### Behavior of Polyoxyethylene-Containing Interpenetrating Polymer Networks and their LiClO<sub>4</sub> Complexes as Phase Transfer Catalysts and Ionic Conductors

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ABSTRACT: Simultaneous grafted interpenetrating polymer networks (IPNs) based on [castor oil-poly(ethylene glycol) (PEG)] polyurethane and poly(alkyl methacrylate) were synthesized by simultaneously coupling castor oil and PEG with 2,4-toluene diisocyanate and by radical polymerization of alkyl methacrylate with castor oil. The gel content of the IPNs is ~96% in most cases. The IPNs were characterized by infrared spectroscopy. The effects of compositional variation of the IPNs on phase transfer catalytic efficiency and mechanical properties, and conductivity of the IPNs complexed with LiClO<sub>4</sub> were also studied. The results show that the IPNs have good phase transfer catalytic ability in the Williamson reaction and exhibit a maximum conversion of potassium phenolate at 55% polyoxyethylene (PEO). The phase transfer catalytic ability of the IPN increases with molecular weight of PEG used in the IPN synthesis and with the length of alkyl groups of the grafts, but decreases with increasing crosslinking degree. The complex of the IPNs with LiClO<sub>4</sub>

### **INTRODUCTION**

Amphiphilic polymers containing hydrophobic segments and hydrophilic polyoxyethylene (PEO) segments have been attracted much attention<sup>1–3</sup> because PEO segments are not only hydrophilic, but also nonionic and crystalline and can complex monovalent metallic cations. These polymers have many uses, including polymeric surfactants, electrostatic charge reducers, compatibilizers in polymer blending, phase transfer catalysts, or solid polymer electrolytes, etc. However, most research about these kinds of amphiphilic polymers is about block copolymers and graft copolymers containing PEO segments. Their mechanical strength is not high, and they cannot be used as a good solid polymer electrolyte film. They also cannot be used as a good phase transfer catalyst, which should be easily recovered and used repeatedly. To overcome these disadvantages, crosslinked polymers or interpenetrating polymer networks (IPNs) containing PEO segments were studied.

exhibits good ionic conductivity at room temperature in the range  $10^{-5}$ -3  $\times 10^{-4}$  S/cm. This ionic conductivity decreases with increasing either the crosslinking degree or the molecular weight of PEG used, but increases with increasing PEO content. The more compatible are the grafts with PEO, the lower is the conductivity. Either butyl methacrylate or ethyl methacrylate is a good choice for the monomer in the synthesis of the IPNs for use as phase transfer catalysts and ion conducting materials. The IPNs showed high tensile strength in the range 10–20 MPa. The good mechanical properties of the IPNs favor their applications as a strong solid polymer electrolyte film and an easily recoverable phase transfer catalyst. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 830–836, 2003

**Key words:** IPNs (see networks); networks; phase transfer catalysis; conducting polymers

Several studies concerning IPNs containing the PEO segments have been reported. Tan et al.<sup>4</sup> prepared simultaneous IPNs based on poly(ethylene glycol) (PEG) diacrylate and bisphenol A diglycidyl ether and studied the effect of compositional variation on the morphology, swelling coefficient, density, and thermal stability. Li et al.<sup>5</sup> synthesized simultaneous IPNs containing PEO segments by polymerizing PEG diacrylate with trimethylol propane and diisocyanate. Wang et al.<sup>6</sup> obtained PEO-containing IPNs by heat mixing PEG with epoxy resin and triethylenetetramine. The IPNs showed high water absorption, and their IPN complexes with ZnCl<sub>2</sub> showed a maximum value of ionic conductivity with increasing ZnCl<sub>2</sub>. Grosz et al.<sup>7</sup> obtained IPNs from polysiloxane, PEG dimethacrylate, and AIBN and studied their behavior as solid polymer electrolytes. Guler et al.8 obtained PEO-containing IPNs by irradiating the solution of PEG in acrylonitrile. The latter was then converted to amidoxime groups. The IPNs were used as an adsorbent material for recovery of uranyl ions by chelation with the amidoxime groups. Kim et al.9 synthesized PEO-grafted polyurethane/polystyrene IPNs and studied the effect of mobile pendant PEO chains on the blood compatibility. We<sup>10</sup> simultaneously pre-

