within the polymer particles. As the polymerization proceeds to a certain extent, the polymer subparticles containing some catalyst crystallites are formed. As the polymerization proceeds further, the polymer subparticles disintegrate to the primary polymer particles containing a catalyst crystallite, which grow as polymerization proceeds. The ca. 1-μm polymer globules on the surfaces of the polymer particles may be agglomerates of some tens of the primary polymer particles.

Registry No. $TiCl_3$, 7705-07-9; polypropylene, 9003-07-0.

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Notes

Consideration of Hydrophobic Attractions in End-to-End Cyclization

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Introduction

Cyclization of polymer chains has been of considerable interest for many years. It is related to fundamental problems such as synthesis of cyclic polymers and DNA cyclization[1] as well as practical problems such as physical property changes due to the addition of cyclic polymer to polymer blends. End-to-end cyclization has been investigated experimentally with the aid of spectroscopy. Sisido and Shimada[2] used the electron transfer between α-naphthyl or *N*-phthalimide groups attached to the ends of a polymer chain, monitored by electron spin resonance (ESR), to study the intramolecular end-to-end reaction. Luminescence techniques such as fluorescence and phosphorescence quenching have also been adopted[3] for polymer chains end-labeled with chromophores. These spectroscopic techniques use the common fact that when the two chromophores are in close proximity, these emit a band, for example, excimer emission, at a frequency distinguishable from the monomeric emission, thus permitting monitoring of the proximity of the ends. The end-to-end cyclization is generally dependent upon the conformation and the dynamics of the polymer chain connecting the two ends.[1,14]

End-to-end cyclization of polymers is known to be diffusion-controlled from extensive fluorescence studies,[1] implying that every encounter between chromophore ends leads to a dimer or excimer. Since the end-to-end cyclization is controlled by diffusion, the observed rate constant is proportional to T/η^0 where η_0 is the solvent viscosity and T is the absolute temperature. Recently, Cheung et al.[4] found anomalous behavior in the study of end-to-end cyclization using pyrene end-labeled poly(ethylene glycol) (Py-PEG-Py) in various solvents. They were able to correlate the measured excimer to monomer intensity ratio, I_e/I_m, which is proportional to the cyclization rate constant in the low-temperature limit, with the inverse solvent viscosity in all solvents except water and methanol where unusually high values of I_e/I_m were observed. Oyama et al.[5] also found similar anomalous behavior for Py-PEG-Py in water and further showed that the deviation of I_e/I_m in water from a diffusion-controlled process increases as the molecular weight of the PEG chain is decreased. In a previous paper,[6] we showed the effect of the addition of methanol on the viscosity-corrected excimer to monomer intensity ratio ($I_e(I_m\eta_0)$) for Py-PEG-Py in water. We found spectroscopic evidence for the existence of ground-state dimers in pure water and that the preformed dimers are diminished by the addition of methanol. From our experimental observations, we concluded that the ground-state dimers form in water-rich solvent due to the hydrophobic attraction between pyrene moieties.

Recently, this type of hydrophobically modified polymer chain has been used as an "associative thickener" in the paint industry.[7] Unlike conventional thickeners, which are usually nonadsorbing water soluble polymer, the associative thickeners interact with hydrophobic surfaces such as latex particles, improving the rheological properties of paint.[7]

The objective of this paper is to, first, derive a simple expression for the cyclization rate constant taking into account the hydrophobic attraction between pyrene ends and, second, to compare these predictions with the experimental results provided in our previous paper.[6]

