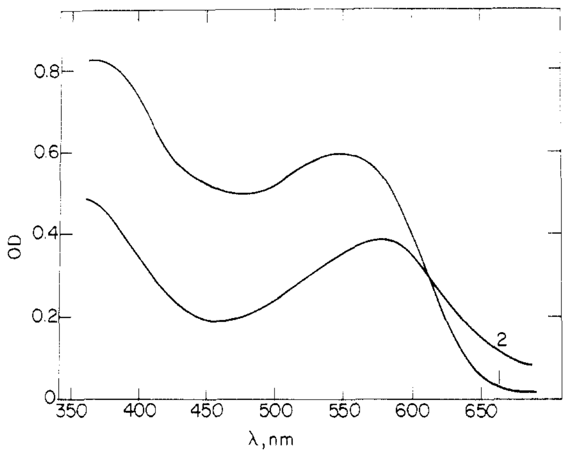

Figure 2. Diffuse reflectance spectra of crystalline (1) and amorphous (2) M_2 polymers. The amorphous polymer was obtained on fast evaporation of MTHF and consequent UV irradiation of the precipitated polymer.

groups participate in the intramolecular stacking whereas the intermolecular stacking involves also the spiropyrans, which are then converted into merocyanines along the direction of the propagation of the crystallization process (possibly along the macromolecular main chains). The merocyanine groups that appear randomly (for example, due to irradiation) *only impair* the zipper crystallization.

In conclusion, it is worthwhile emphasizing that in spite of the ephemerality of the isolation merocyanine moieties, they have a strong tendency to form rather stable phases: quasi-crystals[6,7] and polymer crystals. The stabilization of the merocyanines in these materials is by their dipole–dipole interaction, which is most effective in certain phases. Thus, in the M_2 polymer crystals, the merocyanines are stable even on heating up to 150 °C. (Further heating leads just to destruction of the polymer.) In amorphous polymers fast thermal merocyanine–spiropyran conversion begins at 45 °C (color disappears during a few seconds).

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Registry No. S_2, 91191-22-9; M_2, 57981-89-2; A_2, 89908-24-7; S_6, 91191-23-0; M_6, 89908-30-5.

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Communications to the Editor

Importance of Structure Regularity in Polymer Association[1]

In past years, we have shown that very weak interchromophore interactions, almost undetectable in small-molecule systems, are enhanced in polymers and bring about polymer association even in an extremely dilute solution.[3-7] Exciplex emission from a pair of electron-donating and electron-accepting chromophores bonded to a polymer and its dependence on polymer concentration provide information on self-association of exciplex-forming polymers. Although an exciplex is by definition a complex formed only in the excited state, the pairing chromophores having essentially donor (D) and acceptor (A) natures induce a more or less electron donor–electron acceptor (EDA) interaction in their ground state. The effect is, however, negligibly small in monomer model systems whereas the weak EDA interaction drives polymer association very greatly when D and A units are arrayed along a polymer chain either as main-chain components or as side groups.

Detailed investigation on the effect of polymer molecular weight,[5-7] solvent,[5,7a,c] and polymer main-chain rigidity[7d] on concentration-dependent exciplex emission led to the conclusion that interlocking of EDA chromophores along a polymer chain (zipping) is the origin of polymer association. Observation of an allosteric effect on polymer association in a good solvent[5] further reinforced this conclusion. Furthermore, the rise time of interpolymer exciplex formation is shorter than that of intramolecular exciplex by small model compounds,[8] indicating polymer association prior to photoexcitation.

It is extremely difficult to prove such polymer association in the concentration region of 10^{-5} M (10^{-3}–10^{-4} wt %) by orthodox methods presently available for solution property study. However, we recently succeeded in proving association of exciplex-forming polymers by pulse polarographic determination of diffusion constant as a function of polymer concentration in the concentration region comparable with that of fluorescence spectroscopy.[9] Decrease of diffusion constant was observed for exciplex-forming polymers but not for excimer-forming polymers when the polymer concentration increased.

The structural regularity of the D and A array should promote polymer association. In the following, we will show that an irregular arrangement of D (*N*,*N*-dimethylanilino) and A (1-pyrenyl) groups reduces interpolymer association greatly.

