control reversibly many aspects of the properties of polymer solutions and solid by using photoresponsive polymers.

References and Notes

(1) Part 1: Irie, M.; Menju, A.; Hayashi, K. *Macromolecules* **1979**, *12*, 1176.
(2) (a) Morgan, P. W.; Kwolek, S. L. *Macromolecules* **1975**, *8*, 104. (b) Morgan, P. W. *Ibid.* **1977**, *10*, 1381. (c) Kwolek, S. L.; Morgan, P. W.; Schaefgen, J. R.; Gulrich, L. W. *Ibid.* **1977**, *10*, 1390. (d) Bair, T. I.; Morgan, P. W.; Killian, F. L. *Ibid.* **1977**, *10*, 1396. (e) Panar, M.; Beste, L. F. *Ibid.* **1977**, *10*, 1401.
(3) Agolini, F.; Gay, F. P. *Macromolecules* **1970**, *3*, 349.
(4) Witt, O. N.; Kopitschin, U. E. *Ber. Dtsch. Chem. Ges.* **1912**, *45*, 1134.
(5) Zimmerman, G.; Chow, L.; Paik, U. *J. Am. Chem. Soc.* **1958**, *80*, 3528.
(6) (a) Paik, C. S.; Morawetz, H. *Macromolecules* **1972**, *5*, 171. (b) Tabak, D.; Morawetz, H. *Ibid.* **1970**, *3*, 403.
(7) Oesterhelt, D.; Hess, B. *Eur. J. Biochem.* **1973**, *37*, 316.

Inter- and Intramolecular Interactions of Polymers As Studied by Fluorescence Spectroscopy. 7. Allosteric Self-Association of an Exciplex-Forming Polymer under Extremely Dilute Conditions

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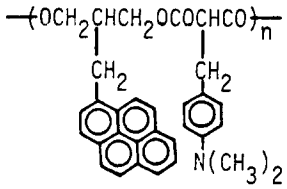
ABSTRACT: Allosteric self-association was found in poly[oxy[2-(1-pyrenylmethyl)propylene]oxy[4-(*N*,*N*-dimethylamino)benzyl]malonyl] (PE(Py-1D)) having an appropriate degree of polymerization under extremely dilute conditions. The polymer (PE(Py-1D)) was prepared by bulk polycondensation of the corresponding 1,3-propanediol with the corresponding diethyl malonate. Comparison of the absorption spectra of PE(Py-1D) with that of monomer model (I) indicated the presence of a weak ground-state interaction between chromophores. The ratio of exciplex emission (F_e) to monomer emission from the local excited state of pyrenyl groups (F_m) increased allosterically with concentration, suggesting interpolymer association in the concentration region below 10^{-5} M. The driving force of interpolymer association was attributed to the weak ground-state interactions between the electron donor (*N*,*N*-dimethylanilino group) and the electron acceptor (pyrenyl group). No exciplex emission was detected in reference experiments mixing monomer model compounds (I and II) containing pyrenyl and *N*,*N*-dimethylanilino groups in the concentration region below 10^{-5} M. Qualitative explanations for the above results are presented on the basis of solvent and molecular weight effects on emission and absorption spectroscopy.

The solution theory of polymers postulates that polymer molecules in dilute solutions are independent of each other. However, polymers containing groups whose interactions are undetectably weak in model monomer systems can exhibit prominent interpolymer association. A typical example is found in antigen–antibody interactions. The driving force for enhanced intermolecular interactions in polymers is attributed to zipping or cooperative effects.

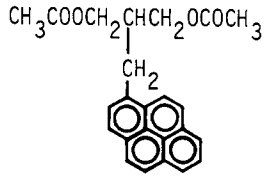
Since 1975, we have been demonstrating the association of weakly interacting groups in synthetic polymers by means of fluorescence spectroscopy.[1-5] Although exciplex-forming electron-donor (D)–electron-acceptor (A) pairs do not generally exhibit observable ground-state interactions in the case of monofunctional compounds, the weak interactions are sufficient to bring about polymer association in which the degree of association depends on the degree of polymerization.[2] Polymer association often accompanies changes in conformation, which affect further association. Consequently, polymer association is not expected to be a simple function of concentration.

