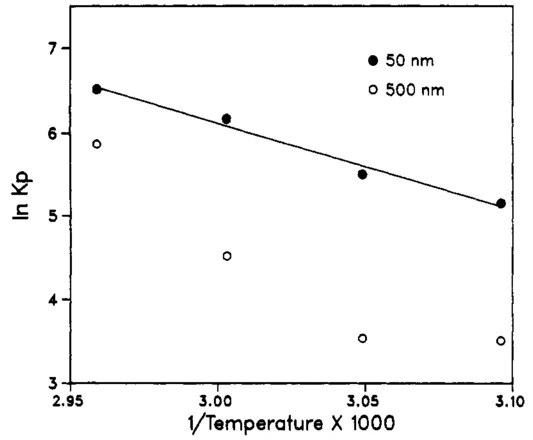

Figure 2. Arrhenius plot of propagation rate constants for small and large particle size latices. Data taken from Table I.

contain contributions from both monomer diffusion and propagation. The activation energy calculated for the propagation reaction for the 50-nm particle size data is 20 kcal/mol. This number is markedly larger than the value observed for radical propagation reactions in solution.[8] Presumably this larger value is a result of the very high viscosities present in the particles under conditions of high conversion.

Recent results reported by Ballard et al.[2] for batch emulsion polymerization of methyl methacrylate may be compared to the results obtained in this study. Although Ballard et al. did not report final particle size, we have inferred from their data that it was about 160 nm, intermediate to the two particles sizes examined in this study. Allowing for the minor compositional difference, their values of $\bar{n}$ and k_p at high conversion are in good agreement with the results of this study. This agreement is reasonable since the late stages of a batch emulsion polymerization should correspond to the steady-state conditions of a semicontinuous emulsion polymerization.

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Amphiphilic and Polymerizable Porphyrins and Their Copolymerization with Phospholipid: Oriented Fixation of Porphyrins in a Bilayer Membrane

This communication describes the synthesis of novel, amphiphilic and polymerizable porphyrin derivatives (1) and their polymers with a polymerizable phospholipid (2). 1 had a high compatibility with lipids and formed a stable bilayer membrane with 2. 1 was copolymerized with 2 in a bilayer state and was covalently and orientedly fixed in a bilayer membrane.

Porphyrins and metalloporphyrins not only are important pigments but also play key roles in biological and biomimetic reaction systems. In these systems much attention has recently been paid to the position and orientation of the porphyrins in matrices: a zinc porphyrin situated in an electron-transfer chain,[1–4] an iron porphyrin as a hemoglobin-like oxygen carrier,[5,6] and a porphyrin fixed in a polymer matrix used for photochemical hole burning.[7,8] In this communication we show that porphyrins can be fixed in a given orientation in a lipid membrane and describe the synthesis of tetraphenylporphyrin derivatives substituted with tetra(α,α,α,α-alkyl) groups having both a polymerizable double bond and a hydrophilic (carboxylic acid) group at their top position (as shown in 1). Because not only the hydrophobic–hydrophilic balance but also the stereostructure of 1 are adjusted to a lipid bilayer, it is expected that 1 will form a stable bilayer membrane with a lipid such as 2, that the polymerizable double bonds of 1 and 2 will be adjacent to each other in a bilayer state, and that in situ copolymerization of 1 with 2 will occur rapidly (Scheme I). Orientation of the porphyrins fixed in the bilayer membrane by the copolymerization was also estimated by electrooptical measurement.

5,10,15,20-Tetrakis(α,α,α,α-*o*-(8′-(((4″-carboxybutadienyl)carbonyl)oxy)-2′,2′-dimethyloctanamido)phenyl)porphyrin (**1a**) was synthesized by reaction of 5,10,15,20-tetrakis(α,α,α,α-*o*-(2′,2′-dimethyl-8′-hydroxyoctanamido)phenyl)porphyrin with muconic acid chloride. The structure including the α,α,α,α-configuration was confirmed by ^{1}H NMR, ^{13}C NMR, UV–vis, and elemental analysis.[10a] Metal insertion in **1a** gave **1b** and **1c**. 5,10,15,20-Tetrakis(α,α,α,α-*o*-(20′-(((2″-carboxypropenyl)carbonyl)oxy)-2′,2′-dimethyleicosanamido)phenyl)porphyrin (**1d**) was synthesized by reaction of 5,10,15,20-tetrakis(α,α,α,α-*o*-(2′,2′-dimethyl-20′-hydroxyeicosanamido)phenyl)porphyrin[5,9] with anhydrous itaconic acid,[10b] and metal insertion gave **1e** and **1f**. 2 was prepared according to the literature.[11]