Results and Discussion. The structures of the samples employed are shown in Figure 1. We have previously reported that I[7a,b] as well as V[7b,c] forms strong interpolymer exciplexes at chromophore concentrations below 10^{-5} M. As a measure of interpolymer exciplex formation, the value of $(F_e/F_m)_c(F_e/F_m)_{c\to 0}$ was taken, where F_e and F_m indicate the maximum fluorescence intensities of exciplex and monomer emission and the subscript c on the parentheses is the chromophore concentration. This index expresses the magnitude of interpolymer interaction relative to intrapolymer interaction, the value being unity at infinite dilution.

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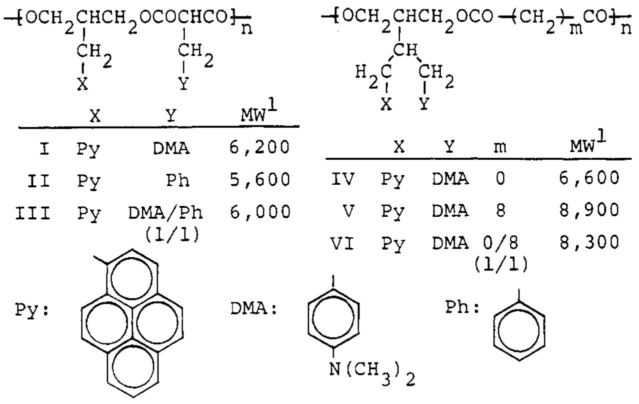

	X	Y	MW^1
I	Py	DMA	6,200
II	Py	Ph	5,600
III	Py	DMA/Ph (1/1)	6,000

	X	Y	m	MW^1
IV	Py	DMA	0	6,600
V	Py	DMA	8	8,900
VI	Py	DMA	0/8 (1/1)	8,300

1: GPC, reduced to standard polystyrene.

Figure 1. Structure and molecular weight of samples.

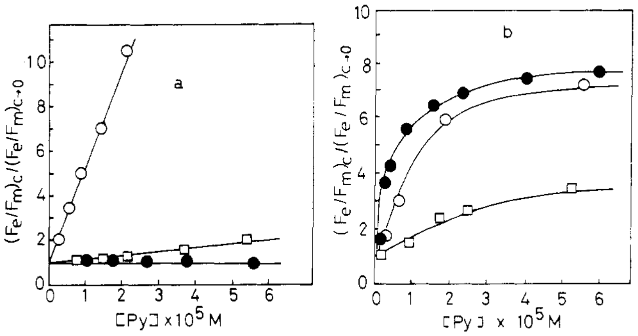

Figure 2. Structure regularity effects on polymer association in DCE. The plots are normalized to $(F_e/F_m)_{c\to0}$. (a) (○) I; (●) II; (□) III. (b) (○) IV; (●) V; (□) VI.

Plots of this value vs. concentration (c) in Figure 2 unequivocally reveal that efficient interpolymer exciplex formation occurs only for polymers having well-defined repeating units. In Figure 2a, II exhibits excimer emission and therefore the polymer association phenomenon is not observed.[7b] Polymer III, prepared by copolycondensation, has a random structure containing equal amounts of phenyl and *N,N*-dimethylanilino groups. This polymer shows exciplex emission when the pyrenyl group is excited. However, the emission is mostly of an intrapolymer nature. Apparently, randomization of the chromophore arrangement reduces the tendency for polymer association.

The results in Figure 2b provide clearer evidence for the role of structural regularity. Both IV and V show a strong tendency toward polymer association regardless of the separation between chromophores, whereas this tendency diminishes markedly when the oxalate and sebacate structures are mixed in the polymer chain. These findings are summarized in Figure 3.

The present results provide additional support for our view that exciplex-forming polymers associate in the ground state via a zipping process and photoexcitation leads to immediate exciplex formation without the need for very much segment rearrangement. The significance of structural regularity will vary with the nature of the interchromophore interaction force. It is at present believed that in the binding force in a weak EDA complex dipole–dipole (or induced dipole) and dipole–quadrupole interactions are more important than charge-transfer forces.[10] Mulliken's theory of charge-transfer complex formation[11] is useful in understanding charge-transfer absorption whereas the formation constant of a weak EDA complex is not explainable by this theory. None of the present polymers exhibit any distinct CT absorption. Slight broadening of the S_0–S_2 band of pyrene is the only difference between exciplex-forming polymers and excimer-forming polymers or the monomer model compounds. Furthermore, the spectral broadening has been shown to be an intrapolymer phenomenon.[7a,c,d] Consequently, the origin of polymer association is not likely to be charge-transfer forces. Providing that dipole–dipole or dipole–multipole interaction is the driving force of polymer association, short-range and directional forces will be more efficient in regular polymers which afford efficient encounters of the exciplex-forming chromophores, as shown in Figure 3. Ethylenic random copolymers containing *p*-cyanophenyl and *N,N*-dimethylanilino groups have also been reported to form intrapolymer exciplex exclusively.[12]

