

Dynamic mechanical and melt rheological properties of sulfonated poly(butylene succinate) ionomers

Sang-Il Han^a, Seung Soon Im^{a,*}, Dong Kuk Kim^{b,*}

^a*Department of Fiber and Polymer Engineering, Hanyang University, 17 Haengdang-dong, Seongdong-gu, Seoul 133-791, South Korea*

^b*Department of Chemistry, Hanyang University, Ansan, South Korea*

Received 2 April 2003; received in revised form 1 July 2003; accepted 22 July 2003

Abstract

A series of poly(butylene succinate) ionomers (PBSi) containing 5-sodium sulfoisophthalate units were prepared by bulk polymerization of succinic acid and 1,4-butanediol in the presence of dimethyl 5-sulfoisophthalate sodium salt (DMSI) up to 5 mol% of diacid monomer. Conspicuous variation of the storage modulus for PBSi was observed, depending on the content of DMSI. The increasing rate of cluster T_g was lower compared to those of amorphous polymer-based ionomers. These results were probably due to the lower clustering ability of semi-crystalline PBSi as compared with amorphous-based ionomers. Non-contact atomic force microscopy confirmed that the size of PBSi-3 clusters was about 40 ~ 50 nm, demonstrating that the clusters were aggregated. Melt rheological analysis was carried out to investigate the effects of ionic groups on the rheological properties as a function of temperature or shear force in the molten state. The melt viscosities of PBSi showed higher values than the parent PBS up to about 190 °C, while with further increasing temperature a falling inflection region of melt viscosity was observed. It was suggested that the relaxation of PBSi chains was due to the thermal dissociation of ionic aggregates. © 2003 Elsevier Ltd. All rights reserved.

Keywords: Poly(butylene succinate) ionomer; Dynamic mechanical analysis; Melt rheology

1. Introduction

An ionomer is defined as an ion-containing polymer with a small amount (usually up to 10 ~ 15 mol%) of ionic groups along the backbone chains or as pendant groups. Ionomers have been extensively studied because of the significant changes in their physical properties due to the formation of ionic aggregates, such as enhanced mechanical properties, high melt viscosity, and increased thermal properties [1–5]. Several models, including the core-shell model of MacKnight et al. the hard-sphere liquid-like interference model of Cooper et al. and the Eisenberg–Hird–Moore (EHM) model have been proposed to explain the significant changes in physical properties caused by ionic interactions [6–8]. They suggested that ion pairs aggregate to form multiplets, which restrict the mobility of the hydrocarbon polymer chain surrounding them. Based on

EHM model, Nishida et al. investigated the dynamic mechanical properties with respect to sodium sulfonated poly(styrene–ethylene–butylene) random ionomer and the filler concept was applied to explain the increase in the storage modulus in the ionic plateau region [9]. Using dynamic mechanical analysis, Kim et al. confirmed that polystyrene (PS)- and poly(methyl acrylate) (PMA)-based ionomers have two glass transition temperatures, and found that both matrix T_g and cluster T_g are affected by the size of multiplets and the nature of ionic groups [10,11]. Despite these studies, little is known about the dynamic mechanical or rheological properties of semi-crystalline polyester ionomers: i.e. how ionic aggregates affect dynamic mechanical and melt rheological properties.

In the present study, we prepared PBS ionomer by two-step polycondensation to extend the fields of application of biodegradable polymers. Copolymerization and blending are important methods for the improvement of the mechanical properties of polymers. However, there are several problems affecting the physicochemical properties of polymers prepared by these methods. For instance, aliphatic copolyesters contain 10–30 mol% of secondary

* Co-corresponding authors. Tel.: +82-2-2290-0495; fax: +82-2-2297-5859 (S.S. Im); tel.: +82-2-400-5495 (D.K. Kim).

E-mail addresses: imss007@hanyang.ac.kr (S.S. Im), dkkim@hanyang.ac.kr (D.K. Kim).

monomers to reduce the crystallinity and thereby enhance their biodegradation rate and ductility. However, aliphatic copolyesters of these compositions show significant melting point depression, due to imperfect lateral packing and/or isomorphism, adversely affecting the temperature range over which they can be used [12,13]. Previously, we analyzed poly(butylene adipate) ionomers that were synthesized to resolve these problems of parent poly(butylene adipate), and confirmed that the incorporation of ionic groups into the main chain led to a reduction of crystallinity without a striking depression of the melting point [14]. Therefore, we expected that introduction of ionic groups into the PBS main chains might not only lead to improved extensibility due to the effective reduction of crystallinity but also provide crucial information of melt rheological property due to the ionic interactions. Here, we report the syntheses, dynamic mechanical properties, and melt rheological properties of PBSi prepared in the presence of dimethyl 5-sulfoisophthalate sodium salt (DMSI) as a secondary monomer.

2. Experimental

2.1. Materials and polymerization

Succinic acid, 1,4-butanediol, and DMSI (Aldrich) were used without further purification. Titanium tetrabutoxide (Aldrich) was also used as received. PBS and its ionomers were prepared by two-step polycondensation [15]. First, calculated amounts of succinic acid and 1,4-butane diol (1:1.2 by mole ratio) were introduced into a reactor equipped with an overhead stirrer and a temperature control device. The monomer mixture was melted and stirred at 20 °C for 2 h, evolving water condensate. Then, the reaction temperature was raised to 250 °C over a period of 30 min with gradual application of reduced pressure to remove low molecular weight condensates. In order to obtain comparable molecular weight to the parent PBS, the reaction temperature was maintained for 4–7 h depending of the feed composition. The poly(butylene succinate) ionomers are denoted by the mole fractions of ionic groups determined by ^1H NMR spectroscopy: e.g. PBSi-3 represents poly(butylene succinate) containing 3 mol% of DMSI.

2.2. Polymer characterization

^1H NMR spectra were recorded using a Bruker 300-MHz spectrometer with $\text{CDCl}_3/\text{TFA-d}$ (deuterated trifluoroacetic acid) polymer solutions containing tetramethylsilane (TMS) as an internal standard. The molecular weight and the molecular distribution of PBS was measured by gel permeation chromatography (GPC, Waters) equipped with a HPLC pump, refractive index detector using PS standards, and styragel[®] HR series (eluent: CHCl_3 35 °C, flow rate:

0.3 ml/min). Solution viscosities of PBSi were measured instead of GPC, because of adsorption on column by ionic groups. Solution viscosities of polymers at a concentration of 0.5 g/dl were measured using a Cannon-Ubbelohde viscometer at 25 °C in phenol/1,1,2,2-tetrachloroethane (3:2) (v/v).