Consideration of Hydrophobic Attraction

To derive a simple analytical expression, we consider a Gaussian polymer chain with negligible excluded volume. Since the Flory–Huggins interaction parameter (χ) for short PEG in water is close to $^1/_2$, the value representing the Θ condition, this approximation is reasonable. A general approach to model the hydrophobic attraction is to use a potential energy between hydrophobic moieties, such as a square-well potential, represented by both a depth (interaction energy) and a range of hydrophobic interaction. Since the interaction energy and the interaction range are generally coupled and there is no explicit expression for the hydrophobic attraction, we further wish to reduce a model potential to one adjustable parameter. There are two ways, in limiting cases, to reduce these two parameters into one. One approach leaves the interaction energy as the only parameter in a "sticky" potential[8] where the range of interaction is negligible. Another approach leaves the range of interaction as the adjustable parameter in a situation where the interaction is fairly high. Since the hydrophobic attraction is generally known to be long

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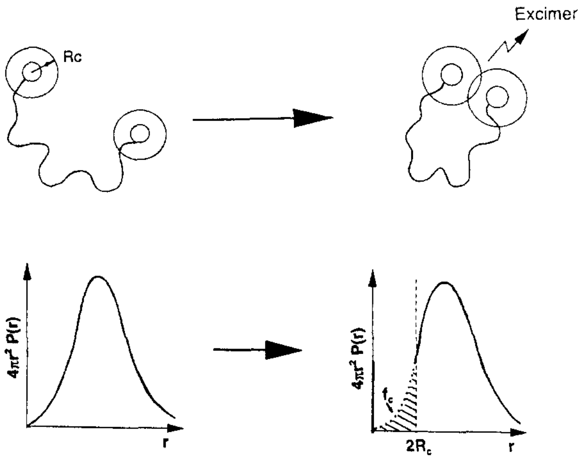

Figure 1. Schematic diagram for the consideration of hydrophobic attraction and modified probability distribution function of end-to-end distance.

ranged, as shown by surface force measurement,[9] the selection of the range of the interaction between two options would be reasonable in our case. Thus, for simplicity, we adopt a "capture process" model to consider the hydrophobic interaction, as depicted in Figure 1. If one pyrene end is within a distance of twice the capture radius from the other, the two are attracted to each other, yielding an excimer emission. Thus, this mathematical manipulation considers the ground-state dimer formation observed for Py-PEG-Py dissolved in water as a fraction of trapped ends.

We assume that the distribution of segments follows a random walk unless the two hydrophobic ends form a ground-state dimer. As soon as one end is within the capture region ($2R_c$) of the other end, two pyrene ends are attracted to each other to form a ring for which end-to-end distance of the pyrene ends is zero. Once a ring is formed, the configuration of the ring chain, which is the convolution of two Gaussian subchains, obviously differs from that of a Gaussian chain. However, our interest is the population of the captured chains rather than the detailed configuration of the dimers since the captured dimers are eliminated from the calculation of the mean-square end-to-end distance. Then, the normalized probability density function of end-to-end vector for a Gaussian chain in three dimensions is

$$P(r,N) = \left(\frac{3}{2\pi N}\right)^{3/2} \exp\left(-\frac{3r^2}{2N}\right) \tag{1}$$

where r is the dimensionless distance of one polymer end from the other, normalized by the segment length, and N is the degree of polymerization. Thus, the fraction of captured pyrene ends is

$$f_c = \int_0^{2R_c} 4\pi r^2 P(r,N)\, dr \tag{2}$$

given from the number of ends found within twice the capture radius, R_c. The modified mean-square end-to-end distance after taking the fraction of captured ends into consideration is then

$$\langle R^2 \rangle = (1 - f_c) \int_{2R_c}^{\infty} 4\pi r^4 P(r,N)\, \mathrm{d}r \tag{3}$$

