Study of the Synthesis and Physical Properties of Fire-Resistant Polyurethane Ionomers

D. Y. CHAO,[1] W. J. KUO,[1] N. H. WANG,[1] C. L. LEE,[1] K. H. YANG[2]

[1] Institute of Applied Chemistry, Chinese Culture University, Hwa Kang, Yang Ming Shain, Taipei, Taiwan, Republic of China

[2] Van Nung Institute of Technology & Commerce, 63-1, Shui-wei Li, Chungli, Taoyuan, Taiwan, Republic of China

ABSTRACT: Fire-resistant polyurethane ionomers successfully synthesized at our laboratory have been proved by infrared spectra. In aqueous solution, the surface tension for fire-resistant polyurethane ionomers made by toluene diisocyanate or isophorone diisocyanate was found to decrease substantially with increasing concentration of 1,4-bis(2-hydroxyethyl)piperazine but to increase gradually with increasing phenylphosphonic acid or 1,4-bis(2-hydroxyethyl)piperazine with the phenylphosphonic acid concentration used to prepare these ionomers. For 1,4-bis(2-hydroxyethyl)piperazine-based polyurethane ionomers made by toluene diisocyanate or isophorone diisocyanate in aqueous solution, the number-average particle sizes of these ionomers decrease drastically with increasing 1,4-bis(2-hydroxyethyl)piperazine concentration, as a result of intramolecular interaction. On the other hand, for both phenylphosphonic acid and 1,4-bis(2-hydroxyethyl)piperazine with phenylphosphonic acid–based polyurethane ionomers, their average particle size increased with increasing phenylphosphonic acid or 1,4-bis(2-hydroxyethyl)piperazine with phenylphosphonic acid concentration. This may be attributed to the results of intermolecular interaction. Obviously, the limiting oxygen index values are seen to be higher for the isophorone diisocyanate type than for the toluene diisocyanate type of fire-resistant polyurethane ionomer. In fact, our experimental results suggest that the isophorone diisocyanate types of fire-resistant polyurethane ionomers provide good fire-resistance. For self-cured films of fire-resistant polyurethane ionomers, the tensile strength at breaking point increases with increasing the concentration of fire retardants, but the elongation at breaking point for these ionomers, on the other hand, appears to decrease with increasing concentration of fire retardants. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 19–26, 1998

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INTRODUCTION

In recent years, the use of fire-resistant polyurethane resin in leather, building, and textile industries has increased rapidly. Owing to environmental protection becoming increasingly important, the organic solvent used as a diluent for synthetic resin has gradually been replaced by water, a non-pollutant solvent. For this reason, the development of water-based fire-resistant resins, special types of resins with high solid content, powder resins, and ultraviolet-curable resins becomes important both at present and in the future.

Fire-resistant[1–3] polyurethane ionomers used as a foam-coating or dipping fabrication for cotton, polyester, dacron/cotton fiber, and other fibers could be prepared as shown in Scheme 1.