Now we have found allosteric self-association of the relatively simple polymer PE(Py-1D) at a unit segment concentration below 10^{-5} mol dm^{-3}.

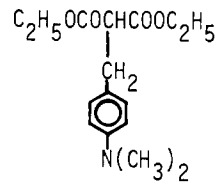
Chart I
Structure of Exciplex-Forming Polymer and the Monomers



PE(Py-1D)



I



II

Experimental Section

Materials. Monomer Models. 2-(1-Pyrenylmethyl)-1,3-propylene diacetate (I) and diethyl [4-(*N*,*N*-dimethylamino)-benzyl]malonate (II) were prepared by methods already reported.[5,6]

Poly[oxy[2-(1-pyrenylmethyl)propylene]oxy[4-(*N*,*N*-dimethylamino)benzyl]malonyl] (PE(Py-1D)). Equimolar amounts of 2-[(1-pyrenyl)methyl]-1,3-propanediol and II were heated to produce bulk polycondensation, using calcium acetate as catalyst. Polycondensation was conducted under a nitrogen atmosphere at normal pressure and at an initial temperature of 160 °C. The reaction vessel was then heated to 210 °C and evacuated gradually to 10^{-2} mmHg over a period of 18 h. IR (KBr disk) 1732 cm^{-1} (>C=O); NMR (Me_2SO-d_6, 90 °C) δ 3.04 (6 H, s, $N(CH_3)_2$), 6.2–6.7 (4 H, m, phenylene), 7.3–8.3 (9 H, m, pyrenyl). Anal. Calcd for $C_{32}H_{29}O_4N$ (repeat unit): C, 78.19; H, 5.95; N, 2.85. Found: C, 77.0; H, 6.25; N, 2.53. The polymer sample was

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Table I
Spectroscopic Properties of Fractionated PE(Py-1D) in Various Solvents

fraction	MW[a]	$\overline{DP}$ n	$\epsilon \times 10^{-4}$ [b] ^1L_a band	hypochromicity,[c] %	broadness of absorption spectrum[d]		
					p-dioxane	mesitylene	1,2-dichloroethane
1	8500	17.3	1.47	62.7	0.52	0.56	0.40
2	6200	12.6	1.83	53.6	0.42	0.44	0.40
3	4600	9.3	2.20	44.2	0.40	0.42	0.39
4	3400	6.9	2.47	37.3	0.39	0.42	0.39
5	2600	5.4	2.60	34.2	0.39	0.42	0.39
10	1200	2.4	2.78	29.4	0.35	0.37	0.35
I	377		3.94	standard	0.34	0.35	0.34

[a] Relative to standard polystyrene. [b] In *p*-dioxane. [c] Difference in ϵ. [d] OD_{335}/OD_{345} (valley/peak ratio).

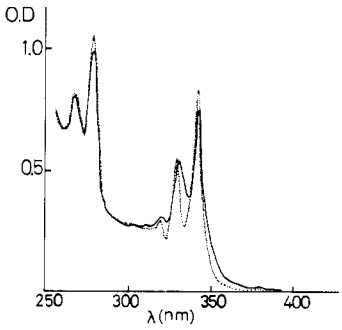

Figure 1. Absorption spectra of PE(Py-1D) (—) and the monomer model I (···). [Py] = 2×10^{-5} M in 1,2-dichloroethane.

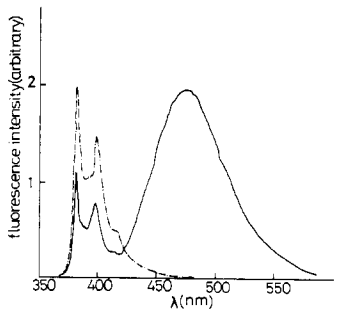

Figure 2. Fluorescence spectra of PE(Py-1D) (—) and I (-·-) in *p*-dioxane. [Py] = 2×10^{-5} M, excitation at 345 nm, 30 °C.

fractionated by means of GPC (HLC-802UR, Toyo Soda Mfg. Co. Ltd.; fractionation column, $G2000HG_6 + G3000HG_6$; chloroform eluent).

