Plasticization in Unclustered Poly(methyl methacrylate) Ionomers

Joon-Seop Kim[†*], Hee-Seok Kim[†], and Adi Eisenberg[‡]

†*Department of Polymer Science & Engineering, Chosun University, 375*
Seosuk-dong Dong-gu, Kwangju 501-759, Korea
‡*Department of Chemistry, McGill University, 801 Sherbrooke Street West,*
Montreal, Quebec, H3A 2K6 Canada
Received January 19, 1998

The dynamic mechanical properties of the unclustered cesium neutralized poly(methyl methacrylate-*co*-methacrylic acid) ionomers plasticized with three different plasticizers of low molecular weight were investigated. It was found that the effectiveness of the plasticization followed the order: glycerol (Gly) $\approx$ 4-decylaniline (4DA) > dioctyl phthalate (DOP). For the ionomer plasticized with Gly, the only effect was a significant decrease in the T_g. Thus it is concluded that the polar plasticizer not only increases the mobility of the ionomer but also dissolves the ionic groups. In the case of the 4DA-plasticized ionomer, both a drastic decrease in the T_g and the appearance of a second glass transition were observed. Therefore, it is suggested that the nonpolar 4DA molecules partition evenly in the poly(methyl methacrylate) matrix and cluster phases via hydrogen bonding between the aniline group of the plasticizer and the carbonyl groups of the ionomer. As a result, the T_g is lowered, multiplets can form, and the material behaves like a clustered ionomer.

Introduction

Ionomers are known as polymers containing relatively small amounts of ionic groups which are attached to the polymer backbone chains.[1] The ionic groups form aggregates, called multiplets,[2] which have significant effects on the properties and microstructure of the polymers.[1] The presence of ionic groups changes significantly the physical properties of ionomers, e.g. melt viscosity, glass transition temperature (T_g), water uptake, etc.[1] In many ionomer systems, a small-angle x-ray scattering peak was observed.[3] In order to correlate and interpret the mechanical data and morphology of random ionomers, the multiplet-cluster model, so-called EHM model, was proposed.[4] According to the model, the multiplet reduces the mobility of surrounding chains. When the ion concentration is low, the reduced mobility regions are not large enough to have their own glass transition temperature. However, as the ion content increases, the regions of reduction in mobility start to overlap; eventually, the regions become large enough to have their own glass transition. Therefore, the ionomers show two-phase behavior. Above a certain ion concentration, the cluster phase even becomes continuous.[5,6]

In the case of polystyrene (PS) ionomers, two glass transitions are seen in dynamic mechanical thermograms; the tan δ peak at low temperature represents the matrix T_g, and the other, at high temperature, the cluster T_g.[5,6] With increasing ion content, the tan δ peaks for the matrix and cluster T_gs shift to higher temperature.[5,6] It was also found that the tan δ peak area for the matrix T_g decreases, whereas that for the cluster T_g increases as the ion content increases; however, the total area under both tan δ peaks remains constant.[6]

For poly(methyl methacrylate) (PMMA) ionomers, two different behavior patterns are seen, depending on the type

of cation used for neutralization. In the poly(methyl methacrylate-*co*-sodium methacrylate) ionomer system, two glass transitions are observed, and both T_gs increase with increasing ion content.[7] However, the total area under the tan δ peaks for the matrix and cluster T_gs decreases with increasing ion content. The plasticization effect on the glass transitions of the PMMA ionomers was also studied.[8] It was found that the addition of a nonpolar plasticizer to the ionomers decreases the matrix and cluster T_gs.

In the case of the cesium neutralized PMMA ionomers,[9] only the matrix tan δ peak was observed; With increasing ion content, the peak position shifts to higher temperature, and the peak area decreases. No small-angle x-ray scattering (SAXS) peak was observed for these PMMA ionomers in bulk, even for the sample containing ca. 7.8 mol% of ions. It was thus concluded that the difference between the cesium neutralized ionomer and the sodium sample is owing to the weaker ionic interaction in the cesium ionomer than in the sodium sample. It was also suggested that the differences between the PMMA and the PS ionomers are owing to the higher dielectric constant of the PMMA polymer matrix than that of the PS matrix. The PMMA matrix, because of its relatively high polarity, can dissolve the ionic groups, which therefore cannot form multiplets. The high glass transition temperature of the PMMA matrix also, in part, prohibits the multiplet formation because the value of kT_g is high relative to the strength of the electrostatic interactions between ion pairs.

