

# On the Study of a PV Fast Maroon HFM Pigment Based Polyurethane Ionomer

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## SYNOPSIS

PV Fast Maroon HFM based polyurethane ionomers were successfully synthesized at our lab, and these ionomer structures have been proven by infrared spectra. In aqueous solution, the surface tension was found to be lower for the HFM pigment based polyurethane ionomer made by isophorone diisocyanate (IPDI) than for the HFM pigment-based polyurethane ionomer made by toluene diisocyanate (TDI), as a result of more hydrophobicity adsorbed at the surface of aqueous solution. The viscosity decreases with increasing the concentration of the HFM pigment used to prepare the HFM pigment based polyurethane ionomer, indicating that the structure of this ionomer is possibly considered to be a type of micelle. In addition, the number-average particle sizes are seen to be decreased with increasing the concentration of HFM pigment employed for making the HFM pigment based polyurethane ionomer. These results also suggest that the HFM pigment based polyurethane ionomer molecule could have a micelle-like structure. However, the 100% modulus property for both the IPDI type or the TDI type of PV Fast Maroon HFM based PU ionomer molecules appears to increase gradually with increasing the concentration of HFM, as a result of more crosslinking formed. © 1996 John Wiley & Sons, Inc.

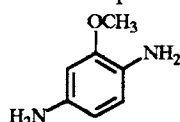
## INTRODUCTION

Owing to environmental protection becoming increasingly important, the organic solvent used as a diluent for pigment resin is gradually replaced by water, a nonpollutant solvent. For this reason, the development of water-based pigment resins becomes important at present.

In general, PV Fast Maroon HFM pigment can, indeed, react with toluene diisocyanate (TDI) or isophorone diisocyanate (IPDI) and dimethylol propionic acid in the presence of other additives to form water-based HFM pigment resins used for leather and other industries. The possible structure of water-based PV Fast Ma-

roon HFM pigment resin could be given as shown in Scheme 1.

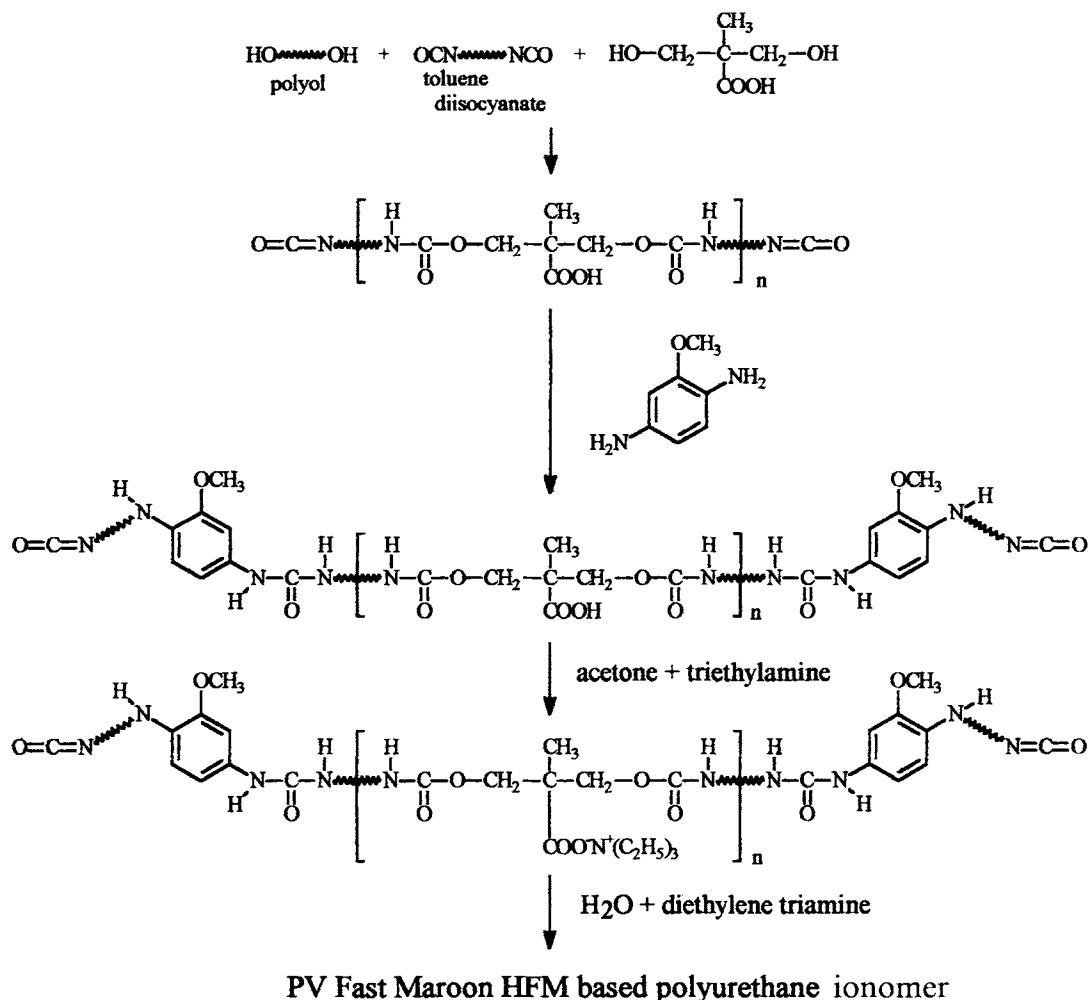
In the process of coloring, PV Fast Maroon HFM,