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pared grafted IPNs based on castor oil–PEG polyurethane and poly(2-vinyl pyridine) by coupling castor oil and PEG with 2,4-toluene diisocyanate (TDI) and by radical polymerization of poly(2-vinyl pyridine) with castor oil. We then studied the electronic–ionic conductivity of the IPNs after complexing the PEO segments with LiClO<sub>4</sub> and the poly(2-vinyl-pyridine) grafts with tetracyanoethylene or tetracyanoquinodimethane.

In this paper we report the synthesis of the amphiphilic, PEO-containing, simultaneously grafted IPNs based on (castor oil–PEG) polyurethane and polymethacrylate. The latter was polymerized from methyl methacrylate (MMA), ethyl methacrylate (EMA), butyl methacrylate (BMA), ethyl acrylate (EA), butyl acrylate (BA), or vinyl acetate (VAc). The effects of compositional variations of the IPNs on the phase transfer catalytic efficiency and mechanical properties as well as the ionic conductivity of their complexes with LiClO<sub>4</sub> were studied to find a good solid polymer electrolyte or an easily recoverable phase transfer catalyst with good mechanical properties.

#### EXPERIMENTAL

### Materials

Castor oil, *N*,*N*-dimethyl aniline (DMA), benzoyl peroxide (BPO), dibutyltin dilaurate (BTL), 2,4-toluene diisocyanate (TDI), toluene, and 1,2-dichloroethane were chemically pure. LiClO<sub>4</sub>·3H<sub>2</sub>O was an analytical reagent. Castor oil was heated at 115°C for 1 h with stirring to remove water. Alkyl methacrylates were purified by washing with 5% NaOH and water successively, followed by drying with CaCl<sub>2</sub> and distillation in the presence of CuCl. PEGs of different molecular weights were laboratory reagents manufactured by Aldrich Chemical Company.

#### Synthesis of the IPNs

The simultaneously grafted IPNs were obtained by reacting trifunctional or three OH groups containing castor oil with excess TDI to form trifunctional prepolymer, followed by reaction with PEG and alkyl methacrylate in the presence of BTL as catalyst and BPO and DMA as redox initiators. The trifunctional castor oil prepolymer was prepared by reacting TDI and dried castor oil at an NCO/OH molar ratio of 2.5 for 1 h with stirring and cooling . Then, the trifunctional castor oil prepolymer was mixed thoroughly with alkyl methacrylate and a warm dichloroethane solution of PEG as well as 1.5% BPO, 1.5% DMA, and 2% BTL based on total weight of the reagents. The mixture was poured into a large culture dish and covered. The mixture was then heated to 50°C for 24 h and 80°C for 4 h. to complete the reaction. The product was vacuum dried at 80°C and stored in a desiccator. The yield was calculated from the weight of dried product divided by the weight of total reactants except the solvent.

### Characterization

The gel content was determined by weighing the sample after extraction with benzene for 24 h and drying at 110°C for 2 h. Infrared (IR) spectra of the extracted IPNs were taken with a Shimadzu IR-435 spectrophotometer.

# Measurement of crystallinity by wide-angle X-ray diffraction (WAXD)

Crystallinity ( $X_c$ ) was measured by WAXD with a Rigaku 3015 apparatus at a scanning rate of 2 °/min. Crystallinity was calculated according to a published method.<sup>11</sup>

### Phase transfer catalysis property in Williamson reaction<sup>12</sup>

Toluene (40 mL), *n*-butyl bromide (2 mL), and a certain amount of copolymer granules were added to a bottle containing potassium phenolate (1.0 g accurately weighed). After purging with N<sub>2</sub>, the system was heated at 90°C for 4 h with stirring. After reaction, 50 mL of distilled water was added with stirring. The IPN was filtered and washed with water. The unreacted potassium phenolate in the filtrate and washing solution was separated from the toluene and titrated with standard HCl, using methyl red as indicator to find the conversion of potassium phenolate into butyl phenolate.

