhibit TTS due to the strong hydrogen bonding that occurred in that polymer. The one exception was the G'–frequency data for 15.8 mol% H-SVP, which did superimpose. But, the same set of shift factors did not superimpose the G'' data. None of the ionomers exhibited TTS, and the pseudo-master curves for the Na- and Zn-salt indicated that the terminal region for the ionomers shifted to much lower frequency compared with the neutral copolymer and the acid derivative.

The failure of TTS for all the acid derivative and salts demonstrated that the phosphonated polystyrene ionomers were thermorheologically complex, even at ion concentrations as low as 2.4 mol%, which is due to the nanophase separation of ionic aggregates. The failure of TTS is consistent with most results for ionomers [2]. However, notable exceptions where successful TTS is reported for ionomers include SPS ionomers with sulfonation levels as high as 5.8 mol% [17] and poly(styrene-*co*-methacrylic acid) with less than 4 mol% metal carboxylate [27]. The success of TTS for the SPS ionomers was attributed to a large relaxation time difference between the ionic interactions and the matrix, such that the two relaxations were not both accessed in the limited frequency range of a typical DMA experiment. The success of TTS for the metal carboxylate system was attributed to the absence of microphase separation at low ionic group concentrations. The viscoelastic behavior of the SVP ionomers described above suggests that the difference in the relaxation times of the matrix and the ionic nanophase is at least as large as for the SPS ionomers, so it is not clear why TTS failed for the SVP ionomers and not the SPS ionomers.

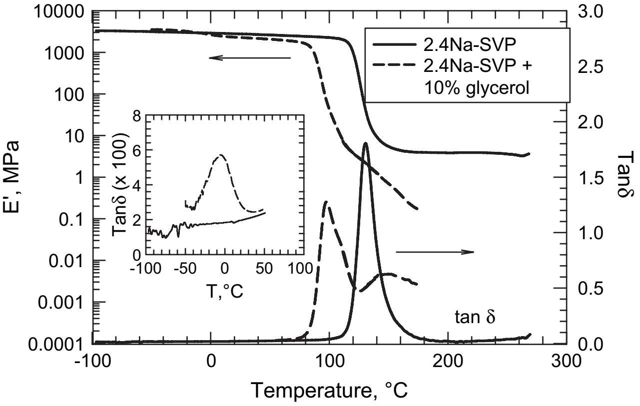

Fig. 8. Dynamic mechanical tensile storage moduli and tan δ of 2.4Na-SVP and 2.4Na-SVP/10% glycerol ($f = 1$ Hz, heating rate = 2 °C/min).

3.4. Properties of glycerol-plasticized M-SVP ionomers

T_g of the 2.4Na-SVP plasticized with 10% glycerol measured by DSC was 95 °C; $T_g = 115$ °C for the neat ionomer. The T_g of glycerol is −86 °C [28]. The Fox equation [29] predicts the glass transition of a miscible amorphous mixture as

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \tag{2}$$

where w_1 and w_2 are the weight fractions of each component with glass transitions of T_{g1} and T_{g2}, respectively. According to the Fox equation, the T_g of the 2.4Na-SVP/10% glycerol blend is expected to be 77 °C, compared to the experimental value of 95 °C. Similar discrepancies have been reported for glycerol-plasticized SPS ionomers [10,13], where a positive deviation from the Fox equation prediction was observed. The T_g of SPS ionomers plasticized with non-polar compounds, such as dioctyl phthalate, agreed well with Fox equation [13]. The difference in the effects of the two types of plasticizers is a consequence of preferential partitioning of the plasticizer in the different phases of the ionomer [8,13]. The non-polar plasticizer interacts exclusively with the hydrocarbon matrix and depresses the matrix T_g by increasing its free volume. On the other hand, polar plasticizers are not miscible with the non-polar hydrocarbon phase and partition into the ionic nano-domains, effectively solvating the ionic interactions. In that case, the depression of the matrix T_g is due to weakening of the restriction on main-chain motions due to the ionic aggregates – that is, the polar plasticizer essentially removes the physical crosslinks due to ionic aggregation.

