Picosecond Fluorescence Studies on Poly(*N*-vinyl-5*H*-benzo[*b*]carbazole) in Solution

Chromophores bound in a polymer chain show intrapolymer excimer emission whose dynamic behavior is sometimes quite different from that of the corresponding concentrated solutions. In the case of poly(*N*-vinylcarbazole) (PVCz), a high-energy second excimer is observed in addition to the normal sandwich excimer.[1-8] Concerning their formation mechanism, Johnson proposed that the second excimer site exists prior to the excitation and that molecular conformational change during the monomer fluorescence lifetime produces the sandwich excimer.[2] A recent picosecond pulse radiolysis study reveals that the second excimer is formed immediately after irradiation with a 10-ps electron pulse, while the sandwich excimer emission shows a rise of several nanoseconds.[4] Similar rise and decay dynamics are observed by photon counting measurement,[5] and these results seem to be consistent with the above proposal. However, Ghiggino et al. reported that the second excimer fluorescence shows a rise of 120 ps, corresponding to the decay of monomer fluorescence.[8] Thus, the formation mechanism of the excimers is still unsettled at the present stage of investigation, and related experimental results should be accumulated. Here, we describe picosecond streak camera studies on poly(*N*-vinyl-5*H*-benzo[*b*]carbazole) (PV5BCz), since this is another polymer showing two kinds of excimers.[9]

Fluorescence spectra of the present polymers and the transmittance of the filters used are shown in Figure 1. In the case of PV5BCz(r), prepared by radical polymerization, the second excimer ($\sim$22 550 cm^{-1}) and the sandwich excimer ($\sim$20 350 cm^{-1}) are observed, while PV5BCz(c), prepared by cationic polymerization, shows monomer fluorescence with vibrational structure and the sandwich excimer.[9] Here, the mean degrees of polymerization of PV5BCz(r) and PV5BCz(c) are about 13 and 8, respectively, and the concentration of the benzo[*b*]carbazole chromophore is $\sim 9 \times 10^{-4}$ mol/L, indicating that the observed excimer emission is due to intramolecular interactions. These samples were excited with a single pulse ($\sim$25 ps) of the third harmonic of a Nd^{3+}:YAG laser, and their emission was recorded by a streak camera (Hamamatsu Temporaldisperser C979). Instead of a monochromator, appropriate filters were used to isolate the fluorescence, since the fluorescence intensity is rather weak under the present experimental conditions. Details of the present laser photolysis system are reported elsewhere.[10]

Fluorescence rise and decay curves of PV5BCz(r) are given in Figures 2 and 3a. In the short-wavelength region, an instantaneous rise determined by the time resolution of our apparatus (ca. 30 ps) is followed by the multiexponential decay. This consists of three decay components with time constants of 60 ps, 560 ps, and longer than a few nanoseconds. In the long-wavelength region, an instantaneous rise is succeeded by a rapid rise that corresponds to the above decay of 60 ps (Figure 2c), and no other distinct change was observed in the present time range. When a Hoya Y-46 filter was used, such a curve was not observed, which may be due to mutual cancellation of the rapid rise and decay components (Figure 2b). In the case of PV5BCz(c), the relative contribution of the 60-ps decay component in the short-wavelength region was very small compared to that of PV5BCz(r), and the above decay component of 560 ps was replaced by a decay process with a time constant of 820 ps. All these results are common to MTHF and toluene solutions.

