

Study of Fluorescence from Fluorescent Dye-Based Polyurethane Ionomer

C. L. Wang,¹ Z. J. Zhang,¹ C. Y. Yang,² D. Y. Chao²

¹Department of Chemistry, Institute of Analytical Science Southwest Normal University, Beibei, Chongqing, P. R. China

²Institute of Applied Science, Hwa Kang, Yang Ming Shan, Taipei, Taiwan

Received 5 August 2002; accepted 23 November 2002

ABSTRACT: 6-Amino-2-(3-chloro-2-hydroxy-propyl)-benzo[de]isoquinoline-1,3-dione (DYE-A) and 2-benzyl-6-hydroxy-benzo[de]isoquinoline-1,3-dione (DYE-B) have been successfully synthesized in our lab, and their structures have been proven by IR, NMR, and mass spectra. The fluorescence performance appears to be better for DYE-A than for DYE-B as a result of DYE-A having more electron donating substituents that are strongly excited when absorbing UV light. These fluorescent dyes have further reacted with toluene diisocyanate and other additives to form the fluorescent dye-based polyurethane (PU) ionomer molecules, and the structures of these molecules have been demonstrated by IR spectra. In aqueous solution, our experimental results indicate that the fluorescence performance is seen to be better for DYE-A than for DYE-B. Increased concentration of DYE-A molecule attached to the backbone of the PU

ionomer molecule may reduce the fluorescence performance of this PU ionomer molecule, resulting from the intramolecular interaction between ionomer molecule itself. For the fluorescent dye-based PU ionomer molecule system, the average particle size of the fluorescent dye-based PU ionomer molecule in water increases with increasing concentration of the fluorescent dyes, as a result of increased free volume of the ionomer molecules. Our experimental results also illustrate that the tensile strength of self-cured film made by the fluorescent dye-based PU ionomer appears to increase with an increase in the concentration of DYE-A. This is the result of increased intermolecular interaction between ionomer molecules. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2723–2737, 2003

Key words: fluorescence; polyurethane ionomer

INTRODUCTION

In general, the fluorescent dyes are considered to be important chemicals that are widely used in both civil and military applications. Most patents indicate that some fluorescent dyes may not be uniformly dispersed or dissolved in normal resin material. Further, fluorescent dye molecules with less hydrophilic groups, such as 2-benzyl-6-hydroxy-benzo[de]isoquinoline 1,3-dione (DYE-B), may not react easily with toluene diisocyanate in the presence of other additives to form fluorescent dye-based polyurethane (PU).^{1–5} Therefore, new fluorescent dye molecules with more electron donating groups need to be developed. The fluorescent dye molecule with electron donating groups, 6-amino-2-(3-chloro-2-hydroxy-propyl)-benzo[de]isoquinoline-1,3-dione (DYE-A), has been successfully synthesized in our lab, and its structure, demonstrated by IR, NMR, and mass spectra, is given in Scheme 1.

This new fluorescent dye, DYE-A, will further react with toluene diisocyanate and other additives to form the structure of the fluorescent dye-based PU ionomer molecule given in Scheme 2.

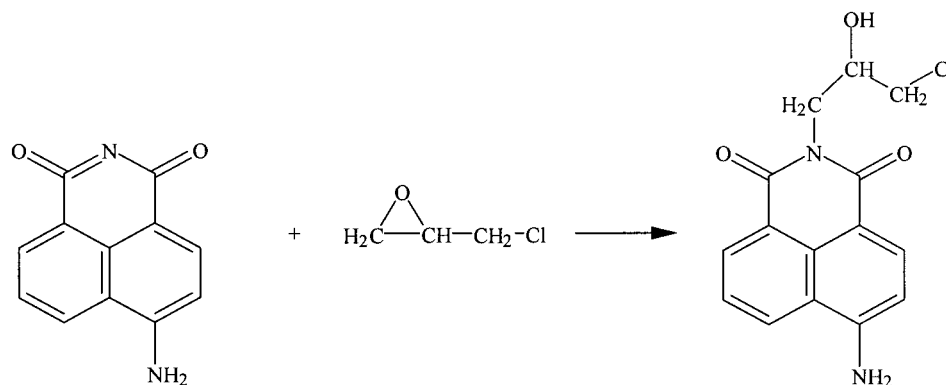
EXPERIMENTAL

Materials

Epichlorohydrin, sodium methoxide, benzylamine, 4-chloro-1,8-naphthalic anhydride, and 4-amino-1,8-naphthalimide were obtained from Acros Organics Co. (USA). Toluene diisocyanate (2,4 TDI, 100%), triethylamine, diethylene triamine, *N,N*-dimethylformamide, and acetone were supplied by Merck Co. (Germany). *N,N*-Dimethylacetamide and dimethylolpropionic acid were purchased from J. T. Baker Chemicals (New Jersey) and Alcolaco Industrial Chemicals (USA), respectively. Polyester (made by the reaction of adipic acid with 1,6-hexanediol and diethylene glycol) with a molecular weight of 2000 (OH number \approx 56), neopentyl glycol, and 1,4-butane diol were received from Taichin Chemical Industry Co. (Kaoshiung, Taiwan).

DYE-A was made by the reaction of 4-amino-1,8-naphthalimide with epichlorohydrin in the presence of sodium methoxide and *N,N*-dimethylformamide at

Correspondence to: D. Y. Chao, Institute of Applied Chemistry, Chinese Culture University, Hwa Kang, Yang Ming Shan, Taipei, Taiwan



Scheme 1

room temperature for 12 h (as part of Mr. C. L. Wang's Ph.D. dissertation).⁶ DYE-B was made by the reaction of 4-chloro-1,8-naphthalic anhydride with benzylamine in the presence of ethanol at 70–78°C and then with NaOH in tetrahydrofuran (THF) at 66°C for 3 h (as part of Mr. C.L. Wang's Ph.D. dissertation). All of these chemicals were used without further purification.

Method

Sodium methoxide (2.6 g), 4-amino-1,8-naphthalimide (10 g), and 100 mL *N,N*-dimethylformamide were charged into a 1000 mL four-necked Pyrex glass flask equipped with a stirrer, thermometer, and condenser. In the above flask 1.05 equivalent of epichlorohydrin was subsequently added and reacted at room temperature for 24 h to form the DYE-A. In order to remove the salts and impurities from the liquids, this new fluorescent dye was washed by 200 mL water and tested by thin liquid chromatography (TLC). After acetone was removed by blowing it out *in vacuo*, the new fluorescent dye, with above 96% purity and 85% yield, was obtained. A 0.0125 equivalent of 1,4-butanediol, 0.018 equivalent of polyester with a molecular weight of 2800 (OH number \approx 40.1), and 0.06 equivalent of dimethylolpropionic acid in the presence of 20 g *N,N*-dimethylacetamide were added to a 1000 mL four-necked reaction kettle equipped with a stirrer, thermometer, and condenser under agitation at 80°C. Subsequently, 0.128 equivalent of toluene diisocyanate and 0.0002 equivalent of DYE-A were added slowly in the above flask at 80–82°C for about a 4 h reaction to form NCO-terminated fluorescent dye (PU) prepolymer. A 0.06 equivalent of triethylamine was then reacted with this NCO-terminated fluorescent dye PU prepolymer and dissolved in 70 g acetone at 700 rpm for about 10 min to form quaternized fluorescent dye PU prepolymer. This quaternized PU prepolymer further reacted with 160 g water in the presence of a small

amount of diethylene triamine to form the fluorescent dye-based PU ionomer.

After removing the acetone by blowing it out *in vacuo*, the fluorescence and the surface tension of this fluorescent dye-based PU ionomer aqueous solution with approximately 20% solids were fully investigated at room temperature using a fluorescence spectrophotometer (F-4500, Hitach, Japan) and a FACE surface tensiometer, CBVP-A3 type (Kyowa Interface Science Co., Japan), respectively. The average particle size of this fluorescent dye-based PU ionomer in water was examined using a Dynamic light-scattering spectrophotometer, DLS-700 (Otsuka Electric Co., Japan). A 1 mm thickness of self-cured film made by a fluorescent dye-based PU ionomer aqueous solution poured into a polypropylene disk that was dried in an oven at 60°C was used for the tensile strength and 100% modulus testing by an Instron 1130 (USA) at room temperature. The experimental error for the above measurement was estimated to be within ± 0.5 .

RESULTS AND DISCUSSIONS

The IR spectra for 4-amino-1,8-naphthalimide and epichlorohydrin are shown in Figures 1 and 2, respectively. The reaction of 4-amino-1,8-naphthalimide with epichlorohydrin in the presence of sodium methoxide and *N,N*-dimethylformamide to form the DYE-A is demonstrated by the formation of the absorbance peaks at around 3650 cm^{-1} (OH), 3300–3450 cm^{-1} (NH), 1160 cm^{-1} (—CH—OH), 1630 cm^{-1} (C=O), 1500–1510 cm^{-1} (NC=O), and 768 cm^{-1} (Cl), given in Figure 3 in comparison to that of Figures 1 and 2.