, at high concentration present in organic solvent, is likely to form aggregates on the surface of the leather. These aggregates will probably result in decreasing the chroma and lightness of HFM pigment on leather. To overcome this problem, the PV Fast Maroon HFM pigment based polyurethane ionomer is possibly used as a foam coating or dipping fabrication for leather.

Because the work on the synthesis and physical properties of water-based PV Fast Maroon HFM pigment resin has not been published so far, we attempted to study the unique way to make this water-based pigment polyurethane resins and to further explore their physical properties.<sup>1-10</sup>

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Scheme 1

## EXPERIMENTAL

### Material

PV Fast Maroon HFM and dimethylol propionic acid were purchased from Aldrich Co. (Milwaukee, WI) and Alcolaco Industrial Chemicals (USA), respectively. Isophorone diisocyanate (IPDI), toluene diisocyanate (TDI), triethylamine, diethylene triamine, and acetone were supplied by Merck Co. Polyester (made by the reaction of adipic acid with 1,6-hexanediol and diethylene glycol with a molecular weight of 2800; OH number  $\approx$  40.1) and *N,N*-dimethyl acetamide (analyzed reagent) were received from Tai Chin Chemical Industry Co. Ltd. (Taiwan) and J. T. Baker Chemicals (USA), respectively. Polyethylene glycol, with a molecular weight of 6000,

was supplied by Sino-Japan Chemical Co. All of these chemicals were used without further purification.

### Method

A 0.022 equivalent of polyester with a molecular weight of 2800 (OH number  $\approx$  40.1), 0.25–1.25% PV Fast Maroon HFM (by weight), and 0.004 equivalent of polyethylene glycol 6000 were charged to a 1000-liter four-necked reaction kettle equipped with a stirrer, thermometer, and condenser containing a 0.088 equivalent of dimethylol propionic acid under agitation at 80°C. Subsequently, a 0.157 equivalent of isophorone diisocyanate was added slowly at around 95°C for about 2 h to form NCO-terminated prepolymer. A 0.044 equivalent of triethylamine was

