Table I summarizes the chemical shift and scalar coupling data for Figures 2 (D-PBd) and 4 (H-PBd). The expected chemical shifts for the D-PBd were calculated on the basis of upfield shifts for the upfield shifts which result from deuteration. These slight decreases in chemical shift are typically ≈–0.25 ppm for an ipso-deuteron and ≈–0.10 ppm for the α-deuteron.[10] The calculated and observed shifts for the D-PBd agree quite well with the largest deviations occurring in the poorly resolved peaks. The observed J splittings result from carbon–deuterium coupling which is not removed by ^1H irradiation. Because the spin of the ^2H nucleus is one, a C–D bond appears as a triplet. The coupling constant J^1_{CD} is expected to be about 20 Hz.[10] As Table I shows, J^1_{CD} is found to be 19.0–19.5 Hz.

As can be seen from the above results, a novel deuterating agent for adding deuterium to olefinic bonds can easily be synthesized by replacing the protons of the hydride group of PTSH with deuterium by using a simple D_2O exchange.

Registry No. PTSH, 1576-35-8; D-PTSH, 109333-73-5; polybutadiene, 9003-17-2.

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Interpolymer Association of Polymers in Extremely Dilute Solution Studied by Normal Pulse Polarography

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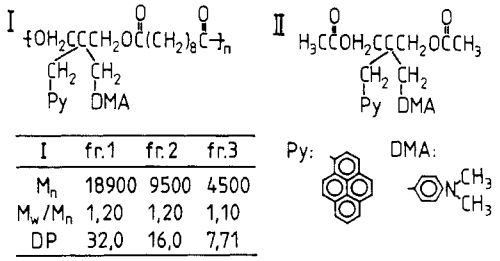
Introduction

Interpolymer association of neutral synthetic polymers, unexpected from conventional solution theory, has been reported for a number of exciplex-forming polymers.[1] Extensive spectroscopic investigation on polymer structural, concentration, and molecular weight effects on intra- and interpolymer exciplex formation revealed that weak interchromophore interactions, typically between aromatic hydrocarbons such as anthracene or pyrene (Py) and *N,N*-dimethylaniline (DMA) groups, both bonded to polymers, were responsible for polymer association.[2] This behavior seems to be common for polymers containing weak electron-donor and -acceptor groups which exhibit donor–acceptor interaction only in the excited state. The ground-state interaction is so weak that the ground-state electronic state is hardly affected and the origin of interaction is believed to be dipole–dipole interaction. Since no such interaction was detected in small molecular model systems, cumulative interactions in polymers in which weak donors and acceptors are regularly arranged were believed to be the essential requirement.



I	fr.1	fr.2	fr.3
M_n	18900	9500	4500
M_w/M_n	1,20	1,20	1,10
DP	32,0	16,0	7,71

Figure 1. Structures of exciplex-forming polymer and its monomer model compound.

This kind of interpolymer association occurs in extremely dilute solution where the chromophore concentration is as low as 10^{-5} M or less and can be evidenced only by the concentration dependence of I^{EX}/I^{LE}, where I^{EX} and I^{LE} are the fluorescence intensities of the exciplex and of the locally excited state of the photoabsorbing species, respectively. Under the condition of high dilution, it is difficult to prove polymer association by methods other than fluorescence spectroscopy since (i) the interaction is too weak to be detected by absorption spectroscopy and (ii) conventional methods for the study of solution properties such as viscometry, osmometry, small-angle light scattering, vapor pressure osmometry, etc., cannot be applied to this highly dilute system. We have been searching for other techniques to demonstrate this interesting polymer association phenomenon.

Electrochemical measurement of the diffusion constant (D) is a candidate method for determining molecular aggregation under extremely dilute conditions. Since D for molecular aggregates decreases with increasing extent of aggregation, the concentration dependence of D provides unequivocal evidence for intermolecular association. This principle has been used for the determination of the association number (AN) of various dye molecules in both aqueous and organic solutions.[3] In this note, we describe spectroscopic and electrochemical studies on the association of exciplex-forming polymers, shown in Figure 1, and of the monomeric model system.

Experimental Section

Both spectroscopic (Hitachi MPF-4 spectrofluorometer) and electrochemical (Fuso polarograph, Model 312) measurements were carried out in *N,N*-dimethylformamide (DMF) at 25 °C. In order to adjust the experimental conditions, both measurements were conducted in the presence of 0.1 M tetra-*n*-butylammonium perchlorate (TBAP). Polymer I and its monomer model compound (II) were prepared according to the literature.[2f] Polymer I was fractionated into three samples by means of gel permeation chromatography (Toyo Soda) (Table I). DMF was refluxed over calcium hydride and then fractionally distilled twice. TBAP as a supporting electrolyte was prepared from the corresponding bromide salt with perchloric acid in water and was recrystallized 3 times from an *n*-hexane–ethyl acetate mixture.

Results and Discussion

Concentration Dependence of Exciplex Formation. The concentration dependence of I^{EX}/I^{LE} by I and II is

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Table I
Fractionation of Polymer Sample I

	polymer I		
	fract 1	fract 2	fract 3
M_n[a]	18900	9500	4500
M_w/M_n[b]	1.20	1.20	1.10
DP[c]	32.0	16.0	7.71

[a] M_n is the number-averaged molecular weight. [b] M_w is the weight-averaged molecular weight. [c] DP is the degree of polymerization.