Fig. 8 compares E' and tan δ for 2.4Na-SVP with and without glycerol. The neat ionomer was clear in appearance, but it became opaque upon the addition of 10% glycerol, which indicates that phase separation occurred in the plasticized ionomer. The opacity of the sample indicated that the phase size was large enough to scatter visible light, ~1 μm. The glass transition of the hydrocarbon matrix shifted to lower temperature by ~20 °C with the addition of glycerol, which agreed with the DSC result. A more dramatic influence of glycerol was the diminution of the rubbery plateau and the much lower temperature onset of viscous flow for the plasticized ionomer. The ionic relaxation peak in tan δ of the ion-rich phase shifted from >250 °C (as discussed above, no peak was actually observed, which was thought to be due to the inability to access high enough temperatures in the DMA experiment) for the neat ionomer to 150 °C for the plasticized material. The crosslinking effect of ionic aggregates was severely weakened by the polar plasticizer, which solvated the ionic association and increased the mobility of the ion-rich phase.

The SAXS data in Fig. 4 show that the characteristic size associated with the ionic aggregates increased to ~4.8 nm, which was about twice that in the neat ionomer. The most popular interpretation of the ionic peak in SAXS is that the characteristic size is a measure of the interparticle distance of the ionic aggregates [30], so the larger separation of the aggregates might indicate a lower crosslink density. The increase in the intensity of the scattering is probably due to the preferential swelling of the ionic aggregates with glycerol. Similar effects of glycerol on the matrix and ion-rich phase glass relaxations of SPS ionomers have been reported [13]. The other characteristic feature of the SAXS pattern of ionomers, the small-angle upturn in intensity, was maintained in the plasticized ionomer. This is believed to be due to an inhomogeneous distribution of isolated ionic groups or multiplets [5].

The opacity of the plasticized sample indicates the presence of phase separation on the scale of approximately μm, which is most likely glycerol. Polystyrene and glycerol are totally immiscible; the addition of as little as 1% glycerol turns PS opaque [13]. Similarly, blends of 2.4E-SVP and 2% glycerol were immiscible. In contrast, SPS ionomers with 8% glycerol were optically clear indicating miscibility [13]. But, the SPS/glycerol mixtures became opaque when the glycerol concentration was increased to >8%, and a broad transition in the region of −100 to 0 °C was attributed to the glass transition of the phase-separated glycerol [13]. That relaxation shifted to lower temperature as the glycerol content increased. The inset in Fig. 9(a) shows a magnification of the low temperature region of the tan δ data for the 2.4Na-SVP and 2.4Na-SVP/10% glycerol. A weak, but distinct, broad transition between −40