When the time-integrated intensities of these components are correlated to the fluorescence spectra shown in Figure 1, the subnanosecond component of PV5BCz(r) is ascribed to the second excimer. The rapid decay of 60 ps is considered to be due to a precursor of both excimers, namely, a monomer fluorescent state, although its spectrum is not detected by conventional spectrophotofluorometry because of its short lifetime. On the other hand, the 850-ps component of PV5BCz(c) should be ascribed to the decay of the monomer fluorescence, since fluorescence spectra of this polymer do not seem to include the second excimer emission (Figure 1). The longest decay component corresponds to the sandwich excimer, with a lifetime of 57 ns.[10] These assignments are supported by the fact that the decay of ca. 60 ps is not so distinct in the case of PV5BCz(c) and are consistent with tacticity considerations. PV5BCz(r) is composed of both syndiotactic and isotactic sequences, showing monomer and two kinds of excimer emissions, while monomer and sandwich excimer fluorescence of PV5BCz(c) is consistent with its isotactic sequence.[9,11]

On the basis of the present results, we propose the mechanism of excimer formation of PV5BCz(r) shown in Figure 4. The notation e may involve excitation of the chromophore, its energy migration to the corresponding sites, and a very slight conformational change including rotational motion, all of which are completed within the time constant of our apparatus. The "monomer fluorescent state" may be different from the monomer excited state involved in the above process e. This monomer fluorescent

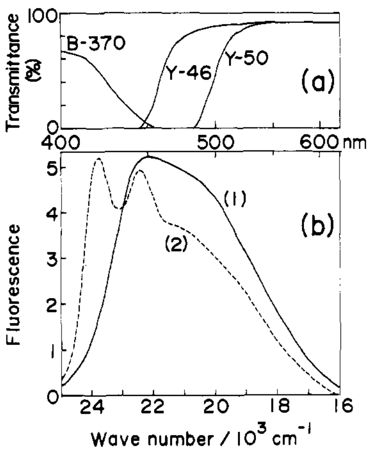

Figure 1. (a) Transmittance of filters used. (b) Fluorescence spectra of PV5BCz(r) (1) and PV5BCz(c) (2) in MTHF–THF mixed solvent.

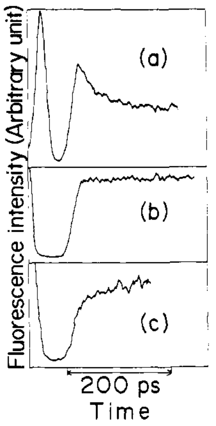

Figure 2. Fluorescence rise and decay curves of PV5BCz(r) in MTHF solution. The filters used are B-370 (a), Y-46 (b), and Y-50 (c). The first sharp pulse is a reference pulse used for calibration and data processing.

0024-9297/82/2215-1213$01.25/0

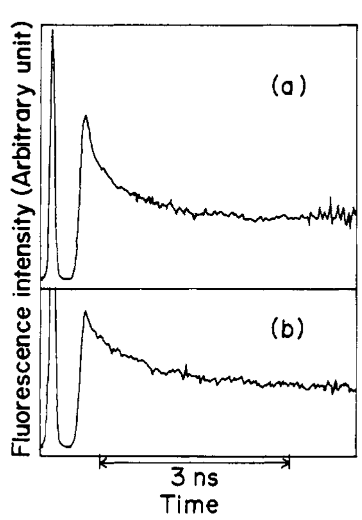

Figure 3. Fluorescence rise and decay curves of PV5BCz(r) (a) and PV5BCz(c) (b) in MTHF solution. A B-370 filter was used.

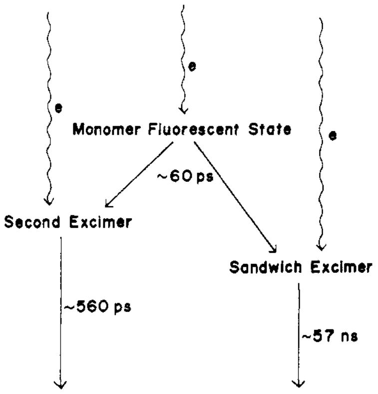

Figure 4. Scheme for excimer formation of PV5BCz(r). See text.

state may possibly be assigned to an excited state trapped in a chromophore that takes a different conformational and configurational structure. Energy migration from this molecule to excimer-forming sites, which may be coupled to a slight movement of the main chain or side groups, determines the time constant of 60 ps. Although the rise curve of the second excimer was not observed directly, it is reasonable to assume that the latter excimer is formed in a way similar to that of the sandwich excimer. The second excimer-forming site may be produced more easily in the ground state than the sandwich excimer. All these sites can be covered by energy migration represented by the process e, since the mean degree of polymerization of the present systems is small. The process of the conversion from the second excimer to the sandwich excimer was not observed and accordingly can be excluded. In the case of PV5BCz(c), the "second excimer" is replaced by another monomer fluorescent state. This excited chromophore may not take such a geometrical structure as that of the second excimer because of its isotactic sequence.