# Formation of complex with LiClO<sub>4</sub> and measurement of conductivity of the complex<sup>13</sup>

A complex of the IPN with LiClO<sub>4</sub> was prepared by immersing an IPN pellet of 15 mm diameter and ~2mm thickness in a tetrahydrofuran solution of Li-ClO<sub>4</sub> at an EO/Li molar ratio of 20/1. After evaporating off the solvent at room temperature, the pellet was dried at 80°C for 1 h and then in a desiccator overnight. The dried pellet (~2 mm thick and 14 mm in diameter) was sandwiched between copper disk electrodes in a large glass cell containing  $P_2O_5$  at the bottom and kept overnight. AC conductivity was measured with a DDS-IIA conductometer operating at 1100–1200 Hz.

### Measurement of mechanical properties

Mechanical properties of the IPNs were determined on a XL-2500 tensile tester with a stretching rate of 300 mm/min. Permanent set was measured as percent elongation at 3 min after the specimen was broken and reunited.

#### **RESULTS AND DISCUSSION**

### Preparation and characterization of the IPNs

We have reported the simultaneous synthesis of IPNs at room temperature from castor oil, TDI, and a vinyl or methacrylic monomer using a redox initiator.<sup>14</sup> The resulting IPNs were mainly grafted IPNs, with vinyl or methacrylic polymer grafted on the double bonds of castor oil, which formed a network by reaction of its three hydroxyl groups with TDI.<sup>15</sup> In this paper, the monomers used are alkyl methacrylates and the castor oil was coupled together with TDI and PEG. Castor oil is a trifunctional component containing three hydroxyl groups, which reacted with TDI first to form a prepolymer and then coupled with PEG containing dihydroxyl groups or difunctional PEG.

The yields of IPNs in most cases were in the range 92–98%. Some alkyl methacrylate was lost during the reaction. The more the charging weight percent of monomer, the more monomer was lost through evaporation and vacuum drying, and the lower was the yield. The gel content of the IPN decreased with increasing charging weight percent of the monomer and with increasing molecular weight of PEG, but increased with increasing charging weight of castor oil. The higher the charging weight percent of the monomer and the less the amount of castor oil used, the less probable was the copolymerization of the monomer with double bonds of castor oil, resulting in decreasing gel content of the product. Most IPNs contain  $\sim$ 96% gel. This amount implies that most of the monomer copolymerized with the double bonds of castor oil to form grafts, whereas a small portion of the monomer homopolymerized. The homopolymer was dis-

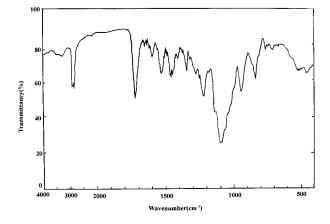


Figure 1 Infrared spectrum of the (castor oil–PEG)PU/PMMA IPN.

solved during extraction, whereas the grafts cannot be dissolved and remained in the gel.

The IR spectrum of the extracted IPN (Fig. 1) shows characteristic peaks at  $1060-1140 \text{ cm}^{-1}$  for the ether linkage of PEO segment, at  $1150 \text{ cm}^{-1}$  for the C—O linkage of ester group, at  $1220 \text{ cm}^{-1}$  for the ester group, at  $1530 \text{ cm}^{-1}$  for the NHCO linkage, at  $1720 \text{ cm}^{-1}$  for the C—O group of ester, at  $860 \text{ cm}^{-1}$  for substituted benzene, and at  $2890-2930 \text{ cm}^{-1}$  for CH<sub>3</sub> and CH<sub>2</sub> groups. Absorption peaks of OH or double bonds almost disappeared, indicating that the IPN was composed of (castor oil–ethylene glycol) polyure-thane and poly(alkyl methacrylate).