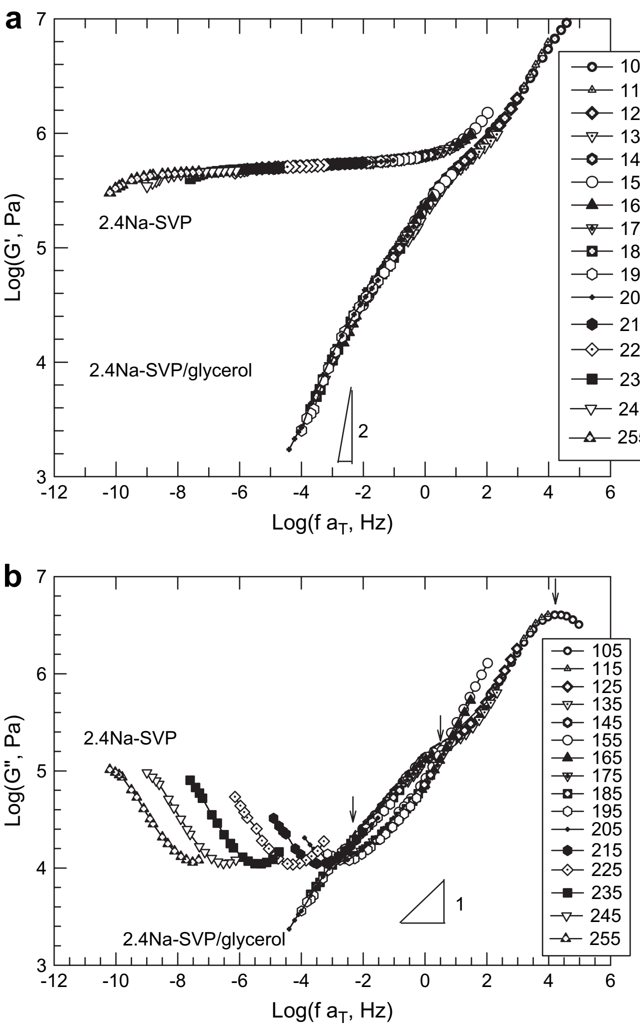

Fig. 9. Dynamic mechanical shear moduli pseudo-master curves for 2.4Na-SVP ionomer and master curves for 2.4Na-SVP/glycerol; $T_{\mathrm{ref}} = T_g + 50$ °C: (a) G'; (b) G''.

and 20 °C was present in the tan δ data for the plasticized ionomer. The peak temperature, ca. −7 °C, is rather high to be a pure glycerol phase. Still, this may be due to a glycerol-rich phase in which glycerol is associated with the ionomer, and it is probably responsible for the opacity of the sample. These data indicate that although the effect of glycerol on the SVP ionomer properties is similar to its effect on SPS ionomers, the miscibility of glycerol in the phosphonate ionomer may be higher.

G' and G'' master curves for G' of 2.4Na-SVP and 2.4Na-SVP/10% glycerol are shown in Fig. 9 ($T_{\mathrm{ref}} = T_g + 50$ °C). TTS data failed for neat ionomer in the low frequency region, which is dominated by the relaxation behavior of the ionic interactions. This is most apparent in the G'' data, which used the shift factors calculated for G'. The preferential interaction of glycerol reduces the intensity of the ionic interactions and dramatically shortens the relaxation times of the nanophase-separated domains. As a result, TTS was reasonably successful for the 2.4Na-SVP/10% glycerol system, which indicates that unlike the neat ionomer, the behavior of the plasticized ionomer was rheologically simple. Although terminal behavior (i.e., slopes of 2 and 1 for the log–log G'–frequency and G''–frequency data, respectively) was not observed in the ionomer pseudo-master curve and the ionomer/plasticizer master curve, the terminal relaxation of the latter was at least 5 orders of magnitude less than that for the neat ionomer. This is consistent with the effective dissociation of the ionic interactions in the plasticized ionomer melt. The G'' master curve for the 2.4Na-SVP/10% glycerol mixture in Fig. 9(b) shows 3 transitions (see arrows), which have tentatively been assigned to the hydrocarbon matrix, a glycerol-rich phase, and an ion-rich phase.

4. Conclusions

Hydrogen bonding and dipole–dipole interactions act as physical crosslinks in the phosphonic acid containing SVP ionomer and its metal salts, respectively, and they produce nanophase separation of the ionic species. The metal–phosphonate interactions are stronger and more temperature persistent than the phosphonic acid interactions, which were manifested by a much broader rubbery region in the thermomechanical behavior of the metal-salt ionomers. The phosphonate interactions were thermally stable up to >250 °C, and the physically crosslinked network produced suppressed viscous flow of the ionomers to very high temperatures. The ratio of q/a of the cation affected the strength and temperature persistence of the ionic interactions. In general, the larger was q/a, the stronger were the interactions and the longer was the extent of the rubbery plateau region in the viscoelastic behavior. Surprisingly, although phosphonic acid is considered as a weaker acid than sulfonic acid, the strength and persistence of the crosslinks produced by the SVP ionomers were greater than for SPS ionomers.

Time–temperature superposition was not applicable for the SVP ionomers, even at ion contents as low as 2.4 mol%, indicating that these materials were thermorheologically complex. This result was due to the nanophase separation of the polar, ionic species that produced two separate relaxation mechanisms. The addition of a polar plasticizer, e.g., glycerol, preferentially solvated the ionic associations and diminished the extent of the rubbery plateau of the ionomer and substantially decreased the terminal relaxation time. Whereas, PS and glycerol are immiscible, nearly 10% (w/w) glycerol dissolved in 2.4Na-SVP, preferentially in the ionic nano-domains. The plasticized compositions appeared to be thermorheologically simple in their linear viscoelastic behavior.