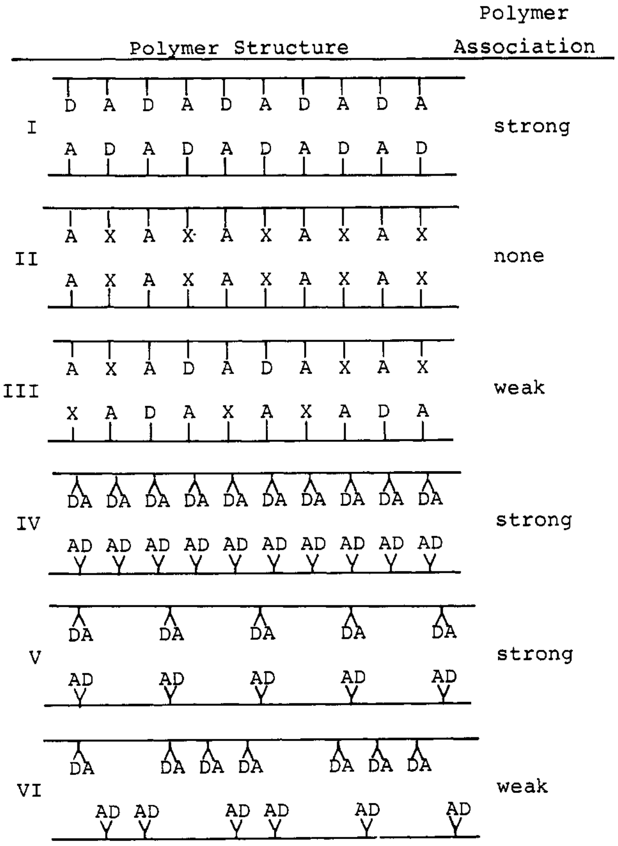

Figure 3. Schematic sketches showing the importance of structure regularity for polymer association. A = 1-pyrenyl, D = 4-(dimethylamino)phenyl, and X = phenyl.

The present results do not necessarily mean that a regular polymer structure is essential in all kinds of polymer association. When the driving force of polymer association is nondirectional and/or of long-range nature, the requirement of structural regularity will not be so stringent. For example, selectivity of polyion complex formation seems to be controlled by pH, solvation, concerted effect, or steric hindrance but not directly by the spacing between ionic groups.[13] Polymer association by hydrophobic interaction, which is short range but nondirectional and not very susceptible to steric effects, is not relevant to the structural regularity effect, as demonstrated in the association of water-soluble random copolymers in aqueous solution.[14]

Experimental Section. Materials. Preparation of polymer I,[5] II,[7b] and V[15] has been reported previously. Polymer IV was prepared in a manner similar to that of polymer V.

Polymer III was prepared by copolycondensation of 2-(1-pyrenylmethyl)-1,3-propanediol with an equimolar mixture of diethyl [4-(dimethylamino)benzyl]malonate and diethyl benzylmalonate using calcium acetate and antimony trioxide as catalysts. The temperature was gradually raised to 160 °C to 210 °C over a period of 18 h while the polymerization vessel was gradually evacuated to a final pressure of 10^{-2} mmHg.

Polymer VI was prepared by copolycondensation of the diol monomer with an equimolar mixture of thiophenol esters of oxalic acid and sebacic acid. The reaction procedure was the same as that for the preparation of V.

The molecular weight of each sample was estimated by a HLC-802UR gel permeation chromatograph (Toyo Soda Mfg. Co. Ltd.) calibrated for standard PS. To obtain samples of approximately equal molecular weight, polymers I, II, and V were fractionated.