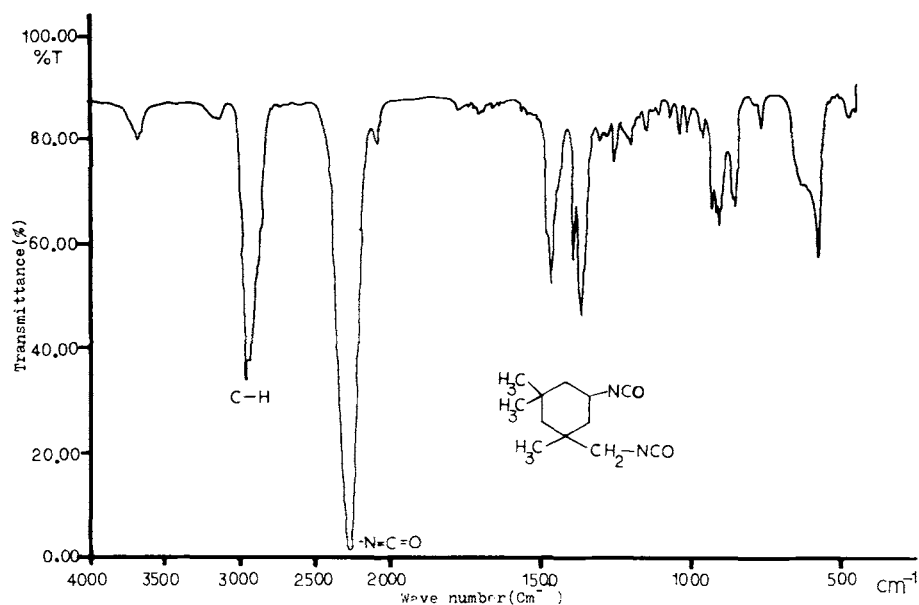


Figure 1 Spectra of isophorone diisocyanate at  $25 \pm 0.05^\circ\text{C}$ .

then reacted with NCO-terminated prepolymer dissolved in 80 g acetone as an organic solvent at 600 rpm for about 20 min to form quaternized NCO-terminated HFM prepolymer. This quaternized NCO-terminated prepolymer reacted further with approximately 320 g water in the presence of a small amount of diethylene triamine to form PV Fast Maroon HFM-based polyurethane ionomers.

After removing the acetone by blowing it out *in vacuo*, the viscosities and surface tensions of HFM pigment based polyurethane ionomer aqueous solutions with approximately 30% solids were investigated at room temperature using a Brookfield viscometer and a FACE surface tensiometer, CBVP-A3 type (Kyowa Interface Science Co., Japan), respectively. The average particle sizes of these HFM based polyurethane ionomers were also examined using a dynamic light-scattering spectrophotometer DLS-700 (Otsuka Electronic Co., Japan). A 1 mm thickness film made by a PV Fast Maroon HFM based polyurethane ionomer aqueous solution poured into a polypropylene disk dried in an oven at  $60^\circ\text{C}$  was used for 100% modulus testing by an Instron 1130 (USA) at room temperature. The experimental error for the above measurements was estimated to be within  $\pm 0.5$ .

## DISCUSSION AND RESULTS

The infrared spectra for IPDI and PV Fast Maroon HFM are given in Figures 1 and 2, respectively. The

$\text{NH}_2$  functional group of PV Fast Maroon HFM will rapidly react with IPDI in the presence of polyester and dimethylol propionic acid to form NCO-terminated polyurethane (PU) prepolymer. This prepolymer, given in Figure 3, is demonstrated by the formation of the absorbance peaks at around  $1240\text{ cm}^{-1}$  (C—O—),  $1540\text{ cm}^{-1}$  (NHCO),  $1620\text{ cm}^{-1}$  (NH),  $1720\text{ cm}^{-1}$  (C=O), and  $3300\text{--}3400\text{ cm}^{-1}$  (NH) and by substantially decreased absorbance peak at around  $2275\text{ cm}^{-1}$  (NCO). In comparison of Figures 1–3, these results suggest that the reaction of IPDI with PV Fast Maroon HFM, polyester, and dimethylol propionic acid, followed with triethylamine, does, indeed, form a PV Fast Maroon HFM based PU ionomer. In aqueous solution, the surface tension measurements for the HFM-based PU ionomer made by IPDI or TDI at room temperature, given in Figures 4–5, were found to be independent of the HFM concentration used to prepare the HFM-based PU ionomer. In addition, the surface tensions were found to be lower for the HFM-based PU ionomer made by IPDI than the HFM-based PU ionomer made by TDI, as a result of more hydrophobic groups of IPDI adsorbed at the air–water interface. Our experimental results also indicate that the PV Fast Maroon HFM based PU ionomer, like surfactant, can substantially lower the surface tension of water, but one cannot obtain the critical micelle concentration (called CMC) from the plot of the logarithm surface tension vs. the HFM concentration. Thus, the PV Fast Maroon HFM based PU ionomer may be consid-