2.3. Thermal and dynamic mechanical analysis

In order to provide identical samples and to ensure a consistency in various measurements (DSC, DMA, tensile test), synthesized polymers were compression molded using a Carver Press at 150 °C and 10,000 psi. The molded films were quenched in ice water and dried in a vacuum oven at 40 °C for 48 h. The melting behaviors of PBSi were studied using a Perkin–Elmer DSC-7 with a heating and cooling rate of 10 °C/min. Dynamic mechanical analysis (TA-DMA 2980) was performed using dual cantilever tensile mode at a frequency of approximately 1 Hz with a heating rate of 3 °C/min under a nitrogen atmosphere. Samples were cooled to –40 °C and then heated gradually to 100 °C at a rate of 3 °C/min. The storage modulus (G'), and $\tan \delta$ were measured as a function of temperature.

2.4. Melt rheological analysis

The rheological behaviors of PBSi were examined with a dynamic oscillatory viscometer (ARES, Rheometric Scientific Inc.) using parallel plates with a diameter of 20 mm and a gap of 1.0 mm. This experiment was performed with a temperature sweep to 280 °C at a rate of 5 °C/min and a frequency sweep from 0.1 to 400 rad/s, with 10% strain level.

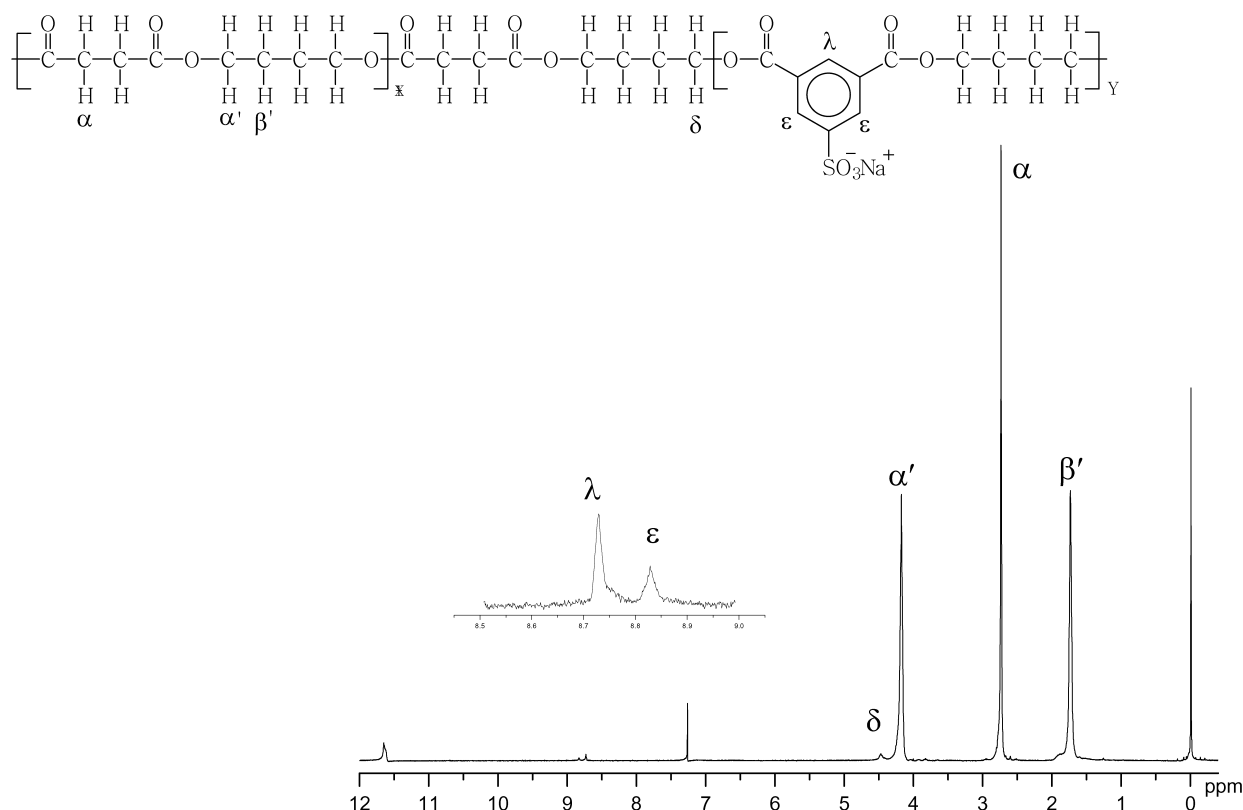
2.5. Stress–strain measurements

The mechanical properties of polymers were evaluated on the dumbbell shape film with a dimension of 3.5 mm width, 14 mm gage length, and 0.3 mm thickness from universal test machine (Instron) with a 1 kN load cell and the grip distance of 26 mm at a cross-head speed of 10 mm/min.

2.6. Morphology

The surface morphology was examined by non-contact mode atomic force microscopy (AFM) (XE-100, PISA) with a cantilever 125 μm in length at resonance frequencies ranging from 265 to 400 kHz.

The morphology of the interfacial surface was investigated using a scanning electron microscope (SEM) (JEOL JSM-6340F). For scanning electron microscopy, the polymer films were fractured under liquid nitrogen and then dried in a vacuum oven at 40 °C for 24 h. The samples were gold-coated by ion sputtering and examined by SEM.

Fig. 1. ^1H NMR spectrum of PBSi-3.

