

Fluorescence from Fluorescent Dye Based Polyurethane Ionomer(III)

Y. C. Chen, R. R. Chiou, H. L. Huang, Y. Z. Tsai, Y. M. Kuo, D. Y. Chao

Institute of Applied Chemistry, Chinese Culture University, Hwa Kang, Yang Ming Shan, Taipei, Taiwan

Received 15 January 2004; accepted 15 November 2004

DOI 10.1002/app.21737

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A series of reactive fluorescent dyes were successfully synthesized and their structure was proven by IR spectra, NMR spectra, elemental analysis, and mass spectra. The fluorescence performance 6-amino-2(-3-phenyl-propyl)-benzo[de]isoquinoline-1,3-dione and 2-benzyl-6-hydroxy-benzo[de]isoquinoline-1,3-dione appears at around 276 and 437.4 nm, respectively, and their quantum yields are 0.662 and 0.562, respectively. It is important to indicate that the fluorescence performance is better for 6-amino-2(-3-phenyl-propyl)-benzo[de]isoquinoline-1,3-dione than for as a result of more electron donating groups linked to the 6-amino-2(-3-phenyl-propyl)-benzo[de]isoquinoline-1,3-dione molecule. These fluorescent dyes further react with toluene diisocyanate and other additives to form fluorescent dye based polyurethane (PU) ionomer molecules, and their

structures are demonstrated by IR spectra. In aqueous solution, the fluorescence performance appears to be better for 6-amino-2(-3-phenyl-propyl)-benzo[de]isoquinoline-1,3-dione based PU ionomer than for 6-amino-2-phenyl-ethyl-benzo[de]isoquinoline-1,3-dione based PU ionomer. For the fluorescent dye based PU ionomer molecule system, the number-average particle sizes of the fluorescent dye based PU ionomer molecules in water increase with increasing concentration of the fluorescent dye, as a result of the increased free volume of the ionomer molecule. This may be the result of increased intermolecular interactions between ionomer- molecules themselves. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 455–465, 2005

Key words: fluorescent dye; polyurethane ionomer

INTRODUCTION

Organic fluorescent dyes with bright colors are important chemicals that are widely used in both civil and military applications such as danger zones, airplanes, ships, ambulances, safety clothes, and transportation signs labeled with fluorescent dye. Because of the problems that organic fluorescent dyes are difficult to react with 2,6-toluene diisocyanate (TDI) (TDI, or other diisocyanates) and organic fluorescent dyes are not well dispersed in normal resins, new fluorescent dyes need to be developed. For this reason, 4-amino-1,8-naphthalimide was chosen as a starting material to react with 1-bromo-3-phenylpropane in the presence of *N,N*-dimethylformamide and sodium hydroxide to form a new fluorescent dye, 6-amino-2(-3-phenyl-propyl)-benzo[de]isoquinoline-1,3-dione (DYE-3).

Because work on the synthesis of this new fluorescent dye has not been published thus far, we therefore attempted to study a unique way to prepare new fluorescent dyes.^{1–5} The new fluorescent dye molecule successfully synthesized at our lab has been demon-

strated to exist by IR, NMR, elemental analysis, and mass spectra. This new fluorescent dye, 6-amino-2(-3-phenyl-propyl)benzo[de]isoquinoline-1,3-dione (DYE-3), will further react with TDI and other additives to form the structure of the fluorescent dye based (PU) ionomer molecule (NCO/OH = 1.3) given in Scheme 1.

EXPERIMENTAL

Materials

1-Bromo-3-phenylpropane and 4-amino-1,8-naphthalimide were purchased from Acro Organic Co. *N,N*-Dimethylformamide, sodium hydroxide, TDI, triethylamine, and diethylene triamine were supplied by Merck Polyester with a molecular weight of 2800 (OH number = 40.1), neopentyl glycol, and 1,4-butanediol were received from Taichin Chemical Industry Co. (Taiwan). Tetrahydrofuran was obtained from J. T. Baker Chemicals. All chemicals were used without further purification.

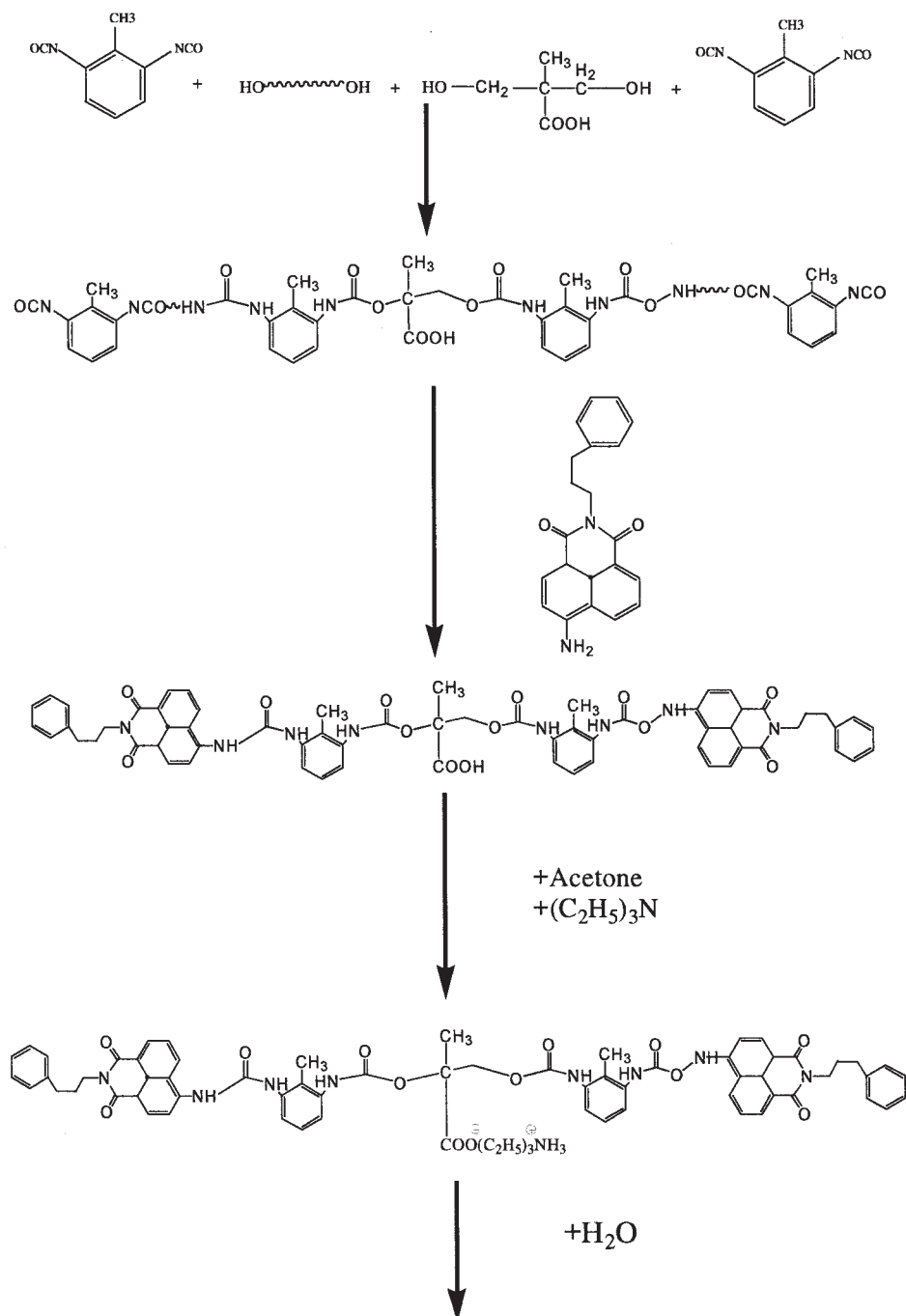
Methods

Ten grams of 4-amino-1,8-naphthalimide were added to a 1000-mL four-necked pyrex glass flask (equipped with a stirrer, thermometer, and condenser) containing 2.6 g of sodium methoxide dissolved in 110 mL of

*Present address: Jintex Corporation Ltd. Taiwan.

