BUTTERWORTH
HEINEMANN

Polymer Vol. 36 No. 16, pp. 3103–3106, 1995

0032-3861/95/$10.00 + 0.00

Intrapolymer excimer formation solely with the full-overlap conformation in poly(2-vinylpyrene)

Akira Tsuchida, Taiji Ikawa and Masahide Yamamoto*
Division of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606, Japan
(Received 14 November 1994; revised 23 January 1995)

Excimer conformation of a novel poly(2-vinylpyrene) (P2VPy) was studied by fluorescence spectra and decay measurements in 2-methyltetrahydrofuran solution. The pyrene chromophores of this P2VPy are substituted at the C_2-symmetry position, and hence formation of only the full-overlap excimer is possible. The excimer emission of P2VPy was compared with that of poly(1-vinylpyrene), in which the pyrene group is able to form both full- and partial-overlap excimers. The excimer emission spectra of both polymers were very similar at room temperature, whereas at low temperatures a large difference between the emission intensities was observed due to the full-overlap excimer formation of P2VPy.

(Keywords: pyrene chromophore; excimer emission; rotamer)

INTRODUCTION

Excimer formation of aromatic vinyl polymers is one of the most efficient photorelaxation processes in solution because the neighbouring aromatic chromophores in the polymers are connected by a C3 methylene chain[1]. An excimer composed of two intermolecular low molecular weight chromophores takes the most stable conformation in solution. On the other hand, for the case of aromatic vinyl polymers, the chromophore conformation is restricted by the connection of the methylene backbone. This restriction sometimes causes multiple excimer formation with different ring overlap structures in an aromatic vinyl polymer. The origin of the dual excimer emission of poly (*N*-vinylcarbazole) is assigned to full- and partial-overlap excimers, which are formed in isotactic and syndiotactic diads, respectively[2,3]. However, when the aromatic chromophore of a polymer is substituted in its non-C_2-symmetry position, a rotamer of an excimer having different ring overlap conformation from the full-overlap excimer can be formed even in the same isotactic diad. Excimer rotamers of this type have been reported for poly(1- and 2-vinylnaphthalene)s and poly(1-vinylpyrene)[4,5].

Pyrene excimers with different ring overlap conformations have been studied extensively using the dimer compounds of 1,3-di(1-pyrenyl)propane and 2,4-di(1-pyrenyl)pentane, in which the two pyrene chromophores are connected by a C3 methylene chain[6–12]. These studies revealed the existence of the full- and partial-overlap excimers of 1-substituted pyrene. As for a polymer, Todesco *et al.* studied the excimer emission of poly(1-vinylpyrene) (P1VPy) by time-dependent measurements and revealed the existence of dual excimer emission originating from the full- and partial-overlap excimers[5]. *Figure 1* shows the molecular structures of poly(2-vinylpyrene) (P2VPy) and P1VPy with their possible pyrene ring overlap conformations. As shown in this figure, 1-substituted pyrene can form two excimer rotamers of full and partial ring overlaps, whereas the 2-substituted pyrene forms only the full-overlap excimer. In the present work, we studied the excimer formation and emission properties of a novel polymer, P2VPy. The pyrene chromophore of this polymer is substituted at the C_2-symmetrical 2-position, and therefore only the full-overlap excimer is expected to be formed.

EXPERIMENTAL

P2VPy and P1VPy were prepared by radical polymerization of the corresponding vinylpyrenes initiated by 2,2′-azobisisobutyronitrile in benzene solvent at 333 K. The molecular weights after several precipitations from benzene solution into methanol were determined by gel permeation chromatography (Tosoh, HLC802UR, polystyrene standard) to be $M_w = 8.1 \times 10^3$, $M_n = 5.6 \times 10^3$ and $M_w = 9.2 \times 10^3$, $M_n = 6.9 \times 10^3$ for P2VPy and P1VPy, respectively. 2-Vinylpyrene (m.p. 102–104°C) was synthesized by the Wittig reaction from 2-pyrenecarboxaldehyde, which was obtained from 2-pyrenecarboxylic acid[10,11,13,14]. Preparation and purification of 2- and 1-ethylpyrene (2EPy and 1EPy, respectively) as monomer analogues of the polymers have already been reported[14].

