diction 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.

Acknowledgment. This work was supported by the NSF-MRL Program through the Center for Materials Research at Stanford University.

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

References and Notes

(1) Semlyen, J. A. *Cyclic Polymers*; Elsevier: London, 1986.
(2) Sisido, M.; Shimada, K. *Macromolecules* **1979**, *12*, 790, 792.
(3) Winnik, M. A. *Acc. Chem. Res.* **1985**, *18*, 73.
(4) Cheung, S. T.; Winnik, M. A.; Redpath, A. E. C. *Makromol. Chem.* **1982**, *183*, 1815.
(5) Oyama, H. T.; Tang, W. T.; Frank, C. W. *Macromolecules* **1987**, *20*, 474.
(6) Char, K.; Frank, C. W.; Gast, A. P.; Tang, W. T. *Macromolecules* **1987**, *20*, 1833.
(7) (a) U.S. Patent 4079, 029, 1978. (b) Santore, M. M.; Russel, W. B.; Prud'homme, R. K., submitted for publication in *Macromolecules*.
(8) Baxter, R. J. *J. Chem. Phys.* **1968**, *49*, 2770.
(9) Israelachvili, J.; Pashley, R. *Nature* **1982**, *300*, 341.
(10) Wilemski, G.; Fixman, M. *J. Chem. Phys.* **1974**, *60*, 866, 878.
(11) Ghiggino, K. P.; Snare, M. J.; Thistlethwaite, P. J. *Eur. Polym. J.* **1985**, *21*, 265.
(12) Jacobson, H.; Stockmayer, W. H. *J. Chem. Phys.* **1950**, *18*, 1600.
(13) James, C.; Evans, G. T. *J. Chem. Phys.* **1982**, *76*, 2680.
(14) Cuniberti, C.; Perico, A. *Prog. Polym. Sci.* **1984**, *10*, 271.

Poly(phosphatidylcholine) Analogues

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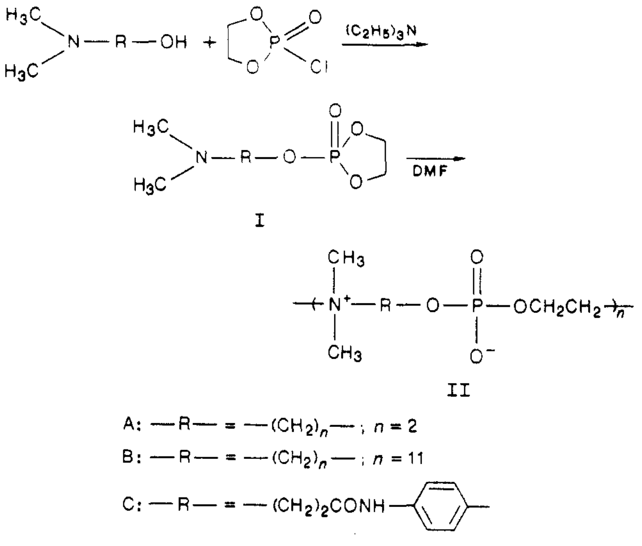
Received August 2, 1988;
Revised Manuscript Received December 9, 1988

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 ^1H 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 ^1H 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 ^1H 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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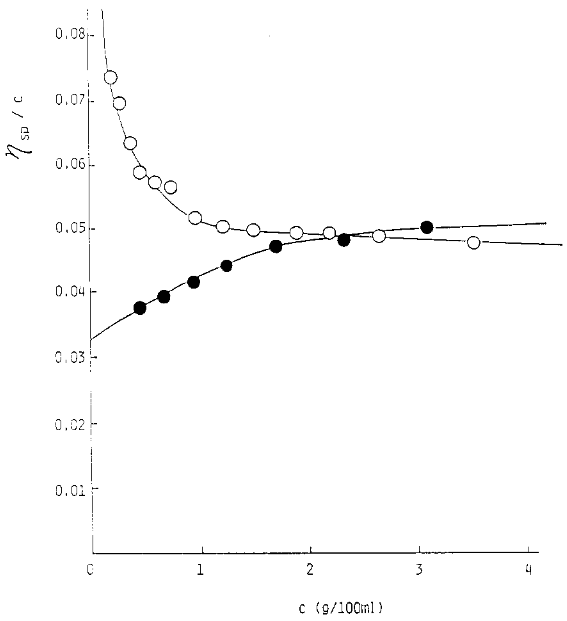

Figure 1. Reduced viscosity of II$_A$ in aqueous solutions at 25 °C: (●) in pure water; (○) in 0.005 mol/L KCl.

°C in the presence and absence of potassium chloride. Figure 1 show plots of the reduced viscosity, η_{sp}/c, versus c for II$_A$ in aqueous solutions, where c is expressed in grams per 100 mL. In pure water, η_{sp}/c was found to increase rapidly upon dilution, whereas the addition of potassium chloride eliminates the increase. Thus, polymer II$_A$ shows polyelectrolyte behavior.

Acknowledgment. We thank the Research Center of Nitto Electric Co. Ltd., Osaka, Japan, for providing facilities for the measurement of GPC.

Registry No. I$_A$, 101707-61-3; I$_A$ (homopolymer), 101707-62-4; I$_B$, 119296-72-9; I$_B$ (homopolymer), 119296-76-3; I$_C$, 119296-73-0; I$_C$ (homopolymer), 119296-77-4; II$_A$, 101647-92-1; II$_B$, 119296-74-1; II$_C$, 119296-75-2; potassium chloride, 7447-40-7.

References and Notes

(1) Finean, J. B. *Form and Function of Phospholipids*; Ansell, G. B., Hawthorn, R. M., Dawson, R. M., Eds.; Amsterdam, 1973; p 171.