The efficacy of fire retardation of polyurethane
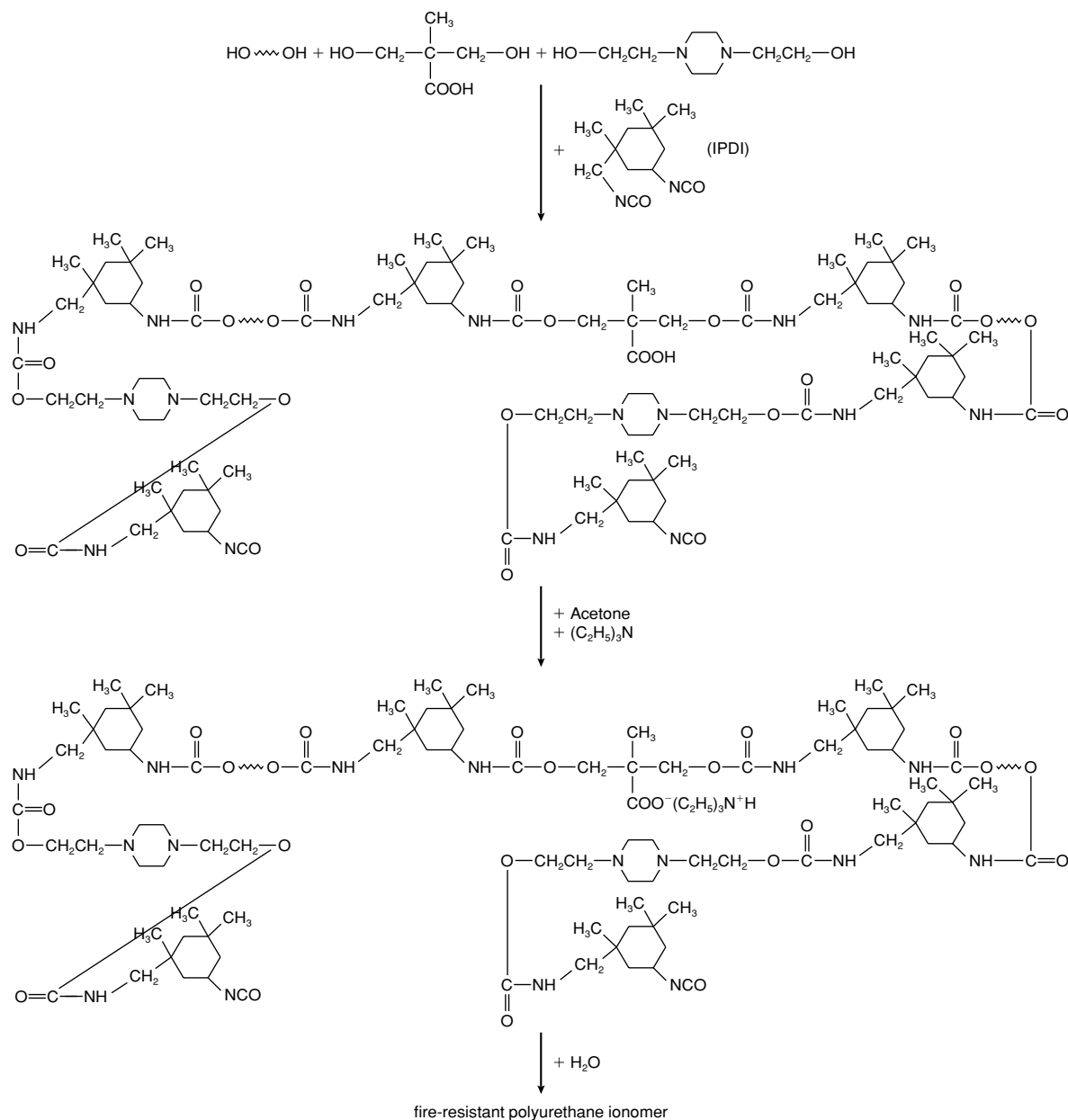
Scheme 1

ionomers on fibers may depend on the amount and type of fire retardants[4-6] incorporated into the polyurethane ionomer.[7-9] This information is very limited in the literature. Therefore, we attempted to explore a unique way of synthesizing the fire-resistant polyurethane ionomers and to further investigate their physical properties, that is, the surface tension, the number-average particle size, the limiting oxygen index, the tensile strength, and the elongation at break.

EXPERIMENTAL

Materials

Toluene diisocyanate (TDI) and isophorone diisocyanate (IPDI) were purchased from Merck Co., and dimethyolpropionic acid was received from Alcolac Industrial Chemicals. Polyester with a molecular weight of 2800 (OH number $\simeq$ 40.1) and polypropylene glycol with a molecular weight
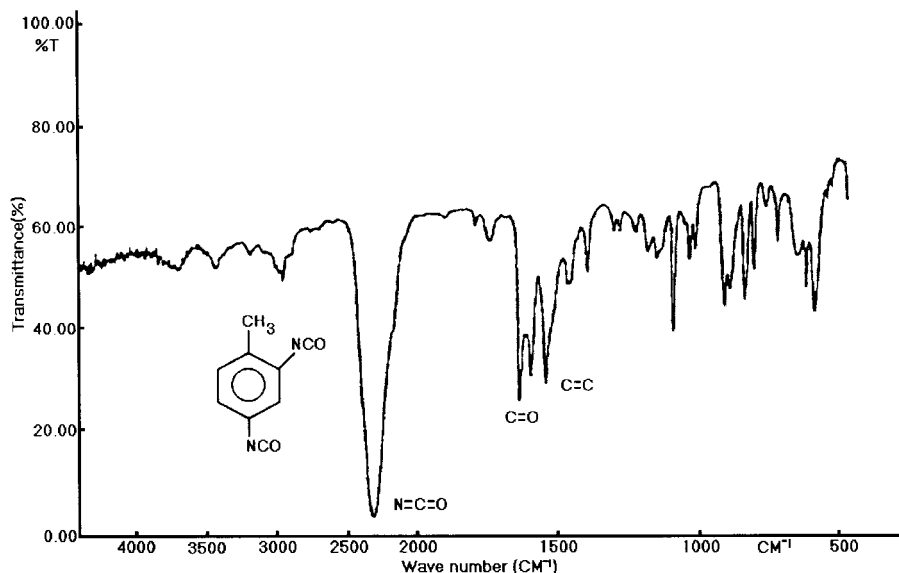
Figure 1 Spectra of TDI at 25 ± 0.05°C.