2-Methyltetrahydrofuran (MTHF) as a solvent for measurements was refluxed and distilled from CaH_2 several times just prior to use. All samples for spectroscopic

---

* To whom correspondence should be addressed

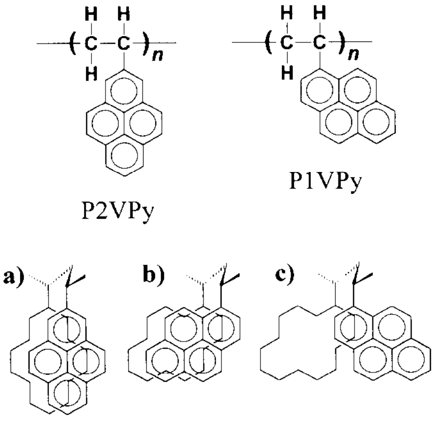

Figure 1 Molecular structures of P2VPy and P1VPy, with full-overlap (a, P2VPy; and b, P1VPy) and partial-overlap (c, P1VPy) structures of two pyrene chromophores of poly(vinylpyrene)s

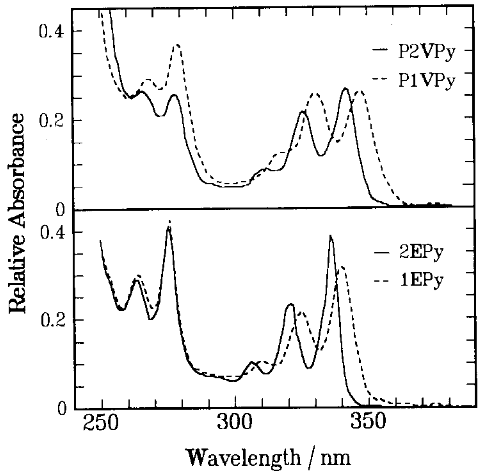

Figure 2 Absorption spectra of P2VPy and P1VPy polymers (top), and their monomer analogues 2EPy and 1EPy (bottom), measured in MTHF solvent at 298 K

measurements were degassed by the freeze–pump–thaw method in a Pyrex ampoule fitted with a 1 cm quartz cell. Low concentrations ($<1\times10^{-4}$ base mol l^{-1}) of the polymers were used for emission measurements to prevent interpolymer interactions.

Absorption spectra were measured by a Shimadzu UV-200S spectrophotometer. Emission spectra were measured with a Hitachi 850 spectrofluorophotometer, the spectral response of which was calibrated using a standard tungsten lamp. For low temperature emission measurements, the sample cell was cooled in a Dewar cell using liquid nitrogen or isopentane/liquid nitrogen mixture. Transient emission decays were measured by the single-photon-counting method (PRA Inc., model 510B). Measurements were made in the two wavelength regions of 400–500 nm and > 500 nm; emission filters of V-40 (Toshiba) + #3380 (Corning) and SC52 (Fuji) × 2 were used for this purpose, respectively.

RESULTS AND DISCUSSION

Radically polymerized P2VPy powder has a slight pale yellow colour even after purification. P2VPy is soluble in MTHF without turbidity at the fairly high P2VPy concentration of 0.8 wt%.

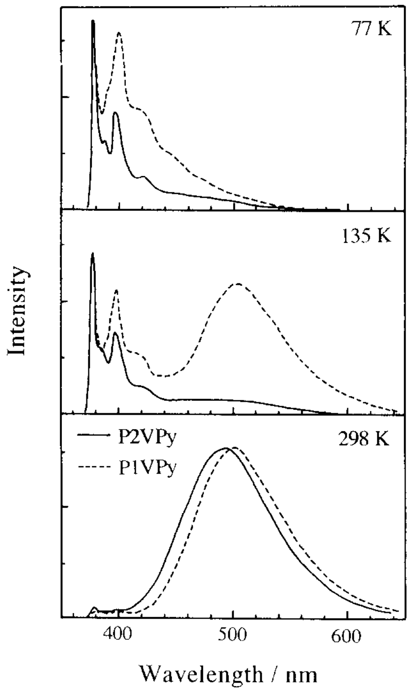

Figure 3 Emission spectra of P2VPy and P1VPy measured in MTHF solvent at 77, 135 and 298 K

Figure 2 shows the absorption spectra of P2VPy and P1VPy (top) and their monochromophoric reference compounds 2EPy and 1EPy (bottom) in MTHF solvent. As already reported for P1VPy[5], the absorption bands of P2VPy also showed large hypochromism compared with those of the model monomer 2EPy. The S_2–S_0 absorption bands of P2VPy at around 300–360 nm are blue-shifted by about 6 nm from those of P1VPy. This shift is considered to be caused by the substitution of the pyrene chromophore at a different position.