A bilayer membrane of 1 with 2 was prepared in an aqueous medium through the normal procedure[12] for liposome preparation ([1]/[2] = 1/(20–50) (molar ratio), [1] = 50 μM). 1 was efficiently taken into the 2 bilayer liposome; only 20 mol of 2 was needed to solubilize 1 mol of 1 completely in water. A DSC thermogram of the 2 liposome containing 1 was measured to estimate the phase transition of the bilayer membrane. The 1/2 liposome showed an endothermic peak at 18 °C, which was assigned to the gel–liquid crystal phase transition temperature (T_c) of the bilayer membrane and agreed with that for the 2 bilayer liposome itself (18 °C). This suggests that the compatibility of 1 with 2 is large enough to form a stable bilayer membrane.

The bilayer liposome of 2 with 1 was allowed to polymerize under UV irradiation. Complete copolymerization of 2 with 1 was confirmed by UV absorption and ^{13}C NMR spectroscopy: disappearance of absorption bands based on the diene of **1a–c** and 2 or the double bond of **1d–f** and

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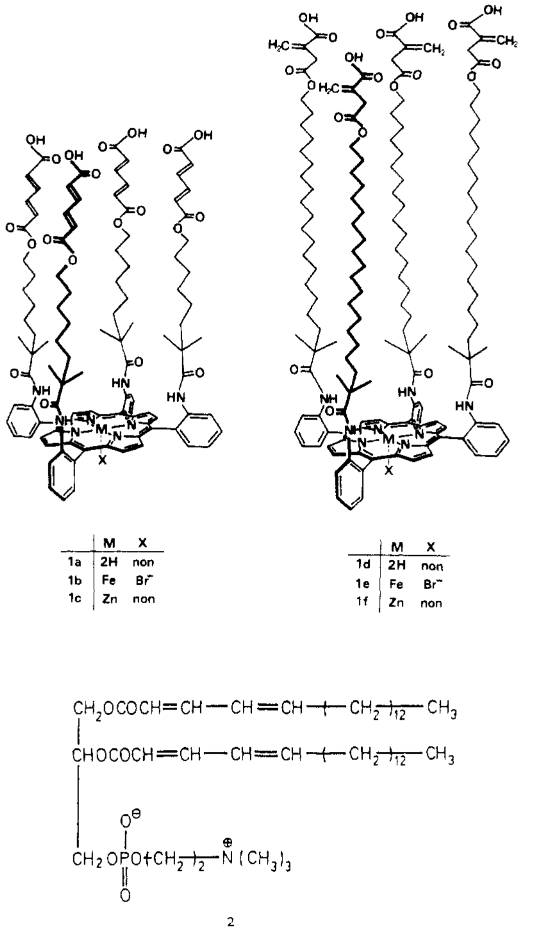
Chart I



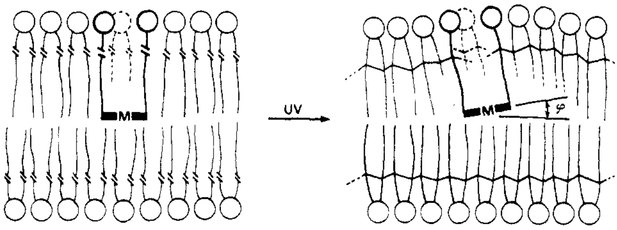
	M	X
1a	2H	non
1b	Fe	Br⁻
1c	Zn	non

	M	X
1d	2H	non
1e	Fe	Br⁻
1f	Zn	non

$$\begin{array}{l} CH_2OCOCH{=}CH{-}CH{=}CH{-}(CH_2)_{12}{-}CH_3 \\ | \\ CHOCOCH{=}CH{-}CH{=}CH{-}(CH_2)_{12}{-}CH_3 \\ | \\ CH_2OP(=O)(O^{\ominus})O(CH_2)_2\overset{\oplus}{N}(CH_3)_3 \end{array}$$

2

Scheme I



disappearance of characteristic signals based on the diene or the double-bond carbons.