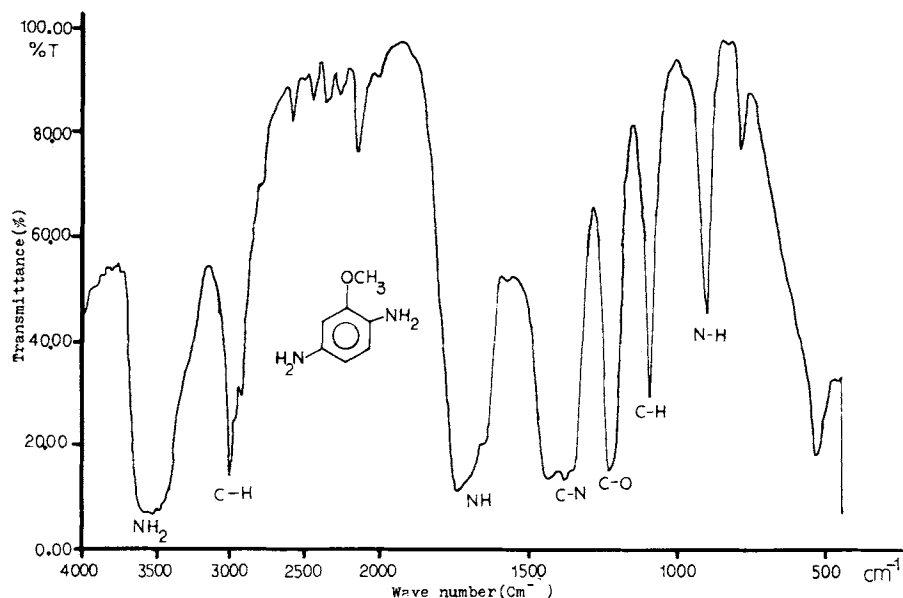


Figure 2 Spectra of PV Fast Maroon HFM at  $25 \pm 0.05^\circ\text{C}$ .

ered as a surface-active agent instead of a surfactant.

The viscosity measurements for PV Fast Maroon HFM based PU ionomer solutions appear to decrease with increasing HFM concentration and then to increase with further increasing HFM concentration, as shown in Figure 6. At a low concentration of HFM ( $\leq 0.5\%$  by weight), the HFM-based PU ionomer molecule, due to its intramolecular inter-

action, may form compact conformation (i.e., small aggregates), resulting in decreasing the viscosity of this ionomer solutions. On the other hand, the HFM-based PU ionomer molecule at a high concentration of HFM ( $>0.5\%$  by weight) is likely to form expanded conformation (i.e., large aggregates), as a result of large free volume resulting from intermolecular interaction of HFM-based PU ionomer molecules. In Figure 6, it also shows that the vis-