The ¹H-NMR (CDCl_3) spectrum shows a signal for the proton of naphthalene, $\delta 7.934$ (naphthalene-H), as shown in Figure 4. According to the mass spectrum given in Figure 5, the molecular weight for the DYE-A molecule ion (M^+) is exactly 304.

These results shown in Figures 1 through 5 suggest that the reaction of 4-amino-1,8-naphthalimide with

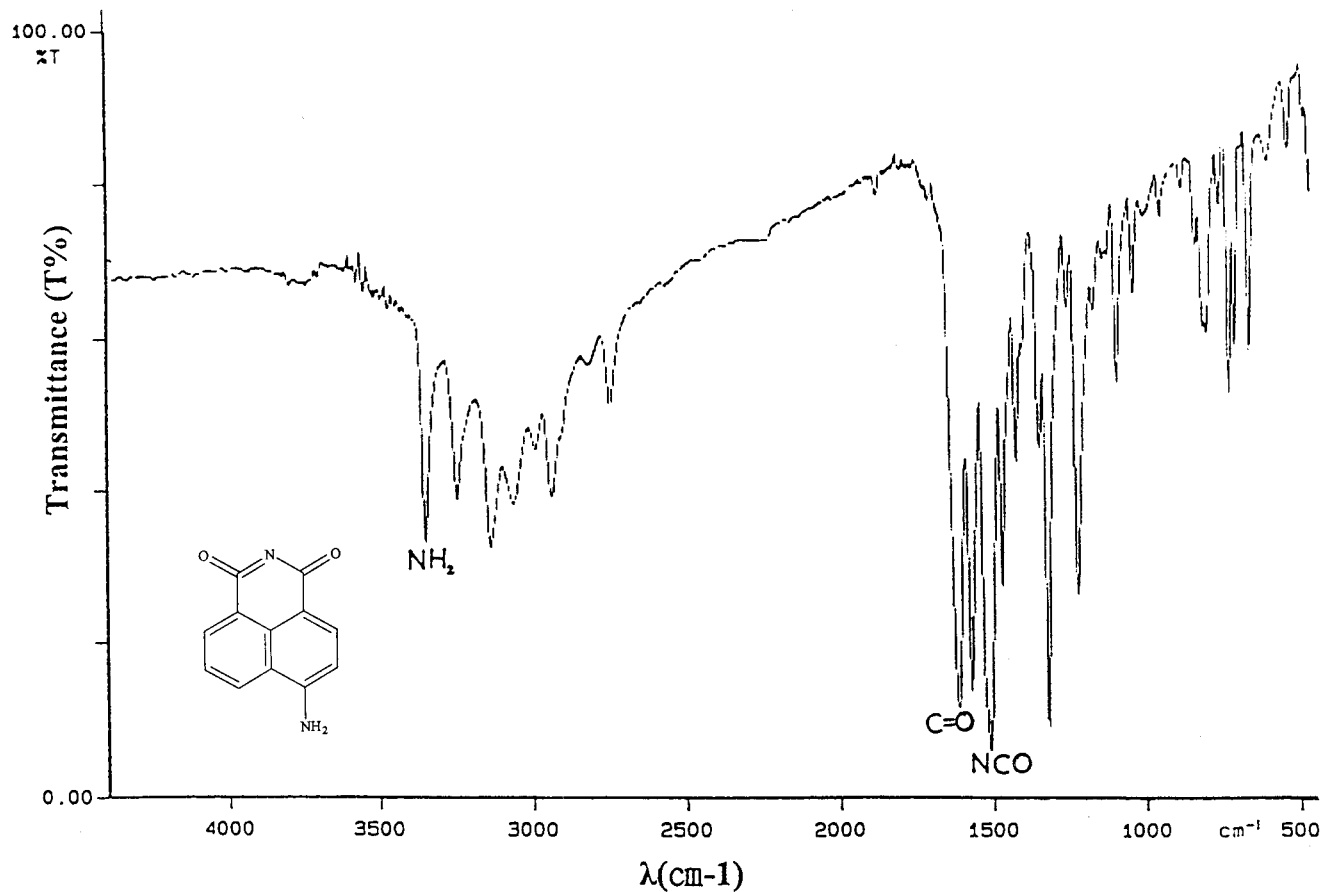


Figure 1 Spectrum of 4-amino-1,8-naphthalimide at $25 \pm 0.05^\circ\text{C}$.

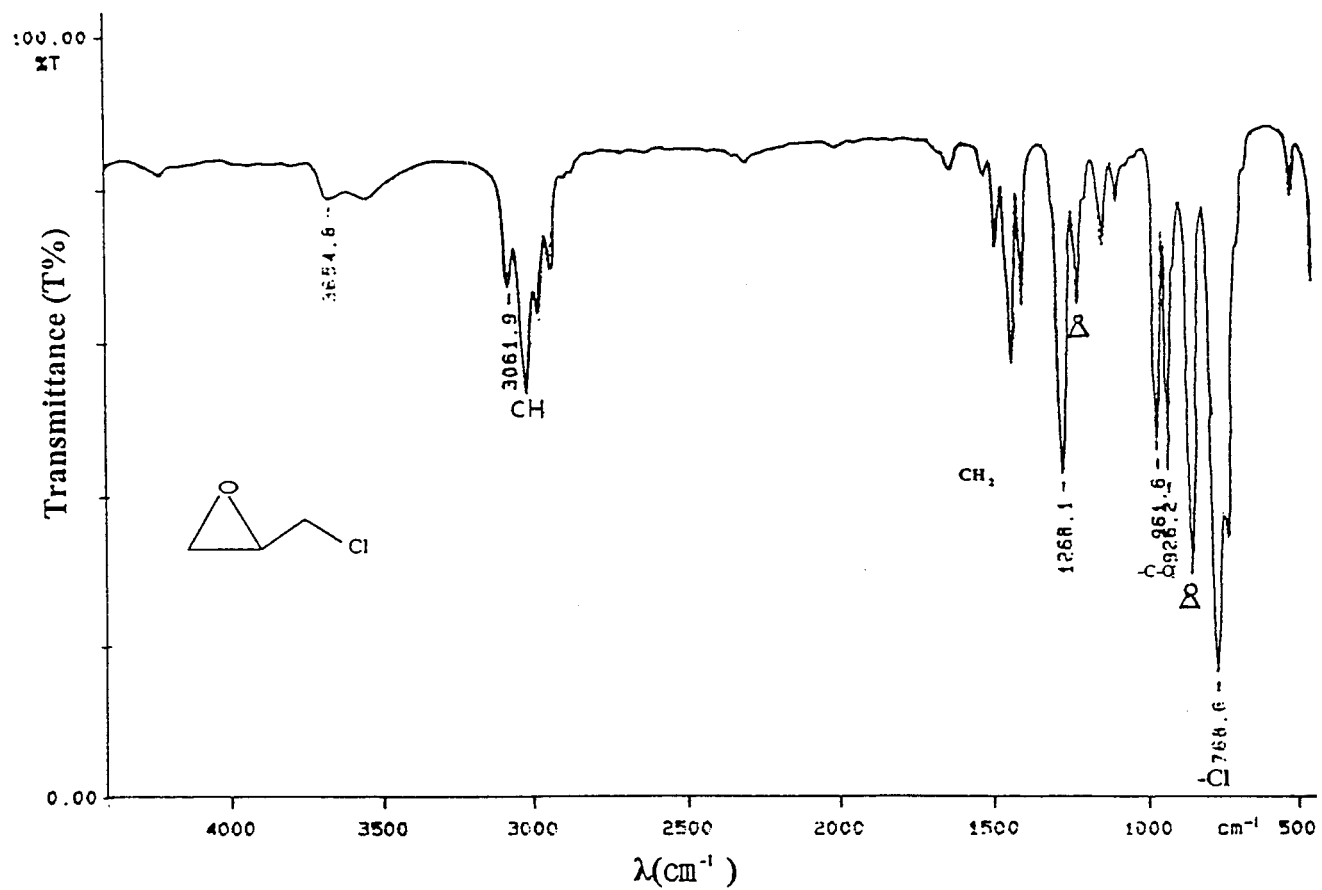


Figure 2 Spectrum of epichlorohydrin at $25 \pm 0.05^\circ\text{C}$.