Solvents. All solvents were purified by accepted procedures from guaranteed grade reagents.

Spectroscopy. The absorption and fluorescence spectra were recorded on a Shimadzu UV-200 spectrometer and a Hitachi MPF-4 spectrofluorometer, respectively. Fluorescence spectroscopy was conducted under an argon atmosphere and no correction was made on the fluorescence spectra.

Results and Discussion

Absorption Spectra. Absorption spectra of PE(Py-1D) and the monomer model (I) are shown in Figure 1. In the S_0–S_2 absorption band, the absorption spectra of PE(Py-1D) showed a 2–3-nm red shift relative to the monomer model compound. The ratio of the maximum absorbance at 346 nm (peak) to the minimum absorbance at 335 nm (valley) is smaller for PE(Py-1D), as shown in Table I. Broader absorption of the pyrenyl groups in PE(Py-1D) than in I and consequently the smaller apparent value of ϵ_{max} are indications of a weak ground-state interaction in the polymer. Furthermore, the spectrum is broadened when the degree of polymerization ($\overline{DP}$) increases and a poor solvent is used. Both an increase in $\overline{DP}$ and a decrease in solubility bring about shrinking of the polymer chain and subsequent enhancement of interactions between chromophores. The solvent–polymer interaction decreases in the order 1,2-dichloroethane $\gtrsim$ dioxane > mesitylene, as judged by the solution viscosity of polymer in these solvents, whereas the broadness of the absorption spectra is in the order mesitylene > dioxane > dichloroethane. When aromatic chromophores are bound to the polymer, the absorption spectrum broadening seems to be more or less a general trend. This phenomenon is more prominent for exciplex systems than for excimer systems. The hypochromicity observed for a variety of polyesters bearing pendant pyrenyl groups is less than 20% in comparison with the monomer or the dimer model compounds.[6] When the pendant groups are naphthalene[7] or anthracene,[6,8] the spectral broadening is no more than that for the pyrene polyesters. The change of polymer backbone from polyester to poly(ester–urethane) does not have much effect on spectral broadening.[8] these results indicate that the hypochromicity in Table I is too large to be attributed to interactions between like molecules.

Pyrene and *N,N*-dimethylaniline are in general not considered complex-forming components in the ground state. However, ground-state weak electron donor acceptor (EDA) interactions between these components have been reported[9] for concentrated solutions. In the present polymer, the EDA pairs are alternately packed along the polyester main chain so that the local concentration is sufficiently high to bring about an observable EDA interaction.

As discussed in a previous article,[1] the enhanced intermolecular exciplex formation in polymeric systems in which the diffusion constant is certainly lower than that of relevant small molecules is not explainable unless some kind of ground-state interaction is taken into account. However, the ground-state association and the exciplex-forming site are not equivalent. Exciplex emission disappears in a frozen 2-methyltetrahydrofuran matrix, indicating the importance of segment mobility in exciplex formation. Consequently, the interpolymer association as evidenced by concentration-dependent exciplex emission provides a favorable moiety for exciplex formation but not an exciplex-forming site itself. Segment mobility is similarly necessary for excimer formation by pyrenyl groups bound to polyester.[10]

Fluorescence Spectra as a Function of Concentration. In order to measure both intra- and intermolecular interactions between pyrenyl and *N,N*-dimethylanilino groups, the intensity ratio of the exciplex emission (F_e, λ_{max} 498 nm) to the emission from the local excited state of pyrene (F_m, λ_{max} 377 nm) shown in Figure 2 was plotted against polymer concentration. The value of F_e/F_m at the low-concentration limit represents intrapolymer exciplex formation. Important results deduced from the figure are as follows: (i) The plots are S-shaped in an appropriate $\overline{DP}$ region, indicating that the interpolymer exciplex for-

