photosensitized polymerization with water-insoluble AIBN provided information about the relative microviscosity of the membrane.

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Registry No. DODPC (homopolymer), 108916-62-7; CF, 76823-03-5; POPC (homopolymer), 116698-35-2.

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Synthesis of Polymerizable and Amphiphilic (Porphinato)irons and Their Copolymers with Polymerizable Phospholipid

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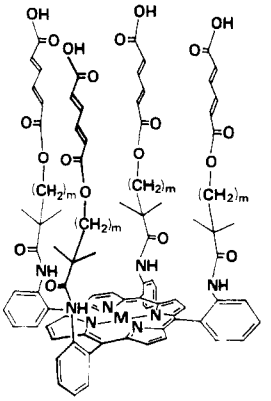
ABSTRACT: This paper describes the synthesis of polymerizable and amphiphilic porphyrins, 5,10,15,20-tetrakis[$\alpha,\alpha,\alpha,\alpha$-*o*-(*n*′-[((4″-carboxybutadienyl)carbonyl)oxy]-2′,2′-dimethylalkanamido)phenyl]porphyrin (**1**) and 5,10,15,20-tetrakis[$\alpha,\alpha,\alpha,\alpha$-*o*-(*n*′-[((2″-carboxypropenyl)carbonyl)oxy]-2′,2′-dimethylalkanamido)-phenyl]porphyrin (**2**), and their copolymers with 1,2-bis(2′,4′-octadecadienoyl)-*sn*-glycero-3-phosphocholine. **1**, **2**, and their (porphinato)iron derivatives have high compatibility with phospholipids and are efficiently copolymerized with the polymerizable phospholipid in a liposome state to give polymerized liposomes covalently containing the porphyrin residues. The oxygen-binding property of the copolymerized (porphinato)iron liposome is also described in comparison with that of a red blood cell.

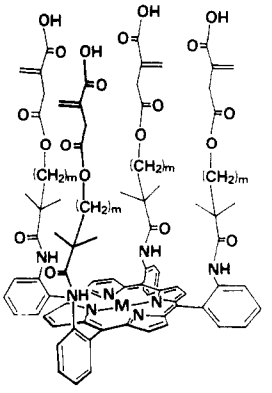
Introduction

Porphyrins and (porphinato)metals play key roles in biological and biomimetic reaction systems[1] and in molecular electronic devices.[2] In these systems much attention has been recently paid to the position and orientation of the porphyrins in matrices: (porphinato)manganese, -zinc, and -iron situated in an electron-transfer chain,[3-5] (porphinato)iron as a hemoglobin-like oxygen carrier,[6,7] and a porphyrin fixed in a polymer matrix used for photochemical hole burning.[8]

We intended to fix porphyrins and (porphinato)metals in a lipid membrane with respect to their orientation, and we preliminarily reported that polymerizable and amphiphilic porphyrins were copolymerized with a polymerizable phospholipid and fixed with a specific orientation in a bilayer membrane.[9] This paper describes the synthesis of novel porphyrin derivatives substituted with tetra($\alpha,\alpha,\alpha,\alpha$-alkyl) groups having both a polymerizable double bond and a hydrophilic (carboxylic acid) group at their top positions: 5,10,15,20-tetrakis[$\alpha,\alpha,\alpha,\alpha$-*o*-(*n*′-[((4″-carboxybutadienyl)carbonyl)oxy]-2′,2′-dimethylalkan(*n*)amido)-phenyl]porphyrins (*n* = 8, **1a**; *n* = 14, **1b**; *n* = 20, **1c**) and their (porphinato)irons (*n* = 8, **1d**; *n* = 14, **1e**; *n* = 20, **1f**) and 5,10,15,20-tetrakis[$\alpha,\alpha,\alpha,\alpha$-*o*-(*n*′-[((2″-carboxypropenyl)carbonyl)oxy]-2′,2′-dimethylalkan(*n*)amido)-phenyl]porphyrins (*n* = 8, **2a**; *n* = 14, **2b**; *n* = 20, **2c**), and their (porphinato)irons (*n* = 8, **2d**; *n* = 14, **2e**; *n* = 20, **2f**).