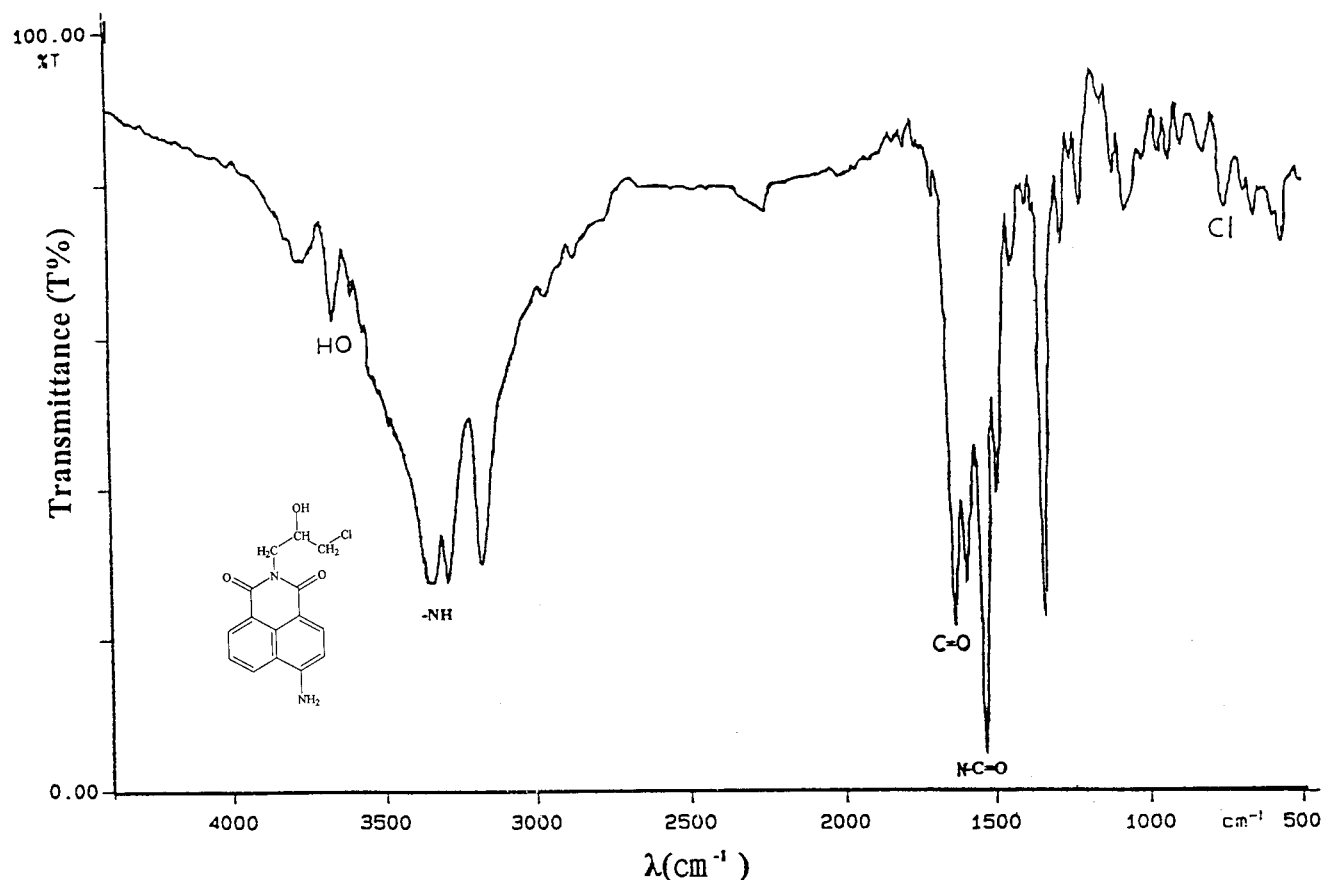


Figure 3 Spectrum of 6-amino-2-(3-chloro-2-hydroxy-propyl)-benzo[de]isoquinoline-1,3-dione at $25 \pm 0.05^\circ\text{C}$.

epichlorohydrin in the presence of sodium methoxide and *N,N*-dimethylformamide to form a new fluorescent dye, DYE-A, does take place. Further, the reaction of toluene with DYE-A and other additives to form the NCO-terminated fluorescent dye-based PU ionomer, given in Figure 6, is demonstrated by the formation of the absorbance peaks at around 768 cm^{-1} (Cl), 1250 cm^{-1} (C—O—), 1540 cm^{-1} (NHCO), 1620 cm^{-1} (NH), 1720 cm^{-1} (C=O), and $3300\text{--}3450\text{ cm}^{-1}$ (NH), and by the almost total disappearance of the absorbance peak at around 2275 cm^{-1} (NCO). The IR spectra for DYE-A and toluene diisocyanate are given in Figures 3 and 7, respectively. In comparison to Figures 6–8, these results suggest that the reaction of toluene diisocyanate with DYE-A and other additives to form a fluorescent dye-based PU ionomer molecule is quite possible.

To further deal with the fluorescence performance of a 0.01 g DYE-A and a 0.01 g DYE-B diluted 20 times in THF, respectively, a fluorescence spectrophotometer (F-4500, Hitach), was used. Their fluorescence spectra are given in Figures 8 and 9. Figures 8 and 9 indicate that the fluorescence performance for both DYE-A and DYE-B is 506.6 and 494 nm, respectively. The quantum yield of the fluorescent dye molecule and of the fluorescent dye-based PU ionomer molecule can be calculated according to the following equation:

$$Y_u = Y_s \times F_u / F_s \times A_s / A_u \quad (1)$$

where Y_u is the quantum yield of the unknown sample to be measured; Y_s is the fluorescence as a standard (quantum yield = 0.90); F_u is the integrated fluorescence intensity of unknown sample; F_s is the fluorescence intensity of fluorescein; A_s is the absorbance intensity of excitation wavelength for the fluorescein, and A_u is the absorbance intensity of excitation wavelength for unknown sample. The quantum yield for both DYE-A and DYE-B is 0.76 and 0.56, respectively. These experimental results suggest that the fluorescence performance is better for DYE-A than for DYE-B, as a result of more hydrophilic groups with electron donating substituents linked to the DYE-A molecule. These increased hydrophilic groups with more electron donating substituents may help the dye molecule to be excited easily when absorbing UV light. We not only studied the fluorescence of the fluorescent dye molecule itself, but also fully investigated the fluorescence performance of the fluorescent dye-based PU ionomer molecules. The experimental results of the fluorescence for these fluorescent dye-based PU ionomer molecules in water are given in Figures 10 and 11. Figures 10 and 11 clearly illustrate that the quantum yield for the fluorescent DYE-A-based PU ionomer molecule or the fluorescent DYE-B-based PU ionomer

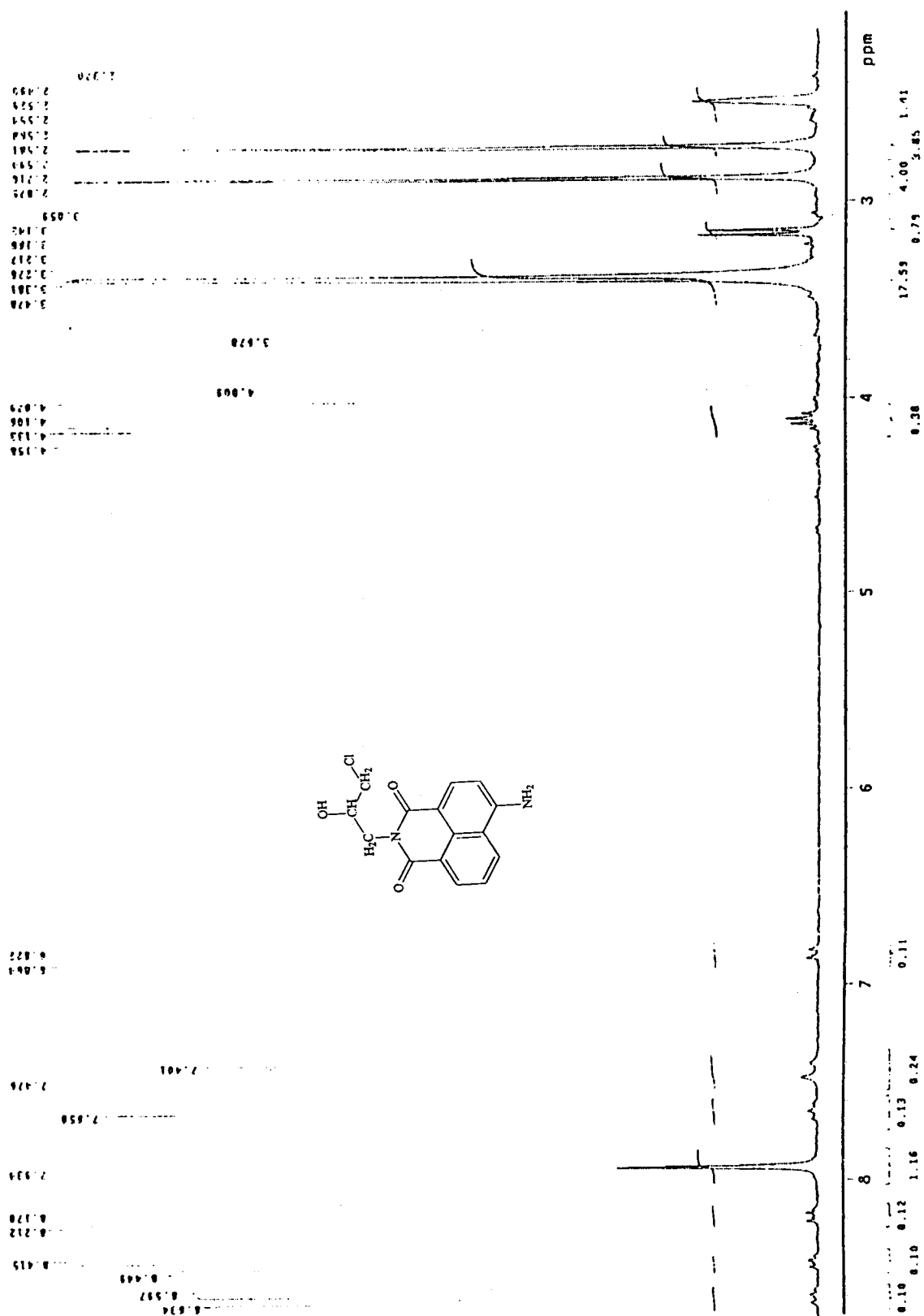


Figure 4 NMR spectrum of 6-amino-2-(3-chloro-2-hydroxy-propyl)-benzo[de]isoquinoline-1,3-dione at $25 \pm 0.05^\circ\text{C}$.