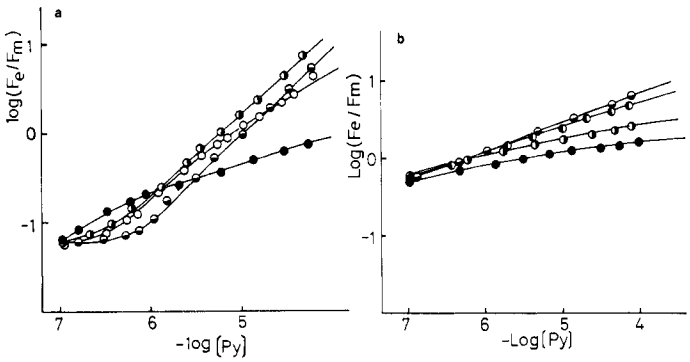

Figure 3. Concentration dependence of exciplex emission by PE(Py-1D) in (a) 1,2-dichloroethane and (b) mesitylene. Excitation at 345 nm. Fractions 10 (●), 5 (◒), 4 (◐), 2 (◑), and 1 (○).

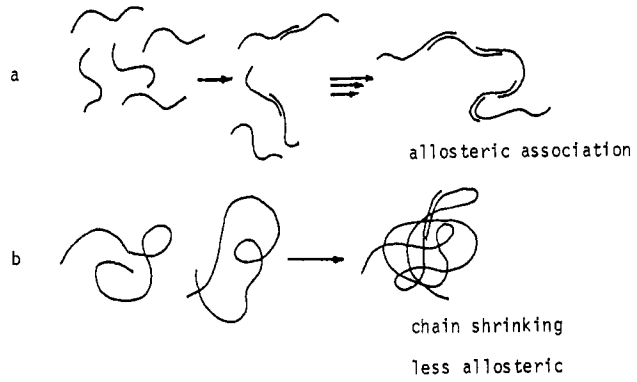

Figure 4. Schematic sketches of interpolymer interactions: (a) medium molecular weight sample; (b) high molecular weight sample.

mation is allosteric in 1,2-dichloroethane (Figure 3a). (ii) The F_e/F_m vs. [C] plots in mesitylene do not show an allosteric trend (Figure 3b). (iii) The degree of intramolecular exciplex formation is small and depends on the solvents used. (iv) There is an optimum $\overline{DP}$ for self-association. The highest molecular weight sample (fraction 1) undergoes self-association efficiently at very low concentration but the interpolymer interaction does not propagate much at higher concentrations. Similarly, the lowest molecular weight sample (fraction 10) exhibits only a weak interpolymer association. (v) In reference experiments with an equimolar mixture of I and II, no exciplex emission was detected in the concentration region examined.

It is noteworthy that molecular association occurs at a chromophore concentration [C] based on a "repeat unit" concentration as low as 10^{-7} mol dm^{-3}. If the concentration is expressed in terms of the polymer chain concentration (i.e., $[C]/\overline{DP}$), the value is further reduced by more than an order of magnitude.

Findings i and iv can be qualitatively explained as follows. With increasing polymer concentration, polymer association is gradually initiated and the apparent $\overline{DP}$ of the polymer increases with the degree of association. To a certain extent, a large $\overline{DP}$ is a favorable condition for polymer association and allosteric behavior appears at a lower concentration with increasing $\overline{DP}$. However, when polymer association proceeds too far, the polymer chains will entangle and saturation of interpolymer association will occur. Further association is suppressed as sketched in Figure 4. The self-association of either a high molecular weight sample or a low molecular weight sample does not increase with increasing concentration. The former is probably due to chain entanglement and subsequent reduction in segment mobility. Interpolymer association, like cross-linking, reduces solubility. Consequently, the ease of interpolymer association decreases with the degree of association for a high molecular weight sample. This phenomenon is certainly a function of polymer–solvent interaction as well. In support of this, Figure 5 shows that interpolymer exciplex formation saturates at an early stage in a poor solvent (mesitylene) whereas it develops smoothly in a good solvent (ethylene dichloride). Finding ii clearly shows the absence of an allosteric tendency in a poor solvent (mesitylene). Self-association could not propagate in this case. To cover a wide concentration region, Figures 3a and 3b are depicted on a logarithmic scale, so the shapes of plots are not comparable with those in Figure 5. These discussions, based on the crude F_e/F_m values, cannot be directly related to the degree of interchromophore interaction since emission probability and lifetime of the exciplex depend on solvent polarity. In polar DCE the exciplex emission probability should be lower than that in mesitylene. Consequently, the slope for DCE in Figure 3 as well as in Figure 5 should have been steeper in reference to the mesitylene system if the plots were based on [exciplex]/[pyrene*] instead of F_e/F_m. The real difference between DCE and mesitylene is therefore expected to be much larger. Since polymer–solvent interaction is also a function of $\overline{DP}$, the F_e/F_m vs. [C] plots depend very much on both $\overline{DP}$ and solvent. When $\overline{DP}$ is too small, the chain length is not sufficient to exhibit these polymer effects. A detailed study of solvent effects is now in progress and will be published in near future.