In the present study, we investigated the effect of plasticization on cluster formation in the unclustered cesium neutralized PMMA ionomers. The goal of the study was to determine whether clustered materials could be obtained from unclustered materials by lowering the T_g of the PMMA ionomer *via* plasticization, and to find out which plasticizer is most effective in the cluster formation. To do so, we chose three plasticizers which have been used mostly in the studies of plasticization of ionomers; one polar

---

*To whom correspondence should be addressed.

plasticizer, *i.e.* glycerol (Gly), and two nonpolar plasticizers, *i.e.* dioctyl phthalate (DOP) and 4-decylaniline (4DA). The 4DA molecule has an amine group on the benzene ring, and the amine group can act as a site for hydrogen bonding.

Experimental

Plasticization. The poly(methyl methacrylate-*co*-cesium methacrylate) ionomer containing 10 mol% of ionic groups was prepared as described in an earlier paper.[9] The plasticized ionomers were obtained by dissolving the ionomers in a mixed solvent of benzene-methanol (9/1 v/v) and adding plasticizers to the ionomer solution on a 24 wt% basis. The ionomer-plasticizer blends were freeze-dried and then further dried under vacuum at 80 °C for one day.

Sample preparation. In order to measure dynamic mechanical properties of samples, the samples were compression-molded at 200 °C at a pressure of *ca.* 20 MPa. The molded samples, with approximate dimensions of 2.5×6.0× 30.0 mm, were annealed at 80 °C under vacuum for one day.

Dynamic mechanical thermal analysis (DMTA). The mechanical properties were determined using a Polymer Laboratories Mark II DMTA was utilized. The measurement was performed in a dual cantilever bending mode, at frequencies of 0.3, 1, 3, 10, and 30 Hz, and a heating rate was 0.5 °C/min. All experiments were performed under a dry nitrogen atmosphere. For each sample, the storage modulus (E'), loss modulus (E''), and loss tangent (tan δ) values were obtained as a function of temperature.

Results and Discussion

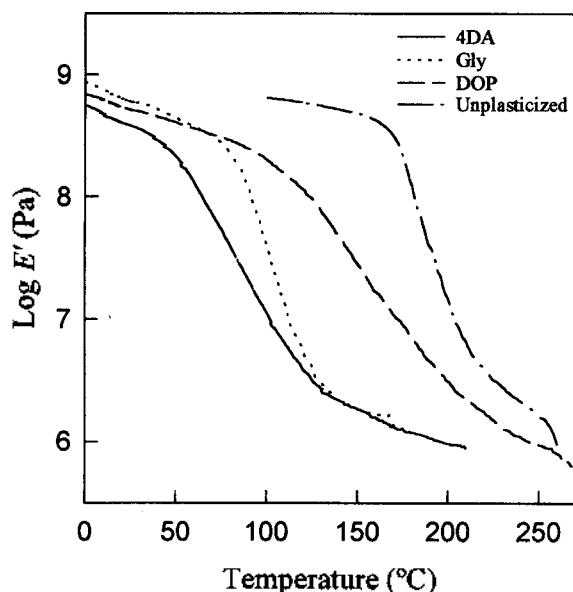Figure 1 shows the storage modulus values against the temperature of the cesium neutralized ionomer and the

ionomers plasticized with three different materials of low molecular weight. The modulus curve of the unplasticized ionomer shows that below ca. 175 °C the modulus value remains relatively constant at *ca.* $10^{8.8}$ Pa, which is considered as the glassy modulus. The modulus starts to decrease at *ca.* 175 °C, which corresponds to the glass transition. In the range of temperature between *ca.* 225 and 250 °C, the curve shows a gentle decrease in a slope which is denoted as a rubbery plateau. The modulus curve of the unplasticized ionomer is similar to that of a nonionic polymer.

The modulus curves of plasticized ionomers also show the glassy modulus, the glass transition, and the rubbery plateau with increasing temperature; however, as expected, the glass transition temperatures shift to lower temperature on addition of plasticizers. Plasticization introduces additional free volume, the mobility of the chains is increased, and the T_gs decrease. The rank of the effectiveness of the plasticization is in this order: Gly $\approx$ 4DA>DOP. It is also seen in Figure 1 that the shape of the modulus curve for the unplasticized ionomer is similar to that for the Gly-plasticized sample while the slope of the modulus curve for the DOP-plasticized ionomer is similar to that for the 4DA-plasticized sample; the temperature ranges for the glass transition of the two former systems are narrower than those for the two latter samples.

