

Synthesis and Characterization of Poly(butylene-2,6-naphthalate) ionomers

윤정은, 조원호, 이상철*

서울대학교 섬유고분자공학과, *금오공대 신소재시스템공학부

1. Introduction

Ionomers are as defined as polymers that contain a small number of ionic groups (less than 10-15%) along nonionic backbone chains. The presence of these ionic cross-links has a strong influence on their physical properties. Ionomers form the multiplets which are aggregates consisting of several ion pairs and containing only ionic materials. According to the EHM (Eigenberg-Hird-Moore) cluster model, multiplets are surrounded by a region of restricted chain mobility. The restricted mobility region would be too small to have its own T_g , but the multiplet itself would increase the T_g of the polymer by acting as a large cross-link. As the ion contents increase, the average distance between multiplets decreases. With higher ionic contents, regions are overlapped and the overlapped regions may have its own T_g .

Most of the studies on ionomers have been limited to addition-type polymers while only a few studies are reported on condensation polymers. It is well-known that the PBN homopolymer is semicrystalline polymer and it has good physical properties. In this study, the PBN-based ionomers are synthesized through condensation polymerization and their thermal and mechanical properties are characterized by DSC and DMTA. Particularly, we compare thermal and mechanical behaviors of the PBN ionomers to those of flexible ionomers and also investigate the effect of ionic groups on aggregates formation of semicrystalline ionomers.

2. Experimental Section

2.1 Synthesis

Poly(butylene-2,6-naphthalate)-based ionomers are synthesized by random copolycondensation of 1,4-butanediol, dimethyl naphthalate and dimethyl 5-(sodiosulfo)isophthalate (DMSI). The synthetic route of the the PBN ionomers is given in *Scheme 1*. These polymers are designated PBN-*X*S. *X* denotes *mol%* of DMSI in copolymer, which was determined by element analysis and ^1H NMR. In

this study, X was varied in the range from 0 to 10 mol%.

2.2 Inherent Viscosity

The inherent viscosity was used to determine the molecular size of the PBN ionomers using a Ubbelohde type viscometer. This was measured at 35°C with a solvent mixture of phenol/1,1,2,2-tetrachloroethane (60/40 by weight) at a concentration of 0.3 g/dL.

2.3 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) was carried out with a Perkin-Elmer DSC-7. PBN ionomers were preheated from room temperature to 120°C and maintained for 5 min in order to remove any water in the ionomers. The samples were then rapidly cooled to 0°C. All samples were heated to 250°C, held at this temperature for 5 min, and quenched to 0°C followed by a second heating to 250°C.

2.4 Dynamic Mechanical Thermal Analysis (DMTA)

A Rheometric Scientific dynamic mechanical thermal analyzer III was used to measure dynamic mechanical properties of ionomers. Samples were compression-molded at 260°C under the pressure of 2 MPa. The dimensions of the molded sample were $8 \times 10 \times 2$ (mm³). The dual cantilever bending mode was utilized at frequency 10Hz at a heating rate of 4°C/min.

2.5 Small Angle X-ray Scattering (SAXS)

The SAXS experiments were carried out at the white beam of the Pohang Accelerator synchrotron radiation source (Pohang, Korea). The scattered X-rays were collected with one-dimensional, position-sensitive detector with a spatial resolution of 125 μm. All samples were examined in the angular q range from 0.08 to 1.85 nm⁻¹.

3. Results

Seven PBN ionomers with different ionic contents were prepared and their compositions of the PBN ionomers were listed in *Table 1*. The compositions were determined from the element analysis.

The DSC thermograms from the first scans and the second scans for all samples are shown in *Figure 1* and *Figure 2*, respectively. When the first scans are compared to the second ones, it is realized that there is a small endotherm peak in the first scans near 140°C which may arise from annealing effect. As shown in *Figure 1* and *Figure 2*, the melting point and heat of fusion decreased

with increasing the ionic content, because ionic domains may interfere with crystallization. For ionomers containing above 4.40 *mol%* ionic groups, the second scans show a small endotherm peak at about 100°C.

However, the SAXS profiles of PBN ionomers (not shown here) do not show any peak corresponding to ionic aggregate. This is probably because the electron density difference is small between matrix polymer and counterion, sodium. Nevertheless, the SAXS profiles show an evidence that ionic groups interfere with the crystallization.