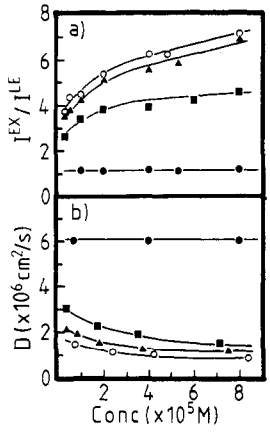

Figure 2. Concentration dependence of exciplex formation (fluorescence spectroscopy) (a) and of diffusion constant (polarography) (b) in DMF containing 0.1 M TBAP at 25 °C. (○) I, fraction 1; (▲) I, fraction 2; (■) I, fraction 3; and (●) II.

presented in Figure 2a. I^{EX}/I^{LE} of I shows a large concentration dependence, while that of II is almost constant regardless of the concentration. The increase in I^{EX}/I^{LE} with increasing concentration indicates that intermolecular exciplex formation (i.e., interpolymer association) is favored at higher polymer concentrations. Above 2×10^{-5} M, I^{EX}/I^{LE} reaches a constant value, indicating that the interpolymer association is saturated above this concentration. Previous studies suggested that the weak ground-state interactions between Py and DMA groups were primarily responsible for the interpolymer association in I.[1,2] Upon excitation of Py, the exciplex is thus produced instantaneously, as revealed by time-resolved fluorescence spectroscopy.[4]

It is worth noting that quaternary ammonium salts such as TBAP quench efficiently Py–DMA exciplex emission with the rate constants 10^9–10^{10} M^{-1} s^{-1} in chloroform.[5] Indeed, I^{EX}/I^{LE} of I at [TBAP] = 0.1 M is smaller than that at [TBAP] = 0, indicating the participation of exciplex quenching by TBAP. However, the concentration dependence of I^{EX}/I^{LE} is similar either in the presence or in the absence of TBAP, and the quenching efficiency of TBAP is smaller than in the case of the small molecule exciplex because of the reduced encounter probability of TBAP with polymer-bonded exciplexes. However, TBAP does not influence the present discussion of the interpolymer interaction.

Concentration Dependence of the Diffusion Coefficient. The diffusion coefficient (D) can be estimated electrochemically by the Cottrell equation (for normal pulse polarography),

$$i_d = nFACD^{1/2}/\pi^{1/2}t_s^{1/2} \quad (1)$$

where i_d is the diffusion current and n, F, A, and C have their usual meanings. t_s is the time interval between pulse application and current measurement (50 ms in this work). D can thus be determined when n and i_d are known. To apply eq 1, an electrochemical reaction should be Nernstian and free from adsorption as well as from side reactions.[6] Reduction of Py ($E \sim -2.0$ V versus SCE) was reversible, showing the slope of the E versus log $[(i_d - i)/i]$ plot to be 60–64 mV. On the other hand, oxidation of DMA ($E \sim +0.8$ V versus SCE) is complicated due to subsequent side reactions. In the present experiments, i_d of the reduction of Py was therefore used for the measurement. On the assumption of $n = 1$ (all Py groups are reduced at once),[7] D values of I and II were determined by normal pulse polarography in the concentration range between 5×10^{-6} and 8×10^{-5} M as shown in Figure 2b. D of I decreases with the degree of polymerization (DP) from 1.40×10^{-6} cm^2 s (DP $\sim$ 8) to 8.40×10^{-7} cm^2/s (DP $\sim$ 32) at the concentration region (6–7) $\times 10^{-4}$ M (out of the scale in Figure 2b) as well as decreases with its concentration: from 3.0×10^{-6} cm^2/s at [I] = 5×10^{-6} M to 1.8×10^{-6} cm^2/s at [I] = 7×10^{-5} M (DP $\sim$ 8). For monomer model compound II, on the other hand, D was essentially independent of its concentration at 6×10^{-6} cm^2/s under identical conditions. The concentration dependence of D in I suggests that polymer association develops with increasing concentration in accord with the results of concentration-dependent fluorescence spectroscopy. The good correlation between the concentration dependence of I^{EX}/I^{LE} and D manifests ground-state interpolymer association. Unfortunately, the association number of I could not be determined since the very small i_d of I below 5×10^{-6} M makes it impossible to estimate D of the unassociated polymer.

We have tried the same polarographic measurement with an excimer-forming polymer of the same backbone structure as I but having phenyl and pyrenyl groups instead of the DMA and pyrenyl groups.[8] The value of D was constant over the concentration range studied, in good agreement with the result that excimer formation in polymers is exclusively intramolecular in this concentration region.[8]

Electrochemical measurement of dilute polymer solution is shown to be almost as sensitive as fluorescence spectroscopy. Whenever a polymer contains electrochemically responsive groups, the present approach will be of general use to study interpolymer interactions.

Registry No. I (copolymer), 81193-12-6; I (SRU), 81192-45-2; II, 81189-04-0.

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