### Phase transfer catalytic activity of the IPNs

It is well known that PEO can complex with alkali metal ions. Because the amphiphilic IPNs contain both the hydrophilic segments of PEO, which can complex with the alkali metal ions, and the hydrophobic castor oil segments and poly(alkyl methacrylate) grafts, they

| Amount of<br>IPN (mg) | Type of<br>Monomer | PEO/Prep/Monomer<br>(weight ratio) | M <sub>nPEG</sub> | Conversion of K<br>Phenolate (%) |
|-----------------------|--------------------|------------------------------------|-------------------|----------------------------------|
| 0                     | EMA                | 70/20/10                           | 3350              | 4.0                              |
| 49                    | EMA                | 70/20/10                           | 3350              | 54.9                             |
| 75                    | EMA                | 70/20/10                           | 3350              | 60.7                             |
| 99                    | EMA                | 70/20/10                           | 3350              | 85.6                             |
| 200                   | EMA                | 70/20/10                           | 3350              | 82.7                             |
| 75                    | EA                 | 60/28/12                           | 2000              | 55.2                             |
| 75                    | MMA                | 60/28/12                           | 2000              | 54.2                             |
| 75                    | BA                 | 60/28/12                           | 2000              | 61.5                             |
| 75                    | VAc                | 60/28/12                           | 2000              | 53.6                             |
| 75                    | MMA                | 70/20/10                           | 3350              | 58.7                             |
| 75                    | EMA                | 70/20/10                           | 3350              | 60.7                             |
| 75                    | BMA                | 70/20/10                           | 3350              | 62.3                             |
| 75                    | VAc                | 70/20/10                           | 3350              | 55.9                             |

TABLE I Effects of the IPN Amount and Type of Monomer on the Phase Transfer Catalytic Effect of the IPNs

| Amount of<br>IPN (mg) | PEO/Prep/Monomer<br>(weight ratio) | Type of<br>Monomer | $M_{ m nPEG}$ | Conversion of K<br>Phenolate (%) |
|-----------------------|------------------------------------|--------------------|---------------|----------------------------------|
| 75                    | 60/28/12                           | EA                 | 2000          | 55.2                             |
| 75                    | 60/25/15                           | EA                 | 2000          | 81.4                             |
| 75                    | 60/21/19                           | EA                 | 2000          | 83.2                             |
| 75 <sup>a</sup>       | 60/21/19                           | EA                 | 2000          | 83.0                             |
| 75                    | 50/23/27 <sup>b</sup>              | EMA                | 2000          | 55.9                             |
| 75                    | 55/25.5/19.5 <sup>b</sup>          | EMA                | 2000          | 69.1                             |
| 75                    | $60/28/12^{\circ}$                 | EMA                | 2000          | 61.2                             |
| 75                    | 65/30/5 <sup>b</sup>               | EMA                | 2000          | 60.9                             |
| 75                    | 50/14.5/35.5 <sup>b</sup>          | EMA                | 3350          | 63.0                             |
| 75                    | 55/15.5/29.5 <sup>b</sup>          | EMA                | 3350          | 84.7                             |
| 75                    | 60/17/23 <sup>b</sup>              | EMA                | 3350          | 65.6                             |
| 75                    | $70/20/10^{\circ}$                 | EMA                | 3350          | 60.7                             |

TABLE II Effects of Crosslinking Degree and PEO Content on the Phase Transfer Catalytic Effect of IPNs

<sup>a</sup> The IPN was used again after recovery.

<sup>b</sup> The weight ratios of Prep/PEG are the same for each series of PEG.

<sup>c</sup> The molar ratio of trifunctional prepolymer/difunctional PEG is nearly the same for the IPN synthesized from PEG with a molecular weight of 2000 at a trifunctional prepolymer/difunctional PEG weight ratio of 28/60 and for the IPN synthesized from PEG with a molecular weight of 3350 at a trifunctional prepolymer/difunctional PEG weight ratio of 20/70.

were tested as the phase transfer catalyst in the Williamson reaction between potassium phenolate solid and *n*-butyl bromide liquid. The results shown in Table I indicate that a very small amount of potassium phenolate reacted in the absence of the IPN. However, the conversion of potassium phenolate increases obviously with increasing the amount of IPN.