Compared with carboxylate- and sulfonate-ionomer, comparatively little research has been done on phosphonate-containing ionomers. Yet, this study demonstrates that the intensity of the ionic interactions and their effect on viscoelastic behavior may be as substantial as what has been reported for sulfonate ionomers. Although, this conclusion may be restricted to the specific ionomers compared herein, where the phosphonate is attached directly to an aliphatic part of the polymer chain and the sulfonate (in SPS) was attached to an aromatic pendent group, it is consistent with a previous conclusion concerning phosphonate and sulfonate ionomers [5].

Acknowledgments

This research was supported in part by grants from the Polymer Program of the National Science Foundation (DMR 0304803) and from the Global Connecticut Fuel Cell Center at the University of Connecticut.

References

[1] Fitzgerald JJ, Weiss RA. J Macromol Sci Rev Macromol Chem Phys 1988;C28:99–185.
[2] Tant MR, Mauritz KA, Wilkes GL, editors. Ionomers: synthesis, structure, properties and applications. London, UK: Blackie; 1997.
[3] Eisenberg A, Kim J-S. Introduction to ionomers. New York: John Wiley & Sons; 1998.
[4] Wu Qi, Weiss RA. J Polym Sci Part B Polym Phys 2004;42:3628–41.
[5] Weiss RA. J Polym Sci Part A Polym Chem 1980;18:2887–99.
[6] Kakati DK, Gosain R, George MH. Polymer 1994;35:398–402.
[7] Pasmann M, Zentel R. Macromol Chem Phys 2002;203:363–74.
[8] Lundberg RD, Makowski HS, Westerman L. Adv Chem Ser 1980;187:67–76.
[9] Bazuin CG, Eisenberg A. J Polym Sci Part B Polym Phys 1986;24:1137–53.
[10] Bazuin CG, Eisenberg A, Kamal M. J Polym Sci Part B Polym Phys 1986;24:1155–69.
[11] Fitzgerald JJ, Kim D, Weiss RA. J Polym Sci Part C Polym Lett 1986;24:263–8.
[12] Fitzgerald JJ, Weiss RA. J Polym Sci Part B Polym Phys 1990;28:1719–36.
[13] Weiss RA, Fitzgerald JJ, Kim D. Macromolecules 1991;24:1064–70.
[14] Bazuin CG. Multiphase polymers: blends and ionomers. In: ACS symposium series, vol. 395; 1989. p. 476–502.
[15] Graessley WW. Polymeric liquids and networks: structure and properties. New York: Garland Science; 2004.
[16] Weiss RA, Lefelar JA. Polymer 1986;27:3–10.
[17] Weiss RA, Fitzgerald JJ, Kim D. Macromolecules 1991;24:1071–6.
[18] Eisenberg A, Navratil M. Macromolecules 1973;6:604–12.
[19] Zhuang H. Miscibility studies of phosphorus-containing polymer blends. Ph.D. Dissertation, Polytechnic University, New York, NY; 1994.
[20] Zhuang H, Pearce EM, Kwei TK. Polymer 1995;36:2237–41.
[21] Lefelar JA, Weiss RA. Macromolecules 1984;17:1145–8.
[22] Hird B, Eisenberg A. Macromolecules 1992;25:6466–74.
[23] Hara M, Jar P, Sauer JA. Polymer 1991;32:1622–6.
[24] Tomita H, Register RA. Macromolecules 1993;26:2791–5.
[25] Eisenberg A. Macromolecules 1971;4:125–8.
[26] Mattera Jr VD, Risen Jr WM. J Polym Sci Part B Polym Phys 1986;24:753–60.
[27] Eisenberg A, Navratil M. J Polym Sci Part C Polym Lett 1972;10:537–42.
[28] Adam G, Gibbs JH. J Chem Phys 1965;43:139–46.
[29] Fox TG. Bull Am Phys Soc 1956;1:123.
[30] Galambos AF, Stockton WB, Koberstein JT, Sen A, Weiss RA, Russell TP. Macromolecules 1987;20:3091–4.