of 1000 (OH number ≃ 113) were obtained from Tai Chin Chemical Industry Co., and Chiunglong Petrochemical Co., respectively. 1,4-bis(2-Hydroxyethyl)piperazine (BHP) and *N,N*-dimethylacetamide were supplied by Aldrich Chemical Co., Inc. Phenylphosphonic acid (PPA) and epoxy resin (BE-188, equiv wt-186) were obtained from Tokyo Kasei Kogyo Co., and Chang Chun Petrochemical Co., Ltd., respectively. Acetone was received from Yakuri Chemicals Co., Ltd. All of

these chemicals were used without further purification.

Methods

A 1000-ml four-necked Pyrex glass flask equipped with a stirrer, thermometer, and condenser was charged with 0.018 equivalent of polyester (molecular weight ≃ 2800; OH number ≃ 40.1), 0.003 equivalent of polyethylene glycol (molecular
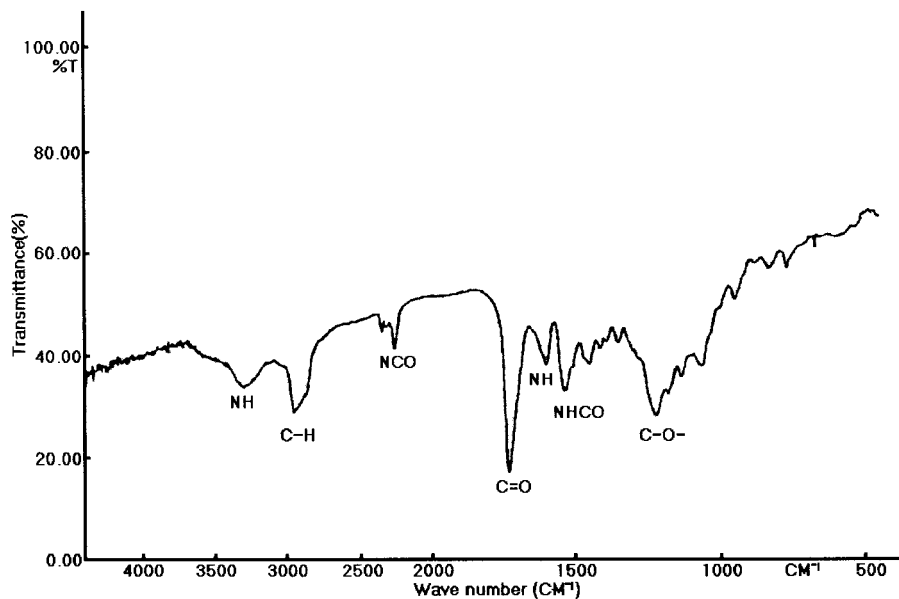

Figure 2 Spectra of fire-resistant NCO-terminated PU prepolymer formed after 2-h reaction at 25 ± 0.05°C.
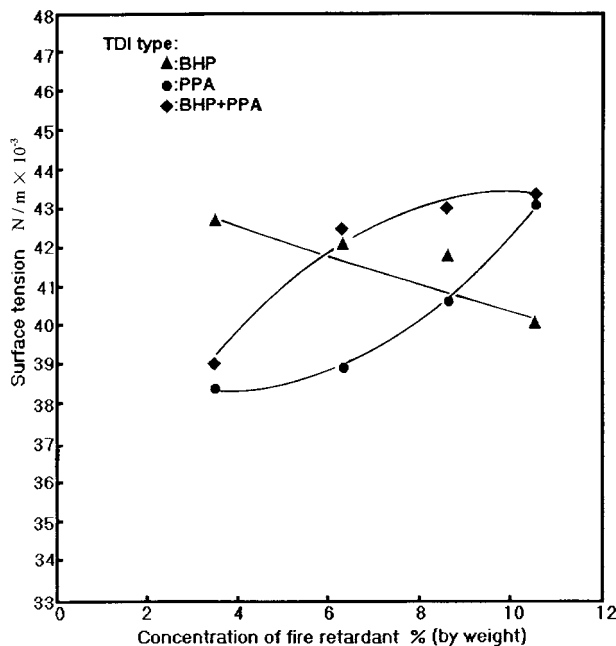
Figure 3 Plot of the surface tension versus the concentration of fire retardants used to prepare TDI-type fire-resistant PU ionomers at $25 \pm 0.05°C$.