Correspondence to: D. Y. Chao.

Contract grant sponsor: National Science Council of Taiwan.



Fluorescent Dye-Based Polyurethane Ionomer

Scheme 1 The synthesis of the fluorescent dye based PU ionomer.

N,N-dimethylformamide under agitation at $25 \pm 0.05^\circ\text{C}$. In the above flask, 4.93 g of 1-bromo-3-phenylpropane or 4.57 g of 2-bromoethylbenzene were subsequently added and reacted at room temperature for 6 h to form 6-amino-2-((-3-phenyl-propyl)-benzo[de]isoquinoline-1,3-dione or 6-amino-2-phenyl-ethyl-benzo[de]isoquinoline-1,3-dione (DYE-

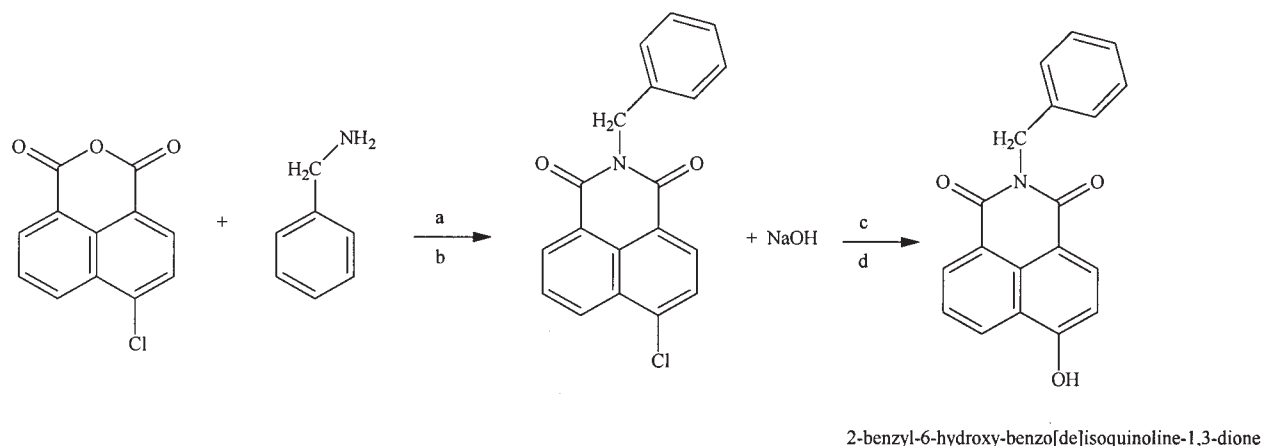
2). Then, ice-water was slowly added into the above flask. 6-Amino-2-((-3-phenyl-propyl)-benzo[de]isoquinoline-1,3-dione was filtered *in vacuo* and dried in an oven. In order to remove the salts and impurities from the liquids, this new fluorescent dye was washed with 200 mL of water and tested by thin layer chromatography. After acetone was removed by blowing it

out *in vacuo*, the pure fluorescent dye with 95% purity and 75% yield was obtained. The amounts of 37.2 g of polyester (MW \approx 2800) 1.5 g of polyethylene glycol (MW \approx 3350), 1.24 g of 1,4-butanediol, and 4.7 g of dimethylol propionic acid in the presence of 35 g of *N,N*-dimethylacetamide were charged into a 1000-mL four-necked reaction kettle equipped with a stirrer thermometer. Then, 14.14 g of TDI and 0.4×10^{-4} – 0.5×10^{-3} equiv of 6-amino-2-(3-phenyl-propyl)-benzo[de]isoquinoline-1,3-dione or 6-amino-2-phenylethyl-benzo[de]isoquinoline-1,3-dione were added slowly into the above flask at 81–82°C for 4 h to form NCO-terminated fluorescent dye based PU prepolymer. A 0.07 equiv of triethylamine was then reacted with this prepolymer dissolved in 65 g of acetone at a speed of 700 rpm for about 10 min to form quaternized fluorescent dye based PU prepolymer. This quaternized PU prepolymer was further reacted with 170 g of 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

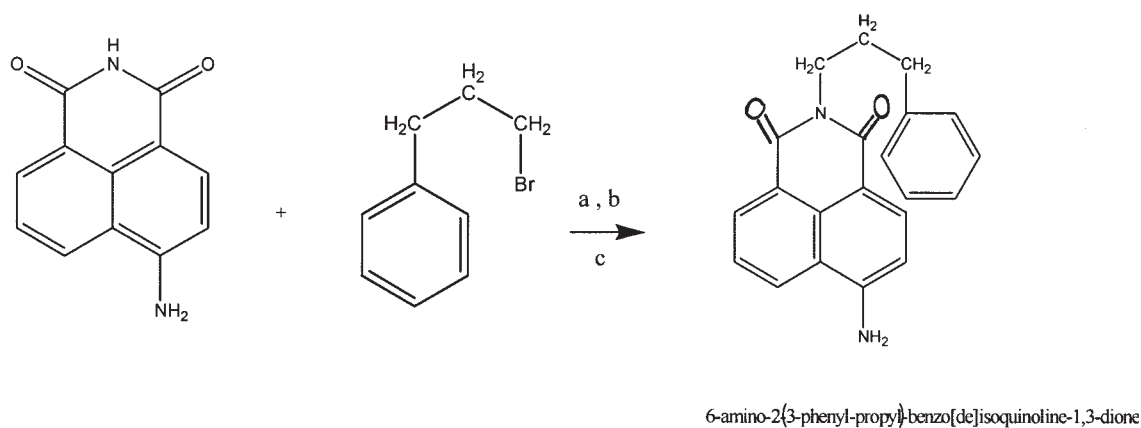
out *in vacuo*, the fluorescence and the average particle size of this fluorescent dye based PU ionomer aqueous solution (\approx 20% solids) were fully investigated at room temperature using a fluorescence spectrophotometer (F-4500, Hitachi) and a dynamic light-scattering spectrophotometer (DLS-700, Otsuka Electric Co.), respectively. The quantum yield of this fluorescent dye can be calculated according to the following equation:

$$Y_U = Y_S \times \frac{F_U}{F_S} \times \frac{A_S}{A_U}$$

where Y_U is the quantum yield of the unknown sample to be measured, Y_S is the fluorescein as a standard (quantum yield = 0.9) F_U is the integrated fluorescence intensity of the unknown sample, F_S is the fluorescence intensity of fluorescein, and A_U is the absorbance intensity of the excitation wavelength for the unknown sample. The structures of these reactive fluorescent dyes are given as follows:



where a is ethanol b is 76°C for 4 h, c is tetrahydrofuran, and d is 66°C for 3 h.