These results indicate that the IPN can complex the potassium ions of the phenolate and transfer them from the solid to the organic solution, thus enhancing the reaction between potassium phenolate and *n*-butyl bromide. Other results shown in Table I indicate that different kinds of grafts synthesized from different monomers in the IPNs also affect the conversion of potassium phenolate. The phase transfer catalytic efficiency increases with the kinds of grafts in the following order: for the IPNs synthesized from PEG with molecular weight of 3350, PVAc < PMMA < PEMA< PBMA; for those from PEG with molecular weight of 2000, PVAc < PMMA < PEA < PBA. It seems that the longer the alkyl groups, the higher is the phase transfer catalytic efficiency. This result is because the efficiency is not only dependent on the PEG segments, which can complex potassium ions from the solid, but is also dependent on the hydrophobic grafts, which can be solvated in the organic solution containing *n*-butyl bromide. The longer the alkyl groups, the more hydrophobic are the grafts.

The effect of PEO content of the IPNs, at the same weight ratios of trifunctional prepolymer/difunctional PEG used in the synthesis of IPNs, on the phase transfer catalytic ability of the IPNs is shown in Table II. A maximum value of potassium phenolate conversion occurs at 55% PEO content of the IPN. This result implies that the phase transfer catalytic efficiency depends not only on the PEO segments, but also on the hydrophobic part of the IPN. At the same PEO content and the same molar ratio of the trifunctional prepolymer/difunctional PEG, the higher the molecular weight of the PEO segment, the higher is the phase transfer catalytic efficiency of the IPN. (Note that the molar ratio of trifunctional prepolymer/difunctional PEG is nearly the same for the IPN synthesized from PEG with molecular weight of 2000 at a trifunctional prepolymer/difunctional PEG weight ratio of 28/60 and for that from PEG with molecular weight of 3350 at a trifunctional prepolymer/difunctional PEG weight ratio of 20/70). The direct correlation of phase transfer catalytic efficiency and PEO segment molecular weight is probably due to the longer coil of PEO segment which can complex with more K<sup>+</sup> ions.

Another correlation shown in Table II is that at the same PEO content, the lower the weight ratio of trifunctional prepolymer/difunctional PEG or the lower the crosslinking degree, the higher is the transfer phase catalytic efficiency. This result indicates that crosslinks restrict the ability of the PEO segments to complex with the potassium ions.

The IPN can be used again as the phase transfer catalyst without serious loss of activity after recovery, as shown in Table II.

# Ionic conductivity of the IPNs complexed with LiClO<sub>4</sub>

The IPNs complexed with LiClO<sub>4</sub> exhibit high ionic conductivity ( $\sigma$ ) at room temperature when complexed with LiClO<sub>4</sub> at an EO/Li molar ratio of 20/1, as shown in Table III. This result is because PEO can complex with Li salt, and the complex shows ionic conductivity. Ionic conductivity ( $\sigma$ ) increases with increasing PEO content, especially when the PEO con-

TABLE IIIEffect of PEO Content of the IPNs at the Same WeightRatio of Prep/PEG on the Conductivity of the Complex<br/>of the IPNs with  $LiClO_4$ 

| PEG/Prep/EMA   |                   | $\sigma \times 10^5$ |
|----------------|-------------------|----------------------|
| (weight ratio) | M <sub>nPEG</sub> | (S/cm)               |
| 55/26/19       | 2000              | 14.9                 |
| 60/28/12       | 2000              | 18.9                 |
| 50/14/36       | 3350              | 0.75                 |
| 55/15.5/29.5   | 3350              | 2.16                 |
| 60/17/23       | 3350              | 6.08                 |
| 65/18/17       | 3350              | 3.71                 |
| 70/20/10       | 3350              | 9.44                 |