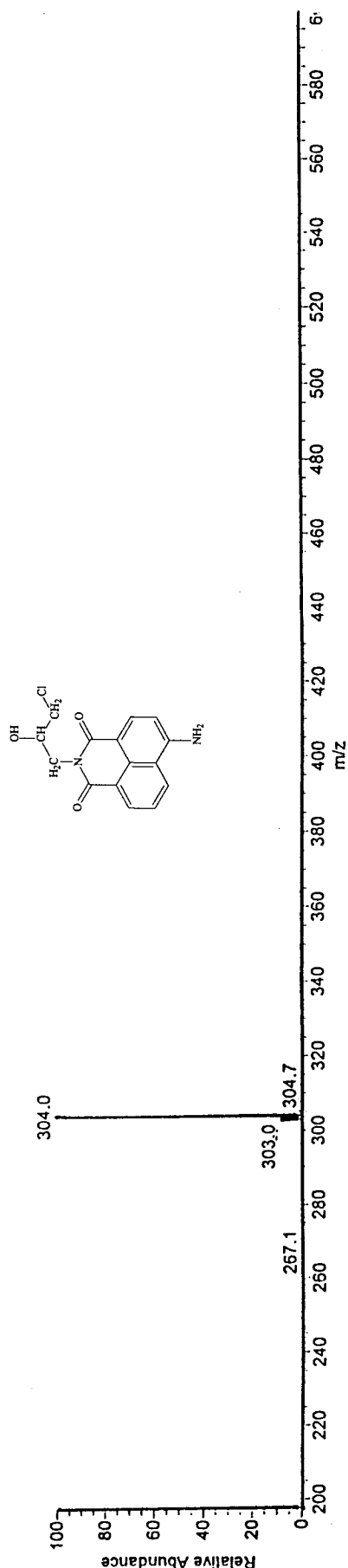


Figure 5 Mass spectrum of 6-amino-2-(3-chloro-2-hydroxy-propyl)-benzo[de]isoquinoline-1,3-dione.

molecule appears to decrease with increasing concentration of the fluorescent DYE-A or the fluorescent DYE-B, as a result of increased intramolecular interaction between hydrophilic groups of the ionomer molecule itself and the intermolecular interaction between ionomer-ionomer molecules themselves. This interaction of electron donating substituents may greatly reduce the aromatics of the PU ionomer molecule to be excited by UV light. However, the fluorescence performance is seen to be better for the DYE-A-based than for the DYE-B-based PU ionomer, as a result of the fluorescent DYE-A molecule having more electron donating groups. Further, increased hydrophilic groups with more electron donating substituents linked to the ionomer molecules may enhance the aromatics of the ionomer molecule to be excited by absorbing UV light. This explains why the fluorescent DYE-A-based PU ionomer has better fluorescence than the fluorescent DYE-B-based PU ionomer. The average particle size of the fluorescent DYE-A- or DYE-B-based PU ionomer molecules in aqueous solution increases with an increase in the concentration of the DYE-A or DYE-B used to prepare the PU ionomer molecules, as described in Figure 12. This is due to increased free volume of the ionomer molecule resulting from strong intermolecular interaction between ionomer-ionomer molecules and between ionomer-water molecules. Therefore, the average particle sizes of these ionomer molecules increase. In aqueous solution, the surface tension measurements, within experimental error, for the fluorescent DYE-A- or DYE-B-based PU ionomers, were found to be independent of the DYE-A or DYE-B concentration used to prepare these ionomers, at room temperature (Fig. 13). This is because the hydrophobic groups of the ionomer molecules adsorbed at the surface of water become saturated. Thus, the surface tension for the fluorescent DYE-A- or DYE-B-based PU ionomer molecule in water remains a constant. The tensile strength for self-cured film made by the fluorescent DYE-A- or DYE-B-based PU ionomer as a function of the concentration of DYE-A or DYE-B is shown in Figure 14. It clearly indicates that, for the fluorescent dye-based PU ionomer system, the tensile strength at the breaking point appears to increase with increasing concentration of the fluorescent DYE-A or DYE-B, as a result of increased intermolecular interaction between ionomer-ionomer molecules. This interaction, resulting from the functional groups of the ionomer molecules, may enhance ionomer molecule crosslinking, thus resulting in increasing the tensile strength of these ionomer molecules. On the other hand, the elongation of dry film made by the fluorescent DYE-A-based PU ionomer molecules at the breaking point appears to decrease with increasing concentration of the fluorescent DYE-A, as shown in Figure 15. Increased fluorescent DYE-A molecule linked to the backbone of the PU

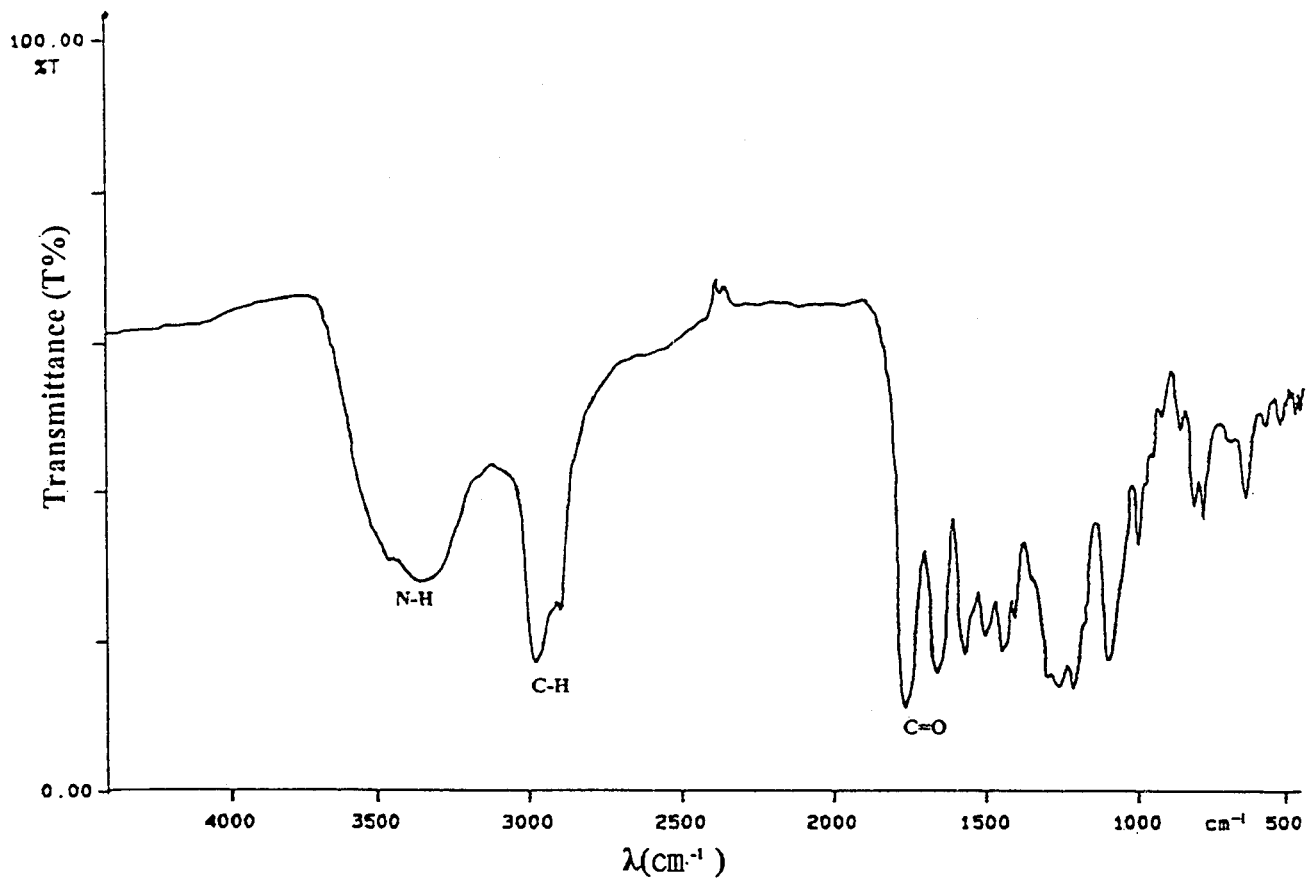


Figure 6 Spectrum of 6-amino-2-(3-chloro-2-hydroxy-propyl)-benzo[de]isoquinoline-1,3-dione based polyurethane prepolymer formed after 4 h reaction at $25 \pm 0.05^\circ\text{C}$.