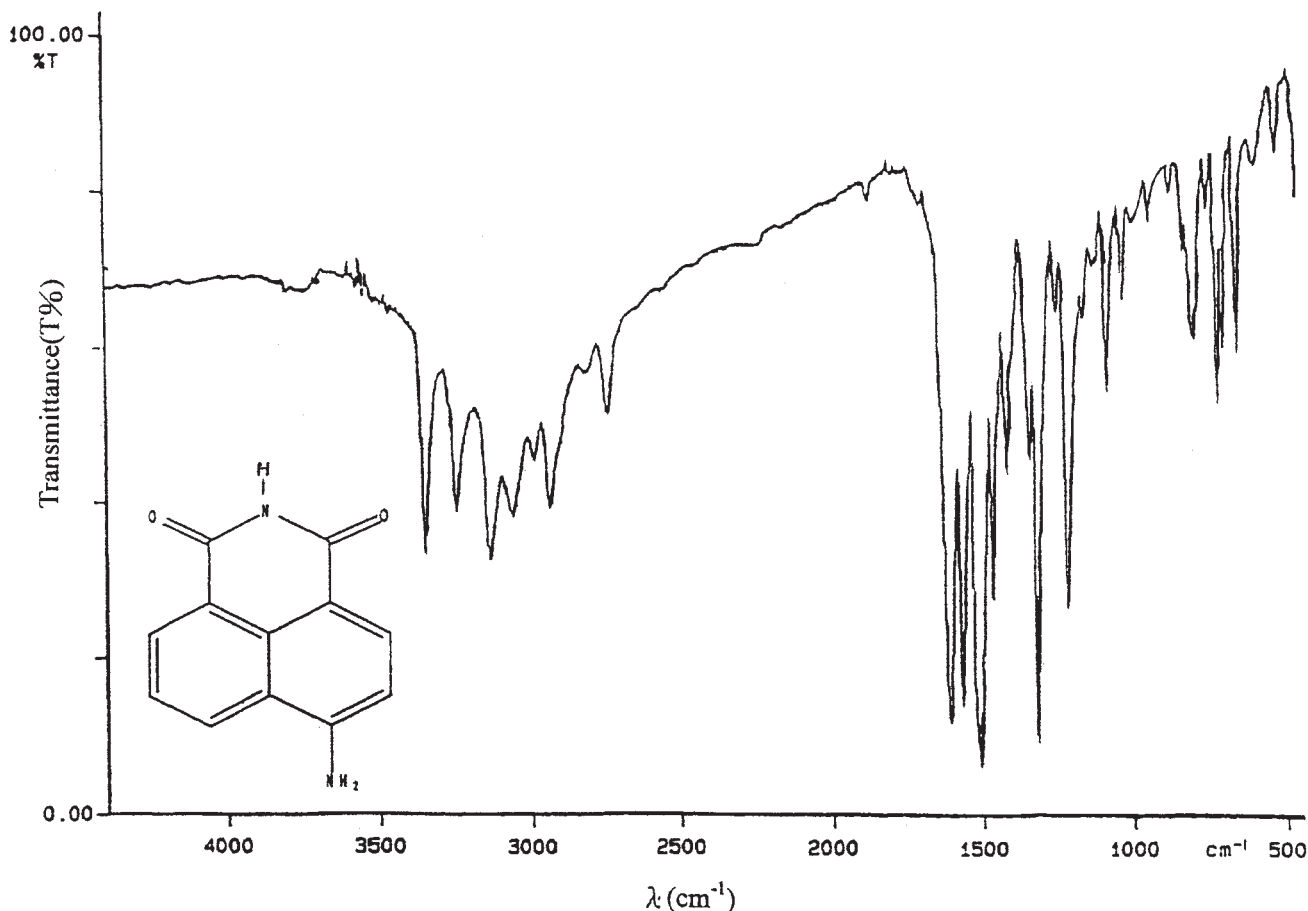


Figure 1 The IR spectrum of 4-amino-1,8-naphthalimide at $25 \pm 0.05^\circ\text{C}$.

where a is *N,N*-dimethylformamide (110 mL), b is sodium methoxide (2.6 g), and c is $25 \pm 0.05^\circ\text{C}$.

RESULTS AND DISCUSSION

The IR spectra for 4-amino-1,8-naphthalimide and 1-bromo-3-phenylpropane are given in Figures 1 and 2, respectively. The reaction of 4-amino-1,8-naphthalimide with 1-bromo-3-phenylpropane in the presence of sodium methoxide and *N,N*-dimethylformamide to form the reactive fluorescent dye 6-amino-2-(3-phenyl-propyl)benzo[de]isoquinoline-1,3-dione is illustrated by the formation of the absorbance peaks at around 3300–3500 (—NH), 3000 (C—H), 1630 (C=O), 1500–1510 (NC=O), and 1260 cm^{-1} (C—O) and by the almost total disappearance of the absorbance peak at $700\text{--}750\text{ cm}^{-1}$ (Br), which is given in Figure 3 in comparison to those of Figures 1 and 2. The $^1\text{H-NMR}$ (CDCl_3) spectrum shows a signal for the respective protons of naphthalene, aromatic C—NH, and oxiran in a reactive fluorescent dye molecule, δ 8.17–8.63 (naphthalene—H), δ 4.0 (aromatic C—NH), and δ 3.16 (oxiran), which are given in Figure 4. In the analysis of the mass spectrum for a reactive fluorescent dye mol-

ecule ($M^+ + 1$), it shows that the molecular weight for this fluorescent dye molecule ion is exactly 331.5, which is given in Figure 5. The elemental analysis (Perkin Elmer 2400 CHN) also indicates that the difference between the theoretical and experimental values (i.e., percentage by weight) for carbon, nitrogen, and hydrogen elements is within 0.4. These results shown in Figures 1–5 suggest that the reaction of 4-amino-1,8-naphthalimide with 1-bromo-3-phenylpropane in the presence of sodium methoxide and *N,N*-dimethylformamide does indeed form 6-amino-2-(3-phenyl-propyl)-benzo[de]isoquinoline-1,3-dione (DYE-3). To further clarify the fluorescence of 0.01 g of DYE-3 diluted 20 times in tetrahydrofuran by using a fluorescence spectrophotometer (F-4500), the excitation and emission spectra are given in Figure 6. The fluorescence for 6-amino-2-(3-phenyl-propyl)benzo[de]isoquinoline-1,3-dione at around 276 nm (Fig. 6) is exhibited, and the quantum yield of this fluorescent dye in comparison to that of fluorescein as a standard is 0.662. In contrast, the quantum yields for 2-benzyl-6-hydroxy-benzo[de]isoquinoline-1,3-dione^{5,6} (DYE-1) and 6-hydroxy-2-phenyl-benzo[de]isoquinoline-1,3-dione⁶ are calculated to be 0.562 and 0.057, respec-