tent is >65%. In the latter case, the PEO segments occur in a continuous phase and can transport Li ions more freely. The molecular weight of the PEG used in synthesis also affects the conductivity. At the same PEO content, the conductivity of the complexed IPNs decreases with an increase of the molecular weight of the PEG used in synthesis from 2000 to 3350. This may be due to the fact that PEO crystallinity increases with molecular weight of PEG (Table IV), thus decreasing the conductivity. (Recall that the molar ratio of trifunctional prepolymer/difunctional PEG is nearly the same for the IPN synthesized from PEG with molecular weight of 2000 at a trifunctional prepolymer/ difunctional PEG weight ratio of 28/60 and for that from PEG with molecular weight of 3350 at a trifunctional prepolymer/difunctional PEG weight ratio of 20/70).

The conductivities of the  $\text{LiClO}_4$  complexes of the IPNs, using different monomers in synthesis, are shown in Table V. The conductivity increases in the following order of monomers: EA < VAc < MMA < BA < EMA < BMA. This order is almost the same as that of increasing difference of solubility parame-

TABLE IVEffect of Molecular Weight of PEG and Type ofMonomer Used in Synthesis on the Crystallinityof the IPNs<sup>a</sup>

| PEG/Prep/Monomer<br>(weight ratio) | Type of<br>Monomer | M <sub>nPEG</sub> | Crystallinity<br>(%) |
|------------------------------------|--------------------|-------------------|----------------------|
| 60/28/12                           | EMA                | 2000              | 21.0                 |
| 60/28/12                           | BMA                | 2000              | 22.6                 |
| 60/28/12                           | BA                 | 2000              | 19.8                 |
| 70/20/10                           | MMA                | 3350              | 37.4                 |
| 70/20/10                           | EMA                | 3350              | 39.2                 |
| 70/20/10                           | BMA                | 3350              | 40.1                 |
| 70/20/10                           | BA                 | 3350              | 38.9                 |
|                                    |                    |                   |                      |

<sup>a</sup> The molar ratio of trifunctional prepolymer/difunctional PEG is nearly the same for the IPN synthesized from PEG with a molecular weight of 2000 at a trifunctional prepolymer/difunctional PEG weight ratio of 28/60 and for the IPN synthesized from PEG with a molecular weight of 3350 at a trifunctional prepolymer/difunctional PEG weight ratio of 20/70.

 TABLE V

 Effect of Type of Monomer used in Synthesis on the Conductivity of the Complex of IPN with LiClO<sub>4</sub>

| •                                  | -                  |                   |                            |
|------------------------------------|--------------------|-------------------|----------------------------|
| PEG/Prep/Monomer<br>(weight ratio) | Type of<br>Monomer | M <sub>nPEG</sub> | $\sigma 	imes 10^5$ (S/cm) |
| 60/28/12                           | MMA                | 2000              | 8.24                       |
| 60/28/12                           | EMA                | 2000              | 18.9                       |
| 60/28/12                           | BMA                | 2000              | 18.5                       |
| 60/28/12                           | VAc                | 2000              | 7.5                        |
| 60/28/12                           | EA                 | 2000              | 3.0                        |
| 70/20/10                           | MMA                | 3350              | 0.39                       |
| 70/20/10                           | EMA                | 3350              | 9.44                       |
| 70/20/10                           | BMA                | 3350              | 17.1                       |
| 70/20/10                           | BA                 | 3350              | 3.99                       |
|                                    |                    |                   |                            |

ters between the graft and PEG or that of decreasing the compatibility between the two components, except PVAc. The compatibility of the grafts with PEG segments corresponds to the difference of their solubility parameters (The solubility parameters of PEO, PEA, PVAc, PBA, PMMA, PEMA, and PBMA are 9.3, 9.35, 9.45, 9.0, 9.15, 9.0, and 8.75, respectively<sup>16</sup>). In most cases, the less the difference of solubility parameters between PEO and the grafts synthesized from the monomer, the more compatible are the grafts formed with the PEO segments and the lower is the ability of the latter to complex with LiClO<sub>4</sub>.