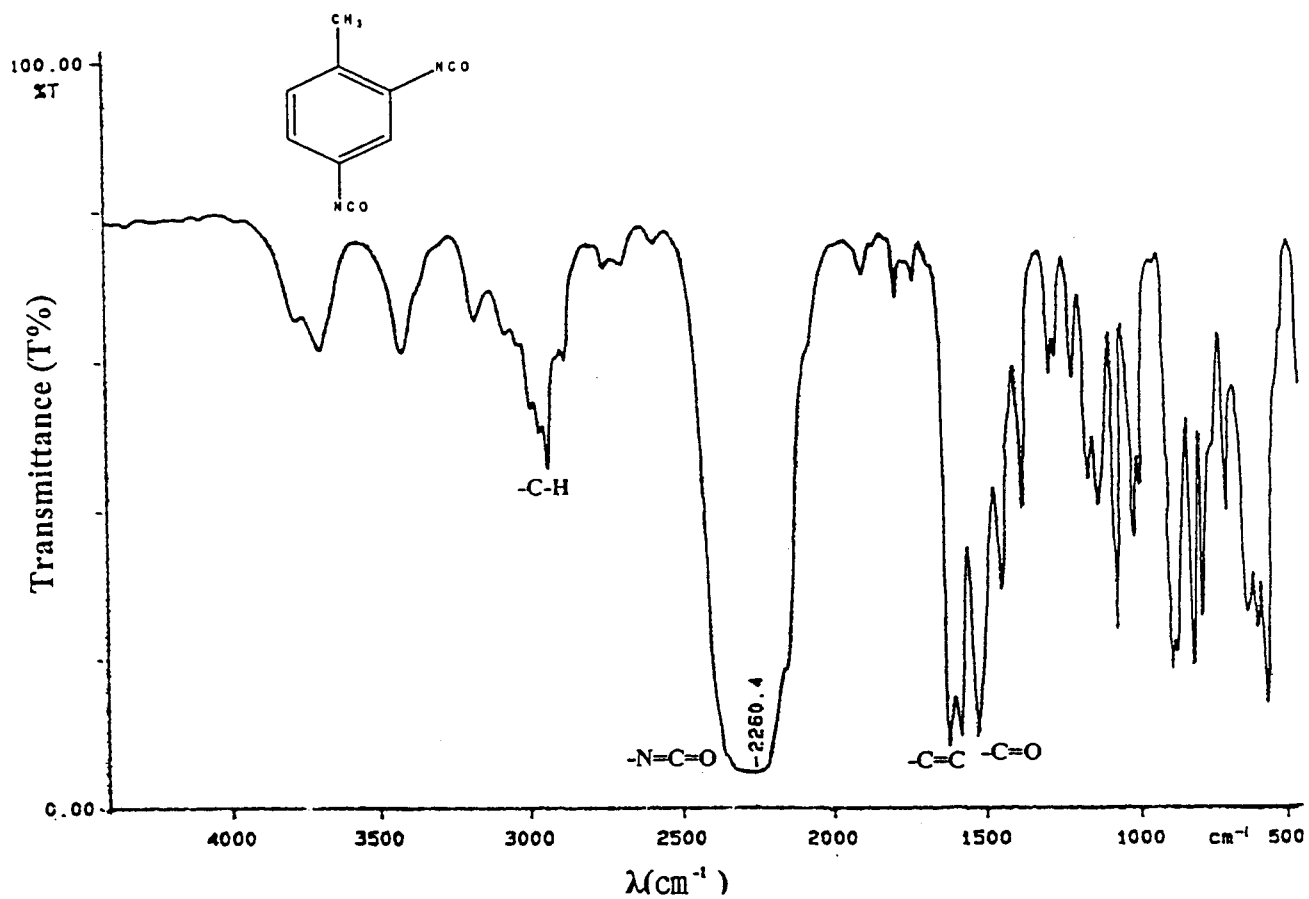


Figure 7 Spectrum of toluene diisocyanate at $25 \pm 0.05^\circ\text{C}$.

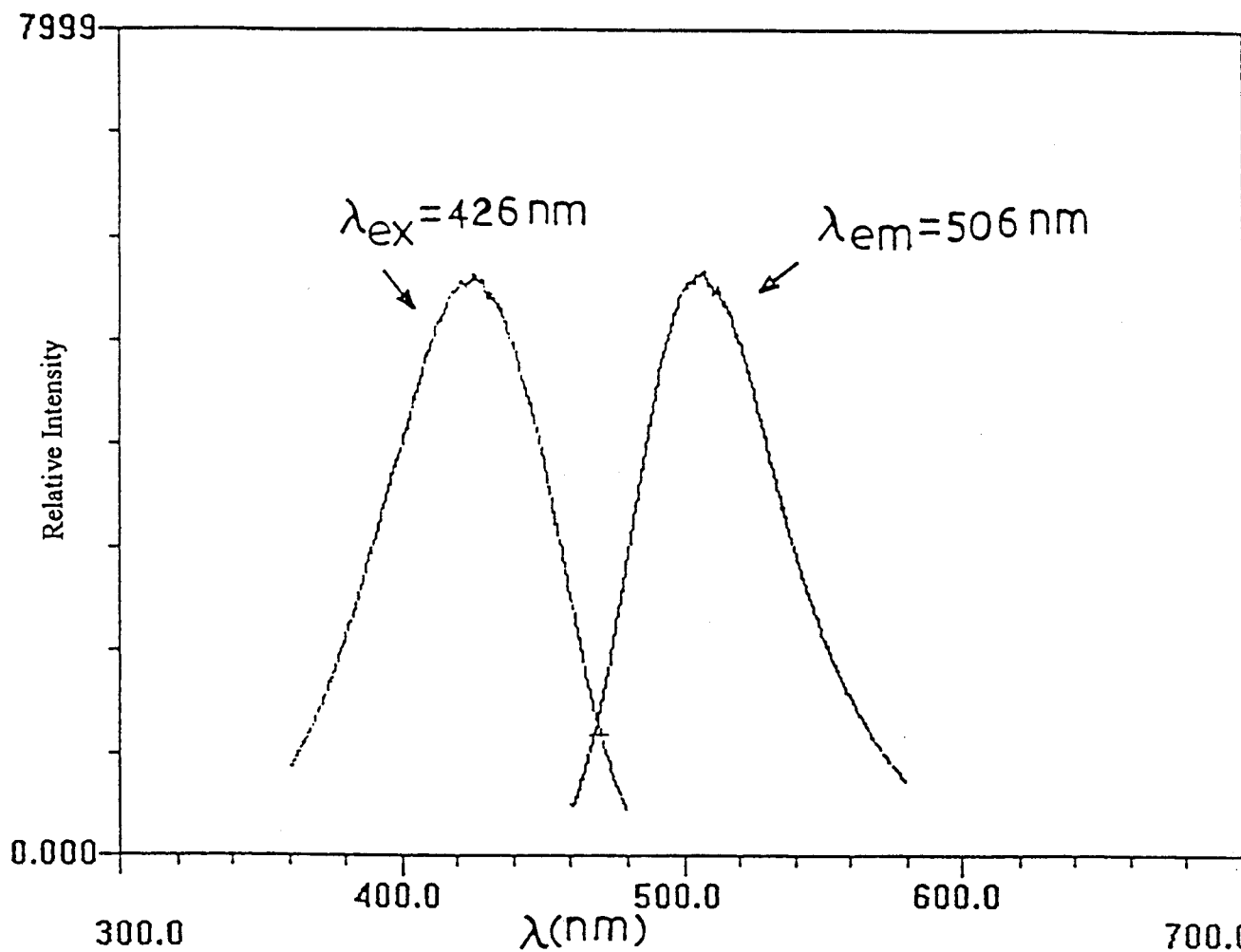


Figure 8 Both excitation and emission spectra of 6-amino-2-(3-chloro-2-hydroxy-propyl)-benzo[de]isoquinoline-1,3-dione at $25 \pm 0.05^\circ\text{C}$.