Figure 3 shows the emission spectra of P2VPy and P1VPy at dilute concentration in MTHF solvent. At 298 K (*Figure 3*, bottom), both P2VPy and P1VPy gave a broad excimer emission band at around 500 nm; P2VPy showed the band at a slightly shorter wavelength region than P1VPy. At this temperature, the molecular motion of the polymer chain is efficient and the equilibrium between an excited monomeric state and the excimer state shifts to the excimer side. Todesco *et al.* showed by time-resolved measurements that the excimer band of P1VPy at room temperature consists of full- and partial-overlap excimer bands[5]. However, the differentiation of these two bands by steady-state measurements is difficult at 298 K as shown in *Figure 3*, since the band positions of the full- and partial-overlap excimers are very close. A shorter lifetime of the partial-overlap excimer (40 ns)[5] compared with that of the full-overlap type (125 ns)[5] may be also responsible for the absence of their separate emission bands by steady-state measurements.

However, upon cooling the sample to 135 K, a large difference was seen in the excimer bands of polymers P2VPy and P1VPy, as shown in the middle of *Figure 3*. At this temperature, the excimer band of P2VPy almost disappeared, whereas that of P1VPy still remained. The MTHF solvent became viscous at this low temperature of 135 K, and the motion of pyrene chromophore was restricted. The partial-overlap excimer of P1VPy is

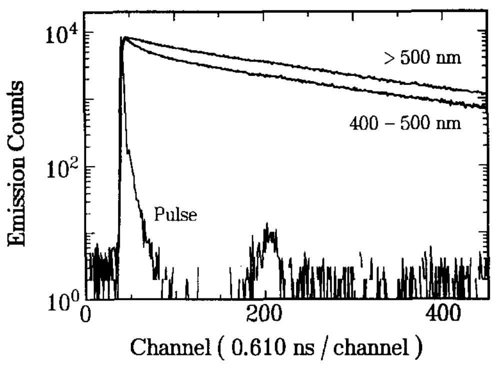

Figure 4 Transient emission decay curves of P2VPy measured at 400–500 nm and at > 500 nm regions in MTHF solvent at 298 K

Table 1 Decay fitting parameters[a,b] of poly(vinylpyrene) excimer emissions measured in MTHF solvent at 298 K

Polymer (wavelength region)	τ_1	τ_2	A_1/A_2	$A_1\tau_1/A_2\tau_2$	χ^{2c}
P2VPy (400–500 nm)	11.6	123.5	0.851	0.0799	1.21
P2VPy (> 500 nm)	16.8	128.4	0.226	0.0296	1.21
P1VPy (400–500 nm)	17.8	100.9	0.478	0.0843	1.27
P1VPy (> 500 nm)	25.7	97.6	0.257	0.0677	1.29

[a] The experimental decay curves were analysed using the equation $I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, where $I(t)$ is the excimer emission decay function. A_i is the pre-exponential factor and τ_i is the decay parameter

[b] The fitting was made from the peak channel of the emission decay

[c] Chi-square of the weighted residuals

considered to be formed more easily than the full-overlap type of P2VPy and P1VPy because it requires less molecular motion. In other words, the excimer of P1VPy formed at this temperature is considered to be mostly of the partial-overlap type.

At 77 K, the MTHF solvent becomes a rigid matrix and motion of the solute polymer is suppressed. The emission spectrum of P2VPy at this temperature (*Figure 3*, top) consists mostly of the monomer band. As for P1VPy, another band at around 400–500 nm was seen to be overlapped on the monomer emission. This band is ascribed to the preformed dimer composed of two neighbouring pyrene chromophores[5]. This preformed dimer is considered to have a kind of partial-overlap conformation of two pyrene groups in the ground state.

