Synthesis and Fluorescence Behavior of Poly[ω -(1,8-naphthalimido)alkyl methacrylates]

Woo-Sik KIM, Dae-Hee OH,* Won-Suk CHANG, and Kwan-Ho SEO

Department of Polymer Science, Kyungpook National University,
Taegu 702-701, Korea

*Department of Surface Coating Engineering, Pusan National University of Technology,
Pusan 608-739, Korea

(Received May 6, 1993)

ABSTRACT: Poly[ω -(1,8-naphthalimido)alkyl methacrylates] (the alkyl: ethyl, propyl, butyl, and pentyl) were synthesized. Inherent viscosities of these polymers were rather low. Poly[ω -(1,8-naphthalimido)alkyl methacrylates] showed weak monomer emission around 380 nm and strong excimer emission around 460 nm in 1,2-dichloroethane. The intensity ratio of the excimer to monomer emissions was independent of the concentration but dependent on the viscosity of the polymers. This result suggests that the polymers form excimers intramolecularly. The ratio showed an even-odd effect for the carbon number of the alkyl groups in the polymers and it increased with the increase in the even or odd carbon number.

KEY WORDS Synthesis / Naphthalimidoalkyl Methacrylate / Fluorescence
/ Intramolecular Excimer / Even-Odd Effect /

For the purpose of designing polymers undergoing chlorophyll-simulated photoreactions, an understanding of interactions between chromophores in polymers is important. For the elucidation of the interactions, it is essential to investigate the effect of the molecular structure of polymers on excimer formation of chromophores.

There are some reports^{1–4} on the effect of the alkyl chain length on excimer formation in polymers having pendant naphthalene rings. Guillet *et al.*¹ reported that the excimer intensity of poly(1-naphthyl acrylate) was stronger than that of poly(1-naphthyl methacrylate) which is stiffer than poly(1-naphthyl acrylate). Ueno *et al.*² reported that the excimer formation of poly(1-naphthyl alanine) was not observed, but the excimer formation of its derivatives which have methylene groups between the main chain and the naphthyl group was observed. Guillet *et al.*³ also reported that the excimer intensity of poly(1-naphthyl-

methyl methacrylate) was greater than that of poly[2-(1-naphthylethyl methacrylate)]. Nakahira *et al.*⁴ reported that the excimer intensity of poly(2-naphthylalkyl methacrylates) was in the order of methyl > propyl > ethyl for the alkyl group. In this case, the intensity of poly(2-naphthylalkyl methacrylate) having more flexible alkyl group became smaller. As described in these reports,^{1–4} the effect of the alkyl chain length on excimer formation varies with different polymers.

We have previously reported the synthesis of poly[2-(1,8-naphthalimidoethyl methacrylate)] as a new polymer containing naphthalene structure and its possibility of excimer formation.⁵ In this study, in order to know the effects of the viscosity(molecular weight) and the alkyl chain length on the excimer formation, poly[ω -(1,8-naphthalimido)alkyl methacrylates] with various alkyl groups were synthesized and their fluorescence behavior was investigated.

EXPERIMENTAL

Materials

Commercial reagents (Aldrich) such as ethanolamine, 3-aminopropanol, 4-aminobutanol, 5-aminopentanol, and 1,8-naphthalic anhydride were used without further purification. Methacryloyl chloride (Aldrich) was used after distillation. Tetrahydrofuran (THF) and dimethylformamide of reagent grade were distilled in the presence of sodium and magnesium sulfate, respectively. Azobisisobutyronitrile (AIBN) was recrystallized from methanol. All of the other reagents were used without purification.

Measurements

Elemental analyses were made with a Perkin-Elmer Model 240 elemental analyzer. IR spectra were recorded on a JASCO-IR 810 spectrophotometer by KBr method. NMR and mass spectra were measured with a Varian T-60A ^1H NMR spectrometer and with a Hewlett Packard Model 5985A GC/MS/DS spectrometer, respectively. Viscosities were measured at a concentration of 0.06 g dl^{-1} in trifluoroacetic acid with a Ubbelohde viscometer at 30°C . Fluorescence spectra were measured at room temperature with a Shimadzu Model RF-500 spectrofluorimeter by using 1,2-dichloroethane as a solvent.

