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Photophysical processes of a copolymer containing naphthalene and carbazole rings

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Abstract

The photophysical processes of copolymer formed by copolymerization of β-naphthyl-methacrylate (NMA) with vinylcarbazole (VCZ) were studied. The results show that when the solution of copolymer (NMA–VCZ) in THF is located in a low concentration range (about 10^{-8} mol/l), the fluorescence emission is in good agreement with that of NMA monomer and the excimer is formed with gradual increase in concentration of copolymer (NMA–VCZ). The fluorescence of copolymer (NMA–VCZ) can be efficiently quenched both by electron donors and acceptors where the quenching effects follow the Stern–Volmer equation. The dimolecular exciplex between copolymer (NMA–VCZ) and *N*,*N*-dimethylaniline (DMA) is formed and the triple exciplex is also observed in the same system. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Copolymer; β-naphthyl-methacrylate; Vinylcarbazole; Excimer; Triple exciplex

1. Introduction

Recently, polymeric light-charge materials have attracted much attention for their potential application in light-emitting devices [1]. Although a great number of polymers have been synthesised and the photoluminescence and electroluminescence properties have also been investigated, the studies on synthesis and photophysical processes of new polymer still remain to be a challenge in this area [2]. We have synthesised a novel copolymer consisting of naphthalene moiety, which emits blue fluorescence with high quantum yield and polyvinylcarbazole (PVCZ) moiety, which can form high-quality thin films with excellent hole-transporting function. In this paper, we report the results of study on the photophysical processes of copolymer β-naphthyl-methacrylate–

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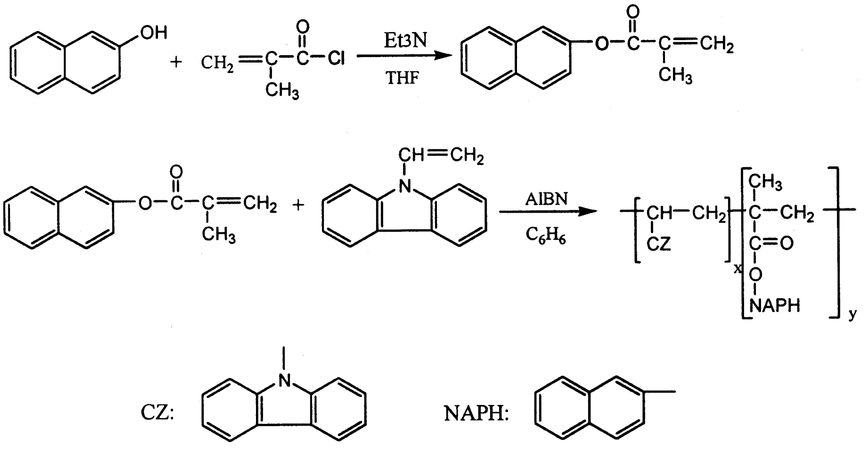

Scheme 1.

vinylcarbazole (NMA–VCZ) using steady fluorescence quenching technique etc. in which the formations of exciplex are especially investigated since the exciplexes are often a middle state of photochemical, photophysical and photobiological primary processes.

2. Experimental

NMA was synthesised by esterification between β-naphthol and methacryloyl chloride in the presence of triethylamine. Then copolymer (NMA–VCZ) was synthesised by polymerisation of NMA (2%) with VCZ (98%) in the presence of 2,2′-azobisisobutyronitrile (AIBN) as initiator. The synthesis and composition of copolymer (NMA–VCZ) are outlined in Scheme 1. The molecular weight of copolymer (NMA–VCZ) is 12 800.

N,*N*-dimethyl-aniline (DMA) and THF were both analytical grade reagents and treated according to standard methods used before.

The measurements of fluorescence were performed on a Perkin-Elmer LS-50B fluorometer with an excitation wavelength of 260 nm. Both excitation and emission bands were set at 3.5 nm on these experimental conditions. All the experiments were carried out at 25 ± 1°C, about which temperature control was maintained by a model 501 superthermostat circulating water bath.

3. Results and discussion

3.1. Luminous properties of copolymer (NMA–VCZ) and formation of excimer

The fluorescence spectra of copolymer (NMA–VCZ) are shown in Fig. 1a. It can be seen when concentration of copolymer (NMA–VCZ) is 5.6×10^{-9} mol/l, the maximal fluorescence emission is at 310 nm which is in good agreement with that of NMA monomer (see Fig. 1b). This means

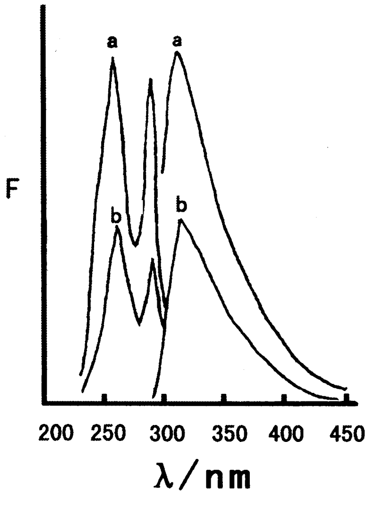

Fig. 1. Excitation and emission fluorescence spectra of copolymer (NMA–VCZ) (a) and NMA (b). Concentration of (a), 5.6×10^{-9} mol/l; and (b), 1.48×10^{-5} mol/l. Excitation and emission wavelength are 260 and 310 nm, respectively.