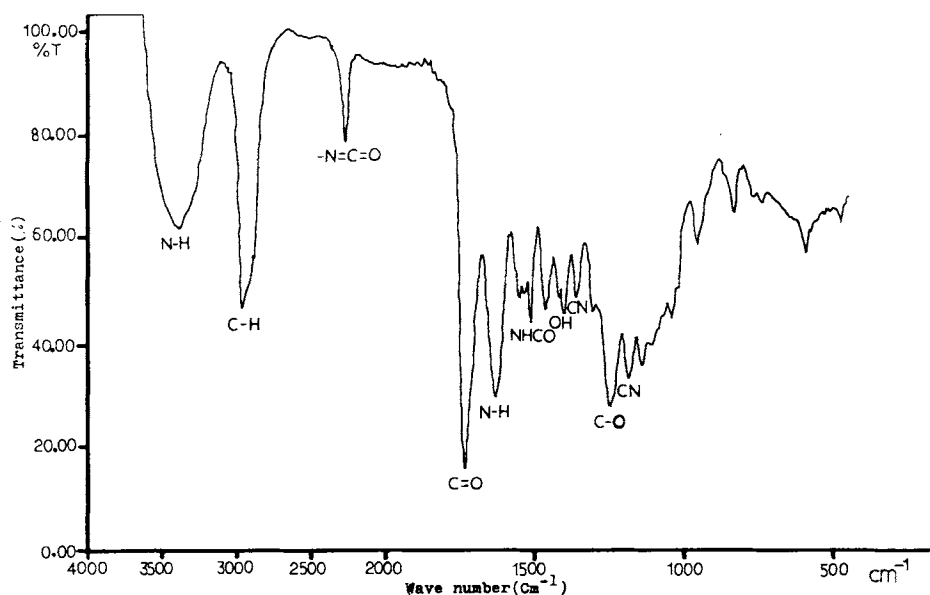
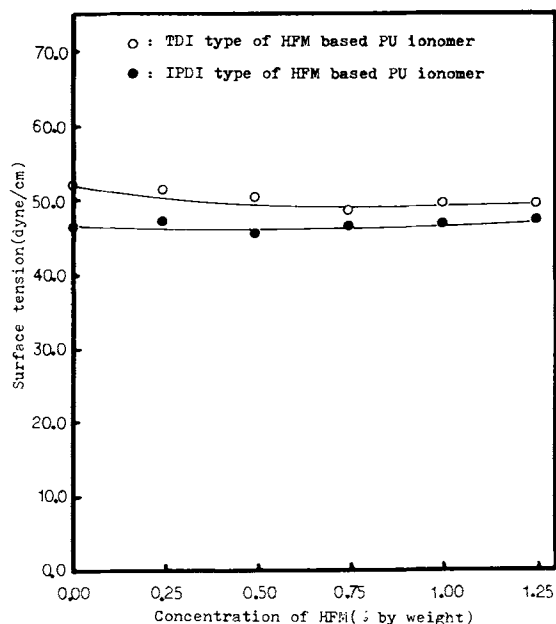
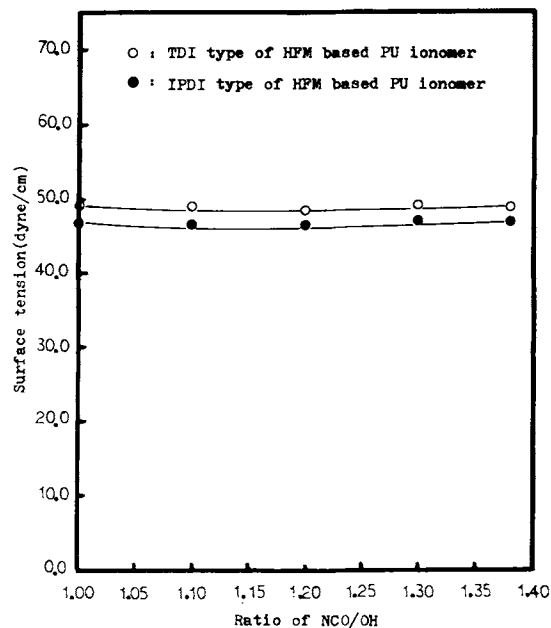


Figure 3 Spectra of PV Fast Maroon HFM based polyurethane ionomer formed after 2 h reaction, at  $25 \pm 0.05^\circ\text{C}$ .



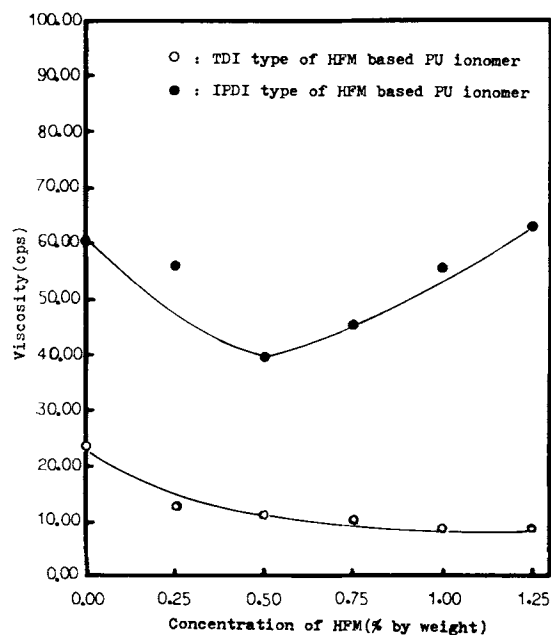
**Figure 4** Plot of the surface tension vs. the concentration of PV Fast Maroon HFM used to prepare HFM pigment based PU ionomer, at  $25 \pm 0.05^\circ\text{C}$ .