Synthesis of Poly(1,8-naphthalimidoalkyl methacrylates)

Four kinds (**3a**, **3b**, **3c**, and **3d**) of poly(1,8-naphthalimidoalkyl methacrylates) were synthesized by the following reactions:

N-3-Hydroxypropyl-1,8-naphthalimide (**1b**), *N*-4-hydroxybutyl-1,8-naphthalimide (**1c**), and *N*-5-hydroxypentyl-1,8-naphthalimide (**1d**) were synthesized by the same synthetic method as **1a**.⁵ The following is a typical synthetic procedure. To 350 ml of THF were added 5.95 g (0.03 mol) of 1,8-naphthalic anhydride and 3.00 g (0.04 mol) of 3-aminopropanol. After the mixture was stirred for 16 h at 70°C , the solvent was evaporated. The reaction mixture was washed with water and recrystallized from ethanol. Hydroxy-1,8-naphthalimides (**1b**, **1c**, and **1d**) showed strong absorption bands of hydroxy group at 3490 cm^{-1} , ester carbonyl group at 1697 cm^{-1} , and naphthalimide carbonyl group at 1655 cm^{-1} in IR spectra. The yields, melting points, mass numbers, chemical shifts of ^1H NMR spectra, and the results of elemental analysis of these imides are given in the following.

1b

Yield, 75%; mp $118\text{--}120^\circ\text{C}$.

^1H NMR (CDCl_3 , δ): 2.1 (2H, CH_2), 3.7 (2H, CH_2), 4.4 (2H, CH_2), 7.9 (2H, naphthalimide), 8.5 (4H, naphthalimide).

Found: C, 70.5%; H, 5.34%; N, 5.89%.

Calculated for $\text{C}_{15}\text{H}_{13}\text{NO}_3$: C, 70.6%; H, 5.10%; N, 5.49%.

1c

Yield, 71%; mp $93\text{--}95^\circ\text{C}$.

^1H NMR (CDCl_3 , δ): 1.6 (4H, CH_2), 3.5 (2H, CH_2), 4.1 (2H, CH_2), 7.9 (2H, naphthalimide), 8.5 (4H, naphthalimide).

Found: C, 70.0%; H, 5.79%; N, 4.97%.

Calculated for $\text{C}_{16}\text{H}_{15}\text{NO}_3$: C, 71.4%; H, 5.50%; N, 5.20%.

1d

Yield, 68%; mp $70\text{--}72^\circ\text{C}$.

^1H NMR (CDCl_3 , δ): 2.7 (6H, CH_2), 3.6 (2H, CH_2), 4.2 (2H, CH_2), 8.2 (6H, naphthalimide).

Found: C, 71.9%; H, 6.08%; N, 4.96%.

Calculated for $\text{C}_{17}\text{H}_{17}\text{NO}_3$: C, 72.1%; H, 5.50%; N, 4.95%.

1,8-Naphthalimidopropyl methacrylate (**2b**), 1,8-Naphthalimidobutyl methacrylate (**2c**), and 1,8-naphthalimidopentyl methacrylate (**2d**) were synthesized by the same synthetic method as **2a**.⁵ A representative synthetic procedure is as follows. To 400 ml of THF were added 5.1 g (0.02 mol) of **1b** and 3.5 ml of triethylamine. To the stirred mixture was added dropwise over 1 h 3.1 g (0.03 mol) of methacryloyl chloride in 50 ml of THF at 0–5°C. Then it was stirred for another 5 h at room temperature. The precipitated salt was removed by filtration. The solvent was evaporated. The crude product was recrystallized from ethanol. Naphthalimidoalkyl methacrylates (**2b**, **2c**, and **2d**) gave absorption bands of ester carbonyl group at 1715 cm^{-1} , imide carbonyl group at 1670 cm^{-1} , and vinyl group at 960 cm^{-1} in IR spectra. The yields, the melting points, the mass numbers (M^+), the molar extinction coefficients (ϵ , $M^{-1}\text{ cm}^{-1}$), the chemical shifts, and the results of elemental analysis of these monomers are given in the following.

2b

Yield, 69%; mp 107–109°C; M^+ , 323; ϵ (333 nm), 13400.

^1H NMR (CDCl_3 , δ): 1.9 (3H, CH_3), 2.2 (2H, CH_2), 4.3 (4H, $(\text{CH}_2)_2$), 5.5 (1H, CH_2 of vinyl), 6.1 (1H, CH_2 of vinyl), 7.7 (2H, naphthalimide), 8.2 (2H, naphthalimide), 8.6 (2H, naphthalimide).

Found: C, 70.4%; H, 5.51%; N, 4.56%.

Calculated for $\text{C}_{19}\text{H}_{17}\text{NO}_4$: C, 70.6%; H, 5.26%; N, 4.44%.

2c

Yield, 56%, mp 69–71°C; M^+ , 337; ϵ (333 nm), 13400.

^1H NMR (CDCl_3 , δ): 1.8 (4H, $(\text{CH}_2)_2$), 1.9 (3H, CH_3), 4.2 (4H, $(\text{CH}_2)_2$), 5.5 (1H, CH_2 of vinyl), 6.1 (1H, CH_2 of vinyl), 7.8 (2H,

naphthalimide), 8.2 (2H, naphthalimide), 8.7 (2H, naphthalimide).