The present dynamic behavior of PV5BCz can be compared with those of PVCz and is summarized as follows. (1) The yield of the instantaneous formation of the sandwich excimer of PV5BCz system is relatively large compared to that of PVCz. (2) The sandwich excimer formation process from the monomer fluorescent state observed in the PV5BCz(r) is similar to that of PVCz except that its formation rate is 2 orders of magnitude larger than that of PVCz. (3) The second excimer does not form the sandwich excimer, which is common to both polymers. Results 1 and 2 may be explained by the difference of the steric restraints produced in the ground state. The sandwich excimer forming site of PV5BCz is more easily formed compared to that of PVCz because of its more bulky group, and a slight conformational change is enough to produce the excimer state. In order to establish the excimer formation mechanism of PVCz and related polymers proposed here, detailed studies involving solvent, viscosity, and temperature effects should be made.

Acknowledgment. We express our sincere thanks to Professor F. C. De Schryver for his helpful discussion. N.M. and H.M. thank the Japanese Ministry of Education, Science and Culture for financial support through a Grant-in-Aid (Special Project Research on Photobiology).

References and Notes

(1) David, C.; Piens, M.; Geuskens, G. *Eur. Polym. J.* **1972**, *8*, 1291. Venikouas, G. W.; Powell, R. C. *Chem. Phys. Lett.* **1975**, *34*, 601.
(2) Johnson, G. E. *J. Chem. Phys.* **1975**, *62*, 4697.
(3) Itaya, A.; Okamoto, K.; Kusabayashi, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2082.
(4) Tagawa, S.; Washio, M.; Tabata, Y. *Chem. Phys. Lett.* **1979**, *68*, 276.
(5) Roberts, A. J.; Cureton, C. G.; Phillips, D. *Chem. Phys. Lett.* **1980**, *72*, 554.
(6) Ghiggino, K. P.; Wright, R. P.; Phillips, D. *Eur. Polym. J.* **1978**, *14*, 567.
(7) Hoyle, C. E.; Nemzek, T. L.; Mar, A.; Guillet, J. E. *Macromolecules* **1978**, *11*, 429.
(8) Ghiggino, K. P.; Archibald, D. A.; Thistlethwaite, P. J. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 673.
(9) Itaya, A.; Okamoto, K.; Kusabayashi, S. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 79.
(10) Masuhara, H.; Ikeda, N.; Miyasaka, H.; Mataga, N. *J. Spectrosc. Soc. Jpn.* **1982**, *31*, 19.
(11) Okamoto, K.; Yamada, M.; Itaya, A.; Kimura, T.; Kusabayashi, S. *Macromolecules* **1976**, *9*, 645.

Akira Itaya* and Ken-ichi Okamoto

Department of Chemical Engineering
Faculty of Engineering, Yamaguchi University
Ube, Yamaguchi 755, Japan

Hiroshi Masuhara,* Noriaki Ikeda, and Noboru Mataga

Department of Chemistry
Faculty of Engineering Science, Osaka University
Toyonaka, Osaka 560, Japan

Shigekazu Kusabayashi

Department of Applied Chemistry
Faculty of Engineering, Osaka University
Suita, Osaka 565, Japan

Received October 21, 1981

Coil-Globule Transition of a Single Polystyrene Chain in Dioctyl Phthalate

The collapse of a polymer coil, the so-called coil-globule transition, has been treated in several theoretical papers.$^{1-7}$ The coil-globule transition can be either continuous or

0024-9297/82/2215-1214$01.25/0