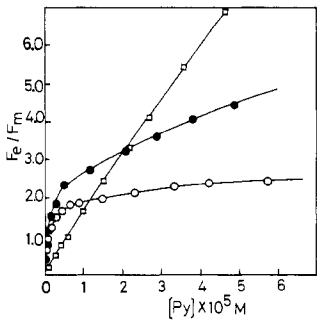

Figure 5. Solvent effect on concentration-dependent exciplex emission by PE(Py-1D). Solvent: 1,2-dichloroethane (□); *p*-dioxane (●); mesitylene (○).

Although we do not know of other results directly relevant to the present system, self-association of an oligopeptide by means of hydrogen bonding in an organic solvent may fall into the category of allosteric association.[11,12] In the concentration region above 10^{-2} mol dm^{-3}, the aggregation number determined by light scattering increases with concentration. The phenomena were interpreted as due to double-stage association[12] in which the associated peptide is subjected to further self-association. Another explanation may also be possible if a higher order complex formation ($nP \rightleftharpoons P_n$, $[P_n] = K[P]^n$ (K is the equilibrium constant)) is assumed. It is unfortunate that no independent method other than fluorescence spectroscopy is available to confirm interpolymer association in extremely dilute solutions.

References and Notes

(1) Tazuke, S; Matsuyama, Y. *Macromolecules* **1975**, *8*, 280.
(2) Matsuyama, Y.; Tazuke, S. *Polym. J.* **1976**, *8*, 481.
(3) Matsuyama, Y.; Tazuke, S. *Macromolecules* **1977**, *10*, 215.
(4) Suzuki, Y.; Tazuke, S. Preprints of the 26th IUPAC Meeting, Tokyo, 1977, Preprint V-1278.
(5) Tazuke, S.; Sato, K.; Banba, F. *Macromolecules* **1977**, *10*, 1224.

(6) Sato, K.; Hayashi, N.; Tazuke, S. *J. Polym. Sci., Polym. Lett. Ed.* **1977**, *15*, 671.
(7) Tazuke, S.; Banba, F. *Macromolecules* **1976**, *9*, 451.
(8) Tazuke, S.; Hayashi, N. *Polym. J.* **1978**, *10*, 443.
(9) Okada, T.; Mataga, N. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2190.
(10) The pyrenyl pendant polyesters[6] do not show any excimer emission in 2-methyltetrahydrofuran at 77 K. Sato, K. M.Sc. Thesis, Tokyo Institute of Technology, 1977.
(11) Okahashi, K.; Ikeda, S. *Biopolymers* **1979**, *18*, 2105.
(12) Ikeda, S.; Okahashi, K. *Biopolymers* **1979**, *18*, 2115.