Incorporation of 1 in the copolymerized liposome was confirmed as follows. After ultracentrifugation (45 000 rpm, 4 h, 10 °C), the supernatant did not contain both 1 and 2. The copolymerized liposome formation was also checked by GPC (Sepharose 4B) monitored by absorptions at 300 and 418 nm based on 2 and 1, respectively. The curves coincided with each other, which means that 1 is included in the liposome. The freeze-dried powder of the 1/2 copolymerized liposome could be resolubilized in water but not in organic solvents, while 1 and 2 before the polymerization were soluble in chloroform. The copolymer was extracted with chloroform: The chloroform did not contain both 1 and 2 and the composition of 1/2 in the extracted copolymer agreed with the feed composition. These results indicate that 1 is copolymerized with 2 and covalently fixed in the polymerized bilayer membrane of 2.

The porphyrin plane of 1 is assumed to be fixed and to be oriented nearly parallel to the polymerized bilayer membrane (Scheme I). This was confirmed by an electrooptical measurement[13] on the 1/2 copolymerized bilayer membrane with a lamellar structure. Dichroism of the porphyrin fixed in the bilayer membrane was monitored under an electric field. The transient absorbance change was very large when the incident light was polarized parallel to the electric field (Table I). It has been reported that a phospholipid bilayer membrane is aligned parallel to an electric field.[13] Thus it is reasonable to consider that the angle (φ) between the porphyrin plane and the lipid bilayer (in Scheme I) is close to zero. It is assumed that the stereostructure and amphiphilic structure of 1 and the copolymerization within the bilayer set the porphyrin plane parallel to the bilayer membrane.

Table I
Reduced Linear Dichroism (ρ) and Orienting Angle of Porphyrin Plane to Electric Field (φ)

ρ^a	$\rho_\infty{}^b$	$\Psi(E)^c$	φ,[c] deg
+0.7	>0.7	>0.96	<5

[a] $\rho = (\epsilon_\parallel - \epsilon_\perp)/\epsilon$, where $\epsilon_\parallel$ and $\epsilon_\perp$ are the extinction coefficients with the light polarized parallel to and perpendicular to the electric field and ϵ is the isotropic extinction coefficient. The ρ value is at 7.5 kV/cm electric field (E). [b] The extrapolation of linear ρ vs. $1/E$ plots to $1/E = 0$ gives the ρ value at infinite electric field (ρ_∞). [c] The relation between E and ρ is given as $\rho = (3/8)(3\cos 2\varphi - 1)\cdot\Psi(E)$ by supposing that the transition moment of porphyrin lies symmetrically in the porphyrin plane. φ is orienting angle of the porphyrin plane to electric field. $\Psi(E)$ is the orientation function to represent the degree of orientation.