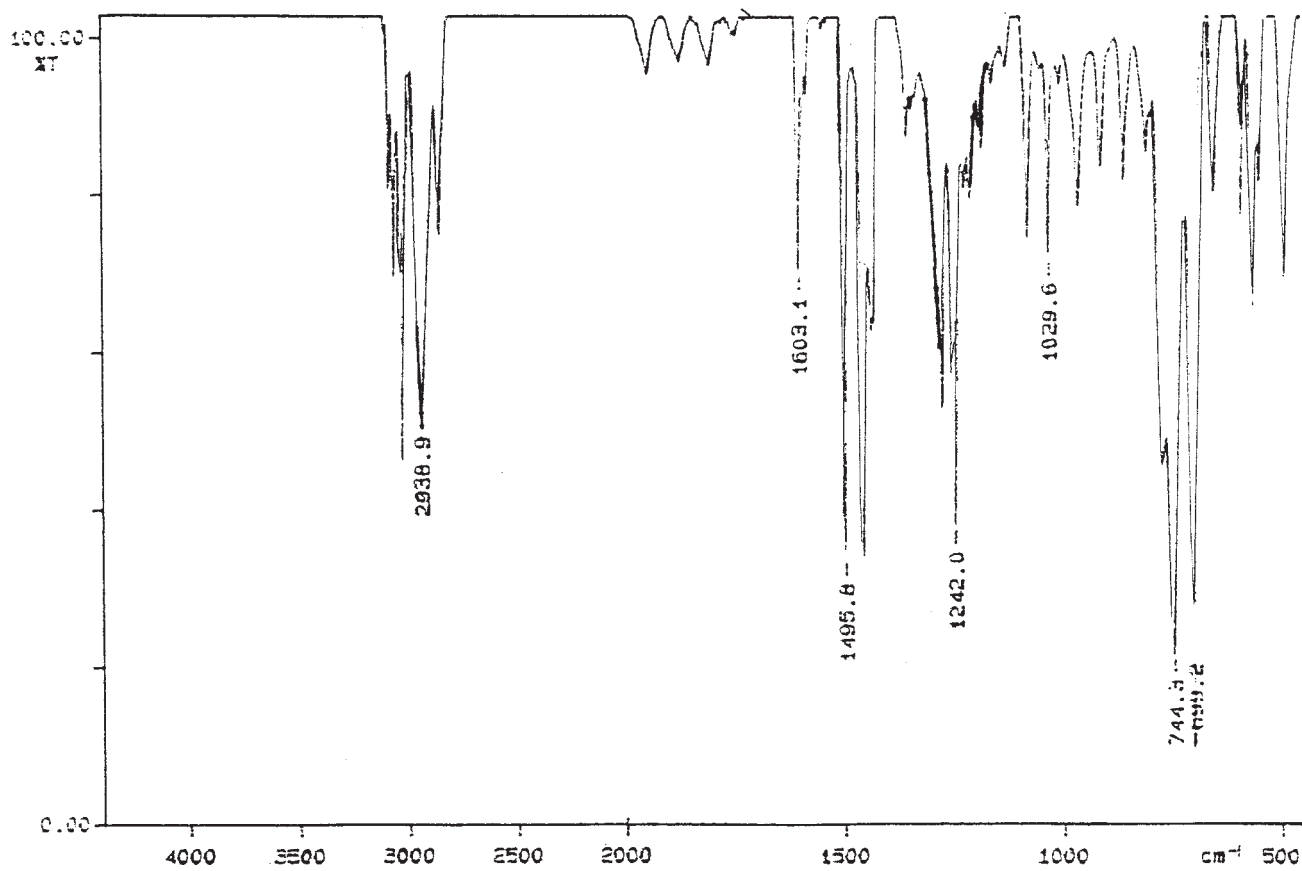


Figure 2 The IR spectrum of 1-bromo-3-phenylpropane at $25 \pm 0.05^\circ\text{C}$.

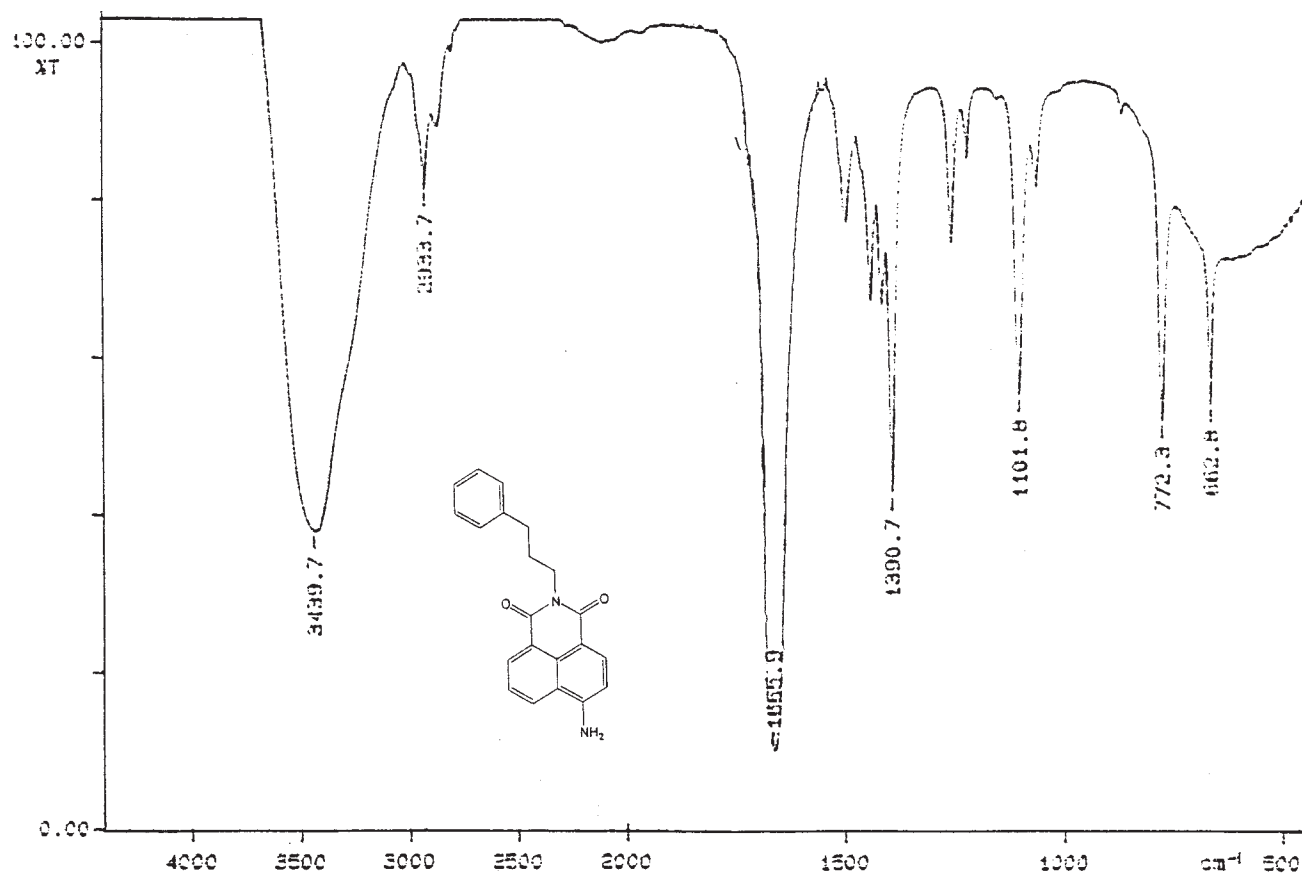


Figure 3 The IR spectrum of 6-amino-2-(3-phenyl-propyl)-benzo[de]isoquinoline-1,3-dione at $25 \pm 0.05^\circ\text{C}$.

