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Intramolecular triplet energy migration in poly(2-vinylnaphthalene) and poly(naphthylalkyl methacrylate)s in solid solution: Effects of side chain length

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Summary

The effect of side chain length on intramolecular triplet energy migration of naphthalene containing polymers was investigated by a delayed fluorescence (DF) spectroscopy for the solid solution of the polymers. The degree of triplet energy migration depends strongly on whether the chromophores are directly attached to the main chain or not.

Introduction

Several studies on the intramolecular triplet energy migration in a solid solution of chromophoric polymers have been reported (1-4). Pash et al. reported that the molecular weight dependence of DF intensity (I_{DF}) for poly(2-naphthyl methacrylate) is much smaller than that of P2VN (1,2). Nakahira et al. also investigated the molecular weight dependence of the ratio of DF intensity to phosphorescence intensity (I_P), I_{DF}/I_P, for poly(2-naphthylmethyl methacrylate) and poly[1-(2-naphthyl)ethyl methacrylate] (3). They showed that the molecular weight dependence of I_{DF}/I_P is not so large for poly(2-naphthylmethyl methacrylate), but large for poly[1-(2-naphthyl)ethyl methacrylate]. They also reported the formation of the triplet trap site in both polymer systems from the shift of phosphorescence spectra. They suggested that the difference of I_{DF}/I_P with different polymer structures is attributed to the ability of trap site formation, in other words, to the difference in the steric hindrance of polymer side chains.

In this study, the molecular weight dependence of the DF intensity for various polymers having naphthalene chromophores was compared in polymer solid solutions and the effect of side chain length on the intramolecular triplet energy migration was investigated. In these polymers, the distance of naphthyl chromophore from the main chains was varied. The sample used in this study was: poly(2-vinylnaphthalene) (P2VN), poly(2-naphthylmethyl methacrylate) (PNMMA), poly(2-naphthylethyl methacrylate) (PNEMA), and poly(2-naphthylpropyl methacrylate) (PNPMA).

Experimental

All the polymers were prepared by AIBN-initiated radical polymerization and purified by repeated reprecipitation from benzene and methanol. Details of the synthetic methods are described elsewhere (6). The different molecular weight samples for each polymer were prepared by fractionation of the polymer with GPC. Four samples with different molecular weight (Mw) were prepared for each polymer: 2.0×10^4, 5.2×10^4, 7.8×10^4, and 1.07×10^5. Delayed luminescence spectra were measured with a Hitachi 850 spectrofluorophotometer fitted with phosphorescence attachment. The prompt emission within 1 ms after the excitation was eliminated by a fast mechanical chopper and a gated electronics of the detection. The decay curves of delayed fluorescence and phosphorescence were measured by a photon counting technique using Xe-flash lamp as a excitation light source. The excitation wavelength was 277 nm. Details of the systems are described elsewhere (5). The polymers were dissolved in 2-methyltetrahydrofuran and sealed in vacuo. The absorbance of the samples was adjusted to be 0.2 at 277 nm for all samples: the concentration of the polymers was less than 5×10^{-7} mol/l. The spectroscopic measurements were carried out at 77 K.

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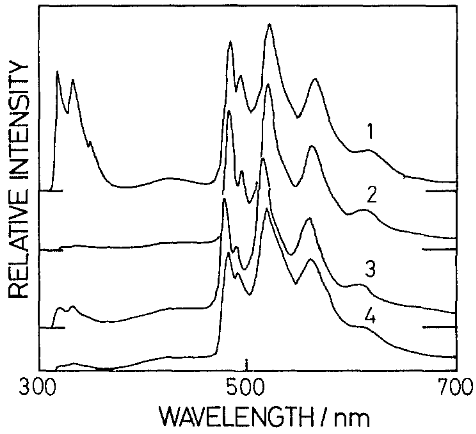

Figure 1 Delayed luminescence spectra of polymers in MTHF at 77 K: (1) P2VN, (2) PNMMA, (3) PNEMA, and (4) PNPMA.

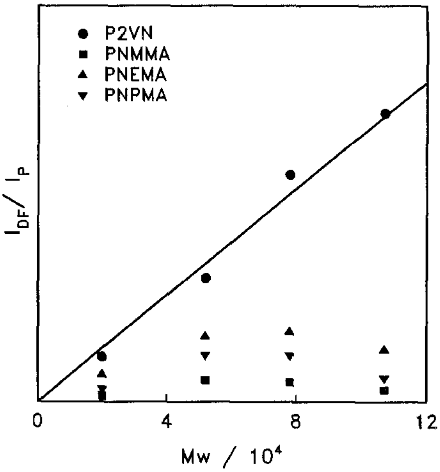

Figure 2 Plot of the ratio of delayed fluorescence intensity to phosphorescence intensity I_{DF}/I_P against the molecular weight of the polymers.