The dependence of the conductivity of the IPNs complexed with  $\text{LiClO}_4$  on the crosslinking degree of the IPNs is shown in Table VI. It is evident that when the PEO content is kept constant, the higher the weight ratio of trifunctional prepolymer/difunctional PEG or the higher the crosslinking degree, the lower is the conductivity. This result may be due to the increase of crosslinks, which restrict the mobility of PEO segments.

### Mechanical properties of the IPNs

The effects of PEO content and crosslinking degree of the IPNs on the mechanical properties of the IPNs are listed in Table VII. It can be seen that the IPNs exhibit good mechanical properties. Tensile strength, which varies in the range10–20 MPa, increases with increasing PEO content, while the weight ratio of the trifunc-

TABLE VIEffect of Crosslinking Degree of the IPNs on theConductivity of the Complex of the IPNs with LiClO4

|                                    | T                  |                | $\frac{4}{\sigma \times 10^5}$    |
|------------------------------------|--------------------|----------------|-----------------------------------|
| PEG/Prep/Monomer<br>(weight ratio) | Type of<br>Monomer | $M_{\rm nPEG}$ | $\sigma \times 10^{\circ}$ (s/cm) |
| 60/28/12                           | EA                 | 2000           | 3.01                              |
| 60/25/15                           | EA                 | 2000           | 5.04                              |
| 60/21/19                           | EA                 | 2000           | 8.00                              |
| 60/17/23                           | EMA                | 3350           | 6.08                              |
| 60/14/26                           | EMA                | 3350           | 23.8                              |
| 60/11/29                           | EMA                | 3350           | 34.5                              |

| TABLE VII<br>Effect of Crosslinking Degree and PEO Content of the<br>IPNs on the Mechanical Properties of the IPNs <sup>a</sup> |                   |                |       |       |  |  |
|---|-------------------|----------------|-------|-------|--|--|
| PEG/Prep/EMA<br>(weight ratio)  | M <sub>nPEG</sub> | $\sigma$ (MPa) | ε (%) | δ (%) |  |  |
| 60/17/23  | 3350              | 15.4           | 615   | 260   |  |  |
| 60/14/26  | 3350              | 13.6           | 125   | 40    |  |  |
| 60/11/29  | 3350              | 16.1           | 60    | 5     |  |  |
| 50/24/26 <sup>b</sup>   | 2000              | 11.7           | 535   | 115   |  |  |
| 55/26/19 <sup>b</sup>   | 2000              | 12.1           | 625   | 120   |  |  |
| $60/28/12^{b}$  | 2000              | 12.2           | 630   | 125   |  |  |
| 65/31/4 <sup>b</sup>  | 2000              | 13.5           | 635   | 135   |  |  |
| 50/14/36 <sup>b</sup>   | 3350              | 13.4           | 95    | 25    |  |  |
| 55/15.5/29.5 <sup>b</sup>   | 3350              | 14.2           | 260   | 105   |  |  |
| 60/17/23 <sup>b</sup>   | 3350              | 15.4           | 615   | 260   |  |  |
| 65/18/17 <sup>b</sup>   | 3350              | 19.2           | 770   | 275   |  |  |
| $70/20/10^{b}$  | 3350              | 19.8           | 740   | 225   |  |  |

<sup>a</sup>  $\sigma$ ,  $\varepsilon$ , and  $\delta$  represent tensile strength, ultimate elongation, and permanent set, respectively.

<sup>b</sup> The weight ratios of Prep/PEG are the same.

tional prepolymer/difunctional PEG remains constant. At the same molar ratio of the trifunctional prepolymer/difunctional PEG, tensile strength of the IPNs increases with the molecular weight of PEG used in synthesis. Both of these results imply that the crystalline PEO segments contribute markedly to the tensile strength. Ultimate elongation, which varies considerably from 100 to 800%, increases with PEO content.