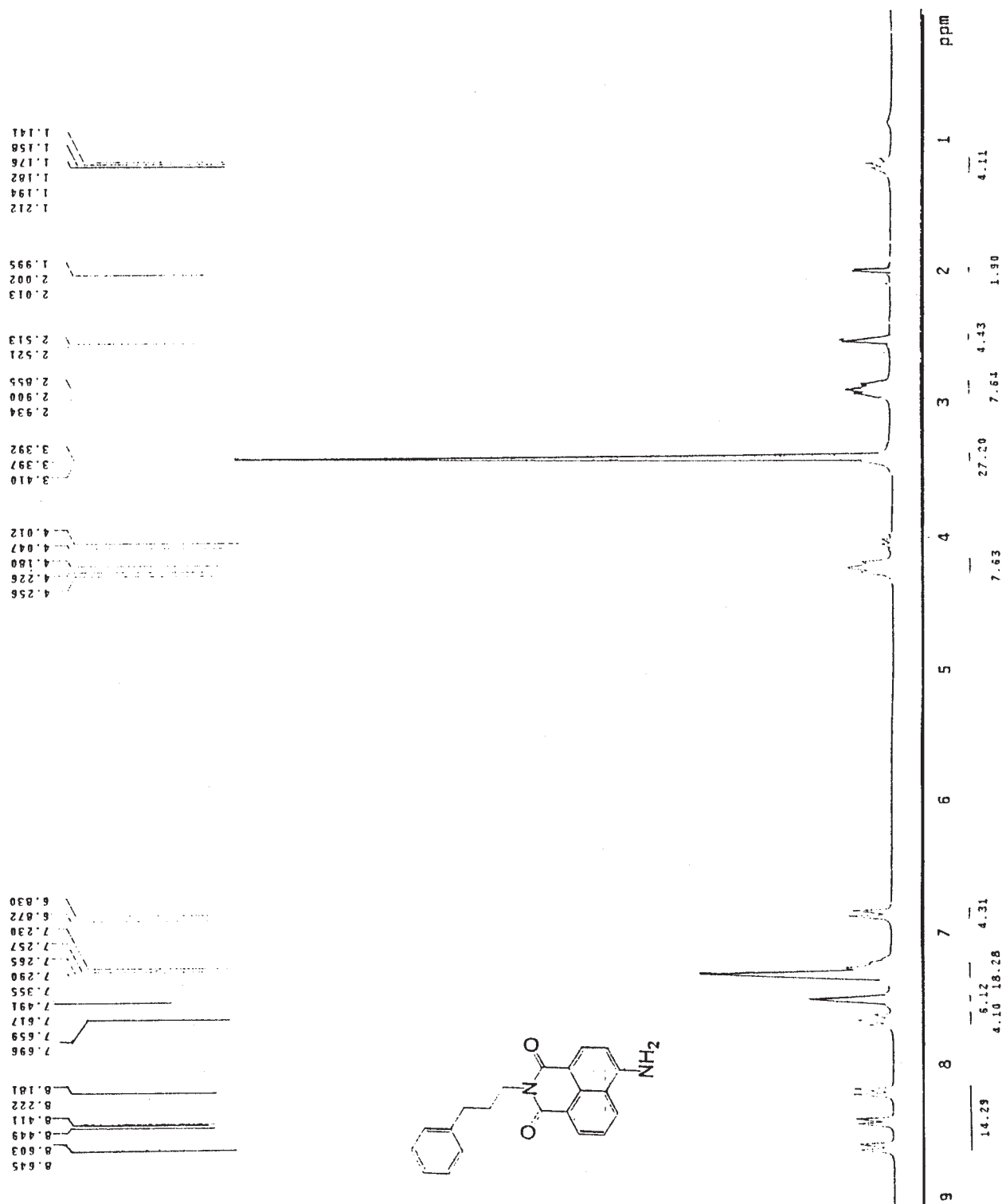


Figure 4 The NMR spectrum of 6-amino-2-(3-phenyl-propyl)-benzo[de]isoquinoline-1,3-dione at $25 \pm 0.05^\circ\text{C}$.

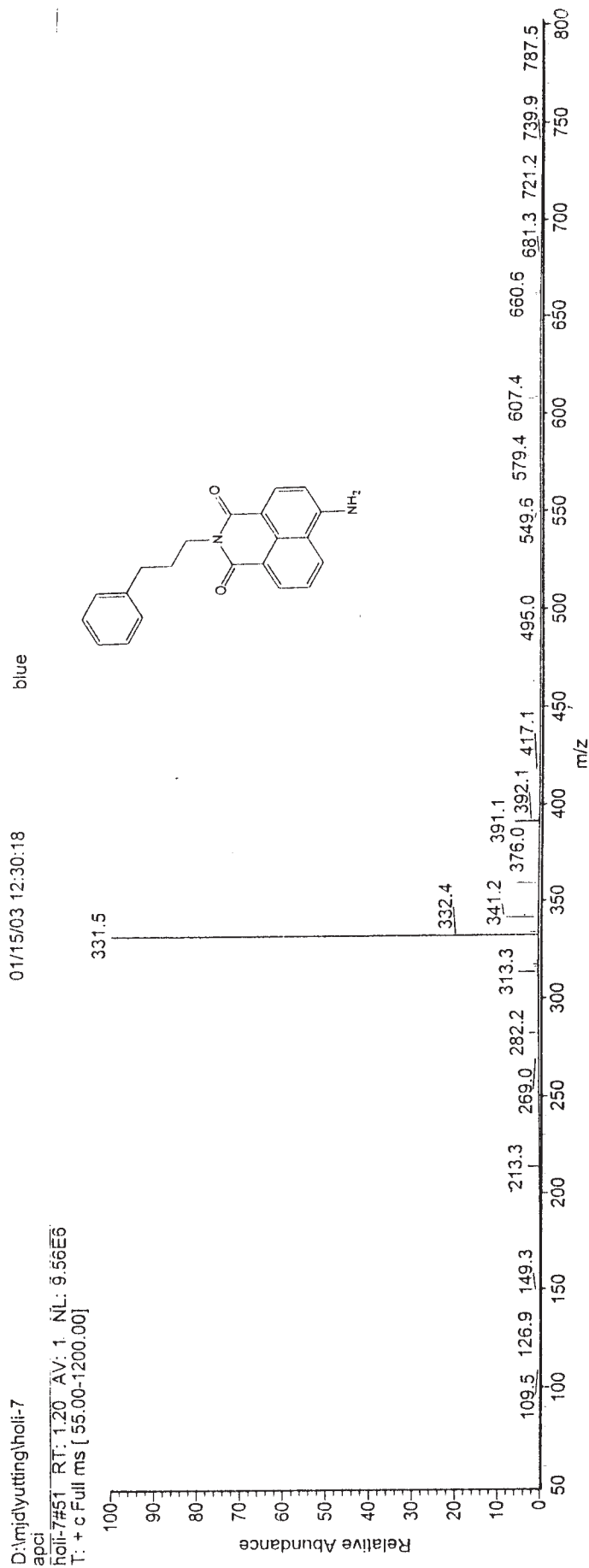


Figure 5 The mass spectrum of 6-amino-2-(3-phenyl-propyl)-benzo[de]isoquinoline-1,3-dione at 25 ± 0.05°C.