Found: C, 70.2%; H, 5.64%; N, 4.16%.

Calculated for $\text{C}_{20}\text{H}_{19}\text{NO}_4$: C, 71.2%; H, 5.63%; N, 4.15%.

2d

Yield, 58%; mp 65–67°C; M^+ , 351; ϵ (333 nm), 13400.

^1H NMR (CDCl_3 , δ): 1.8 (6H, $(\text{CH}_2)_3$), 1.9 (3H, CH_3), 4.2 (4H, $(\text{CH}_2)_2$), 5.5 (1H, CH_2 of vinyl), 6.1 (1H, CH_2 of vinyl), 7.8 (2H, naphthalimide), 8.2 (2H, naphthalimide), 8.7 (2H, naphthalimide).

Found: C, 72.1%; H, 6.15%; N, 4.08%.

Calculated for $\text{C}_{21}\text{H}_{21}\text{NO}_4$: C, 71.8%; H, 5.98%; N, 3.99%.

3a was synthesized in the previous work.⁵

2b was polymerized by the same method of the polymerization as **2a**: In a 50 ml ampoule were placed 15 ml of dimethylformamide, 1 g of **2b**, and 1 mol% of AIBN with respect to **2b**. The ampoule was sealed under nitrogen and heated at 65°C for 48 h. The reaction mixture was poured into a large excess of methanol to precipitate the polymer. The precipitate was filtered and dried under vacuum. Polymerizations of **2c** and **2d** were carried out similarly. The yields, inherent viscosities (η_{inh} , dl g^{-1}), and the chemical shifts of these polymers are given in the following.

3b

Yield, 80%; η_{inh} , 0.13.

^1H NMR (CF_3COOH , δ): 1.4 (3H, CH_3), 2.4 (4H, CH_2), 4.5 (4H, CH_2), 8.0 (6H, naphthalimide).

3c

Yield, 82%; η_{inh} , 0.17

^1H NMR (CF_3COOH , δ): 1.2 (3H, CH_3), 2.0 (6H, CH_2), 4.3 (4H, CH_2), 8.0 (6H, naphthalimide).

3d

Yield, 77%; η_{inh} , 0.11

^1H NMR (CF_3COOH , δ): 1.3 (3H, CH_3), 2.1 (8H, CH_2), 4.3 (4H, CH_2), 8.0 (6H, naphthalimide).

RESULTS AND DISCUSSION

Figure 1 compares UV spectra of **2b** and naphthalene in 1,2-dichloroethane. **2b** showed broad bands in the range of 295 to 375 nm. However, naphthalene exhibited similar bands in the range of 245 to 295 nm. The ϵ values of **2a**, **2b**, **2c**, and **2d** at 333 nm were determined to be 13,400 in 1,2-dichloroethane, the size of the alkyl groups in these monomers having no effect on ϵ .

These polymers were soluble in chloroform, trifluoroacetic acid, etc. The solubility of these

Figure 1. UV spectra of **2b** (—) and naphthalene (····) in 1,2-dichloroethane.

Figure 2. Fluorescence spectra of **2b** (—) and **3b** (---) in 1,2-dichloroethane: [Residue] = 1×10^{-6} M; excitation 330 nm.

polymers increased with the increase in the size of the alkyl groups. The inherent viscosities of these polymers were rather low (0.08 to 0.17 dl g^{-1}).

Fluorescence spectra of **2b** and **3b** are shown in Figure 2. **2b** exhibited only monomer emission band around 380 nm. The polymer (**3b**) showed a weak emission band around 380 nm and a strong and broad emission band around 460 nm. The band of **3b** around 380 nm was assigned to be a monomer emission band because the emission maximum wavelength of **3b** was the same as that of **2b**. In order to know whether the red-shifted band is due to an excimer formation of **3b** or not, absorption and excitation spectra of **3b** were measured, as shown in Figure 3. The excitation spectrum was measured at emission wavelength of 460 nm, which corresponds to the emission maximum wavelength of **3b**. As given in Figure 3, even though the relative intensities of 333 nm and 348 nm in the two spectra are a little different, the peaks of the bands in the spectra are similar. This result suggests that the broad emission band around 460 nm in Figure 2 is an excimer emission band.^{6,7}

To know the effect of the concentration of the polymers (**3a**, **3b**, **3c**, and **3d**) on the intensity ratio of excimer emission (I_e) to monomer emission (I_m), the ratios were plotted against the concentration (Figure 4). The ratios scarcely changed with the concentration,

Figure 3. Absorption (—) and excitation spectra of **3b** at monitoring emission of 460 nm (---) in 1,2-dichloroethane at [Residue] = 1×10^{-5} M.