The full-overlap excimer formation of P2VPy in fluid solution at room temperature is clear from the above discussions on the emission spectra. The conformational relaxation of an excimer inherent to the polymer system was also observed by decay measurements for the full-overlap excimer of P2VPy. *Figure 4* shows the excimer emission decay of P2VPy measured by the single-photon-counting method in MTHF solvent at 298 K. The emission decays were measured at short (400–500 nm) and long (> 500 nm) wavelength ranges of the excimer band. As shown in the figure, neither decay could be fitted by a single exponential decay function. Therefore, the decays were tentatively analysed by a biexponential fitting to obtain a rough value of the excimer lifetime, although the exact physical meaning of the parameters is not clear. *Table 1* shows the analysed decay parameters by a least-squares fitting for the full-overlap excimer emission of P2VPy. The parameters for P1VPy measured under the same conditions are also listed in the table as a reference. For the P1VPy system, the partial-overlap excimer as well as the full-overlap excimer contributes to the decays since the emission bands of full- and partial-overlap excimers could not be separated by filters. The longer decay value obtained by the biexponential fitting was about 125 ns for P2VPy. As shown in *Table 1*, the fraction of the shorter decay component in the 400–500 nm wavelength region ($A_1/A_2 = 0.815$) is larger than that of the shorter decay component in the > 500 nm wavelength region ($A_1/A_2 = 0.226$). The intrapolymer excimer of P2VPy is formed in the TT full-overlap conformation of the pyrene diad as mentioned above. However, even in this TT full-overlap conformation there are still various microenvironments due to inhomogeneity caused by the polymer chain conformation. Immediately after the photoexcitation, the unstable full-overlap excimers in various microenvironments in the P2VPy chain are expected to have various relaxation times to fall to the most stable excimer. In other words, an intrapolymer pyrene excimer whose conformation is slightly distorted from that of the most stable one gives the excimer emission in the short wavelength region and then it changes conformation to attain the energy minimum according to the molecular motion of the polymer chain. The shorter decay values (about 10–20 ns) in *Table 1* are considered to be the relaxation time of the distorted full-overlap excimers formed in P2VPy.

CONCLUSION

P2VPy forms a full-overlap excimer of the pyrene chromophores, whereas P1VPy forms both full- and partial-overlap excimers in solution at 298 K. Excimer emission decay measurements of P2VPy showed the existence of a distorted full-overlap excimer, which is relaxed to the most stable full-overlap excimer within 10–20 ns in the TT conformation of the pyrene diad.

ACKNOWLEDGEMENTS

This work was supported by a Grant-in-Aid from the General Sekiyu Research & Development Encouragement & Assistance Foundation and partly defrayed by Research on Priority Areas, Photochemical Reactions (No. 06239107) from the Ministry of Education, Science and Culture of Japan.

REFERENCES

1 Hirayama, F. *J. Chem. Phys.* 1965, **42,** 3163
2 De Schryver, F. C., Vandendriessche, J., Toppet, S., Demeyer, K. and Boens, N. *Macromolecules* 1982, **15,** 406
3 Vandendriessche, J., Palmans, P., Toppet, S., Boens, N., De Schryver, F. C. and Masuhara, H. *J. Am. Chem. Soc.* 1984, **106,** 8057
4 Semerak, S. N. and Frank, C. W. *Adv. Polym. Sci.* 1984, **54,** 31
5 Todesco, R. V., Basheer, R. A. and Kamat, P. V. *Macromolecules* 1986, **19,** 2390
6 Winnik, F. M. *Chem. Rev.* 1993, **93,** 587
7 Tanaka, J. A., Masuhara, H. and Mataga, N. *Polym. J.* 1986, **18,** 181
8 Zachariasse, K. A., Busse, R., Duveneck, G. and Kühnle, W. *J. Photochem.* 1985, **28,** 237
9 Zachariasse, K. A., Duveneck, G., Kühnle, W., Leinhos, U. and Reynders, P. in 'Photochemical Processes in Organized Molecular Systems' (Ed. K. Honda), Elsevier, Amsterdam, 1991, p. 83
10 De Schryver, F. C., Collart, P., Vandendriessche, J., Goedeweeck,

R., Swinnen, A. M. and Van der Auweraer, M. *Acc. Chem. Res.* 1987, **20,** 159

11 Collart, P., Toppet, S. and De Schryver, F. C. *Macromolecules* 1987, **20,** 1266

12 Siemiarczuk, A. and Ware, W. R. *J. Phys. Chem.* 1989, **93,** 7609

13 Tanikawa, K., Ishizuka, T., Suzuki, K., Kusabayashi, S. and Mikawa, H. *Bull. Chem. Soc. Jpn* 1968, **41,** 2719

14 Tsuchida, A., Tsujii, Y., Ohoka, M. and Yamamoto, M. *J. Phys. Chem.* 1991, **95,** 5797