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(10) (a) Data for **1a**: ^{1}H NMR ($CDCl_3$, Me_4Si standard, ppm) δ −2.30 (s, 2 H, inner pyrrole proton (H)), −0.21 (s, 24 H, 2′,2′-dimethyl H), 0.20–2.00 (m, 40 H, alkyl chain H (porphyrin (P)-(*meso*-Ph)-$NHCOC(CH_3)_2(\mathit{CH_2})_5CH_2O$–), 3.90 (t, 8 H, alkyl chain H (P-(*meso*-Ph)-$NHCOC(CH_3)_2(CH_2)_5\mathit{CH_2}O$–), 6.10–6.30 (d,d, 8 H, outer diene H (*CH*═CH—CH═*CH*)), 7.00–7.20 (d,d, 8 H, inner diene H (CH═*CH*—*CH*═CH)), 7.10–7.90 (m, 24 H, phenyl H (P-(*meso-Ph*)), 8.70 (s, 4 H, amido H (P-(*meso*-Ph)-*NH*$COC(CH_3)_2$–), 8.80 (s, 8 H, β-H of porphyrin ring); ^{13}C NMR ($CDCl_3$, Me_4Si standard, ppm) δ_C 24.3 (2′,2′-dimethyl carbon (C)), 24.8 (alkyl chain C (P-(*meso*-Ph)-$NHCOC(CH_3)_2CH_2\mathit{CH_2}$–), 28.6–29.6 (alkyl chain C (P-(*meso*-Ph)-$NHCOC(CH_3)_2CH_2CH_2(CH_2)_3$–), 41.0 (alkyl chain C (P-(*meso*-Ph)-$NHCOC(CH_3)_2\mathit{CH_2}$–), 42.3 (tertiary C of pivaloyl group (P-(*meso*-Ph)-$NHCO\mathit{C}(CH_3)_2$–), 64.8 (alkyl chain C (P-(*meso*-Ph)-$NHCOC(CH_3)_2CH_2CH_2(CH_2)_3\mathit{CH_2}$–), 114.9 (*meso*-C of porphyrin ring), 120.8, 123.2, 130.1, 130.7, 134.4, 138.5 (3-, 5-, 4-, 1-, 6-, 2-C's of phenyl, respectively), 127.9, 128.5 (outer dienes (4 and 1) C's of muconic acid group, respectively), 131.8 (β-C of porphyrin ring), 140.7, 141.0 (inner dienes (3 and 2) C's of muconic acid group), 146.2 (α-C of porphyrin ring), 165.8 (top carbonyl C of muconic acid group), 166.2 (inner carbonyl C of muconic acid group), 174.6 (carbonyl C of pivaloyl group (P-(*meso*-Ph)-NH*CO*–); IR (KBr pellet, cm^{-1}); 1620 ($\nu_{C{=}C}$), UV–vis (chloroform, nm) 254, 418, 513, 545, 589, 645; elemental anal. C, H, N (found: C, 85.0; H, 7.6; N, 7.4; calcd: ($C_{108}H_{122}N_8O_{20}$) C, 84.7; H, 8.0; N, 7.3. (b) Data for **1d**: ^{1}H NMR ($CDCl_3$, Me_4Si standard, ppm) δ_H −2.28 (s, 2 H, inner pyrrole H), −0.21 (s, 24 H, 2′,2′-dimethyl H), 0.20–2.00 (m, 136 H, alkyl chain H (P-(*meso*-Ph)-$NHCOC(CH_3)_2$-$(\mathit{CH_2})_{17}CH_2O$–), 2.20 (s, 8 H, CH_2 of itaconic acid group (P-(*meso*-Ph)-$NHCOC(CH_3)_2(CH_2)_{17}CH_2OCO\mathit{CH_2}C({=}CH_2)$-