3. Results and discussion

3.1. Synthesis of PBSi

PBS and PBSi were synthesized by a two-step process consisted of direct esterification and polycondensation. DMSI was restrictively incorporated up to 5 mol% because DMSI has poor solubility in the reaction mixture. Fig. 1 shows a representative ^1H NMR spectrum of PBSi-3. The complete disappearance of methyl hydrogens in DMSI at 3.95 ppm confirmed that ionic monomers were covalently incorporated into the PBSi chains. The integration ratio between the peak at 4.45 ppm arising from methylene hydrogens ($-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$) adjacent to the DMSI repeating unit and the peak at 4.12 ppm arising from methylene hydrogens ($-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$) adjacent to the succinic acid repeating unit was used to determine the compositions of DMSI in the copolymer. ^1H NMR analyses indicated that the spectroscopically determined DMSI contents in PBSi samples corresponded to the respective feed compositions. The compositions and characteristics of PBSi are summarized in Table 1. The inherent viscosity (η_{inh}) of PBSi ranged between 0.75 and 1.20 dl g^{-1} and decreased with increasing ionic content. The presence of an ionic moiety in the reaction medium may bring about a significant change in the reactivity of the functional group, which would be responsible for the observed slower polycondensation step.

3.2. Thermal and dynamic mechanical analysis

As shown in Table 1, the PBSi-1 ~ 5 showed slight reductions in melting point (ca. 1 K/mol% of ionic group) with increasing ion content. Nevertheless, the crystallization temperatures were significantly reduced. The exothermal peak of PBSi showed lower intensity with increasing ion content (Fig. 2). These results, together with the observation that PBSi showed a higher degree of supercooling ($T_m - T_c$) with increasing ion content for crystallization, indicates that the incorporation of ionic groups caused a reduction in the regularity of polymer chains. Wide-angle X-ray diffraction (WAXD) patterns for PBS and its ionomers are shown in Fig. 3. The pattern for the parent PBS exhibited strong peaks at 19.3° , 21.7° , 22.4° , and 28.7° , which were assigned to (020), (021), (110), and (111) planes, respectively [16,17]. In the case of PBSi-1 ~ 5, WAXD patterns were broader but with no significant changes in d -spacing. It can be claimed that the ionic units might be rejected out of crystalline region and lead to a low degree of perfection of packing for crystallization of PBSi. McLean et al. previously reported that the morphology of semi-crystalline ionomer consists of imperfect lamellar stacks with ionic domains segregated into regions outside of the lamellar stacks [18]. The crystallinity of the parent PBS was 40.8%, while the crystallinity for ionomers decreased with increasing ion content. In the case of PBSi-5, the value was 35.9%,

Table 1
Polymerization data and thermal properties of PBS and its ionomers

Polymer code	Composition		GPC result		Reaction time (h)	η_{inh}^a (g dL ⁻¹)	T_g^b (°C)	T_m^c (°C)	T_c^c (°C)	$T_m - T_c$ (°C)	ΔH_f (J/g)
	Molar ratio in feed ^d (succinic acid/DMSI)	Molar ratio in real composition ^e (succinic acid/DMSI)	$M_n \times 10^{-4}^f$	M_w/M_n^f							
PBS	100/0	100/0	4.3	2.01	2 + 4	1.26	−10.7	114.5	80.1	34.4	79.7
PBSi-1	99/01	99/01	— ^f	— ^f	2 + 4	0.94	−9.2	113.6	71.2	42.4	77.2
PBSi-3	97/03	97/03	— ^f	— ^f	2 + 5	0.92	−6.8	112.0	64.3	47.7	73.4
PBSi-5	95/05	95/05	— ^f	— ^f	2 + 7	0.75	−3.0	110.7	55.8	54.9	63.5

^a 0.5 g/dL in phenol/1,1,2,2-tetrachloroethane (3/2) (v/v).

^b Measured by DMA, 3 °C/min.

^c Measured by DSC, 10 °C/min.

^d Molar ratio of DMSI to succinic acid in total diacid feed.

^e Real composition was determined by ¹H NMR.

^f GPC data for ionomers were not measured because of adsorption on column by ionic groups.

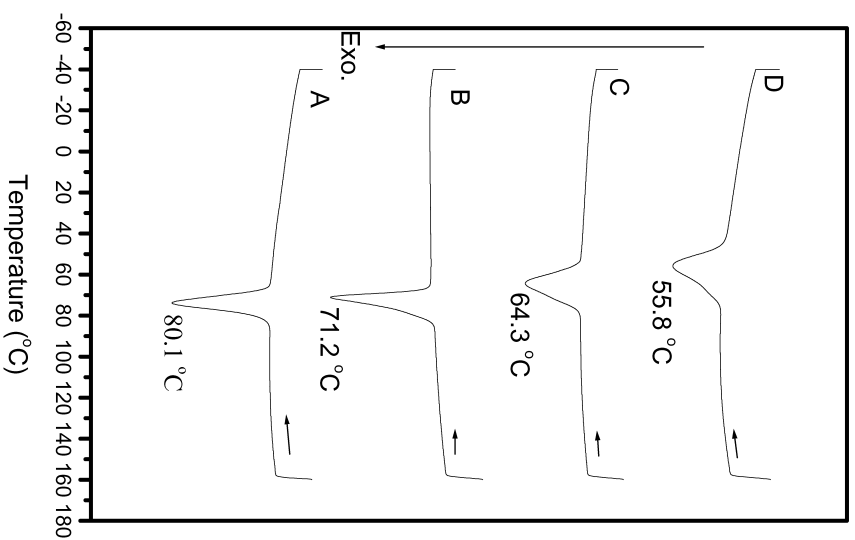


Fig. 2. DSC traces of PBSi at a cooling rate of 10 °C/min. A, PBS homopolymer; B, PBSi-1; C, PBSi-3; D, PBSi-5.

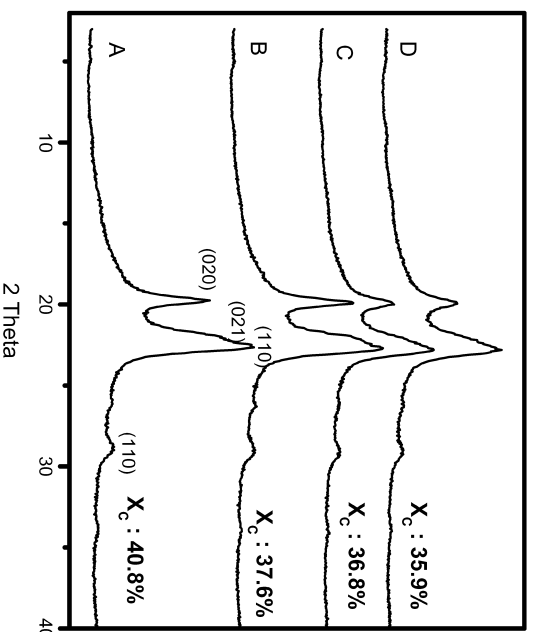


Fig. 3. WAXD patterns of PBSi films crystallized in ice water. A, PBS; B, PBSi-1; C, PBSi-3; D, PBSi-5. The crystallinity was calculated by deconvolution of the WAXD patterns using a curve-fitting program.