Using the Gaussian probability density distribution function given in eq 1, we are able to derive analytic expressions for f_c and $\langle R^2 \rangle$, respectively:

$$f_c = 4\pi\left(\frac{m}{\pi}\right)^{3/2}\left\{-\frac{R_c}{m}e^{-4mR_c^2} + \frac{1}{4m}\left(\frac{\pi}{m}\right)^{1/2} \operatorname{erf}\,(2R_c m^{1/2})\right\} \tag{4}$$

$$\langle R^2 \rangle = (1 - f_c)4\pi\left(\frac{m}{\pi}\right)^{3/2}\left\{e^{-4mR_c^2}\left(\frac{R_c}{m}\right) \times \left[4R_c^2 + \frac{3}{2m}\right] + \frac{3}{8m^2}\left(\frac{\pi}{m}\right)^{1/2} \operatorname{erfc}\,(2R_c m^{1/2})\right\} \tag{5}$$

where $m = 3/(2N)$ and R_c is the dimensionless capture radius again normalized by the segment length. In the limiting case of a Gaussian chain without capture ends, we recover $\langle R^2 \rangle = N$ (dimensionless) by setting $R_c = f_c = 0$.

The large body of theoretical studies on diffusion-controlled end-to-end cyclization[10] show that the cyclization rate constant (k_{cy}) is directly proportional to I_e/I_m in the low-temperature limit where excimers are irreversibly formed and the k_{cy} is related to the mean-square end-to-end distance as follows:

$$k_{cy} \sim I_e/I_m \sim \langle R^2 \rangle^{-\alpha} \tag{6}$$

where α varies from a value of $^3/_2$ to 2 depending on the solvency and the degree of draining of polymer chains. For example, α is $^3/_2$ for a nondraining chain and 2 for a free-draining chain in a Θ solvent, while in a good solvent, α is slightly larger than $^3/_2$.[1] The value of α has been found to be as low as unity, as shown from the dynamic study of pyrene end-tagged poly(ethylene oxide) in organic solvents such as toluene and tetrahydrofuran.[11]

As we mentioned earlier, the excimers formed in water are ground-state dimers and thus do not reflect the cyclization dynamics. Therefore, the static contribution should be much more important than the dynamic contribution. The equilibrium cyclization probability of end-to-end vectors in close proximity of chain ends scales as $\langle R^2 \rangle^{-3/2}$ for Gaussian chains, as shown by Jacobson and Stockmayer.[12] James and Evans[13] pointed out that the dependence of k_{cy} on $\langle R^2 \rangle$ is determined primarily by the equilibrium probability distribution rather than the cyclization dynamics. Consequently, the value of α, fixed at $^3/_2$, is valid for the situations considered here.

Results and Discussion

Figure 2 shows the effect of the capture radius on the excimer to monomer intensity ratio for Gaussian chains of various degrees of polymerization. The excimer to monomer intensity ratio, I_e/I_m, at arbitrary R_c is normalized by that in the absence of hydrophobic interaction. Up to $R_c = 1.4$, I_e/I_m remains unchanged and the molecular weight has no effect on the relative excimer-to-monomer intensity ratio $[(I_e/I_m(R_c))/(I_e/I_m(R_c{=}0))]$. However, as R_c is further increased, $(I_e/I_m(R_c))/(I_e/I_m(R_c{=}0))$ begins to deviate from unity and the degree of polymerization has a more pronouned effect on the relative excimer-to-monomer intensity ratio. We also show in Figure 2 that a short chain, i.e., for a degree of polymerization (N) of 100, is more sensitive to the capture radius than a longer Gaussian chain. When the degree of polymerization exceeds 500, the hydrophobic attraction has little effect on the excimer to monomer intensity ratio. This prediction is physically reasonable since short chains should be more strongly affected by the hydrophobic attraction due to their small end-to-end distances.

The above prediction can be compared with experimental results provided earlier.[6] We[6] reported photostationary I_e/I_m values for aqueous solutions of Py-PEG-Py

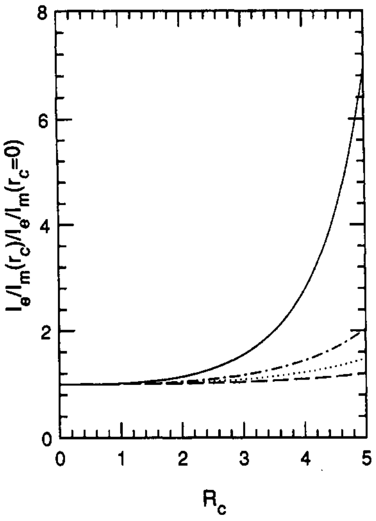

Figure 2. Theoretical prediction of the excimer to monomer intensity ratio relative to the excimer to monomer intensity ratio without hydrophobic attraction against the dimensionless capture radius for degrees of polymerization: N = 100 —, N = 200 -·-, N = 300 ···, N = 500 ---.