weight $\simeq 6000$), 0.009 equivalent of epoxy resin (BE-188, equiv wt $\simeq 186$) and 0.06 equivalent of dimethylolpropionic acid in the presence and absence of 1,4-bis-(2-hydroxythyl)piperazine (0–12% by wt), phenylphosphonic acid (0–12% by wt), and 1,4-bis(2-hydroxyethyl)piperazine with phenylphosphonic acid (1 : 1 equivalent ratio; 0–12% by wt), respectively. A 0.108 equivalent of IPDI was subsequently added and reacted in the presence of dibutyltin dilaurate (0.2% by wt) as a catalyst at around 100°C for 5 h to form an excess diisocyanate (NCO)-terminated polyurethane (PU) prepolymer. A 0.034 equivalent of triethylamine was then reacted with NCO-terminated PU prepolymer dissolved in 78 g of acetone to form a quaternized NCO-terminated PU prepolymer. After approximately 340 g of water was added to the above quaternized fire-resistant PU prepolymer, the fire-resistant PU ionomers with 30% solid content were obtained. After the acetone was completely removed from fire-resistant PU ionomer liquids by evaporation, the surface tensions and the number-average particle size of these ionomer liquids were fully investigated with a FACE surface tensiometer, CBVP-A3 type (Kyowa Interface Science Co., Japan) and a dynamic light-scattering spectrophotometer DLS-70 (Otsuka Electronic Co., Japan), respectively, at room temperature. The 1-mm dry film of fire-resistant

PU ionomer with 10% solid content was prepared for tensile and elongation testing by Instron 1130.

A dry fire-resistant PU ionomer film of 12 mm length and 4.5 mm width was placed in a limiting oxygen index (LOI) chamber to be burned in the presence of a controlled ratio of oxygen and nitrogen gases. After this film was burned for 3 min, the LOI measured was based on the following equation:

$$LOI = \frac{O_2 \text{ (L/minute)}}{O_2 \text{ (L/minute)} + N_2 \text{ (L/minute)}} \times 100\% \quad (1)$$

where O_2 and N_2 represent the amounts of oxygen and nitrogen gases per minute flowing into the combustion chamber. The experimental error for the aforementioned measurements was estimated to be within ± 0.5.

RESULTS AND DISCUSSION

The infrared (IR) spectra for TDI and fire-resistant NCO-terminated PU prepolymer are given in
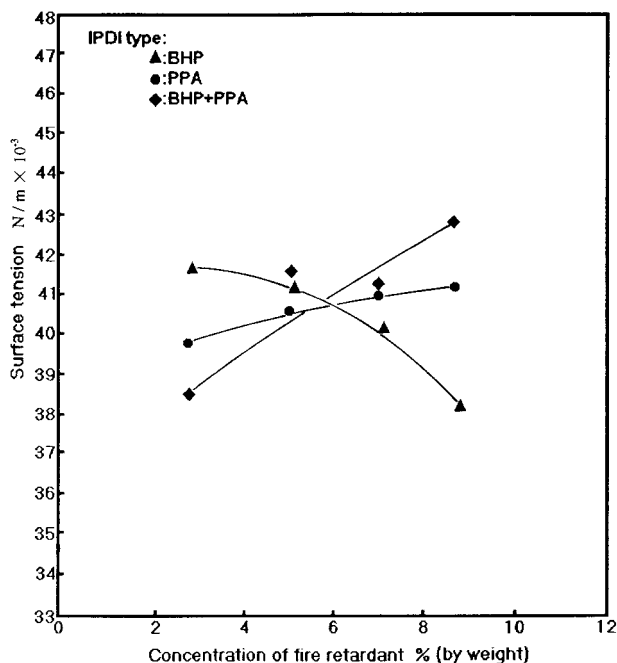