Fluorescence Spectroscopy. A Hitachi MPF-4 spectrofluorometer was used. Spectrograde 1,2-dichloroethane (DCE) was further distilled immediately before use for spectroscopy. The monomer and exciplex intensities were determined at the maximum wavelengths, as already reported. No correction was made for the wavelength-dependent sensitivity of the spectrometer. The sample solution was deaerated by argon bubbling.

Registry No. I (copolymer), 76769-89-6; I (SRU), 91210-44-5; II (copolymer), 91210-52-5; II (SRU), 91210-45-6; III (copolymer), 91210-53-6; IV (copolymer), 91210-55-8; IV (SRU), 91210-46-7; V (copolymer), 91210-56-9; V (SRU), 91210-47-8; VI (copolymer), 91210-57-0.

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Shigeo Tazuke* and Hui Lian Yuan[2]
Research Laboratory of Resources Utilization
Tokyo Institute of Technology
4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

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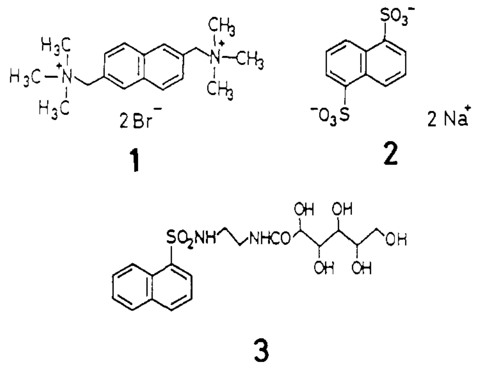
pH-Sensitive Permeation of Ionic Fluorescent Probes from Nylon Capsule Membranes[1,2]

The permeability of microcapsules has been investigated rather extensively because of its importance in designing and constructing sustained drug release devices and artificial cells.[3-6] However, these earlier studies dealt with the permeations of small, simple substances such as NaCl and glucose in the neutral-pH region.

Chart I



We report here that the permeation of ionic, water-soluble fluorescent probes (**1** and **2**, Chart I) from a large nylon capsule membrane is greatly affected by the ambient pH and is reversibly controlled by pH changes of the outer medium. This is the first example of pH-sensitive permeation control across capsule membranes. The permeability of NaCl or a nonionic probe **3** was not affected by the ambient pH.

Large, ultrathin nylon-2,12 capsules were prepared from ethylenediamine and 1,10-bis(chlorocarbonyl)decane by interfacial polymerization in the presence of a small amount of a cross-linking agent (trimesoyl chloride), by the method described in previous papers.[7-15] The presence of the cross-linking agent gave strong capsule membranes. The capsules (diameter: 2.5 mm, membrane thickness: 1 μm) were dialyzed against 0.01 mol dm^{-3} phosphate buffer (pH 7.0) containing a fluorescent probe (1.0×10^{-3} mol dm^{-3}) to give capsules with the trapped probe.

The permeability of the capsule toward the fluorescent probe was followed by detecting increases in the fluorescence intensity at 340 nm (excitation at 280 nm for **1** and at 290 nm for **2** and **3**) in the outer water phase. Permeation rates P were calculated from the following equation:[8,10,15]

$$P = \frac{kV}{AC} = \frac{1}{6}\frac{kd}{\Delta C} \tag{1}$$

where k, V, and A are the slope of increases in fluorescence intensity with time (see Figure 1), the volume of the outer water phase, and the surface area of a capsule, respectively; C denotes the concentration of the probe trapped in the inner phase and can be substituted by ΔC (the change of the fluorescence intensity after crushing a capsule). P (cm s^{-1}) depends on the capsule diameter, d, the slope, k, and the fluorescence intensity after crushing a capsule, ΔC. The pH values of the outer medium were controlled by addition of HCl or NaOH.

Figure 1 shows reversible changes in the permeation of fluorescent probes from nylon capsules at different pH values of the outer medium. The permeability of NaCl was not affected by changing the ambient pH from 2 to 12. When the cationic probe **1** was employed as a permeant, the permeability was drastically reduced below that of NaCl at an ambient pH 2. When the pH of the outer medium was changed from 2 to 12, the permeability was immediately enhanced by a factor of ca. 100 and reduced again almost to the same slow rate by returning the ambient pH to 2. In the case of the permeation of the anionic probe **2**, the reverse occurred. The permeability was enhanced in the acidic medium (pH 2) and reduced in the basic medium (pH 12) by a factor of ca. 50. This pH-sensitive permeability regulation could be repeated over

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