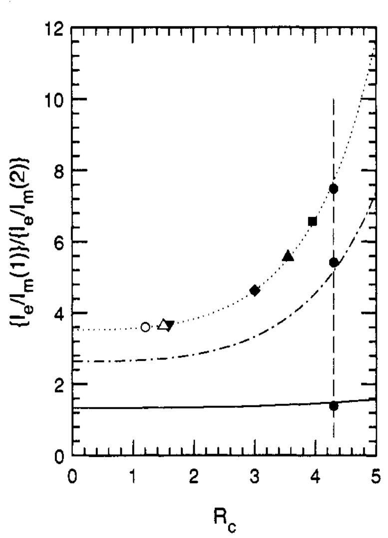

Figure 3. Effect of the dimensionless capture radius on the relative excimer to monomer intensity ratio ($\{I_e/I_m(1)\}/\{I_e/I_m(2)\}$): ···, (1) M_w = 4800 (N = 110) - (2) M_w = 11 200 (N = 255); -·-, (1) M_w = 4800 - (2) M_w = 9200 (N = 210); —, (1) M_w = 9200 - (2) M_w = 11200; and data showing the effect of adding methanol ●, in water; ■, 10% MeOH; ▲, 20% MeOH; ◆, 30% MeOH; ▼, 40% MeOH; ○, 60% MeOH; △, 100% MeOH.

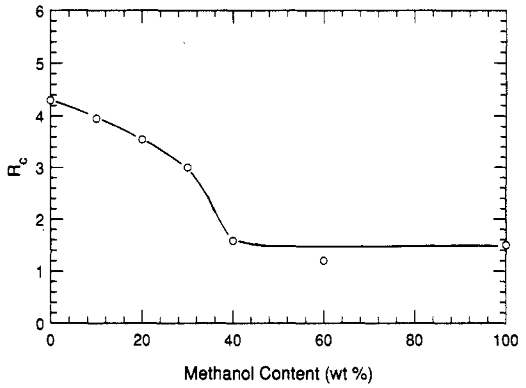

Figure 4. Effect of methanol addition on the decrease in dimensionless capture radius.

having molecular weights of 4800, 9200, and 11 200 based on PEG backbone. We showed that the short chain (M_w = 4800) gives the largest discrepancy from the Wilemski–Fixman prediction[10] for diffusion-controlled cyclization, where k_{cy} should scale with $N^{-3/2}$. We attributed this discrepancy to hydrophobic attraction. In the present study, we determine the capture radius or range of hydrophobic interaction by comparing the predictions given here with the experimental data. The segment length defined in eq 1–5 is equal to the length of a poly(ethylene glycol) repeat unit, approximately 4.4 Å, since poly(ethylene glycol) is flexible. Figure 3 shows the theoretical predictions of the effect of capture radius on three ratios of I_e/I_m representing ratios of three degrees of polymerization to be compared with the experimental data reported in Table III of ref 6. When molecular weights for the pair are both high, i.e., 9200 and 11 200, the ratio of I_e/I_m is almost insensitive to the capture radius (solid line). However, whenever the short Py-PEG-Py (i.e., M_w = 4800) is included in the pair, the ratio becomes very sensitive to the capture radius. Comparing the prediction with experimental data shows quite good agreement for all three ratios at R_c = 4.3 Å. In actual distances, this is equivalent to about 20 Å, so that the range of hydrophobic interaction is approximately 40 Å for hydrophobic pyrene ends. This value is within the region of hydrophobic attraction observed for linear hydrocarbon chains (~100 Å) measured with a surface-force apparatus.[9] Since the hydrophobic interaction between aromatic molecules is generally weaker in magnitude than linear hydrocarbon molecules, we believe this value to be reasonable.