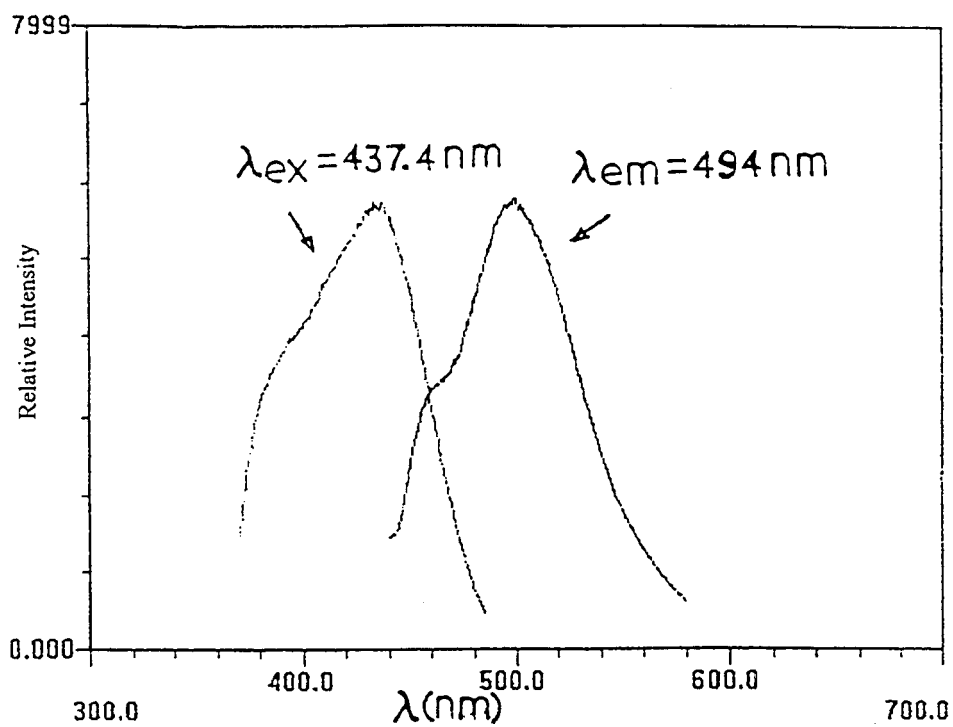


Figure 9 Both excitation and emission spectra of 2-benzyl-6-hydroxy-benzo[de]isoquinoline-1,3-dione at $25 \pm 0.05^\circ\text{C}$.

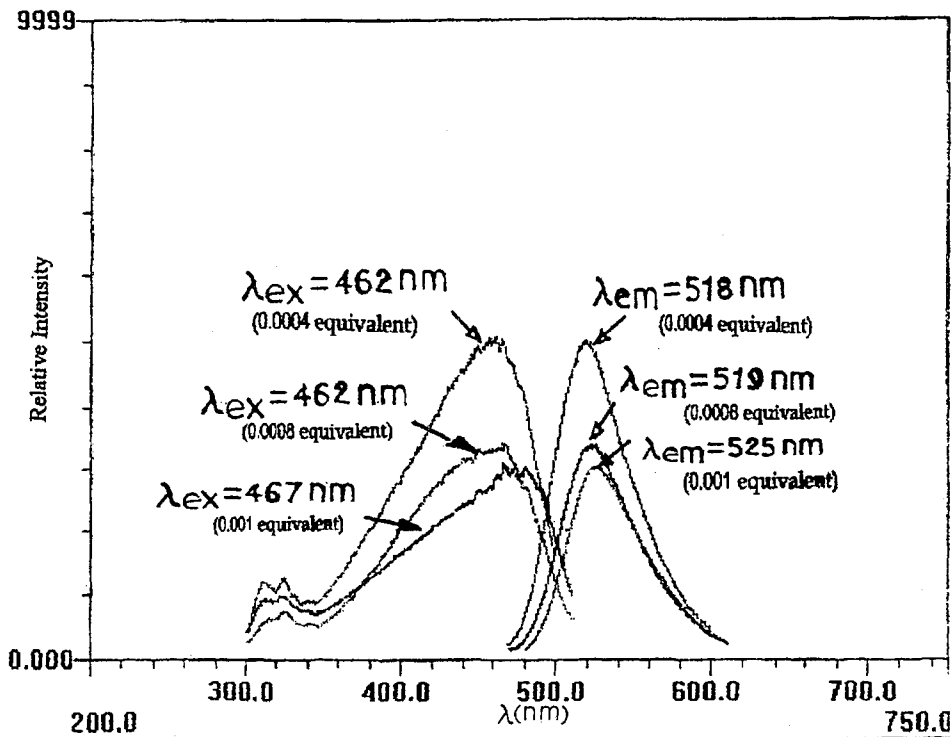


Figure 10 Both excitation and emission spectra of 6-amino-2-(3-chloro-2-hydroxy-propyl)-benzo[de]isoquinoline-1,3-dione dye-based PU ionomer (0.0004, 0.0008, 0.001 equivalent) at $25 \pm 0.05^\circ\text{C}$.

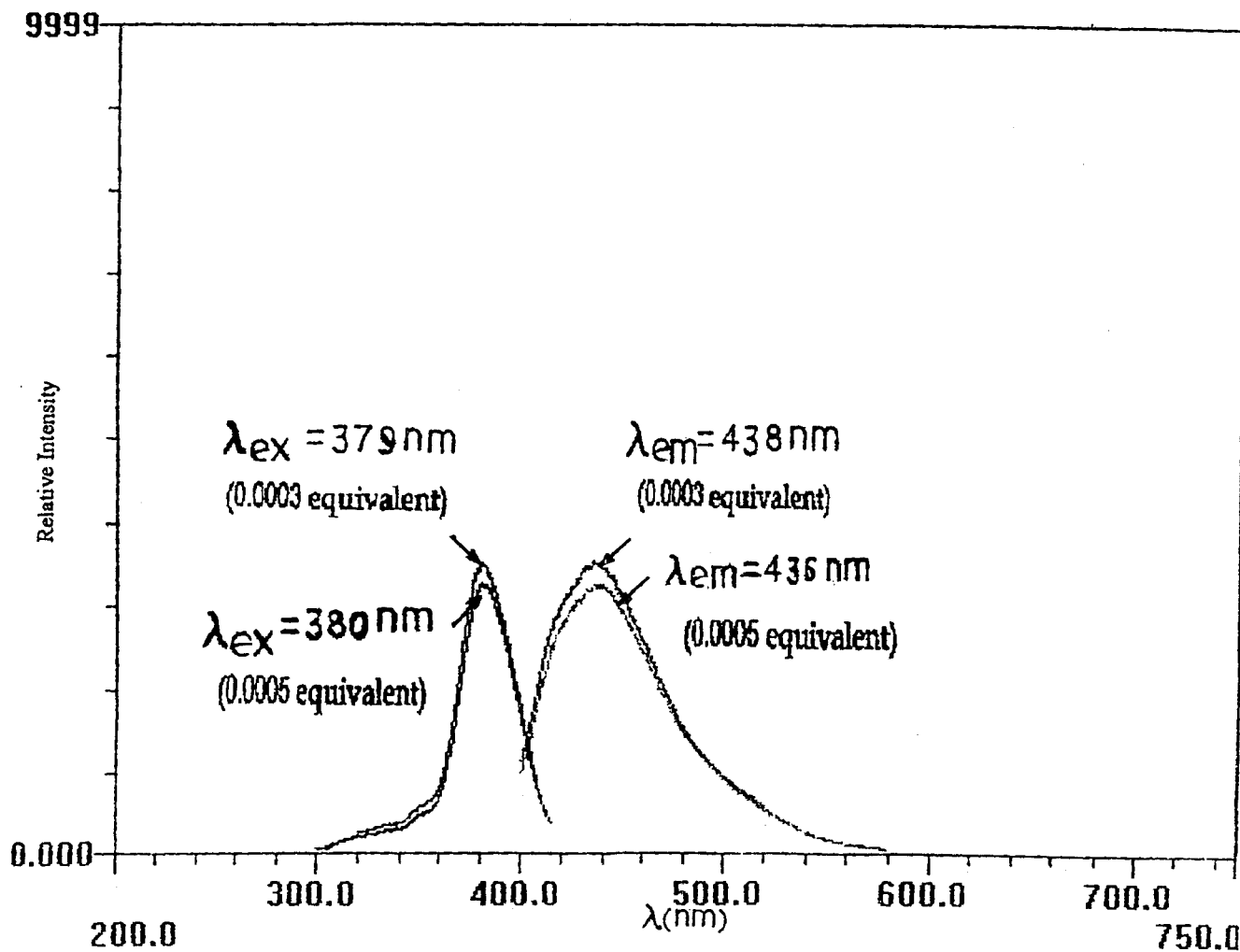


Figure 11 Both excitation and emission spectra of 2-benzyl-6-hydroxy-benzo[de]isoquinoline-1,3-dione dye-based PU ionomer (0.0003, 0.0005 equivalent) at $25 \pm 0.05^\circ\text{C}$.