Figure 4. Concentration dependence of I_e/I_m in 1,2-dichloroethane: (○) 3a; (●) 3b; (□) 3c; (■) 3d.

Figure 5. Viscosity dependence of I_e/I_m in 1,2-dichloroethane: (○) 3a; (●) 3b; (□) 3c; (■) 3d; [Residue] = 1×10^{-6} M; excitation 330 nm.

indicating that the polymers form excimers intramolecularly.⁷ As shown in Figure 4, the order of the I_e/I_m ratios was $3a < 3c < 3b < 3d$.

The I_e/I_m ratios for the polymers (3a, 3b, 3c, and 3d) were plotted against the inherent viscosity (Figure 5). The ratio increased with the increase in the viscosity. This result seems to indicate that poly[ω -(1,8-naphthalimido)-alkyl methacrylates] form intramolecular excimer between nearest as well as nonnearest neighbor chromophores.^{8,9} So far, the effect of

molecular weight on an excimer formation seems not to be investigated in detail.^{8,9}

As given in Figure 5, the order of the ratios for the size of the alkyl groups in the polymers was $3a < 3c < 3b < 3d$ in the range of viscosity. Thus, the ratio apparently showed an even-odd effect for the carbon number of the alkyl groups in the polymers and it increased with the increase in the even or odd number of alkyl groups. The latter result was supported by the results of Guillet *et al.*¹ and Ueno *et al.*² which were explained by the flexibility of the side chain. This result, however, was in the reverse of Nakahira's result⁴ that the ratio of poly(2-naphthyl-alkyl methacrylates) decreased with the increase in the odd number of alkyl groups. Our polymers are stiffer than Nakahira's polymers because the naphthalimido group is bulkier than the naphthyl group. Therefore, the effect of alkyl groups on our polymers and Nakahira's polymers on the ratio can be different. Also, it is thought that polymers with a suitable flexibility form an excimer easily. Though α,ω -diesters prepared from ethylene glycol homologs, $\text{HO}(\text{CH}_2)_m\text{OH}$ ($m=2-5$), and 1-naphthoic acid are not polymers, the ratios of the esters showed an even-odd effect and it increased with the increase in the even or odd carbon number of m .¹⁰ The tendency of the ratio toward the carbon number of m was similar to that of our polymers toward the carbon number of alkyl groups in 3a–3d. The former result was rationalized by an equilibrium rotational isomeric state analysis.¹⁰ The analysis was based on taking an easy conformation of intramolecular nearest chromophores for an excimer formation. Considering the analysis,¹⁰ our result can be explained by effect of the carbon number of the alkyl spacers on conformations conducive to an excimer formation.

CONCLUSION

Poly[ω -(1,8-naphthalimidoalkyl)methacrylates] (**3a**, **3b**, **3c**, and **3d**) were synthesized. The viscosities of these polymers were rather low. The I_e/I_m ratios of these polymers (**3a** to **3d**) scarcely depended on the concentration but significantly depended on the viscosity. These results suggest that they form intramolecular excimers with the nearest and nonnearest neighboring groups. The ratio showed an even-odd effect for the carbon number of the alkyl groups in the polymers and it increased with increasing the even or odd carbon number.

Acknowledgement. The authors thank the Korea Science and Engineering Foundation for the financial support of this work (KOSEF 871-1005-006-2).

REFERENCES

1. L. Merle-Aubry, A. Holden, Y. Merle, and J. E. Guillet, *Macromolecules*, **13**, 1138 (1980).
2. A. Ueno, T. Osa, and F. Toda, *J. Polym. Sci., Polym. Lett. Ed.*, **16**, 539 (1978).
3. D. A. Holden, P. Y. K. Wang, and J. E. Guillet, *Macromolecules*, **13**, 295 (1980).
4. T. Nakahira, I. Maruyama, S. Iwabuchi, and K. Kojima, *Makromol. Chem.*, **180**, 1853 (1979).
5. W. S. Kim, D. H. Oh, and K. H. Seo, *Polym. Commun.*, **29**, 108 (1988).
6. A. C. Somersall and J. E. Guillet, *Macromolecules*, **6**, 218 (1973).
7. S. Tazuke and F. Banba, *Macromolecules*, **9**, 451 (1976).
8. J. S. Aspler and J. E. Guillet, *Macromolecules*, **12**, 1982 (1979).
9. Y. Suzuki and S. Tazuke, *Macromolecules*, **14**, 1742 (1981).
10. F. Mendicuti, B. Patel, and W. L. Mattice, *Polymer*, **31**, 453 (1990).