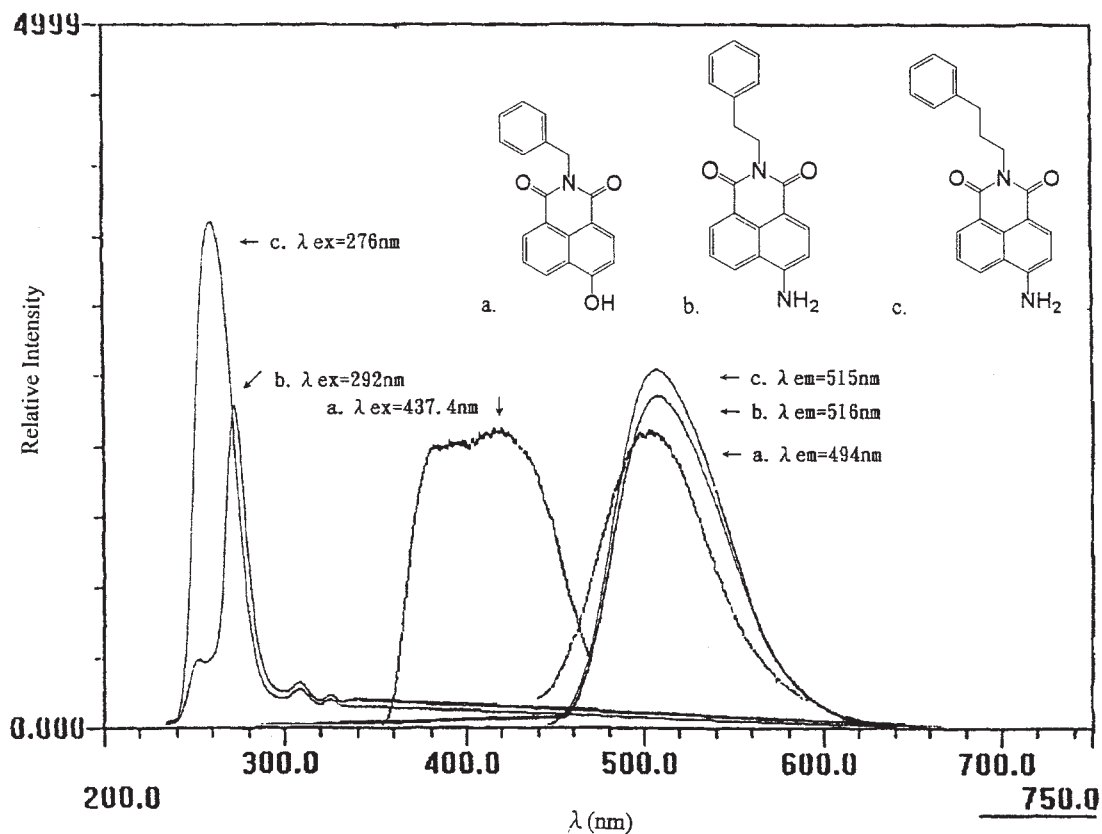


Figure 6 The excitation and emission spectra of different fluorescent dyes at $25 \pm 0.05^\circ\text{C}$.

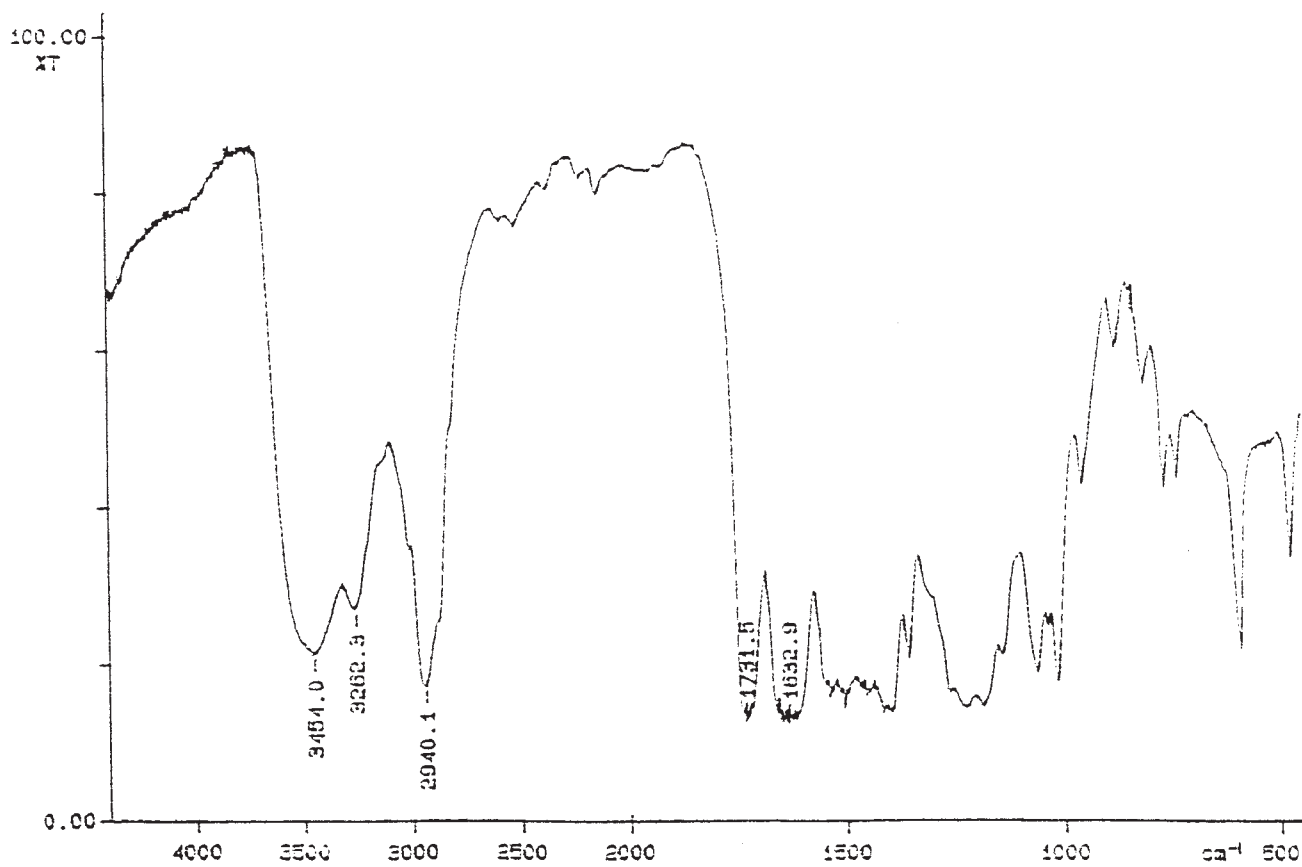


Figure 7 The IR spectrum of 6-amino-2-(3-phenyl-propyl)-benzo[de]isoquinoline-1,3-dione based polyurethane prepolymer formed after 100-min reaction at $25 \pm 0.05^\circ\text{C}$.