High-Conversion Polymerization Fluorescence Probes. 1. Polymerization of Methyl Methacrylate

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ABSTRACT: The effect of polymerization of methyl methacrylate on the fluorescence intensities of a series of donor–acceptor molecules ([*p*-(*N*,*N*-dialkylamino)benzylidene]malononitriles) has been investigated. The fluorescence of the probes increases gradually (1.5 times) as conversion increases to 60%. Further increase in conversion causes a sharp increase in fluorescence (20–40 times), reaching a limiting value at the limiting conversion. This sudden rise in the fluorescence occurs when the polymerization approaches the glassy state. In this region, mobility becomes restricted and internal molecular relaxation of the probes becomes controlled by the microscopic free volume provided by the polymer. This leads to a decrease in the nonradiative rate and consequently to an increase in fluorescence. Bulk polymerization of methyl methacrylate was carried at 50, 70, and 90 °C in the presence of the fluorescent probe. A correlation between the limiting fluorescence yield and the limiting conversion was found. It is assumed that these results reflect the influence of free volume on the molecular relaxation of the probes.

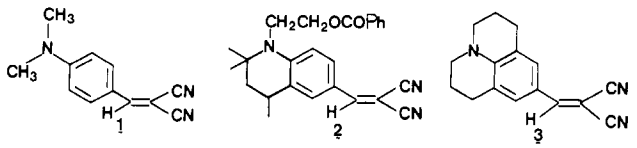
Introduction

In bulk polymerization the reaction system is converted from a low molecular weight liquid (the monomer) via solutions of the polymer in the monomer of various concentrations to the polymeric mass. This process is accompanied by dramatic physical and structural changes. As polymer concentration increases, a point is reached where appreciable chain entanglements occur and eventually a glassy-state transition may result. These physical changes often have a significant effect on both rate of polymerization and molecular weight development, which, in turn, markedly affect the kinetics of the polymerization reaction.

It is well-known that in free radical polymerization of vinyl monomers, the classical polymerization kinetics do not apply at high conversions. The deviation of the rate of polymerization from the classical kinetic behavior is usually observed after some initial conversion and this deviation is characterized by a rapid decrease of the termination rate, k_t, relative to the rate of propagation, k_p. The significant reduction in termination rate (due to polymer chain entanglement) often causes an almost "explosive" increase in radical population and polymerization rate, R_p. This process is termed autoacceleration. The extent of the autoacceleration on the rate of polymerization depends a great deal upon molecular weight development.

Despite the many theoretical and experimental contributions made on the subject,[1-7] it is quite evident that none of the proposed kinetic models can quantitatively describe free radical polymerization to moderately high conversion. Also, relative magnitudes of termination and propagation rates or evaluation of effects such as free volume and segmental and/or translation motion is virtually impossible to assess from an experimental standpoint.

Our intention in the work described here was to examine the effects of the physical changes occurring during radical polymerization of methyl methacrylate (MMA) on the flluorescence of a series of donor–acceptor (D–A) molecules, [*p*-(*N*,*N*-dialkylamino)benzylidene]malononitriles (**1–3**).



On the basis of electrochemical and spectroscopic studies,[8] we have assigned the lowest excited singlet state of these materials to an intramolecular charge transfer (ICT) complex of the form D^+–A^-. The radiative decay rate, k_r, in fluid media was calculated to be 2.8×10^8 s^{-1}. The singlet lifetime is estimated to be 3–10 ps in solution, which corresponds to a nonradiative decay rate, k_{nr}, of the order of 10^{11} s^{-1}. The extremely fast deactivation rate of the singlet excited state of these materials was attributed to torsional relaxation, which is consistent with recent proposals.[8-10] We have also shown that environmental factors restricting the internal molecular rotation of dyes **1–3** lead to a decrease in k_{nr} and consequently an increase in fluorescence yield ($\phi_F = k_r/(k_r + k_{nr})$). For instance, when these dyes were embedded in a polymer matrix such as poly(vinyl acetate), ϕ_F increased by a factor of 2–6. Furthermore, the fluorescence yield approached unity in rigid glasses at 77 K (a 500-fold increase). These dyes are, therefore, excellent microscopic probes for the physical changes occurring during the course of free radical polymerization of vinyl monomer since their fluorescence yield is very sensitive to dynamic properties of the microenvironment.

The polymerization of methyl methacrylate (MMA) appears to be the most suitable system to evaluate initially, in view of the following: (1) there is a strong gel effect associated with such polymerization; (2) chain transfer reactions are unimportant; and (3) polymer chains are produced mainly by termination reactions. Hence, k_t, k_p,

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