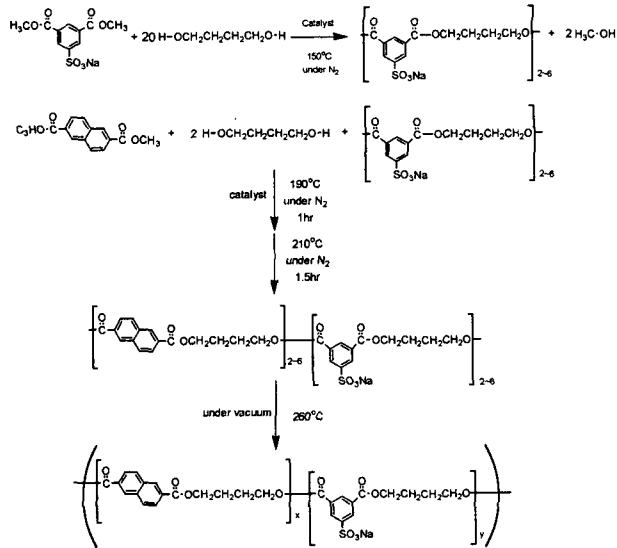
A plot of the loss tangent as a function of temperature for PBN ionomers is shown in *Figure 3*. Two peaks were observed for samples containing 4.40 *mol%* ionic groups. The peak around 80°C is due to the glass transition of matrix polymer, PBN. With increasing ionic contents, this temperature shifts toward higher value. The shoulder at high temperature is due to the transition behavior of the restricted regions of cluster proposed by EHM cluster model. Moreover increasing ionic contents results in an increase in the elastic modulus at the rubbery plateau region (*Figure 4*). These results are attributed to the formation of the ionic domains which act as the physical cross-links.

4. Conclusion

PBN ionomers with different ionic content were synthesized and their thermal and mechanical properties were characterized. In case of PBN ionomers, the ionomers with ionic contents above 4.40 *mol%* show two separated phases as evidenced by DMTA. The presence of two $\tan \delta$ peaks indicates that each phase has its own transition temperature. Above 4.40 *mol%* the elastic modulus increases with the contents of ionic groups particularly at the rubbery plateau region. It is also observed that the melting point and the heat of fusion increase with increasing the ionic content in DSC experiments. It is noteworthy that two endotherms are observed in the DSC thermograms for samples with the ionic groups above 4.40 *mol%*. This is another evidence for formation of ionic aggregates.

5. Reference

- 1) A. Eigenberg and J.-S. Kim, *Introduction to Ionomers*, John Wiley & Son; New York, 1996
- 2) A. Eigenberg and B. Hird, *Macromolecules*, **25**, 6466(1992)
- 3) K. R. Gorda and D. G. Peiffer, *J. Polym. Sci., Part B: Polym. Phys.*, **30**, 281(1992)



Scheme 1. Synthesis of PBN ionomers

Table 1. Samples of PBN ionomers

sample code	mol% of ionic contents	η_{inh}
PBN	0	0.6325
PBN-1.25S	1.25	0.7058
PBN-1.91S	1.91	0.5753
PBN-4.40S	4.40	0.4525
PBN-5.51S	5.51	0.3409
PBN-8.45S	8.45	0.2805
PBN-10.87S	10.87	0.3134

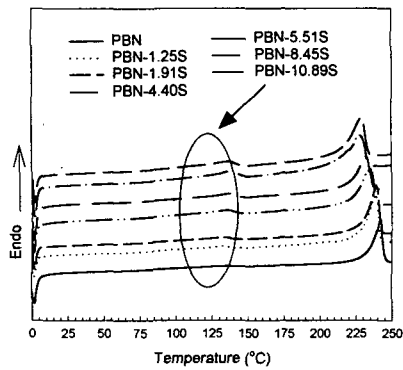


Figure 1. Second scans of PBN ionomers

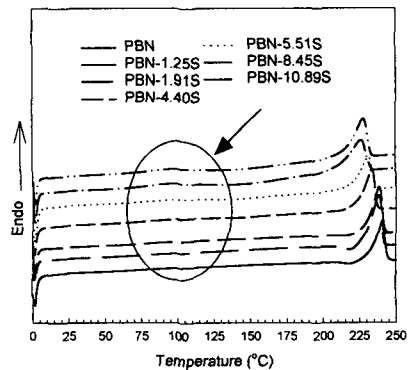


Figure 2. Second scans of PBN ionomers

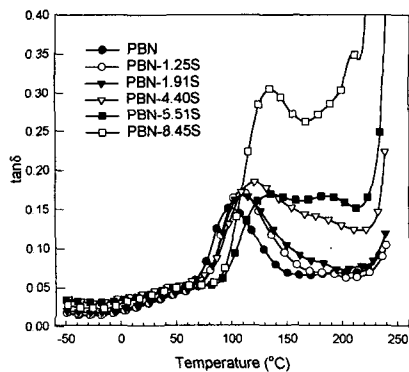


Figure 3. Loss tangent of PBN ionomers

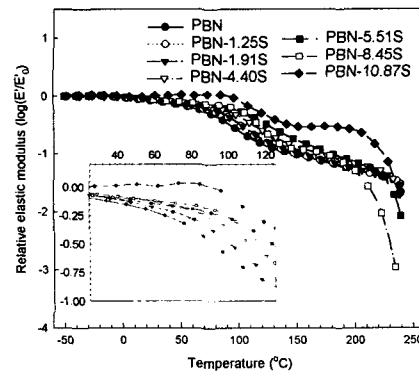


Figure 4. Relative elastic modulus of PBN ionomers