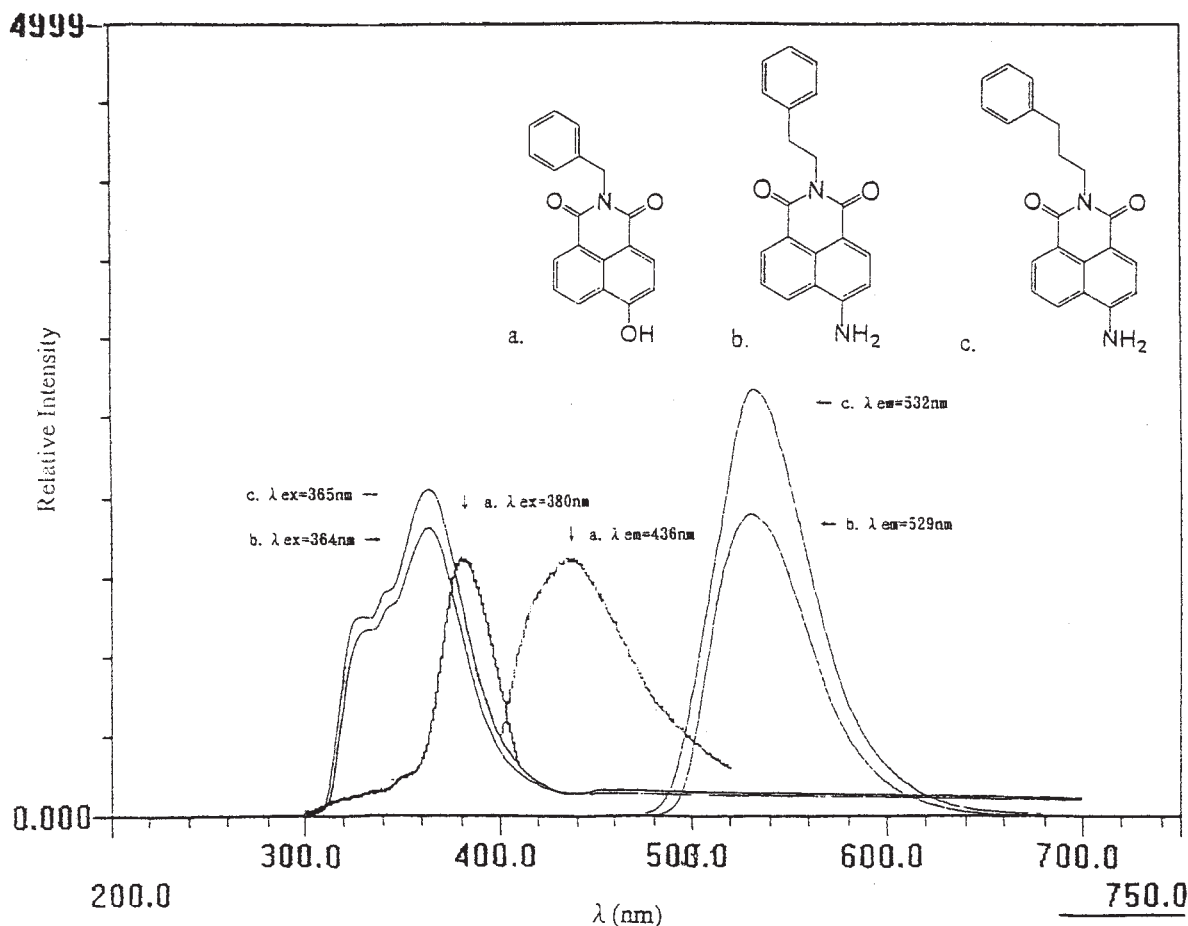


Figure 8 The excitation and emission spectra of different fluorescent dye based polyurethane ionomers at $25 \pm 0.05^\circ\text{C}$.

tively. These results suggest that the fluorescence performance is better for DYE-3 than for 6-amino-2-phenyl-ethyl-benzo[de]isoquinoline-1,3-dione (DYE-2) or DYE-1, as a result of more electron donating groups linked to the DYE-3 molecule. Thus, these increased electron donating groups may help the fluorescent dye molecule to be excited easily by absorbing UV light. Furthermore, the reaction of TDI with 6-amino-2-(3-phenyl-propyl)benzo[de]isoquinoline-1,3-dione (DYE-3) or DYE-2 and other additives to form NCO-terminated fluorescent dye based PU prepolymer (Fig. 7) is illustrated by the formation of the absorbance peaks at around 1250 (C—O), 1540 (NHCO), 1620 (NH), 1720 (C=O), 3400 (NH), and 3650 cm^{-1} (OH) and by almost the total disappearance of the absorbance peak at around 2275 cm^{-1} (NCO). The IR spectra for DYE-3 and TDI are given in Figures 3 and 6, respectively. In comparison to Figures 3, 6, and 7, these results suggest that the reaction of TDI with DYE-3 and other additives to form a fluorescent dye based PU ionomer molecule is quite possible. To further elucidate the fluorescence performance of a 0.01-g DYE-3 based PU ionomer and a 0.01-g DYE-2 or DYE-1 based PU ionomer diluted 20 times in water

using a fluorescence spectrophotometer (F-4500) their fluorescence spectra are given in Figure 8. Figure 8 illustrates that the quantum yield for the fluorescent DYE-3 based PU ionomer molecule is better than that of DYE-2 or DYE-1 based PU ionomer molecules. This may be due to the result of more electron donating groups attached to the DYE-3 based PU ionomer molecule.

In addition, increased electron donating groups (i.e., hydrophilic groups) attached to the ionomer molecules may enhance the aromatics of the ionomer molecule to be excited easily by absorbing UV light. The number-average particle size of the fluorescent DYE-3 or DYE-1 based PU ionomer molecule in aqueous solution as a function of the concentration of the fluorescent DYE-3 or DYE-1 is given in Figure 9. Figure 9 shows that, for the DYE-3 based PU ionomer or DYE-1 based PU ionomer in aqueous solution, the number-average particle size of this ionomer appears to increase with increasing concentration of the fluorescent DYE-3 or DYE-1 used to make the fluorescent dye based PU ionomer molecules. This is the result of increased free volume of the ionomer molecule resulting from strong intermolecular interactions between

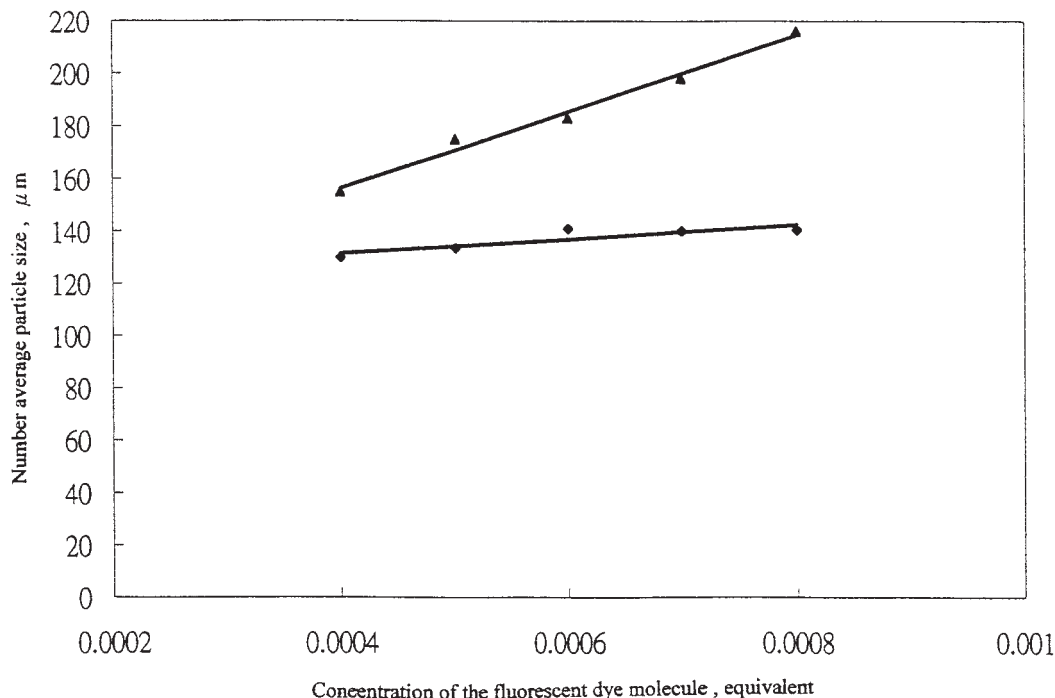


Figure 9 The plot of the number-average particle size versus the concentration of the fluorescent dye used to prepare the fluorescent dye based polyurethane ionomer at $25 \pm 0.05^\circ\text{C}$.

ionomer molecules and between ionomer and water molecules. Thus, the number-average particle size of this ionomer molecule increases. However, the number-average particle size is larger for the DYE-3 based PU ionomer molecule than for the DYE-1 based PU ionomer molecule, as a result of the large molecules of the DYE-3 based PU ionomer molecule.