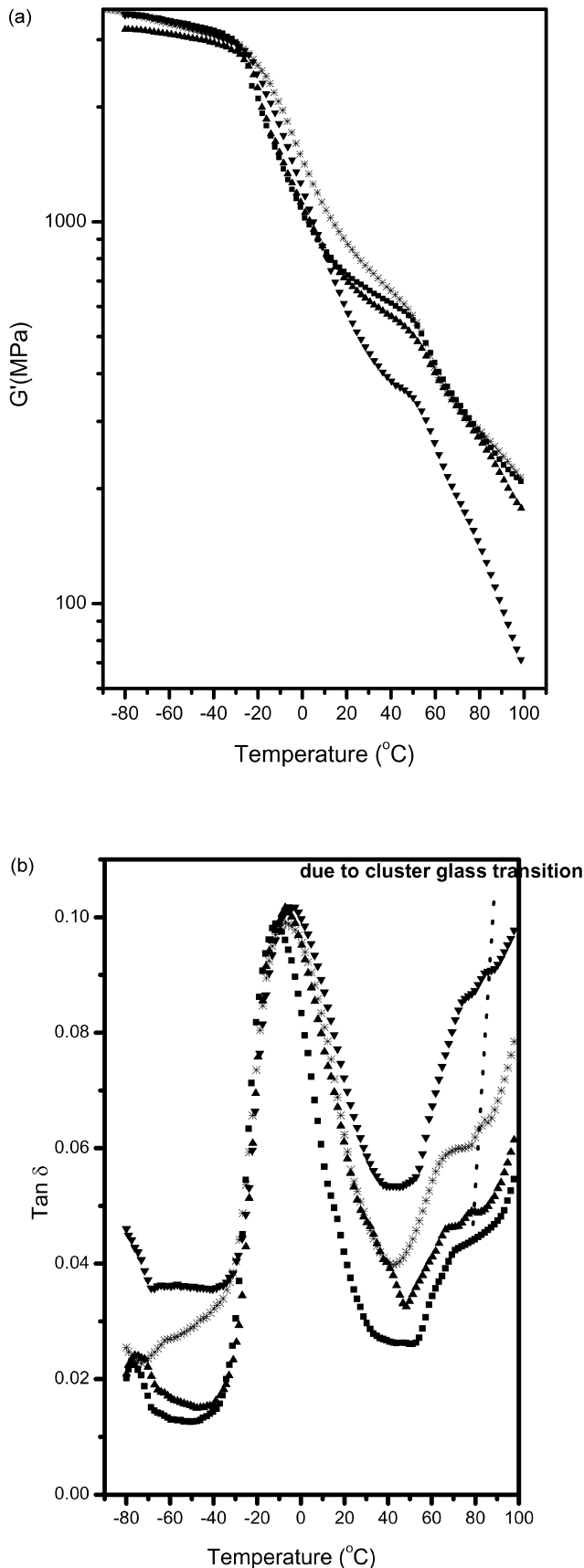


Fig. 4. Storage modulus (a) and $\tan \delta$ (b) of PBSSis versus temperature. PBS (■); PBSSi-1 (▲); PBSSi-3 (*); PBSSi-5 (▼).

representing a decrease of about 5% as compared with that of the parent PBS.

Fig. 4(a) and (b) show storage modulus (G') and $\tan \delta$ of PBSSi-1 ~ 5 plotted against temperature. PBSSi-3 showed the highest storage modulus up to the rubbery plateau region, which was probably related to the strong physical cross-linkage by electrostatic attractive forces between ionic groups. On the other hand, the storage modulus for PBSSi-5 dropped rapidly above the glass transition region with increasing temperature, which may have been due to the reverse effect of physical cross-linkage resulting from preferential intramolecular ion-pair associations. Generally, intramolecular ion-pair associations lead to the collapse of polymer chain, which may cause the reduction of both the radius of gyration and the viscosity [19]. Xie et al. investigated the ionic aggregation of sodium salts of sulphonated PS and found that intrachain ionic aggregation occurred above a critical sulphonation level of 4.0 mol% [20]. As shown in Fig. 4(b), the $\tan \delta$ curves for PBSSi-1 ~ 5 showed two T_g . The main peak was assigned as the T_g of the matrix, while the shoulder at higher temperature reflected the T_g corresponding to the ion cluster region. The matrix T_g shifted to higher temperatures with increasing ion content. As the cluster T_g was visualized as a shoulder or a small peak in the region of 80–100 °C and/or partially overlapped with the $\tan \delta$ curves because of polymer flow, the dotted line represented the position for cluster T_g peaks. The increasing rates of T_g for the matrix and cluster are expressed by the following equations:

$$\text{Cluster } T_g = -10.2 + 1.1 \text{ } ^\circ\text{C} \times (\text{mol\% of ion content})$$

$$\text{Matrix } T_g = 75.6 + 1.8 \text{ } ^\circ\text{C} \times (\text{mol\% of ion content})$$

The increasing rates of matrix T_g and cluster T_g were different from those for amorphous polymer-based ionomers. For instance, the increasing rate for matrix T_g of the PS-based ionomer is in the range of 3–5 °C/mol%, and the increasing rate for cluster T_g is in the range of 3–9 °C/mol%

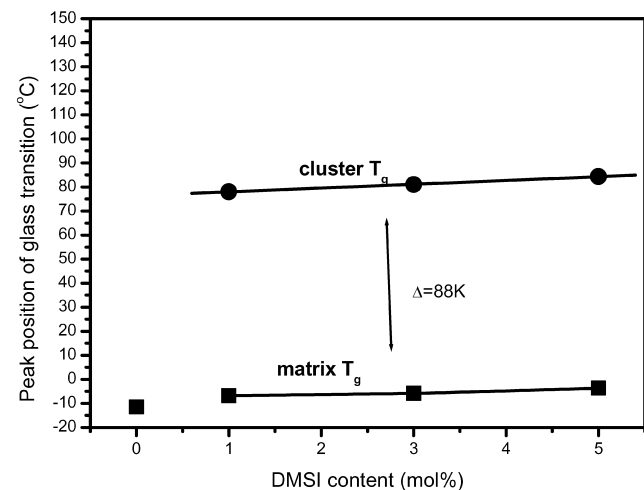


Fig. 5. Glass transition temperatures of matrix and cluster regions as a function of ion content.