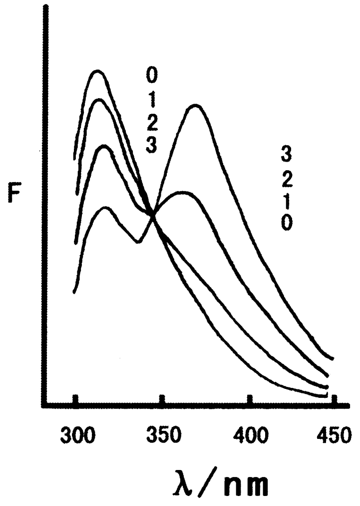

Fig. 2. Fluorescence spectra of copolymer (NMA–VCZ) and its excimer. Concentration of copolymer (NMA–VCZ) (mol/l), 0, 5.6×10^{-9}; 1, 1.13×10^{-8}; 2, 2.24×10^{-8}; 3, 4.49×10^{-8}. Excitation wavelength, 260 nm.

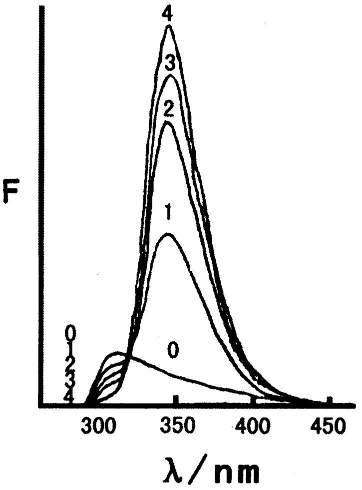

Fig. 3. Fluorescence spectra of copolymer (NMA–VCZ) and exciplex. Concentration of copolymer (NMA–VCZ), 4.1×10^{-9} mol/l. Concentration of DMA (mol/l), 0, 0.00; 1, 6.06×10^{-6}; 2, 1.21×10^{-5} 3, 1.82×10^{-5}; 4, 4.24×10^{-5}.

that the copolymer (NMA–VCZ) mainly manifests the part of luminous behaviour of NMA containing naphthalene ring in low concentration range. Under this condition, when the concentration of copolymer (NMA–VCZ) was fixed at 5.6×10^{-9} mol/l (Fig. 2, 0), the fluorescence was quenched efficiently with the progressive increase in concentration of copolymer (NMA–VCZ) itself (Fig. 2, 1–3), and at a relatively longer wavelength a new emission band appeared at 370 nm and the spectra passed an isostilbic point of 345 nm. Evidently, the fluorescence emission at 370 nm contributed to the excimer formed between copolymer (NMA–VCZ) molecules [3].

3.2. Formation of bimolecular exciplex

Fig. 3 gives the fluorescence spectra of copolymer (NMA–VCZ) in the presence of DMA. It can be seen that the fluorescence of copolymer (NMA–VCZ) was also efficiently quenched with increasing concentration of DMA. At the same time, a new structureless emission band appeared at a relatively longer wavelength of 345 nm and all the spectra passed an isostilbic point of 320 nm. The fluorescence quenching pattern was similar to that of copolymer (NMA–VCZ) concentration quenching described above, which indicated that a bimolecular exciplex was formed between copolymer (NMA–VCZ) and DMA.

The ratio of the fluorescence intensity of exciplex, F_E, to that of copolymer (NMA–VCZ), F_M, was plotted as a function of [DMA], and a straight line was obtained with a good correlation ($\gamma > 0.998$). From the slope of the line, an estimate of the probability of exciplex formation, K_e [4], could be made as 6.32×10^5. This suggested that the degree of exciplex formation between copolymer (NMA–VCZ) and DMA was stronger. Plot of F_M^0/F_M, i.e. the ratio of fluorescence intensity versus [DMA] also gave a straight line which conformed to Stern–Volmer equation $F_M^0/F_M = 1 + K_{sv}[DMA]$, so it could be estimated that K_{sv}, the apparent quenching coefficient, was 7.04×10^4 M^{-1} [5]. The result suggested that the quenching effect mainly came from the stronger charge-transfer process of NMA with DMA, among which the exciplex was dominant.