The tensile strength for self-cured film made by the fluorescent DYE-3 or DYE-1 based PU ionomer as a function of the concentration of fluorescent DYE-3 or DYE-1 is given in Figure 10. 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 fluorescent DYE-3 or DYE-1, as a result of increased intermolecular interaction between ionomer molecules. This interaction resulting from the functional group of the ionomer molecules may enhance the ionomer molecule to crosslink readily, thus resulting in increases in the tensile strength of these ionomer molecules. Conversely, the tensile strength at the breaking point is greater for the DYE-1 based PU ionomer molecule than for the DYE-3 based PU ionomer molecule. This is because more electron donating groups attached to the backbone of the PU ionomer molecules may reduce the intermolecular interaction between ionomer molecules, thus causing the tensile strength of these molecules to become weak.

CONCLUSION

A series of reactive fluorescent dyes can be successfully synthesized by using 4-amino-1,8-naphthalimide

as a starting material to react with 1-bromo-3-phenylpropane or 1-bromo-2-phenylethane in the presence of other additives. Our experimental results indicate that the fluorescence performance appears to be better for 6-amino-2-(-3-phenyl-propyl)benzo[de]isoquinoline-1,3-dione than for DYE-2 or DYE-1. This is the result of more electron donating groups attached to the fluorescent dye molecule, thus causing the dye molecule to be strongly excited by absorbing UV light. The reaction of the fluorescent DYE-3, DYE-2, or DYE-1 molecule with TDI and other additives to form the structure of the fluorescent DYE-3, DYE-2, or DYE-1 based PU ionomer molecule was demonstrated by IR spectra. In aqueous solution, it was found that the fluorescence performance is better for the fluorescent DYE-3 based PU ionomer than for the fluorescent DYE-2 or DYE-1 based PU ionomer, as a result of more electron donating groups attached to the backbone of the PU ionomer molecules. The number-average particle sizes of the fluorescent DYE-3 or DYE-1 based PU ionomer molecules in aqueous solution increase with increasing concentration of the fluorescent DYE-3 or DYE-1 molecule. This may be the result of increased free volume of the ionomer molecule resulting from strong intermolecular interactions between ionomer-molecules themselves and between ionomer and water molecules. The tensile strength of a self-cured film made by the fluorescent DYE-3 or DYE-1 based PU ionomer molecules increases with increasing concentration of the fluorescent DYE-3 or DYE-1 molecule as a result of increased intermolecular interaction be-

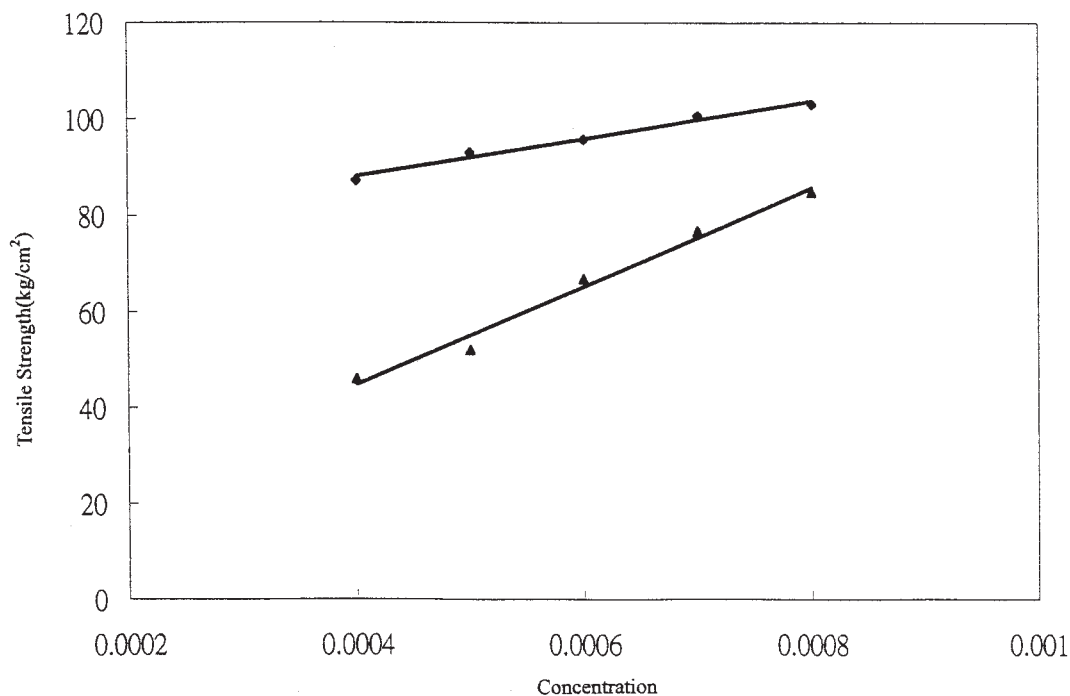


Figure 10 The lot of the tensile strength versus the concentration of the fluorescent dye used to prepare the fluorescent dye based polyurethane ionomer at $25 \pm 0.05^\circ\text{C}$.

tween ionomer molecules themselves. However, the tensile strength at the breaking point appears to be better for DYE-1 than DYE-3 based PU ionomer molecules. It is believed that more electron donating groups linked to the backbone of the PU ionomer molecules are likely to reduce the intermolecular interaction between ionomer molecules, thus causing the tensile strength of DYE-3 based PU ionomer molecules to decrease.

We thank the National Science Council of Taiwan for the financial support of this research.

References

1. Brown, F. K.; Brown, P. J.; Bickett, D. M.; Chambers, C. L. *J Med Chem* 1994, 37, 674.
2. Wang, C. L.; Kuo, Y. M.; Chao, D. Y. *Polym Adv Technol* 2000, 11, 127.
3. DeSilva, A. P.; Sandanayake, K. R. A. S. *Tetrahedron Lett* 1991, 32, 42.
4. Prasanna DeSilva, A.; Nimal Gunaratne, H. Q.; Lynch, P. L. M. *J Chem Soc Perkin Trans* 1995, 2, 685.
5. Wang, C. L.; Zhang, Z. J.; Yang, C. Y.; Chao, D. Y. *J Appl Polym Sci* 2003, 89, 8923.
6. Wang, C. L.; Zhang, Z. J.; Chen, C. Y.; Kuo, Y. M.; Chao, D. Y. *Hwa Kang J Sci* 2003, 20, 257.