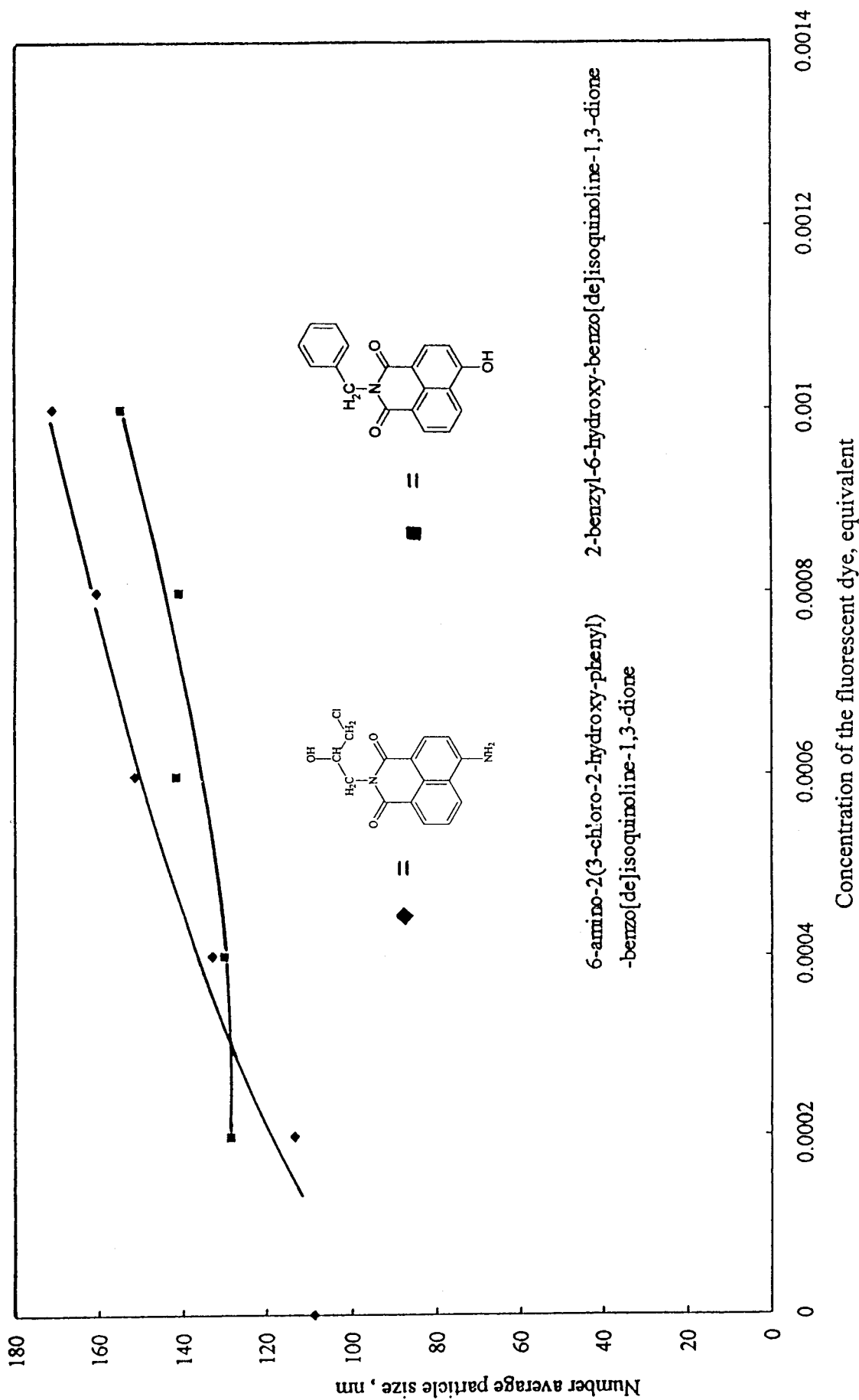


Figure 12 Plot of the average particle size versus the concentration of fluorescent dye used to prepare the fluorescent dye-based PU ionomer at $25 \pm 0.05^\circ\text{C}$.

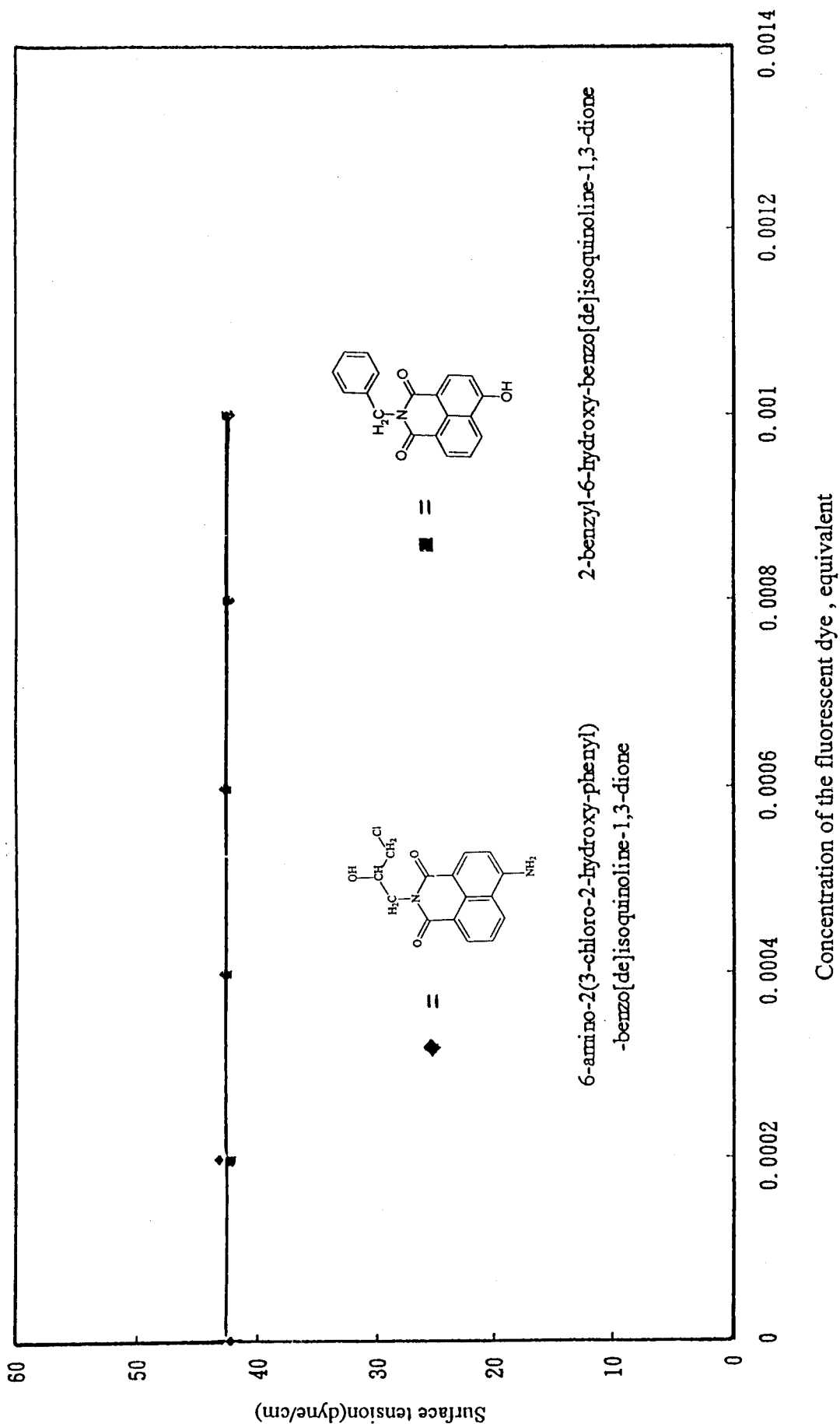
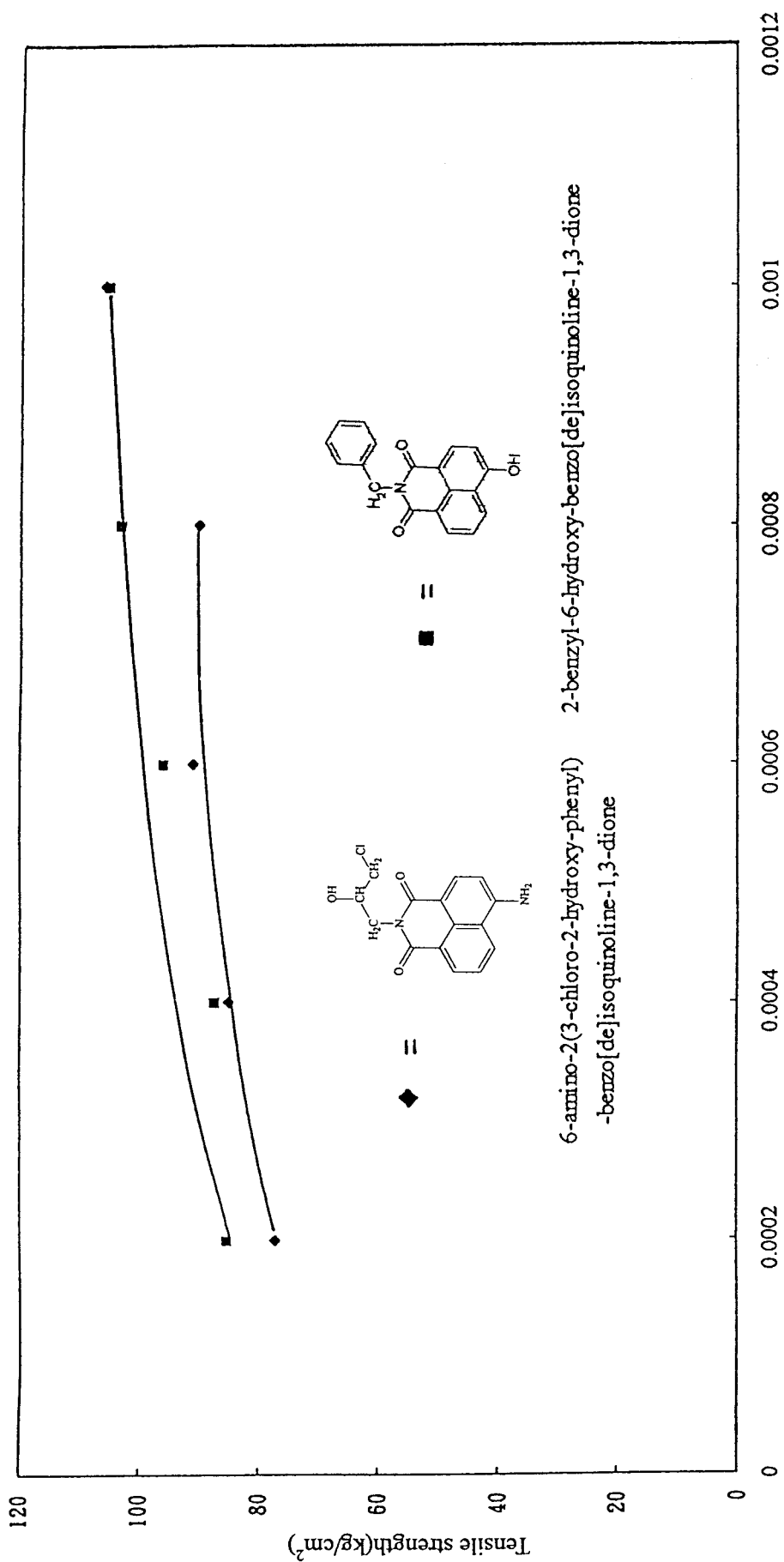