The loss tangent (tan δ) values of the four systems as a function of temperature are shown in Figure 2. The tan δ peak for the unplasticized ionomer is seen at *ca.* 200 °C, and no second peak is visible, as was also observed before.[9] Upon plasticization, the tan δ peak shifts to lower temperature.

In the case of the Gly-plasticized sample, the T_g is seen at ca. 110 °C. The width and height of the tan δ peak are similar to those of the unplasticized ionomer. It should be mentioned that the shape of these two tan δ peaks are similar to that of the homopolymer, *i.e.* a one-phase material.
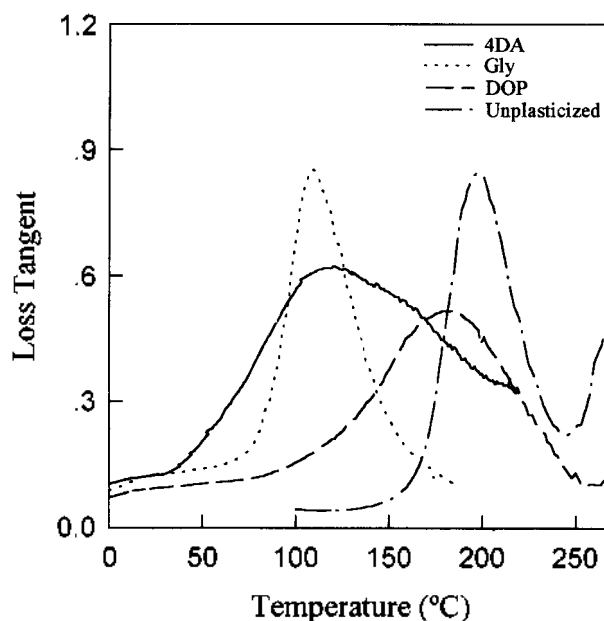

Figure 1. Storage modulus (E') curves as a function of temperature measured at 1 Hz for the unplasticized poly(methyl methacrylate-*co*-cesium methacrylate) ionomer (10 mol% of ions) and the ionomers plasticized with 4DA, Gly, and DOP (24 wt%).

Figure 2. Loss tangent curves as a function of temperature measured at 1 Hz for the unplasticized ionomer and the plasticized ionomers.

Unexpectedly, the T_g of the Gly-plasticized ionomer is lower by *ca.* 25 °C than that of the PMMA homopolymer which is *ca.* 135 °C as determined by DMTA.[9] This result implies that the glycerol molecules reside in the matrix and thus decrease the matrix T_g. The glycerol molecules also dissolve the ionic groups, leading to the weakening of interactions between ionic groups. These two effects contribute to the decrease in the T_g by 90 °C. Thus, it can be concluded that while the matrix T_g is decreased drastically by plasticization with glycerol, the cluster T_g cannot be observed as the presence of the polar plasticizer weakens interactions in multiplets.

In the case of the nonpolar DOP-plasticized ionomer, the temperature of the peak maximum is ca. 180 °C. Evidently the DOP molecules decrease the T_g of the ionomer but only slightly. The morphology of this system must be very different from that of the Gly-plasticized ionomer. It is also seen that whereas the width of the peak is broader the height is lower than those of the unclustered ionomer, which means that the glass transitions take place over a wider range of temperatures. It needs to be mentioned that normally the width of the peak is related to the heterogeneity of the polymer phases. However, at this time we do not have any clear explanation for the width of the peak.

For the 4DA-plasticized system, the peak maximum is located at *ca.* 120 °C, and the width of the peak is very broad. It is also seen that there is a shoulder on the curve at *ca.* 170 °C, which may represent the second T_g. To see the effect of the plasticization on the tan δ peak (measured at 0.3 Hz) more clearly, a curve deconvolution was performed using a Peakfit (Jandel Scientific) computer program. The best fit was achieved by fitting the curve with two exponentially modified Gaussian peaks with an exponential background. The deconvolution result is shown in Figure 3. In the figure, it is clear that there are two peaks associated with the glass transitions of the matrix and cluster phases; one peak maximum is at ca. 110 °C and the other at 165 °C.