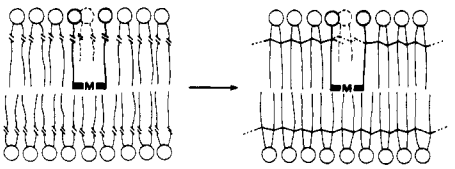


		m = n - 2		
		6	12	18
M	2H	1a	1b	1c
	Fe	1d	1e	1f

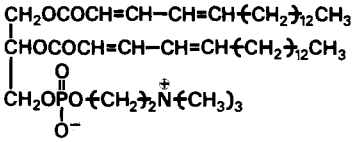


		m = n - 2		
		6	12	18
M	2H	2a	2b	2c
	Fe	2d	2e	2f

Scheme I



Because not only the hydrophobic–hydrophilic balance but also the stereostructure of 1 and 2 is adjusted to a lipid bilayer, it is expected that 1 and 2 will form a stable bilayer membrane with a lipid, that the polymerizable double bonds of 1, 2, and a polymerizable lipid will be adjacent to each other in a bilayer state, and that in situ copolymerization of 1 and 2 with the polymerizable lipid will occur rapidly (Scheme I). We use in this paper 1,2-bis(2′,4′-octadecadienoyl)-*sn*-glycero-3-phosphocholine (**3**)[10] as a polymerizable phospholipid and describe the copolymerization of the porphyrins 1 and 2 with the phospholipid 3 and the stability of the copolymerized liposomes. The oxygen-binding property for the copolymerized (porphinato)irons is also described in comparison with that of a red blood cell.



3

Results and Discussion

Synthesis of Polymerizable and Amphiphilic Porphyrins. The synthetic route of the polymerizable and amphiphilic porphyrin derivatives 1 and 2 is presented in Scheme II. 5,10,15,20-Tetrakis[$\alpha,\alpha,\alpha,\alpha$-(*o*-aminophenyl)]porphyrin[11] is reacted with *n*-(benzyloxy)-2,2-dimethylalkanoic(*n*) acid (n = 8, 14, 20) according to our previous papers[12,13] to yield 5,10,15,20-tetrakis[$\alpha,\alpha,\alpha,\alpha$-*o*-(2′,2′-dimethyl-*n*-hydroxyalkan(*n*)amido)phenyl]-porphyrin (n = 8) **5a**; n = 14, **5b**; n = 20, **5c**). Reaction of **5** with muconic acid chloride gives **1a–c**. Structures, including the $\alpha,\alpha,\alpha,\alpha$-configuration, were confirmed by ^{1}H NMR, ^{13}C NMR, UV–vis, and elemental analysis (see Experimental Section). Iron insertion into **1a–c** gives corresponding (porphinato)iron derivatives (**1d–f**). **2a–c** are synthesized by the reaction of 5,10,15,20-tetrakis[$\alpha,\alpha,\alpha,\alpha$-*o*-(*n*′-hydroxy-2′,2′-dimethylalkan(*n*)amido)-phenyl]porphyrin (n = 8, **5a**; n = 14, **5b**; n = 20, **5c**) with anhydrous itaconic acid, and the following iron insertion gives **2d–f** (see Experimental Section). The reference samples of 1 and 2, 5,10,15,20-tetrakis[$\alpha,\alpha,\alpha,\alpha$-*o*-(*n*′-((methacrylcarbonyl)oxy)-2′,2′-dimethylalkan(*n*)-amido)-phenyl]porphyrin (n = 8, **4a**; n = 14, **4b**; n = 20, **4c**) and