Figure 4 Plot of the surface tension versus the concentration of fire retardants used to prepare IPDI-type fire-resistant PU ionomers at $25 \pm 0.05°C$.
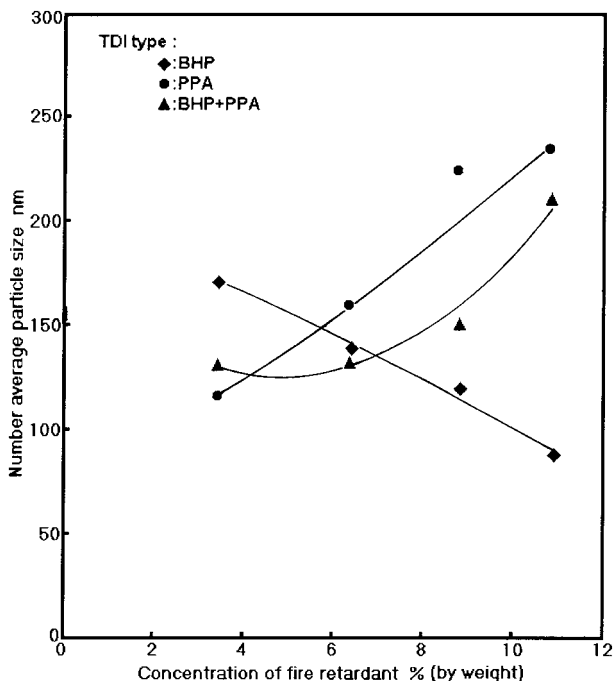
Figure 5 Plot of the number-average particle size versus the concentration of fire retardants used to prepare TDI-type fire-resistant PU ionomers at 25 ± 0.05°C.

Figures 1 and 2, respectively. The OH functional group of 1,4-bis(2-hydroxyethyl)piperazine, phenylphosphonic acid, or BHP mixed with PPA reacted rapidly with TDI in the presence of epoxy resin, dimethylol propionic acid, and polyester to form fire-resistant NCO-terminated PU prepolymer (Fig. 2). This is demonstrated by the formation of the absorbance peaks at around 1540 cm^{-1} (NHCO), 1620 cm^{-1} (NH), 1720 cm^{-1} (C = O), 1240 cm^{-1} (C—O—), and 3300–3400 cm^{-1} (NH) and by a substantially decreased absorbance peak at around 2275 cm^{-1} (NCO) in comparison to the absorbance peak of NCO given in Figure 1. These IR spectra suggest that the BHP, PPA, or BHP with PPA is considered to be incorporated into the main chain of the NCO-terminated PU prepolymer.

The measurements of the surface tensions for the TDI type of fire-resistant PU ionomer aqueous solution as a function of the concentration of BHP, PPA, and BHP with PPA, respectively, are given in Figure 3. It clearly indicates that the surface tension decreases with increasing the concentration of BHP used to prepare a fire-resistant PU ionomer, as a result of increased hydrophobic chains of BHP at the surface of the aqueous solution. As the BHP, a fire-resistant component, was

replaced by PPA or BHP with PPA used to make the fire-resistant PU ionomer, the surface tension of this ionomer aqueous solution was found to increase gradually with increasing concentration of PPA or BHP with PPA. Owing to the hydrogen bond interaction between ionomer molecules themselves and ionomer-water molecules, resulting from more hydrophilic groups of PPA attached to the backbone of the fire-resistant PU ionomer molecule, hydrogen bond interaction may enable the hydrophobics of the fire-resistant PU ionomers adsorbed at the air–water interface to become even more ordered. Thus, the surface tension increases. For the IPDI type of fire-resistant PU ionomers, on the other hand, the surface tension data (Fig. 4) are seen to decrease rapidly with an increase of BHP concentration but to increase gradually with increasing concentration of PPA or BHP with PPA. The reason is the same as aforementioned for the TDI type of fire-resistant PU ionomer system. However, the surface tension data are seen to be slightly lower for the IPDI type than for the TDI type of PU ionomer aqueous solution. This is the result of more hydrophobic chains of IPDI-type PU ionomer molecules being adsorbed at the air–water interface. The number-average particle size as a function of
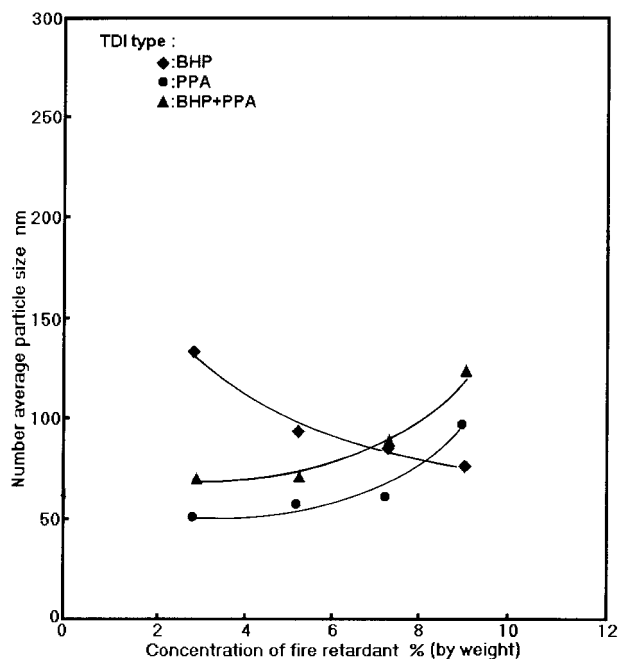