[21–23]. In the present study, the increasing rates for matrix T_g and cluster T_g of the semi-crystalline PBSi were 1.8 and 1.1 °C/mol%, respectively (Fig. 5). Furthermore, while the differences in matrix and cluster T_g for amorphous ionomers, such as PS- and PMA-based ionomers, are ca. 55 and 40 K, the differences in matrix and cluster T_g for PBSi were ca. 88 K [11,24,25]. Kim et al. reported that the increasing rate of cluster T_g is related to the degree of clustering depending on the polarity of the polymer, and found that the difference in the two T_g increases with stronger ionic interactions between ionic groups and decreasing cluster size [26]. Despite this, the rate of increase of cluster T_g and the difference in the two T_g for PBSi was not comparable with those of amorphous-based ionomers. Considering the fact that ionic domains are segregated into region outside crystalline lamellae [18], it indicates that for semi-crystalline PBSi the degree of clustering may be responsible for dimensions of crystalline lamellae. AFM in non-contact mode was applied to observe the surface morphology of PBSi-3 film (Fig. 6). In contrast to the smooth surfaces of the parent PBS, AFM images of PBSi-3 confirmed the homogeneous distribution of clusters measuring approximately 40–50 nm.

3.3. Melt rheological and tensile properties

Melt rheology data (Fig. 7(a) and (b)) verified the presence of strong ionic interactions in the polymer melts. In the temperature region below 190 °C, PBSi-1 ~ 5 have higher melt viscosity than the parent PBS, even though their inherent viscosities in solution are lower than that of the parent PBS, as shown in Table 1. PBSi-3 had the highest melt viscosity among the ionomers examined. As the melt viscosity of ionomers is generally determined by the intrinsic molecular weight of the polymer and reversible physical cross-linkage due to the ionic association/dissociation mechanism of formation of ionic aggregates [27], this result indicates that the strong physical cross-linkage between ionic groups has a greater effect on the melt rheological properties than the molecular weight. The parent PBS showed monotonous decrease of the melt viscosity, η , with increasing temperature, while PBSi-3 and PBSi-5 showed a falling inflection region. This result indicates that the restricted chain mobility close to ionic aggregates is relaxed, mainly due to thermal dissociation of ionic aggregates at temperatures above 190 °C. $\tan \delta$ curves in the melt are shown as a function of temperature in Fig. 7(b). Considering the multiplets-cluster model proposed by Eisenberg et al. for PBSi-3 and PBSi-5 the shoulder and peak 1 nearby 240 ~ 280 °C may be considered the evidence of the relaxation of chains in direct contact with the multiplets. On the other hand, it seems appropriate that the broad peak of PBSi-5 is deconvoluted to two peaks. In the case of PBSi-5, formation of larger multiplets may be possible because of its high ion content. Accordingly, the peak 2 at lower temperature region, 210 ~ 240 °C may be

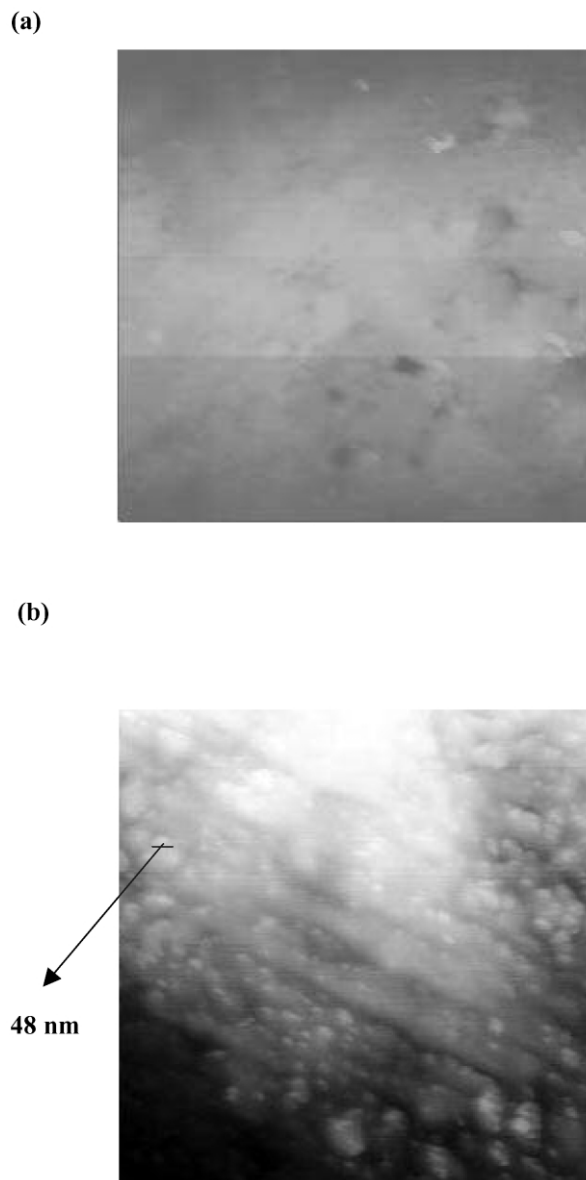


Fig. 6. Phase images of a PBS surface (a) and PBSi-3 surface (b) in non-contact mode AFM. Scan boxes are 500 × 500 nm for each plot, and the height is 0–10 nm. The (b) shows the surface where ion clusters are aggregated with diameter on the order of 40–60 nm. Arrows indicate the diameter of ion cluster in (b), representatively.

attributed to the relaxation of relatively distant chains from multiplets.