Figure 13 Plot of the surface tension versus the concentration of the fluorescent dye used to prepare the fluorescent dye-based PU ionomer at $25 \pm 0.05^\circ\text{C}$.



Concentration of 6-amino-2(3-chloro-2-hydroxy-propyl)-benzo[de]isoquinoline-1,3-dione , equivalent

Figure 14 Plot of the tensile strength versus the concentration of the fluorescent dye used to prepare the fluorescent dye-based PU ionomer at $25 \pm 0.05^\circ\text{C}$.

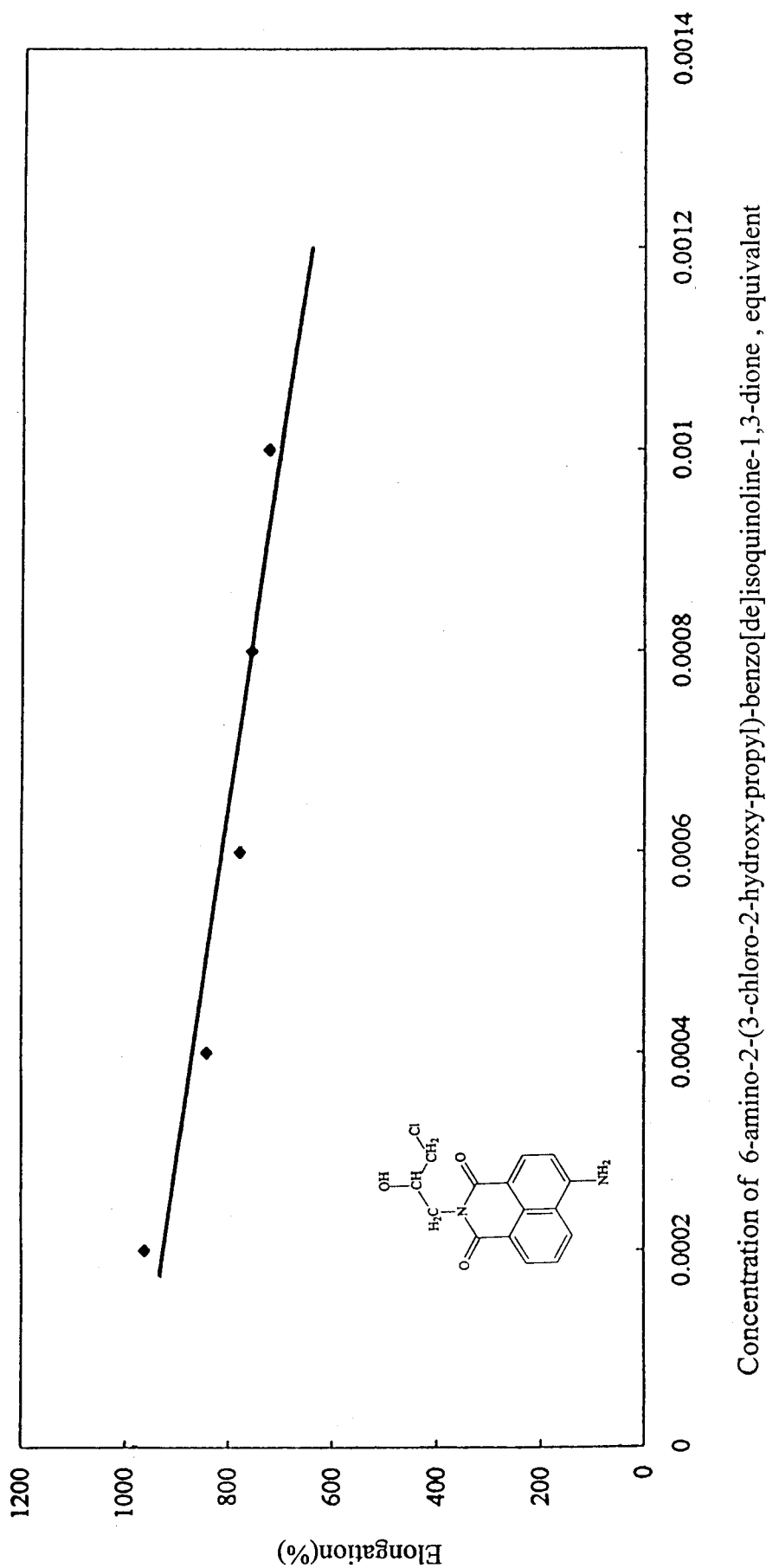


Figure 15 Plot of the elongation versus the concentration of 6-amino-2-(3-chloro-2-hydroxy-propyl)-benzo[de]isoquinoline-1,3-dione used to prepare the 6-amino-2-(3-chloro-2-hydroxy-propyl)-benzo[de]isoquinoline-1,3-dione dye-based PU ionomer at $25 \pm 0.05^\circ\text{C}$.

ionomer molecule may greatly reduce the intermolecular interaction between ionomer-ionomer molecules, thus causing the elongation of the ionomer molecule to decrease.

CONCLUSIONS

Both fluorescent DYE-A and DYE-B molecules have been successfully synthesized in our lab, and their structures have been proven by IR, NMR, and Mass spectra. In THF, the fluorescent DYE-A has better fluorescence performance than the fluorescent DYE-B. This is the result of the fluorescent DYE-A molecule having more electron donating groups, which may help the DYE-A molecule to be strongly excited when absorbing UV light. The fluorescent DYE-A or DYE-B molecule further reacted with toluene diisocyanate and other additives to form the structure of the fluorescent DYE-A- or DYE-B-based PU ionomer molecule has been demonstrated by IR spectra. In aqueous solution, it has also been found that the fluorescence performance is better for the fluorescent DYE-A-based PU ionomer than for the fluorescent DYE-B-based PU ionomer. Furthermore, increased concentration of the fluorescent DYE-A molecule linked to the backbone of the PU ionomer molecule greatly reduces the ability of the ionomer molecules to be excited when absorbing UV light, resulting from increasing intramolecular interaction between ionomer molecule itself. Thus, the fluorescence performance for increased concentration

of the DYE-A molecule used to prepare the DYE-A-based PU ionomer becomes poor. In aqueous solution, the average particle sizes of the fluorescent DYE-A- or DYE-B-based PU ionomer molecules increase with an increase in the concentration of the fluorescent DYE-A or DYE-B molecule. This may be the result of increased free volume resulting from strong intermolecular interactions between ionomer-ionomer molecules themselves and between ionomer-water molecules. The tensile strength of self-cured film made by the fluorescent DYE-A- or DYE-B-based PU ionomer molecule appears to increase with increasing concentration of the fluorescent DYE-A or DYE-B molecule, as a result of increased intermolecular interaction between ionomer-ionomer molecules themselves. On the other hand, the elongation of dry film made by these ionomer molecules is seen to decrease with increasing concentration of the fluorescent DYE-A molecule. This is the result of increased intramolecular interaction between ionomer molecule itself.

References

1. Lorenz, O.; Rose, G. *Angew Makromol Chem* 1975, 45, 85.
2. Lorenz, O.; Hick, H. *Angew Makromol Chem* 1978, 72, 115.
3. Dieterich, O. *Adv Org Coat Sci Technol Ser* 1979, 1, 55.
4. Wang, C. L.; Kuo, Y. M.; Chao, D. Y. *Polym Adv Technol* 2000, 11, 127.
5. Chen, Y. *J Appl Polym Sci* 1992, 46, 435.
6. Abstracted in part from C. L. Wang's dissertation, to be submitted to the Southwest Normal University, Beibei, Ghongqing, P.R. China, 2003.