Figure 6 Plot of the number-average particle size versus the concentration of fire retardants used to prepare IDPI-type fire-resistant PU ionomers at 25 ± 0.05°C.
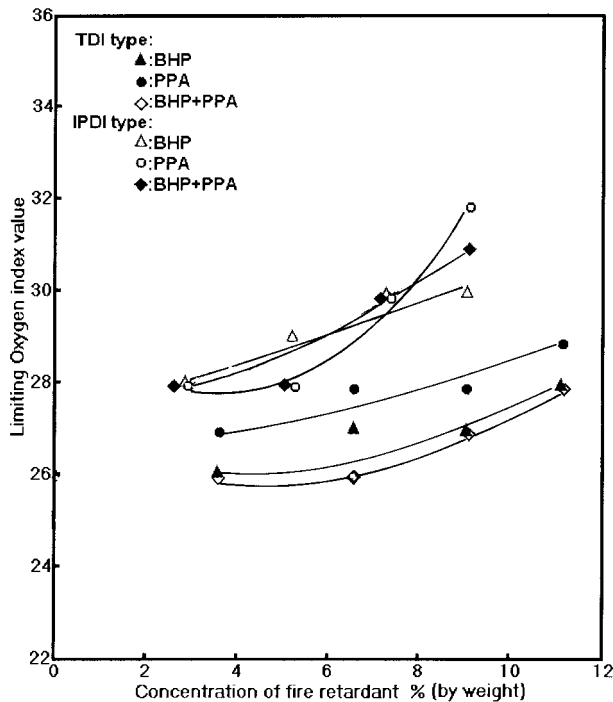
Figure 7 LOI value for fire-resistant PU ionomers as a function of the concentration of fire retardants.

the concentration of BHP, PPA, and BHP with PPA for the TDI type of fire-resistant PU ionomer is given in Figure 5. Figure 5 shows that the number-average particle size drastically decreases with increasing concentration of BHP, but increases significantly as the concentration of PPA or BHP with PPA increases further. This is because the increased OH functional group of the BHP molecule attached to the backbone of ionomer molecules with less steric effect may enhance the intramolecular interaction of ionomer molecules. The TDI-type ionomer molecule due to the intramolecular interaction is likely to form compact conformation or small aggregates. Therefore, the number-average particle size decreases. Furthermore, as a fire-resistant agent (BHP) was replaced by PPA or BHP with PPA, the number-average particle size seems to increase with an increase of the concentration of PPA or BHP with PPA. This may be attributed to an increased amount of PPA or BHP with PPA attached to the main chain of PU ionomer molecules with steric effect strongly preventing the intramolecular interaction to occur. However, the intermolecular interaction may dominate the whole process for PU ionomer molecules containing PPA or BHP with PPA present in the aqueous solution. This