To investigate the rheological behavior as a function of shear force at temperatures which the ionic groups appear to be almost completely associated or partially dissociated, the melt rheological data were determined by increasing shear force at temperatures of 150 and 220 °C. The loss tangents ($\tan \delta$) of the PBSi at 150 and 220 °C are plotted against frequency in Fig. 8(a) and (b). $\tan \delta$ is generally measured as an indicator of the solid-like elastic or liquid-like viscous properties of a system. At 150 °C, PBSi-3 had a lower $\tan \delta$ and greater elasticity than the parent PBS at all frequencies examined, and at

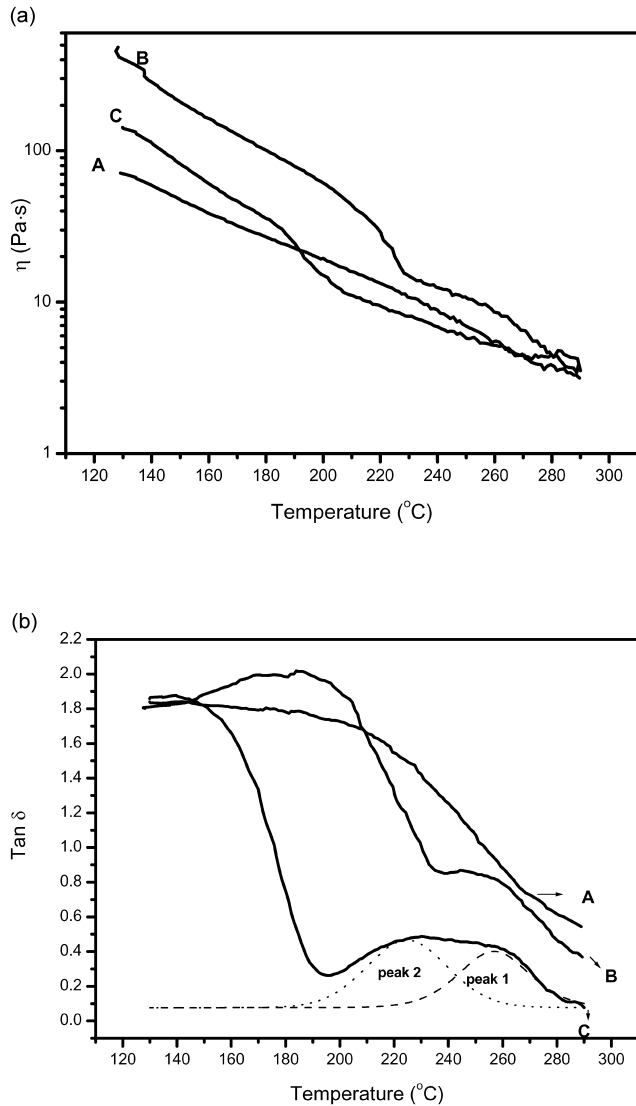


Fig. 7. Melting viscosity (a) and $\tan \delta$ (b) versus temperature for PBSis. A, PBS; B, PBSi-3; C, PBSi-5.

220 °C $\tan \delta$ curves of PBSi-3 and PBSi-5 were broad peaks with maxima in the frequencies of 15 and 35 rad/s, respectively, which would be the result of the significant transition on ionic aggregation. To investigate this transition in detail, Cole–Cole plots were plotted as shown in Fig. 9(a) and (b). As shown in Fig. 9(a), PBS and PBSi examined showed similar curves with slopes of about 1.9 over all frequencies. This value is similar to the slope (2.0) of most isotropic and homogeneous systems reported previously [28–30]. This result indicates that PBSi-1 ~ 5 show no significant changes in shear force over all frequencies and approach homogeneous systems irrespective of shear force at 150 °C. On the other hand, at 220 °C inflection points were observed on the Cole–Cole plots (Fig. 9(b)) of PBSi-3 and PBSi-5 in the vicinity of the G'' values of 300 and 60 Pa, respectively. For PBSi-3, the slope changed from 0.49 to

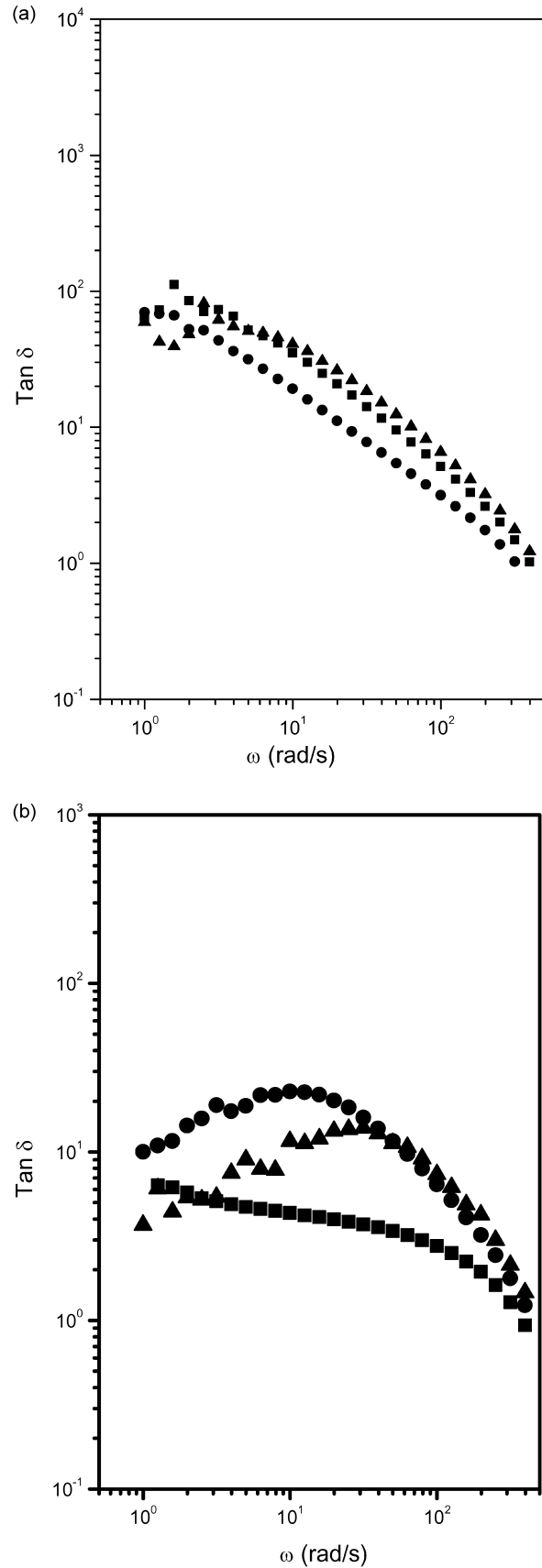


Fig. 8. $\tan \delta$ of PBSis as a function of frequency at 150 °C (a) and 220 °C (b). PBS (■); PBSi-3 (●); PBSi-5 (▲).