(2) (a) Fendler, J. H. *Membrane Mimetic Chemistry*; Wiley: New York, 1982; Chapter 6. (b) Fendler, J. H. *Science (Washigton, D.C.)* **1985**, *223*, 888.

(3) Nakai, S.; Nakaya, T.; Imoto, M. *Makromol. Chem.* **1977**, *178*, 2963.

(4) Nakai, S.; Nakaya, T.; Imoto, M. *Makromol. Chem.* **1978**, *179*, 2343.

(5) Umeda, T.; Nakaya, T.; Imoto, M. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 285.

(6) Furukawa, A.; Shoji, H.; Nakaya, T.; Imoto, M. *Makromol. Chem.* **1987**, *188*, 265.

(7) Umeda, T.; Nakaya, T.; Imoto, M. *Makromol. Chem., Rapid Commun.* **1983**, *3*, 457.

(8) Sugiyama, K.; Nakaya, T. *Makromol. Chem., Rapid Commun.* **1986**, *7*, 679.

(9) Minezaki, S.; Nakaya, T.; Imoto, M. *Makromol. Chem.* **1974**, *175*, 3017.

(10) Data: mp 129–131 °C; Yield 80%; IR (KBr) 1630 (m), 1655 (vs), 1598 (m) 1505 (vs) cm^{-1}; ^{1}H NMR (CD$_3$OD) δ 2.25 (s, 6, CH$_3$), 2.40–2.80 (m, 4, NCH$_2$CH$_2$CO), 4.96 (s, 2, CONH, OH). 6.70 (d, 2, aromatic ring protons), 7.30 (d, 2, aromatic ring protons). Anal. Calcd for C$_{11}$H$_{16}$O$_2$N$_2$: C, 63.44; H, 7.74; N, 13.45. Found: C, 63.29; H, 7.82; N, 13.17.

(11) Yasuzawa, M.; Nakaya, T.; Imoto, M. *J. Macromol. Sci., Chem.* **1986**, *A23*, 963.

(12) ^{1}H NMR (CDCl$_3$): (I$_A$) δ 2.55 (s, 6, CH$_3$), 2.65 (m, 2, NCH$_2$) 4.13 (m, 2, CH$_2$O), 4.36 (m, 4, methylene H of phospholane ring); (I$_B$) δ 1.43 (m, 18, CH$_2$), 2.56 (s, 6, CH$_3$), 2.67 (m, 2, NCH$_2$), 4.14 (m, 2, OCH$_2$), 4.37 (m, 4, methylene H of phospholane ring); (I$_C$) δ 2.50 (s, 6, CH$_3$), 2.40–2.80 (m, 4, NCH$_2$CH$_2$CO), 6.70 (d, 4, aromatic ring protons).

(13) II$_A$: ^{1}H NMR (CD$_3$OD) δ 3.30 (s, 6, CH$_3$), 3.50 (m, 4, N$^+$CH$_2$), 4.10–4.40 (m, 4, OCH$_2$); IR (neat) 1235 and 1080 cm^{-1} (POO$^-$). II$_B$: δ 1.32–1.50 (m, 18, CH$_2$), 3.32 (s, 6, N$^+$CH$_3$), 3.51 (m, 4, N$^+$CH$_2$), 4.12–4.43 (m, 4, OCH$_2$); IR (neat) 2840 (CH$_2$), 1235, 1080 cm^{-1} (POO$^-$). II$_C$: δ 3.33–3.40 (m, 6, N$^+$CH$_3$, 2, CH$_2$CO), 3.55 (m, 2, N$^+$CH$_2$), 4.15–4.46 (m, 4, OCH$_2$), 5.02 (s, 1, CONH), 6.70–6.75 (m, 4, aromatic ring protons); IR (KBr) 1660 (CONH), 1600, 1500 (Ph), 1236, 1060 cm^{-1} (POO$^-$). Elementary analyses of polymers II$_A$–II$_C$ were in good to excellent agreement with theory.

Communications to the Editor

Poly(*exo*-5-hydroxynorbornene): A Functional Polymer Using Metathesis Polymerization of an Organoborane Derivative

Polymers that have a variety of functional groups are finding applications in areas such as solid-phase synthesis, polymer-bound catalysts, polymer-bound drugs, etc. The sensitivity of most organometallic catalysts toward functional monomers with heteroatoms, such as O, S, and N, has often hampered their utilization in the synthesis of functional polymers.

Ring-opening metathesis polymerization of functional monomers has met with only limited success.[1] Some very recent investigations using RuCl$_3$ catalysts, however, appear to hold more promise in terms of their application for the synthesis of functional polymers.[2] Considerable progress in the synthesis of transition metal (W and Mo) alkylidene complexes[3] during the past few years has led to a greater understanding of the steric and electronic environment around the metal center necassary for these complexes to effect living polymerization and also to be functional group compatible. At present, living ring-opening metathesis polymerization has been possible only with cyclic olefins that possess considerable ring strain, such as norbornene. In general, the living and functional group tolerant catalysts are thus relatively less active and therefore are most effective for the polymerization of strained ring olefins.[4] Our approach to functional polymers has been directed toward the development of monomers that are stable to transition-metal catalysts and are quantitatively convertible to functional polymers after polymerization. This approach would allow us to access a much wider range of monomers by using more reactive catalysts that are usually very susceptible to functional groups. The transformation of organoboranes to a variety of functional groups has been well established in small organic molecules.[5] We have recently demonstrated that alkenylboranes can be polymerized by a Ziegler–Natta process and that the poly(borane)s thus produced can be quantitatively converted to poly(alcohol)s.[6] Such monomers can further be copolymerized with 1-alkenes to give hydrocarbon polymers with varying degrees of functionalization.[7] We have now extended this approach to the synthesis of functional polymers by ring-opening metath-