interaction may substantially increase the free volume of PU ionomer molecules in aqueous solution. Thus, the number-average particle size increases. Under approximately the same experimental condition, the same experimental trend happens to the system of IPDI-type fire-resistant PU ionomer (Fig. 6). The explanation of Figure 6 is the same as that described in Figure 5, but the magnitude of the average particle size is larger for the PU ionomer made by TDI than for the PU ionomer made by IPDI. As a result of our experimental data, it appears that the TDI-type ionomer molecule may have stronger intermolecular interaction than the IPDI-type ionomer molecule as a whole. This may be why the average particle size of the TDI-type ionomer molecule is large. The LOI values for fire-resistant PU ionomer molecules as a function of various concentrations of BHP, PPA, and BHP with PPA are shown in Figure 7. For the TDI-type PU ionomer, the LOI values at BHP, PPA, or BHP/PPA concentration less than or equal to 10% by weight are lower than 28 as an effective fire-resistant value. On the other hand, at a concentration of BHP, PPA, or BHP/PPA greater than 10% by weight, the LOI values are slightly greater than 28. It appears that the LOI value is likely to be independent of the concentration of BHP, PPA, or BHP/PPA used to
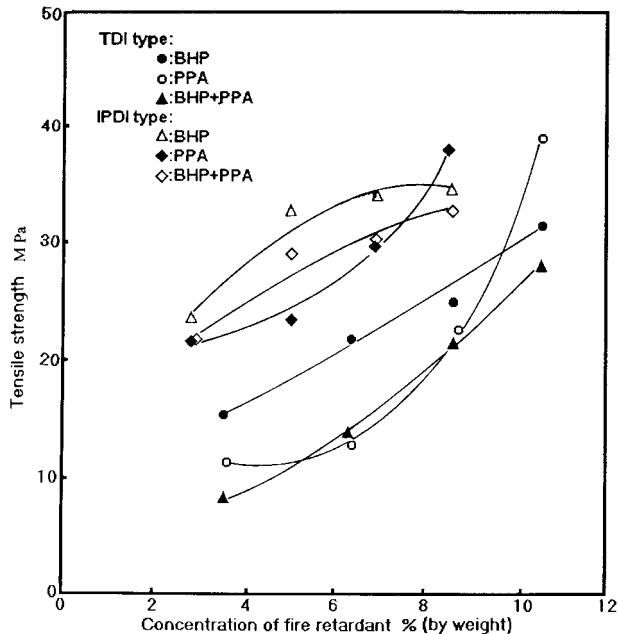

Figure 8 Plot of the tensile strength of dry film versus the concentration of fire retardants used to prepare TDI- and IDPI-type fire-resistant PU ionomers at 25 ± 0.05°C.
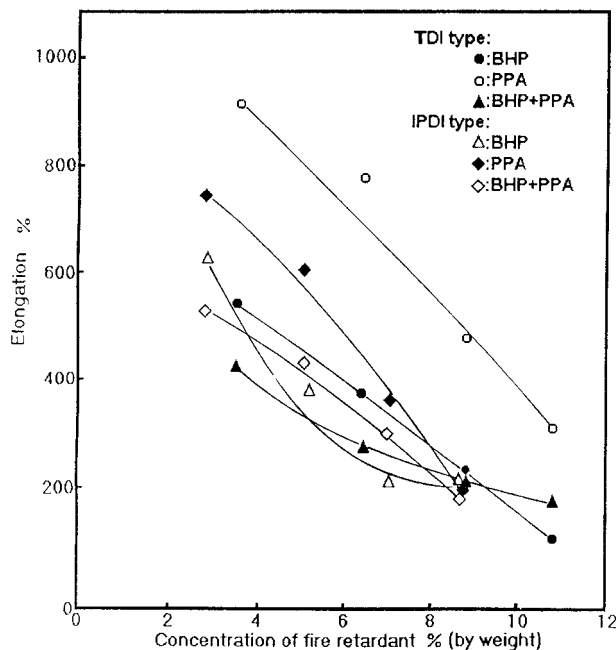
Figure 9 Plot of the elongation of dry film at the breaking point versus the concentration of fire retardants used to prepare TDI- and IDPI-type fire-resistant PU ionomers at $25 \pm 0.05°C$.

make TDI-type fire-resistant PU ionomers. More important, the LOI values for BHP-, PPA-, or BHP/PPA-based PU ionomers made by IPDI are significantly larger than 28, as the BHP, PPA, or BHP/PPA concentration increases. Obviously, the PO (phosphoric oxide) free radical from PPA-based PU ionomer molecules may readily react with hydrogen (H) or hydroxide (OH) free radical produced by the combustion of gases (that is, the mixture of oxygen and nitrogen gases) to form the less active HPO intermediate. As a result of less H and OH free radicals present in burning gases, the dry film of BHP-, PPA-, or BHP/PPA-based PU ionomers would be difficult to be burned out. Thus, the BHP, PPA, or BHP/PPA may be considered to be a good fire retardant for use in preparing IPDI-type instead of TDI-type PU ionomers.