COOH), 3.50 (t, 8 H, alkyl chain H (P-(*meso*-Ph)-NHCOC-$(\mathrm{CH_3})_2(\mathrm{CH_2})_{17}\mathit{CH}_2$O–), 5.90 (s, 8 H, side-chain $\mathrm{CH_2}$ of itaconic acid group (P-(*meso*-Ph)-NHCOC$(\mathrm{CH_3})_2$-$(\mathrm{CH_2})_{17}\mathrm{CH_2OCOCH_2C}(=\mathit{CH}_2)$COOH), 7.10–7.90 (m, 24 H, phenyl H), 8.70 (s, 4 H, amido H), 8.80 (s, 8 H, β-H of porphyrin ring); ^{13}C NMR ($\mathrm{CDCl_3}$, $\mathrm{Me_4Si}$ standard, ppm δ_C 24.2 (2′,2′-dimethyl C), 24.8 (alkyl chain C (P-(*meso*-Ph)-NHCOC-$(\mathrm{CH_3})_2\mathrm{CH_2}\mathit{CH}_2$–), 29.2–31.6 (alkyl chain C (P-(*meso*-Ph)-NHCOC$(\mathrm{CH_3})_2\mathrm{CH_2CH_2}(\mathit{CH}_2)_{15}$–), 40.5 (alkyl chain C (P-(*meso*-Ph)-NHCOC$(\mathrm{CH_3})_2\mathit{CH}_2$–), 42.4 (tertiary C of pivaloyl group (P-(*meso*-Ph)-NHCO*C*$(\mathrm{CH_3})_2$–), 62.4 (alkyl chain C of itaconic acid group (P-(*meso*-Ph)-NHCOC$(\mathrm{CH_3})_2\mathrm{CH_2CH_2}$-$(\mathrm{CH_2})_{15}\mathrm{CH_2OCO}\mathit{CH}_2$–), 65.5 (alkyl chain C (P-(*meso*-Ph)-NHCOC$(\mathrm{CH_3})_2\mathrm{CH_2CH_2}(\mathrm{CH_2})_{15}\mathit{CH}_2$–), 114.9 (*meso* C of porphyrin ring), 121.3, 123.6, 130.2, 131.3, 134.1, 138.5 (3-, 5-, 4-, 1-, 6-, and 2-C's of phenyl group), 122.2 (side-chain vinylidene C of itaconic acid group (P-(*meso*-Ph)-NHCOC-$(\mathrm{CH_3})_2\mathrm{CH_2CH_2}(\mathrm{CH_2})_{15}\mathrm{CH_2OCOCH_2C}(=\mathit{CH}_2)$COOH), 130.9 (inner vinylidene C of itaconic acid group (P-(*meso*-Ph)-NHCOC$(\mathrm{CH_3})_2\mathrm{CH_2CH_2}(\mathrm{CH_2})_{15}\mathrm{CH_2OCOCH_2}\mathit{C}(=\mathrm{CH_2})$COOH), 131.8 ($\beta$-C of porphyrin ring), 146.2 (α-C of porphyrin ring), 167.9 (top carbonyl C of itaconic acid group (P-(*meso*-Ph)-NHCOC$(\mathrm{CH_3})_2\mathrm{CH_2CH_2}(\mathrm{CH_2})_{15}\mathrm{CH_2OCOCH_2C}(=\mathrm{CH_2})\mathit{COOH}$), 168.9 (inner carbonyl C of itaconic acid group (–OC*O*$\mathrm{CH_2C}(=\mathrm{CH_2})$COOH)), 175.5 (carbonyl C of pivaloyl group (P-(*meso*-Ph)-NH*CO*C$(\mathrm{CH_3})_2$–); IR (KBr pellet, cm^{-1}) 1640 ($\nu_{C=C}$), UV–vis (chloroform, nm) 228, 417, 512, 544, 588, 643; elemental anal. C, H, N; (found: C, 84.5; H, 9.8; N, 5.7; calcd ($\mathrm{C_{152}H_{214}N_8O_{20}}$) C, 84.8; H, 10.0; N, 5.2.

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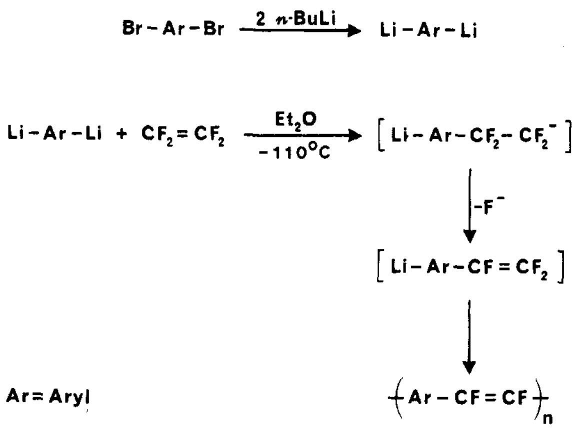
The Synthesis of New Poly(arylenedifluorovinylenes) from Aromatic Dianions and Tetrafluoroethylene

Conjugated organic polymers recently have been shown to exhibit dramatic increases in electrical conductivity when oxidized or reduced by electron acceptors or donors.[1] Since the conductivity varies from insulating to conducting depending on the structure of the polymer and the nature of the dopant, there is much interest in elucidating the structure–property relationships that give rise to the observed electrical properties. Poly(phenylenevinylene) is among the conjugated organic polymers that have received attention as promising conducting materials, and a number of structure–conductivity studies of this polymer recently have appeared.[2-4] In this communication, the synthesis of new fluorinated poly(arylenevinylene) via a novel polymerization reaction is reported.