We[6] also showed how the enhanced I_e/I_m in water decreases by the addition of methanol. By comparing these data with the theoretical prediction, we are able to show quantitatively the reduction of hydrophobic interaction in various water–methanol mixtures. Since the experimental data for water–methanol mixtures are given for only two molecular weights, i.e., M_w = 4800, 11 200, the top curve in Figure 3 is used. We take the ratio of the two I_e/I_m values at the same methanol content to cancel solvent viscosity effects. As illustrated in Figure 3, the range of hydrophobic interaction decreases with increasing methanol content. The decrease in capture radius is not linear with methanol content as shown in Figure 4. The capture radius decreases as the methanol content is increased to 40% but remains constant as more methanol is added. Thus, the hydrophobic effect is not completely eliminated in pure methanol since it is a polar solvent.

As mentioned earlier, if excimers are formed by a diffusion-controlled process, I_e/I_m should be inversely proportional to solvent viscosity. Thus, when I_e/I_m is multiplied by solvent viscosity (η_0), all solvents yielding diffusion-controlled excimers should have the same $(I_e/I_m)\eta_0$ for a given polymer molecular weight at a fixed temperature. As expected, $(I_e/I_m)\eta_0$ in pure methanol remains higher than $(I_e/I_m)\eta_0$ in solvents where excimers form solely due to diffusion-controlled process, implying that there is a hydrophobic effect in pure methanol. For example, $(I_e/I_m)\eta_0$ in methanol is 0.0856, whereas $(I_e/I_m)\eta_0$ where there is no hydrophobic attraction yields 0.0686[5] for Py-PEG-Py (M_w = 4800). This corresponds to the observation made by Cheung et al.[4] that I_e/I_m or k_{cy} in methanol deviates from I_e/I_m or k_{cy} predicted by a diffusion-controlled mechanism; however, the deviation is not as extensive as it is in water. Excitation spectra in methanol also indicate the disappearance of most ground-state dimers, presumably due to the significant reduction in the hydrophobic attraction.

In conclusion, we have estimated the range of the hydrophobic attraction between pyrene moieties attached to a polymer chain in water and its subsequent decrease upon the addition of methanol with a sample theoretical prediction taking a capture process between the ends of a Gaussian chain into consideration. The range of hydrophobic interaction between pyrene ends is approximately 40 Å as determined from experimental data for three different molecular weights. The addition of methanol decreases the range of hydrophobic attraction up to 40% with the range staying constant beyond that methanol content. This implies that the hydrophobic attraction is not completely eliminated even in pure methanol.

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Registry No. Py-PEG-Py, 82870-83-5; MeOH, 67-56-1.

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Poly(phosphatidylcholine) Analogues