This finding indicates that the 4DA molecules reside in the PMMA matrix phase and thus decreases the T_g. Therefore, the multiplets form, whose proximity is sufficient to show typical behavior of a clustered material. Tong and Bazuin studied the clustered poly(ethyl acrylate) ionomers plasticized with a 4DA and found that matrix and cluster T_gs are decreased in parallel with increasing plasticizer content.[11] Thus they suggested that the 4DA, a nonpolar plasticizer, is distributed evenly in the cluster and matrix phases *via* a strong hydrogen bonding between the aniline group and the carbonyl group of the poly(ethyl acrylate). The same effect is operative in the present study. The 4DA molecules partition in the nonionic PMMA phase and plasticize the nonionic phase preferentially. Thus the plasticizers lower the T_g of the PMMA, rather than having the aniline group reside preferentially near the ionic group. It should be mentioned that the cluster formation in unclustered materials by plasticization was also found by Wollmann *et al.* in the polystyrene ionomers.[12] They found that when a unclustered poly(styrene-*co*-4-vinylpyridinium methyl iodide) ionomer was plasticized with diethylbenzene, clustering was induced by the plasticizers of low polarity, which was observed by dynamic mechanical techniques.

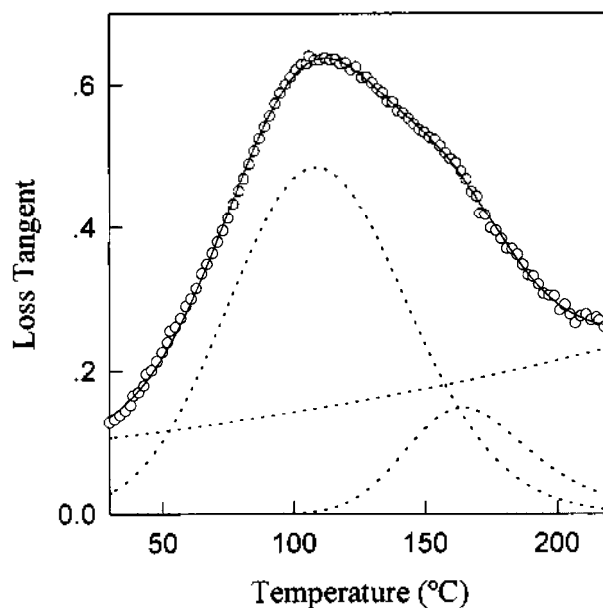From Figure 3, we can see that the peak for the cluster T_g

Figure 3. Deconvoluted loss tangent curves as a function of temperature for the 4DA-plasticized ionomer sample measured at 0.3 Hz.

is smaller than that for the matrix T_g. At this point, it needs to be recalled that in poly(styrene-*co*-sodium methacrylate) ionomer system containing *ca.* 10 mol% of ions, the area under the cluster T_g peak is bigger than that for the matrix T_g.[5,6] This difference may be due to two factors. First, the persistence length of the poly(methyl methacrylate) is shorter than that of the polystyrene.[7] Second, in the PMMA ionomers, the strength of the ionic interaction between ionic groups in the multiplet that was induced by plasticization is still much weaker than that in the cesium neutralized PS ionomers. Thus clustering is not extensive in the plasticized PMMA ionomers. At this state, however, it can be concluded that the mixing of 4DA with the unclustered poly (methyl methacrylate-*co*-cesium methacrylate) ionomer can induce clustering. More work needs to be done on the morphology of these plasticized systems.

Conclusion

The unclustered cesium neutralized PMMA-based ionomers were plasticized with three different plasticizers of low molecular weight. The effectiveness of plasticization is ranked in the following order: Gly ≈ 4DA > DOP. When the ionomer is plasticized with the 4DA, the nonpolar 4DA molecules are believed to reside evenly in the PMMA matrix region because of strong hydrogen bonding between the aniline group of the plasticizer and the carbonyl group of the PMMA. This results in a lowering of the T_g of the ionomer. Once the plasticization lowers the T_g and additional free volume is introduced, multiplets can form; as a result, the material shows two glass transitions, characteristic of a clustered ionomer. In the system plasticized with the Gly, the polar plasticizer not only decreases the T_g of the ionomer, but also acts as a solvent for the ionic groups. Therefore, only a significant decrease in the T_g was

observed, without cluster formation.