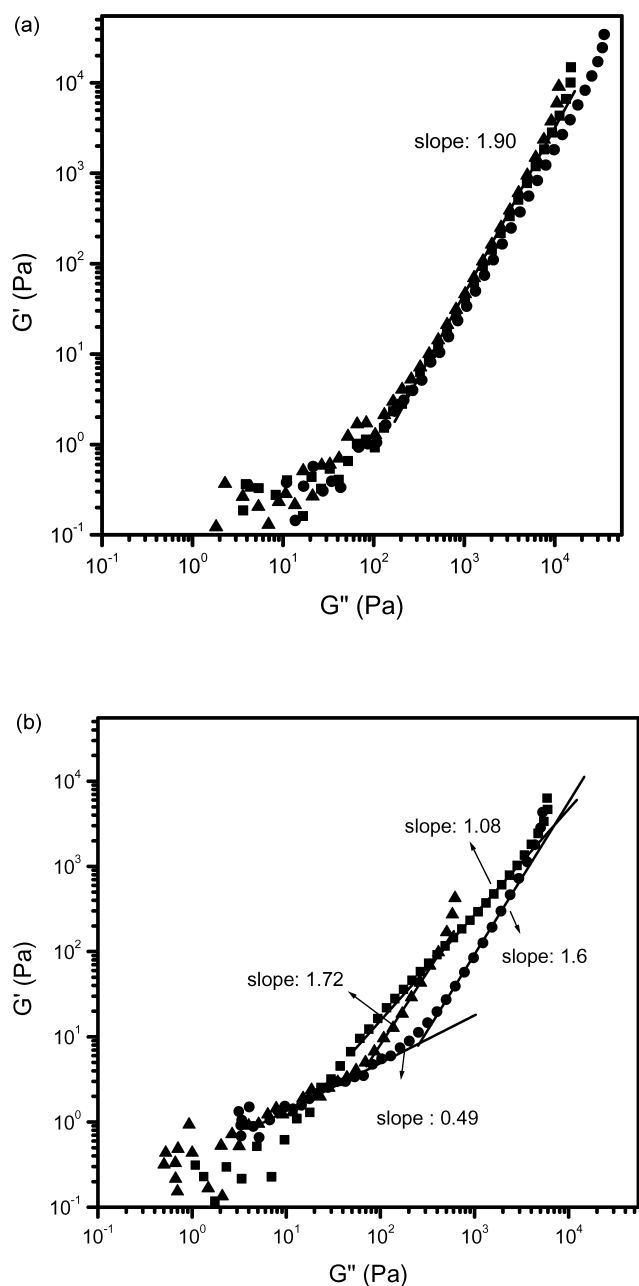


Fig. 9. Cole–Cole plots of PBSis at 150 °C (a) and 220 °C (b). PBS (■); PBSi-3 (●); PBSi-5 (▲).

Table 2
Tensile properties of PBS ionomers

Polymer	Tensile strength (MPa)	Elongation at break (%)	Modulus (MPa)
PBS	26.3 (6.9)	96.0 (7.3)	331.5 (48.5)
PBSi-1	26.4 (0.3)	204.7 (27.8)	315.0 (12.6)
PBSi-3	43.0 (4.0)	514.5 (75.8)	306.2 (11.8)
PBSi-5	22.3 (5.8)	17.4 (9.8)	368.0 (96.2)

Values in parentheses are standard deviations.

1.60 and for PBSi-5 the slope increased from 0.49 to 1.72. These results indicate that the homogeneity of the polymer melt changes with increasing shear force. At the high temperature of 220 °C, PBSis are thought to behave as heterogeneous systems with both ionic association and partial dissociation, and the reduced slope prior to the