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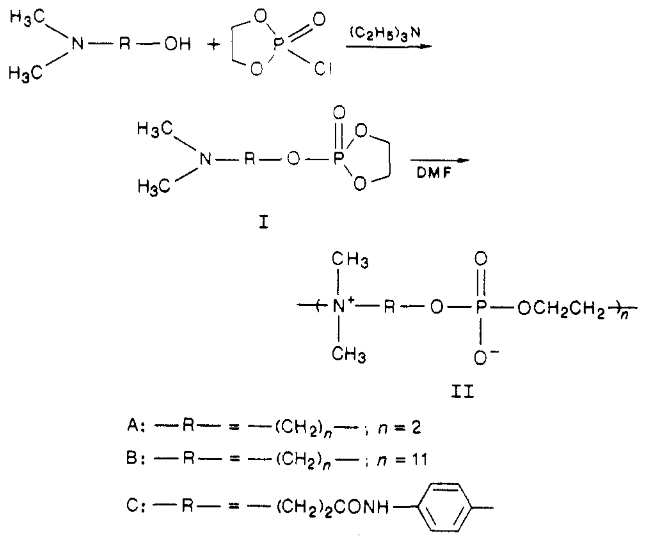
Considerable attention has recently been paid to phospholipids because they are known to be important building units of biological membranes.[1,2] From this point of view, it seemed attractive to investigate the behavior of polymeric phospholipid analogues. During the past 10 years, a large amount of our effort has been directed toward the syntheses and properties of polymers containing phosphatidylethanolamine[3,4] or choline[5,6] analogues in the side chains. In addition, we have recently reported the syntheses and some properties of polymers containing phosphatidylcholine analogues in the main chains.[7,8] Our continuing interest in this type of ring-opening polymerization prompted us to design new monomers having both dimethylamino and 2-oxo-1,3,2-dioxaphospholan-2-yloxy functions as terminal groups, where the linkages between the terminal groups are as listed below.

We now wish to report the first synthesis of poly(phosphatidylcholine) analogues whose structures are particularly interesting as biochemical models. Thus, monomers I were synthesized and their subsequent polymerization was carried in DMF to give the corresponding poly(phosphatidylcholine) analogues II.



As starting materials, 2-(dimethylamino)ethanol, 11-(dimethylamino)decanol, and *p*-[(dimethylamino)ethanamido]phenol were used. 11-Bromoundecanol was prepared by lithium aluminum hydride reduction of 11-bromoundecanoyl chloride which has been synthesized by reaction of 11-bromoundecanoic acid[9] with thionyl chloride. *p*-[(Dimethylamino)ethanamido]phenol[10] was prepared by reaction of dimethylamine with *p*-acrylamidophenol[11] which had been obtained by the reaction of p-acryloyl chloride with *p*-aminophenol.

Monomers I_A–I_C were prepared in good yield by reaction of the appropriate materials with 2-chloro-2-oxo-1,3,2-dioxaphospholane in THF in the presence of a 3-fold excess of triethylamine at −10 °C for 2 h. Charactrization of these monomers was based on their ^{1}H NMR spectra.[12] The polymerization was carried out by heating these monomers in DMF at 60 °C for 20 h. In a typical experiment, the ^{1}H NMR spectra change of the polymerization of I_A was followed. The peak due to NCH_3 protons of I_A at $\delta = 2.55$ ppm disappeared, whereas a new peak due to N^+CH_3 protons appeared at 3.30 ppm. Peaks arising from the phospholane ring OCH_2 protons appeared at 3.50 and 4.10–4.40 ppm and were assigned to the ring-opened N^+-CH_2 and OCH_2 protons, respectively. These observations indicate that the ring-opening polymerization of I_A afforded a new polyionene-containing phosphatidylcholine analogous structural units along the main chain. Characterization of the resulting polymers was based on their ^{1}H NMR and IR spectra as well as elemental analyses.[13] These polymers are hygroscopic and soluble in water and methanol but almost insoluble in acetone, diethyl ether, and benzene.

Gel permeation chloromatography (GPC) measurements of these polymers were carried out in water with TSK-GEL-(G5000PW + G3000PW) columns. From the relationship between retention time and molecular weights derived for narrow-distributed standard poly(ethyleneglycol)s, the weight-average molecular weights of II_A, II_B, and II_C were estimated as 15 000, 16 000, and 10 000, respectively.

In previous work,[6,7] we have found that vinyl polymers having phosphatidylcholine in the side chains show the properties of polyelectrolytes in their viscosity behavior in aqueous solution. In contrast with these studies, we have recently found that polymers containing phosphatidylcholine analogues in the polymer backbone do not show polyelectrolyte behavior but show instead a linear increase of reduced viscosity versus concentration of the polymer.[7] Accordingly, it is very interesting to determine whether the new polymers are polyelectrolytes or not. Therefore, viscosity measurements were performed at 25

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