References

1. Eisenberg, A.; King, M. *Ion-Containing Polymer, Physical Properties and Structure*; Academic Press: New York, U. S. A., 1977.
2. Eisenberg, A. *Macromolecules* **1970**, *3*, 147.
3. Wilson, F. C.; Longworth, R.; Vaughan, D. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1968**, *9*, 505.
4. Eisenberg, A.; Hird, B.; Moore, R. B. *Macromolecules* **1990**, *23*, 4098.
5. Hird, B.; Eisenberg, A. *J. Polym. Sci., Part B: Polym. Phys.* **1990**, *28*, 1665.
6. Kim, J.-S.; Jackman, R. J.; Eisenberg, A. *Macromolecules* **1994**, *27*, 6541.
7. Ma, X.; Sauer, J. A.; Hara, M. *Macromolecules* **1995**, *28*, 3953.
8. Ma, X.; Sauer, J. A.; Hara, M. *Polymer* **1997**, *38*, 4425.
9. Gronowski, A. A.; Jiang, M.; Yeager, H. L.; Wu, G.; Eisenberg, A. *J. Membr. Sci.* **1993**, *82*, 83.
10. Jiang, M.; Gronowski, A. A.; Yeager, H. L.; Wu, G.; Kim, J.-S.; Eisenberg, A. *Macromolecules* **1994**, *27*, 6541.
11. Tong, X.; Bazuin, C. G. *J. Polym. Sci.: Part B: Polym. Phys.* **1992**, *20*, 389.
12. Wollmann, D.; Williams, C. E.; Eisenberg, A. *Macromolecules* **1992**, *25*, 6775.

Electronic Band Structure of N and P Dopants in Diamond

Dae-Bok Kang

Department of Chemistry, Kyungsung University, Pusan 608-736, Korea
Received January 11, 1998

The properties of the n-type impurities nitrogen and phosphorus in diamond have been investigated by means of electronic band structure calculations within the framework of the semiempirical extended Hückel tight-binding method. For diamond with the nitrogen and phosphorus substitutional impurities, calculated density of states shows the impurity level deep in the band gap. This property can be derived from the substantial <111> relaxation of the impurity and nearest-neighbor carbon atoms, which is associated with the population of an antibonding orbital between them. The passivated donor property of the P-vacancy complex which lies deep in the gap is also discussed.

Introduction

Recent advances in diamond-film growth techniques have stimulated an interest in the use of diamond as a semiconductor in electronic devices.[1] Diamond films produced by low-pressure methods have a wide array of potential applications due to their unique mechanical, thermal, optical, and semiconducting properties. Despite the significant process in the field of diamond growth, the problem of reproducible doping by donor and acceptor impurities to obtain p-n junction remains unresolved. It is well known that p-type conductivity can be obtained by boron doping. The results reported so far on n-type doping are controversial.[2] There is continuing interest in making shallow n-type diamond to develop the p-n technologies of the semiconductor industry applicable to future diamond-based devices. Nearly all of the n-type diamond which has been reported to result from either doping during film growth or ion implantation is highly resistive. An understanding of the behavior of impurities in diamond is important as a tool in the search for a possible n-type dopant.

Substitutional nitrogen and phosphorus with five valence

electrons are prototype n-type impurities in diamond. While the isolated nitrogen impurity is well characterized experimentally,[3-8] the phosphorus doping has not been widely reproduced.[9,10] The problem of nitrogen and phosphorus impurities in diamond has also been addressed using a number of theoretical techniques.[11-16] Nonetheless, a complete quantitative description of the impurity energetics and structure is still lacking. Self-consistent molecular orbital calculations by Astier *et al.* predicted a deep donor level occurring at 1.3 eV below the diamond conduction band edge for the substitutional nitrogen impurity.[11] This level was degenerate and therefore assumed to be Jahn-Teller unstable with respect to a distortion. However, self-consistent Green's function calculations on this impurity in diamond find a non-degenerate shallow level (0.15 eV below the conduction band edge) and therefore no Jahn-Teller instability.[12] The authors suggest that the off-center distortion of nitrogen is driven by local bonding effects. Theoretical calculations[13] based on the local-density approximation show that phosphorus is a deep donor at 1.09 eV below the bottom of the conduction band; however, calculations[14,15] using the plane-wave pseudopotential method predict that phosphorus would