3.3. Formation of triple exciplex

As shown in Fig. 4, when concentration of copolymer (NMA–VCZ) and DMA is fixed at 4.1×10^{-9} and 4.2×10^{-5} mol/l, respectively, the emission intensity of bimolecular exciplex formed by copolymer (NMA–VCZ) with DMA is maximised. On the basis of the maximal emission spectrum, the fluorescence of bimolecular exciplex is again quenched with addition of copolymer (NMA–VCZ), meantime, a new broad structureless emission band appears at a relative further long wavelength of 400 nm, and similarly all the spectra pass an new isostilbic point of 362 nm. These experimental results show that trimolecular exciplex (triple exciplex), i.e. AAD is formed. The fluorescence peak at 400 nm arose from the triple exciplex [6,7]. As described earlier, plot of F_T/F_E versus concentration of copolymer (NMA–VCZ) is also linear and K_T can be obtained as 7.55×10^4.

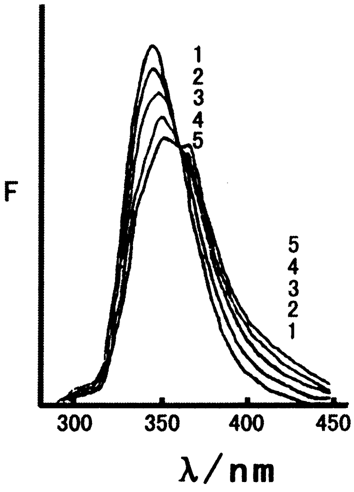

Fig. 4. Fluorescence spectra of a triple exciplex. Concentration of copolymer (NMA–VCZ)(mol/l), 1, 4.1×10^{-9}; 2, 7.2×10^{-8}; 3, 1.41×10^{-7}; 4, 2.11×10^{-7}; 5, 2.80×10^{-7}. Concentration of DMA 4.24×10^{-5} mol/l.

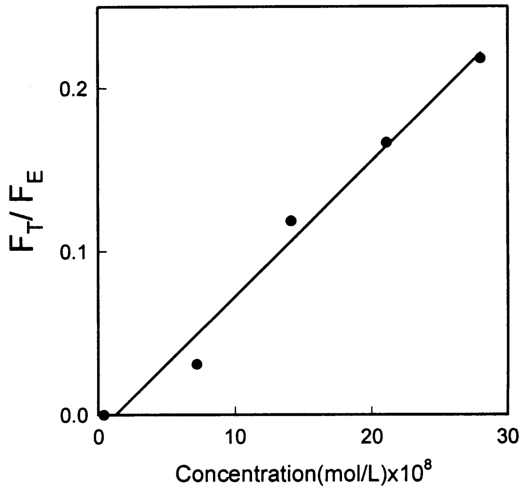

Fig. 5. Dependence of F_T/F_E on concentration of copolymer (NMA–VCZ). Concentration of DMA, 4.24×10^{-5} mol/l.

The whole photophysical processes can be summarised as follows:

$$\mathrm{A} \xrightarrow{hv} \mathrm{A}* \qquad \text{(light-excitation)} \tag{1}$$

$$\mathrm{A}* \xrightarrow{K_1} \mathrm{A} + hv_{\mathrm{M}}$$

(fluorescence emission of single molecule) (2)

$$\mathrm{A}* \xrightarrow{K_2} \mathrm{A} \qquad \text{(decay of non-radiation)} \tag{3}$$

$$\mathrm{A}* + \mathrm{D} \xrightarrow{K_3} (\mathrm{AD})*$$

(formation of bimolecular exciplex) (4)

$$(\mathrm{AD})* \xrightarrow{K_4} \mathrm{A} + \mathrm{D} + hv_{\mathrm{E}}$$

(fluorescence emission of biomolecular exciplex) (5)

$$(\mathrm{AD})* \xrightarrow{K_5} \mathrm{A} + \mathrm{D} \qquad \text{(decay of non-radiation)} \tag{6}$$

$$(\mathrm{AD})* + \mathrm{A} \xrightarrow{K_6} (\mathrm{AAD})*$$

(formation of triple exciplex) (7)

$$(\mathrm{AAD})* \xrightarrow{K_7} \mathrm{AAD} + hv_{\mathrm{T}}$$

(fluorescence emission of triple exciplex) (8)

$$(\mathrm{AAD})* \xrightarrow{K_8} \mathrm{AD} + \mathrm{A} \qquad \text{(decay of non-radiation)} \tag{9}$$

According to the steady-state equilibrium, the following equation can be obtained through Eqs. (7)–(9):

$$\frac{\bar{d}(\mathrm{AAD})*}{\bar{d}t} K_6(\mathrm{AD})*(\mathrm{A}) - (K_7 + K_8)(\mathrm{AAD})* = 0 \tag{10}$$

hence the Eq. (11) is obtained as follows:

$$\frac{(\mathrm{AAD})*}{(\mathrm{AD})*} = \frac{K_6}{K_7 + K_8}(\mathrm{A}) \tag{11}$$

This means that the ratio of fluorescence intensity of triple exciplex to that of bimolecular exciplex is proportional to the concentration of copolymer (NMA–VCZ). The above result is plotted in Fig. 5. It can be seen that the experimental result is in agreement with Eq. (11). By this, it is demonstrated that the mechanism for the formation of triple exciplex, $(AD)^* + A \rightarrow (AAD)^*$, is primary [7].

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