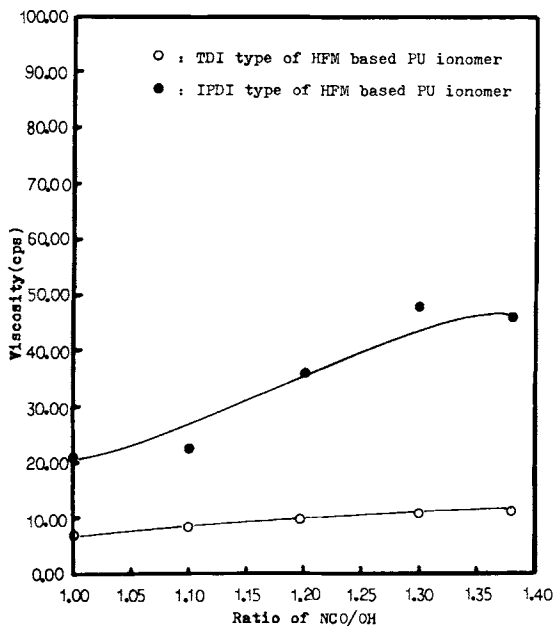
**Figure 5** Surface tension for PV Fast Maroon HFM based PU ionomer as a function of NCO/OH ratio at  $25 \pm 0.05^\circ\text{C}$ .

cosity of the HFM-based PU ionomer made by TDI is seen to be decreased with increasing the concentration of the HFM. This is the result of intramolecular interaction of the HFM-based PU ionomer molecule, resulting in forming compact conformation. However, the viscosity data are seen to be larger for the HFM-based PU ionomer made by IPDI. As expected, this is the result of large molecular weight of the HFM-based PU ionomer made by IPDI. Figure 7 shows that the viscosities increase with increasing the ratio of NCO/OH for the HFM-based PU ionomer molecule made by IPDI, and slightly increase with increasing the ratio of NCO/OH for the ionomer molecule made by TDI. This is because increased NCO functional groups may enhance the intermolecular interaction of ionomer molecules, resulting in forming expanded conformation, for instance, large aggregates. For the IPDI type of the HFM-based PU ionomer molecule, the number-average particle size of this ionomer molecule increases slightly with increasing the HFM concentration, as shown in Figure 8. Because the free volume of the ionomer molecule due to intermolecular interaction increases, the number-average particle size of this ionomer molecule increases. Figure 8 also indicates that, for the TDI type of HFM-based PU ionomer molecule, the number-average particle size of the ionomer molecule decreases with increasing HFM concentration. This is because the ionomer molecule

with less steric effect, probably generating strong intramolecular interaction, may lead to form compact conformation. Thus, the average particle size of the ionomer molecule decreases. Figure 9 illus-



**Figure 6** Plot of the viscosity vs. the concentration of PV Fast Maroon HFM used to prepare HFM pigment based PU ionomer, at  $25 \pm 0.05^\circ\text{C}$ .



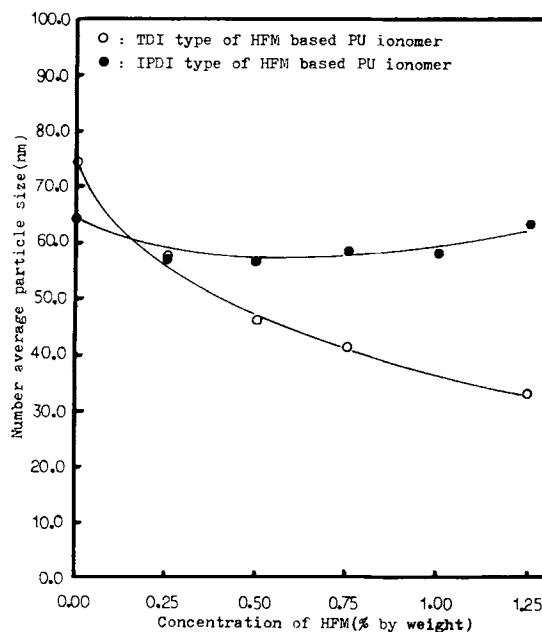
**Figure 7** Viscosity for PV Fast Maroon HFM based PU ionomer as a function of NCO/OH ratio at  $25 \pm 0.05^\circ\text{C}$ .

trates that, for both the IPDI type and the TDI type of HFM-based PU ionomer molecule, the number-average particle size of the ionomer molecule increases with increasing the ratio of NCO to OH. The reason is due to the increased NCO functional group on the main chain of the HFM-based PU ionomer molecule readily to interact with other ionomer molecules present in water. This intermolecular interaction may increase the free volume of the ionomer molecule. Therefore, the average particle size of the ionomer molecule increases.

The modulus property of self-cured films for both the IPDI type and the TDI type of HFM-based PU ionomer molecules, given in Figure 10, appears to increase gradually with increasing the concentration of HFM. This is the result of more crosslinking formed, resulting from more functional groups (i.e.,  $\text{—NH—}$ ) attached to the backbone of HFM-based PU ionomer molecules.