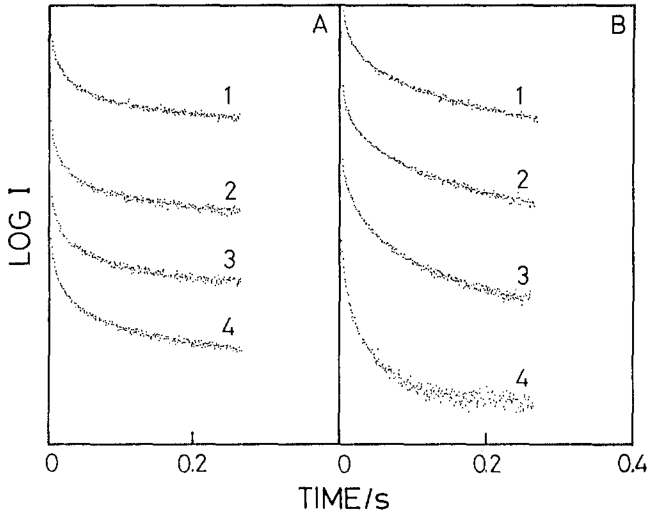

Figure 3 Effect of molecular weight on the decay curve profiles of the delayed fluorescence at 336 nm in MTHF at 77 K: (A) PNEMA and (B) P2VN. The molecular weights are (1) 1.07 x 10^5, (2) 7.8 x 10^4, (3) 5.2 x 10^4, and (4) 2.0 x 10^4.

Results and Discussion.

Figure 1 shows the delayed luminescence spectra of the polymers whose molecular weights(Mw) are the same, 1.07 x 10^6 at photostationary condition. P2VN showed strong delayed fluorescence (DF), but PNAMAs (PNMMA, PNEMA, and PNPMA) showed relatively weak DF. The energy migration in P2VN was much more efficient than that in PNAMAs.

It should be noted that the spectral shift of phosphorescence spectra was not observed in the solid solution for all samples. In the films for PNAMAs, however, a large spectral shift was observed due to the trap site formation (5). In these films, inter-chromophore interaction induces the formation of a triplet trap site because the concentration of the chromophores in the films is higher than that in the solid solution. The present findings indicate the absence of a triplet trap site in the solid solution. As mentioned above, Nakahira et al. reported the large spectral shift of PNMMA phosphorescence, and their result is in poor agreement with ours. The reason is not clear at this stage.

Figure 2 shows the plot of the I_{DF}/I_P against the Mw of the polymers. I_{DF}/I_P for P2VN increased linearly with the molecular weight from 2.0 x 10^4 to 1.0 x 10^6. On the other hand, I_{DF}/I_P for PNAMAs were saturated above a molecular weight of 5.0 x 10^4.

Figure 3A and Figure 3B show the change of decay profiles of delayed fluorescence at 336 nm with molecular weight for PNEMA and P2VN, respectively. The decay curves were multi-exponential (more than two) for both systems. The decay time of P2VN decreased with increasing its molecular weight. The slow decays of larger molecular weight samples indicate that the annihilation of mobile excitons for large molecular weight samples takes a long time compared with that for small molecular weight samples. On the other hand, PNEMA did not show clear molecular weight dependence. Neither polymer, PNMMA nor PNPMA show clear molecular weight dependence.

As judged from phosphorescence spectra, there seems to be neither a triplet trap site nor triplet excimer (Figure 1), and the major phosphorescence quenching process in polymer systems is ascribed to T-T annihilation, which provides multi-exponential decays for PNEMA or P2VN. The results shown in Figure 2 and Figure 3 indicate that the T-T annihilation occurs more efficiently in P2VN than in PNAMAs. The linearity of I_{DF}/I_P vs. Mw for P2VN shows that the probability that a polymer chain has two triplet excitons at the same time increases with the molecular weight of the polymer and that the triplet exciton in P2VN migrates along the polymer chain of more than a few hundred monomeric units. On the other hand, PNAMAs show weak molecular weight dependence and weak delayed fluorescence. This suggests that triplet energy migration is poor for PNAMAs. The high efficiency of triplet energy migration for P2VN is caused by the fact that the naphthalene moieties are directly attached to the main chain, and neighboring naphthalene moieties are forced to be close to each other. On the other hand, for PNAMAs, there are ester and methylene groups between the main chain and naphthalene moiety, so the neighboring naphthalene moieties are rather far apart. It should be noted that the triplet-triplet energy migration occurs by the exchange mechanism through the overlap of electron clouds (7). As a consequence, triplet energy migration in the solid solution of chromophoric vinylpolymers depends strongly on whether the chromophores are directly attached to the main chain or not. That is, the inter-chromophore distance strongly affects the efficiency of triplet energy migration. This is one of the key points to design the high efficiency systems of triplet energy migration. Besides the inter-chromophore distance, both the trap site and the excimer site also must be taken into consideration, since the trap site and the excimer site prevent the energy migration (6).

References

1. Pash NF, Webber SE (1978) Macromolecules 11: 727
2. Pash NF, Webber SE (1978) Macromolecules 11: 733
3. Nakahira T, Ishizuka S, Iwabuchi S, Kojima K (1980) Makromol Chem Rapid Commun 1: 759.
4. Yokoyama M, Tamamura T, Nakano T, Mikawa H (1976) J Chem Phys 65: 272
5. Katayama H, Tawa T, Ito S, Yamamoto M (1992) Submitted in J Chem Soc Faraday Trans
6. Ito S, Katayama H, Yamamoto M (1988) Macromolecules 21: 245
7. Dexter DL (1953) J Chem Phys 21: 836

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