Also shown in Table VII is that the tensile strength of the IPN decreases at first and then increases, whereas the ultimate elongation and permanent set decrease considerably when the weight ratio of trifunctional prepolymer/difunctional PEG or the crosslinking degree decrease and the grafts increases at constant PEO content and molecular weight of PEG used. Tensile strength of the IPNs depends on three main factors; they are, chemical crosslinks, grafts, and crystallinity. The chemical crosslinks diminished with decreasing the weight ratio of the trifunctional prepolymer/difunctional PEG, resulting in less tensile strength. With further decreasing of the crosslinks, the effect of crystallinity and grafts overcome that of crosslinks, resulting in an increase in the tensile strength.

The dependence of mechanical properties on type of monomer used in synthesis is shown in Table VIII. It can be noted that at the same PEO content and crosslinking degree, the crystallinity is lower for the IPNs containing PEG with molecular weight of 2000 than those containing PEG with molecular weight of 3350 (Table IV), and the tensile strength decreases in the following order of monomers: MMA > VAc > EMA > BMA > BA. This order is nearly the same as the order of decreasing glass transition temperature  $(T_g)$  of the grafts synthesized from the monomers, except PVAc ( $T_{gs}$  for the PMMA, PVAc, PEMA, PBMA, and PBA grafts are 105, 32, 65, 20, and -54°C, respectively). For the IPNs containing PEG with molecular weight of 3350, the crystallinity is higher and the tensile strength decreases in following order: BMA > EMA = BA> MMA. This order is nearly the same as that of decreasing crystallinity (i.e., BMA > EMA > BA> MMA; Table IV).

### CONCLUSIONS

The phase transfer catalytic ability of the IPNs exhibit a maximum value at 55% PEO and increases with increasing molecular weight of PEG used in the synthesis (from 2000 to 3350) and the length of alkyl groups of the grafts, but decreases with increasing crosslinking degree. The complexes of the IPNs with LiClO<sub>4</sub> exhibit very good ionic conductivity in the range  $10^{-5}$ -3  $\times$   $10^{-4}$  S/cm. This conductivity increases with decreasing crosslinking degree and the molecular weight of PEG used (from 3350 to 2000), but with increasing PEO content. The more the compatibility of the grafts with PEO, the lower is the conductivity. With regard to the phase transfer catalytic ability and ion conductivity, it is better to use EMA or BMA as the monomer in the synthesis of IPN. The IPNs show good tensile strength in the range 10–20

 TABLE VIII

 Effect of Type of Monomer used in Synthesis on the Mechanical Properties of the IPNs<sup>a</sup>

| PEG/Prep/Monomer<br>(weight ratio) | Type of<br>Monomer | $M_{ m nPEG}$ | $\sigma$ (MPa) | ε (%) | δ (%) |
|------------------------------------|--------------------|---------------|----------------|-------|-------|
| 60/28/12                           | MMA                | 2000          | 13.4           | 720   | 110   |
| 60/28/12                           | EMA                | 2000          | 12.2           | 630   | 125   |
| 60/28/12                           | BMA                | 2000          | 11.9           | 625   | 130   |
| 60/28/12                           | VAc                | 2000          | 12.0           | 695   | 135   |
| 60/28/12                           | BA                 | 2000          | 11.7           | 545   | 105   |
| 70/20/10                           | MMA                | 3350          | 19.3           | 725   | 230   |
| 70/20/10                           | EMA                | 3350          | 19.8           | 740   | 225   |
| 70/20/10                           | BMA                | 3350          | 22.4           | 1000  | 285   |
| 70/20/10                           | BA                 | 3350          | 19.8           | 895   | 275   |

<sup>a</sup>  $\sigma$ ,  $\varepsilon$ , and  $\delta$  represent tensile strength, ultimate elongation, and permanent set, respectively.

MPa, with the ultimate elongation mostly in the range 100–1000% and the permanent set mostly in the range 25–300%. The good mechanical properties of the IPNs favor their application as a strong solid polymer electrolyte film and an easily recoverable phase transfer catalyst.

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