The tensile strength and elongation properties of self-cured films of fire-resistant PU ionomers are given in Figures 8 and 9. Figure 8 clearly indicates that the tensile strength of dry films at breaking point gradually increases with increasing concentration of fire retardants of PU ionomers, as a result of increased crosslinking associated with intraionomer and/or interionomer molecular interactions resulting from increased functional groups (that is, $-COO-$, $-O-$,

$HO-P-OH$, $-N-CH_2CH_2OH$) in the backbone of PU ionomer molecules. This interaction between ionomer molecules themselves and/or between ionomer molecule and water forming hydrogen bonding may enhance the crosslinking of the PU ionomer molecule. Thus, the tensile strength of fire-resistant PU ionomer molecule becomes stronger. However, the tensile strength is seen to be stronger for PPA- than for BHP- or BHP/PPA-based PU ionomers at high concentration ($\geq 8\%$ by wt), as a result of more crosslinking formed, resulting from more functional groups (that is, $-COO-$, $-O-$, $HO-P-OH$) attached to the backbone of PU ionomer molecules. The elongation of dry films of fire-resistant PU ionomer molecules at breaking point (Fig. 9), on the other hand, is exactly opposite to the result illustrated in Figure 8. For fire-resistant PU ionomer molecules, the crosslinking was found to be weaker for the PU ionomer molecule with PPA than for the PU ionomer molecule with BHP at low concentrations ($<8\%$ by wt), thus causing the elongation of the PU ionomer molecule with PPA alone to be higher.

CONCLUSION

Fire-resistant PU ionomers, which have been successfully synthesized at our laboratory, are demonstrated to be BHP-, PPA-, and BHP/PPA-based PU ionomers by Fourier transform infrared spectra. The experimental results indicate that the surface tension for TDI-type or IPDI-type fire-resistant PU ionomer molecules in aqueous solution was found to decrease substantially with increasing concentration of BHP but to increase gradually with increasing the PPA or the BHP with PPA concentration used to prepare these ionomers. This may be the result of sufficient amounts of hydrophobics of PU ionomer molecules being adsorbed at the air–water interface and of the rearrangement of their orientation at the interface. For BHP-based PU ionomers made by TDI or IPDI in aqueous solution, the average particle sizes of these ionomers decrease drastically with increasing BHP concentration, as a result of intramolecular interaction. Contrarily, for both PPA- and BHP/PPA-based PU ionomers, their average particle sizes increase with increasing concentration of PPA or BHP with PPA; this may be attributed to the result of intermolecular interaction.

The LOI values appear to be higher for IPDI-type than for TDI-type fire-resistant PU ionomers. These

results suggest that IPDI-type BHP-, PPA-, or BHP/ PPA-based PU ionomers in fact provide good fire-resistant properties. For self-cured films of fire-resistant PU ionomers, the tensile strength at breaking point increases with increasing concentration of fire retardants, but the elongation at breaking point for these ionomers is seen to decrease with increasing concentration of fire retardants. This indicates that the strength of crosslinking with respect to the amount of fire retardants linked to the backbone of PU ionomers significantly affects the mechanical properties of these fire-resistant PU ionomers. However, our results indicate that poor tensile strength compared with that of commercial plastics is mainly due to the relatively poor crosslinking of the PU ionomer molecule.

REFERENCES

1. J. Troitzsch, *Makromol. Chem. Macromol. Symp.,* **74,** 125 (1933).
2. J. K. Rogers, *Mod. Plast. Int.,* **57,** Sep. (1992).
3. A. S. Wood, *Mod. Plast. Int.,* **46,** Sep. (1991).
4. J. F. Lee and D. Y. Chao, *Colloid Polym. Sci.,* **272,** 1508 (1994).
5. O. Lorenz and H. Hick, *Angew. Makromol. Chem.,* **72,** 115 (1978).
6. D. Dieterich and H. Reiff, *Angew. Makromol. Chem.,* **26,** 85 (1972).
7. Y. M. Kuo, C. T. Wu, and D. Y. Chao, *J. Appl. Polym. Sci.,* **60,** 2265 (1994).
8. J. J. Lee, Z. K. Chi, Y. M. Kuo, and D. Y. Chao, *J. Appl. Polym. Sci.,* **57,** 1005 (1995).
9. J. J. Lee, R. M. Shieh, H. H. Chang, and D. Y. Chao, *J. Appl. Polym. Sci.,* **60,** 2265 (1996).