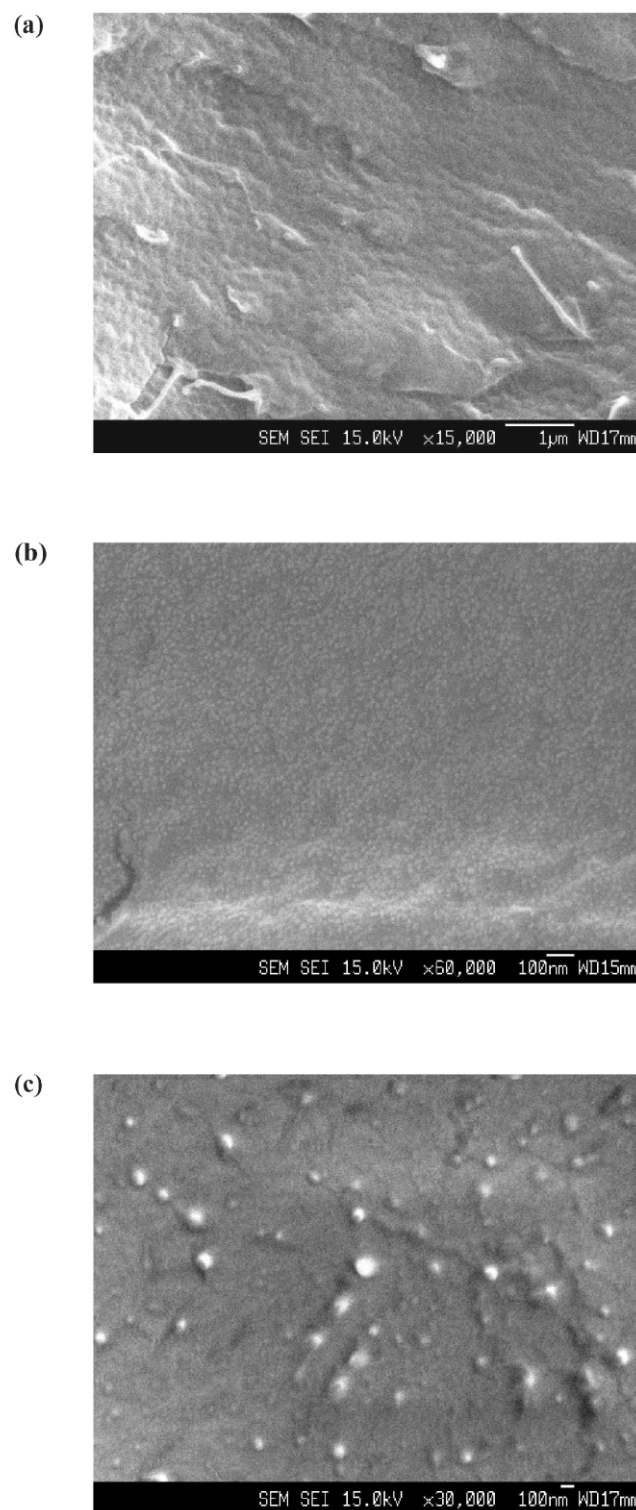


Fig. 10. Scanning electron micrographs of interfacial surfaces for PBSis.

inflection point reflects the breakdown of physical cross-linkages by ionic force. With increasing shear force, physical cross-linkages are broken and thus PBSis appear to approach the homogeneous state.

The tensile properties of PBSi are shown in Table 2. PBSi-3 exhibited markedly improved tensile strength as compared with the parent PBS. The tensile strength of PBSi-3 was approximately 40 MPa and its elongation at breakage was 550%. However, PBSi-5 showed somewhat reduced tensile strength and markedly decreased elongation. In general, the tensile strength depends largely on the molecular weight of the polymer. However, the physical bonding of ionic groups makes even low molecular weight ionomeric polymers behave as high molecular weight species. Another possible explanation for the improved mechanical properties is that ion clusters may play a role as filler on the nanometer scale. The SEM images shown in Fig. 10 support this role of clusters as filler. The PBSi-3 film seems to be comprised of a continuous matrix phase with monodispersed clusters. In contrast, PBSi-5 includes occasional clusters measuring about 100 nm, which may be responsible for the formation of larger multiplets. This kind of morphology is believed to contribute to the mechanical properties of ionomers.

4. Conclusions

PBSis were successfully synthesized in the presence of DMSI by two-step melt polymerization. The DMA data and SEM images provide evidence for cluster formation. The rates of increase in matrix T_g and cluster T_g were slightly lower than those of amorphous polymer-based ionomers, and these PBSis showed marked differences ($\Delta = 88$ K) in matrix T_g and cluster T_g , which was attributable to the lower level of clustering. The clusters of PBSi-3 in the bulk phase measured about 40 nm, demonstrating that the clusters were aggregated. Melt rheological data verified the thermally reversible ionic interactions, suggesting that intermolecular ion-pair association and intramolecular ion-pair association are major factors determining the physical properties of ionomers. PBSi-3 showed markedly improved tensile strength as compared to the parent PBS homopolymer.

Acknowledgements

This work was supported by the Brain Korea 21 Project, the Basic Research program of the Korea Science and Engineering Foundation (grant No. R01-1999-000-00194-0) and the Korea–Japan Basic Scientific Promotion Program (grant No. F01-2001-000-20038-0).

References

1. Lu X, Weiss RA. *Macromolecules* 1993;26:3615.
2. Kim JS, Hong MC, Nah YH. *Macromolecules* 2002;35:155.
3. Takahashi T, Watanabe J, Minagawa K, Takimoto JI, Iwakura K, Koyama K. *Rheol Acta* 1995;34:163.
4. Szymczyk A, Roslaniec Z. *Polym Adv Technol* 1999;10:579.
5. Nguyen D, Kim JS, Guiver MD, Eisenberg A. *J Polym Sci, Part B: Polym Phys* 1999;37:3226.
6. MacKnight WJ, Taggart WP, Stein RS. *J Polym Sci, Polym Symp* 1974;45:113.
7. Yarusso DJ, Cooper SL. *Macromolecules* 1983;16:1871.
8. Eisenberg A, Hird B, Moore RB. *Macromolecules* 1990;23(18):4099.
9. Nishida M, Eisenberg A. *Macromolecules* 1996;29:1507.
10. Kim JS, Jackman RJ, Eisenberg A. *Macromolecules* 1994;27:2789.
11. Kim JS, Nah YH, Jarng SS, Kim W, Lee Y, Kim YW. *Polymer* 2000;41:3099.
12. Howard GJ, Knutton S. *Polymer* 1969;9:527.
13. Schulken RM, Boy RE, Cox RH. *J Polym Sci* 1964;C6:17.
14. Yoo YT, Lee BJ, Han SI, Im SS, Kim DK. *Polym Degrad Stab* 2003;79:257.
15. Ko MS, Han SI, Kim TY, Im SS, Yoo YT, Kim DK. *Polym J* 1998;30(7):538.
16. Ihn KJ, Yoo ES, Im SS. *Macromolecules* 1995;28:2460.
17. Park JW, Kim DK, Im SS. *Polym Int* 2002;51:239.
18. McLean RS, Doyle M, Sauer BB. *Macromolecules* 2000;33:6541.
19. Lundberg RD, Phillips RR. *J Polym Sci, Polym Phys Ed* 1982;20:1143.
20. Xie R, Weiss RA. *Comp Theor Polym Sci* 1997;7:65.
21. Hird B, Eisenberg A. *J Polym Sci, Part B: Polym Phys* 1990;28:1665.
22. Hird B, Eisenberg A. *Macromolecules* 1992;25:6466.
23. Gauthier M, Eisenberg A. *Macromolecules* 1990;23:2066.
24. Ma X, Sauer JA, Hara M. *Macromolecules* 1995;28:3953.
25. Kim JS, Kim HS, Eisenberg A. *Bull Korean Chem Soc* 1998;19:623.
26. Kim JS, Wu G, Eisenberg A. *Macromolecules* 1994;27:814.
27. Kang H, Long TE. *Polym Mater Sci Engng* 2001;84:909.
28. Oh SJ, Kim BC. *J Polym Sci, Part B: Polym Phys* 2001;39:1027.
29. Han CD, Kim J, Kim JK. *Macromolecules* 1989;22:383.
30. Chung SC, Hahn WG, Im SS, Oh SG. *Macromol Res* 2002;10(4):221.