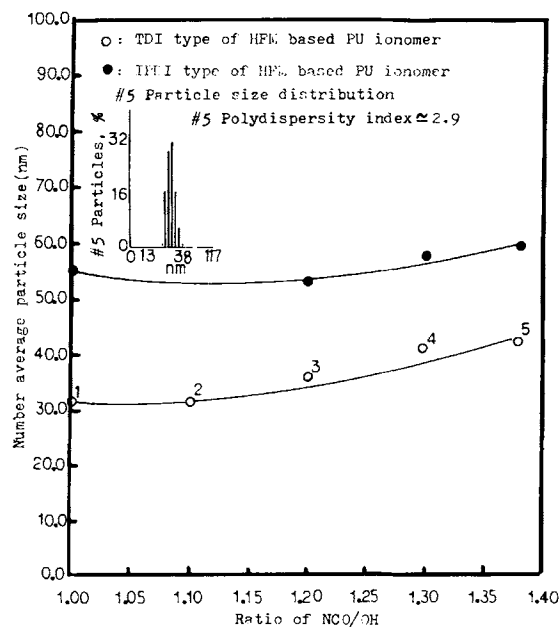
## CONCLUSION

Pigment-based PU ionomers that have been successfully synthesized at our lab are demonstrated to be a PV Fast Maroon HFM-based PU ionomer by FTIR spectra. In aqueous solution, the surface tension measurements were found to decrease with in-

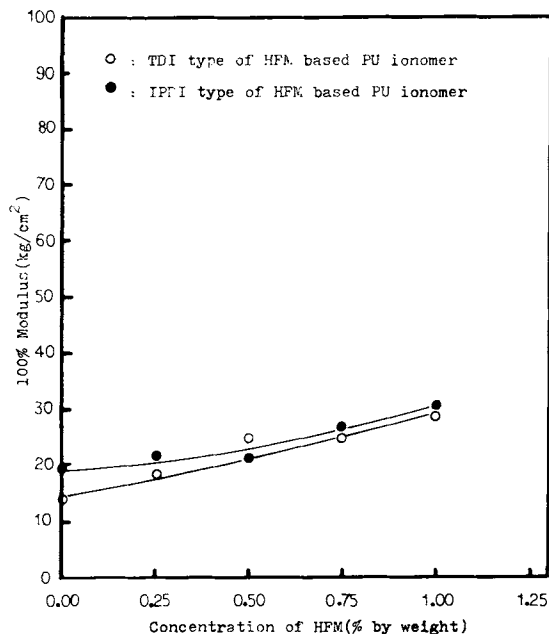


**Figure 8** Plot of the number average particle size vs. the concentration of PV Fast Maroon HFM used to prepare HFM pigment based PU ionomer, at  $25 \pm 0.05^\circ\text{C}$ .

creasing the concentration of the HFM pigment, and to be lower for the HFM pigment-based PU ionomer made by IPDI than for the HFM pigment-based PU ionomer made by TDI, as a result of more hydro-



**Figure 9** Number average particle size for PV Fast Maroon HFM based PU ionomer as a function of NCO/OH ratio at  $25 \pm 0.05^\circ\text{C}$ .



**Figure 10** Plot of the 100% modulus vs. the concentration of PV Fast Maroon HFM used to prepare HFM pigment based PU ionomer, at  $25 \pm 0.05^\circ\text{C}$ .

phobicity adsorbed at the air–water interface. For HFM pigment-based PU ionomers in aqueous solution, the viscosities of these ionomer solutions appear to decrease with increasing the concentration of the HFM pigment used to prepare these ionomers, indicating that they may have the compact conformation, for instance, the small aggregates (like small micelles). Furthermore, the number-average particle sizes of these ionomer solutions are also seen to be decreased with increasing the concentration of the HFM pigment. All these results suggest that the HFM pigment based PU ionomer molecules are likely to have a micelle-like structure.

The experimental results indicate that the 100% modulus of self-cured films for both the IPDI type and the TDI type of HFM pigment based PU ionomer molecules increases gradually with increasing the HFM concentration. This is the result of more crosslinking formed due to more functional groups (i.e.,  $-\text{NH}-$  groups) attached to the backbone of the HFM pigment based PU ionomer molecule.

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