Theoretical considerations suggest that fluorine is a particularly desirable substituent for conducting polymers.[5,6] LCAO–SCF–MO calculations[5] predict that poly(fluoroacetylene) and poly(difluoroacetylene) should have decreased band gaps relative to poly(acetylene) due to lowering of the levels of the LUMO's as a result of the high electronegativity of fluorine and raising of the levels of the HOMO's due to electron donation through fluorine's lone pairs. It also has been proposed that fluorine substitution in poly(acetylene) may afford greater oxidative stability.[5] Furthermore, steric effects should be minimal with fluorine substitution and thus, fluorination should not interfere with coplanarity of a conjugated π-network.[1a,7] A preliminary account of the synthesis of the fluorinated analogue[8] of poly(1,6-hexadiene)[9] lends support to these predictions.

Scheme I



Poly(arylenevinylenes) for structure–conductivity studies have been prepared by the Wittig reaction,[2] by dehydrohalogenation of *p*-xylylidene dihalides,[2] via coupling of dibenzoylarylenes,[3] or, recently, from bis(sulfonium chloride) intermediates.[4] The route to new fluoro-substituted poly(arylenevinylenes) reported here employed polymerization of tetrafluoroethylene with aryl dianions. We envisioned that the reaction of aryl dianions with tetrafluoroethylene would afford poly(arylenedifluorovinylene) via an addition–elimination[10] step-growth polymerization, with the dianion and tetrafluoroethylene serving as difunctional monomers in the polymerization reaction (Scheme I). The model reaction for this polymerization, nucleophilic vinylic substitution of tetrafluoroethylene with aryl monoanions to give aryl-substituted trifluoroolefins and 1,2-diaryl-1,2-difluoroolefins, is well-established.[11]

Two aromatic monomers, *p*-dilithiobenzene and 4,4′-dilithiobiphenyl, were considered for the preparation of fluorinated analogues of poly(phenylenevinylene). The attempted preparation of *p*-dilithiobenzene by halogen–metal exchange[12,13] of *p*-dibromobenzene in ethyl ether at 0 °C with 2 equiv of *n*-butyllithium afforded predominantly monolithiobromobenzene (analyzed by gas chromatography after methanol quench). Efforts to optimize the formation of dilithiobenzene in ethyl ether were complicated by reactions with solvent and by loss of stoichiometric equivalency as a result of coupling of *n*-butyllithium with butyl bromide, the byproduct of the exchange reaction (characterized by GC–MS). The reaction of 2 equiv of *n*-butyllithium with *p*-dibromobenzene in refluxing petroleum ether (15 h) gave primarily dilithiobenzene (85%), but subsequent reaction with tetrafluoroethylene afforded only a low yield of uncharacterized product. Dilithiation was much more facile with 4,4′-dibromobiphenyl. Halogen–metal exchange of 4,4′-dibromobiphenyl in ethyl ether with 2 equiv of *n*-butyllithium proceeded smoothly and gave a quantitative yield of the desired dianion (0 °C, 1 h).

For the preparation of poly(biphenyldiyldifluorovinylene), tetrafluoroethylene was condensed into a stirred mixture of 4,4′-dilithiobiphenyl in dry, distilled ethyl ether at –110 °C. The reaction mixture was maintained at –110 °C under a nitrogen atmosphere for 3 h at which time it was allowed to warm slowly to room temperature. The resulting bright yellow solid was extracted (Soxhlet) for 6 days with ethanol, water (to remove LiF), ethanol, and ether and then dried at 80 °C under reduced pressure to

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