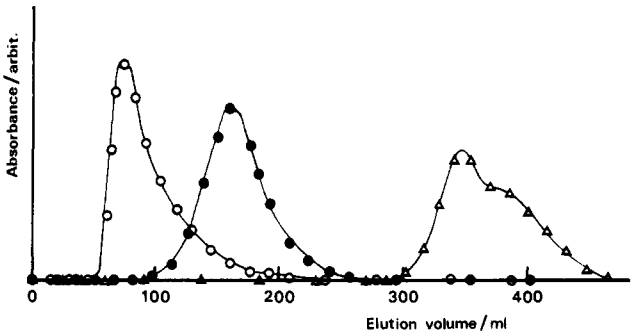
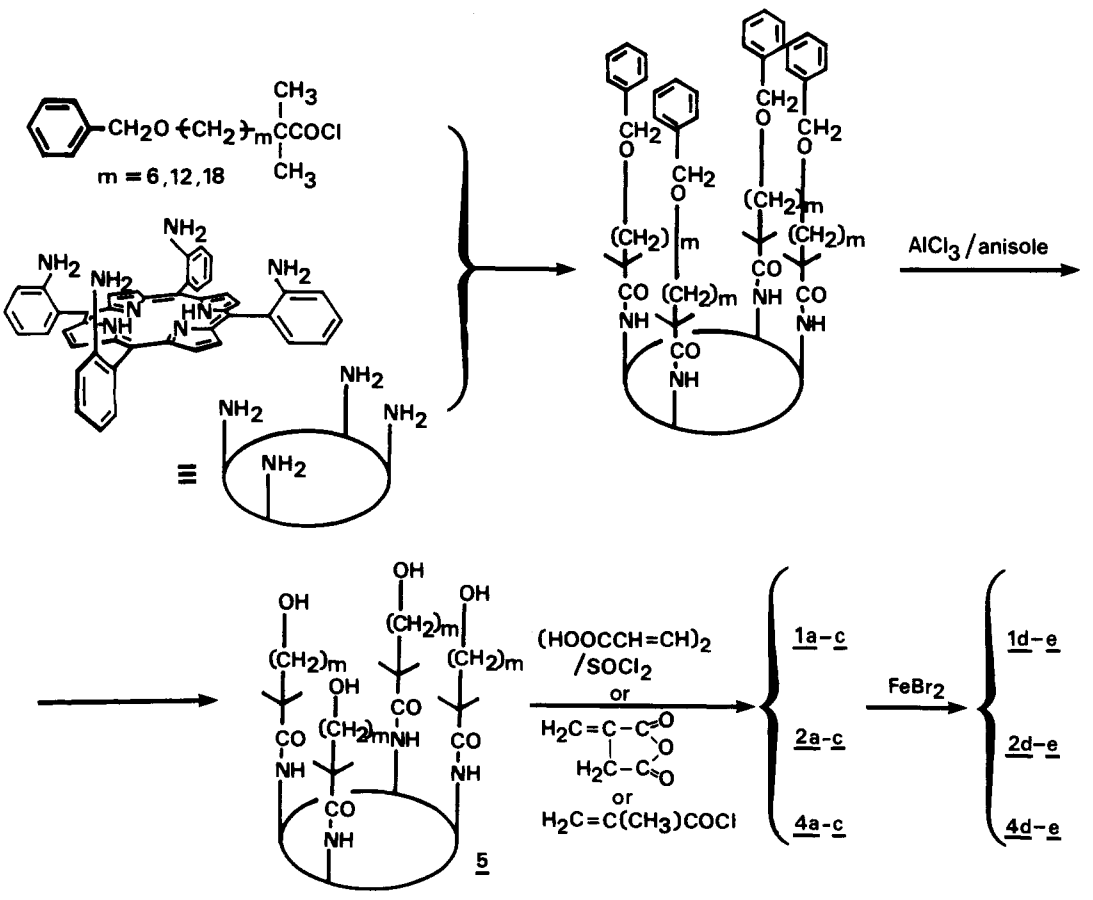


Figure 1. GPC elution curves of the porphyrin/lipid copolymerized liposome. Confirmation of the copolymerization of the porphyrin with the lipid: ○, 1/3 copolymer; ●, polymerized 3 without 1; △, 1/3 mixture before the polymerization.

Scheme II



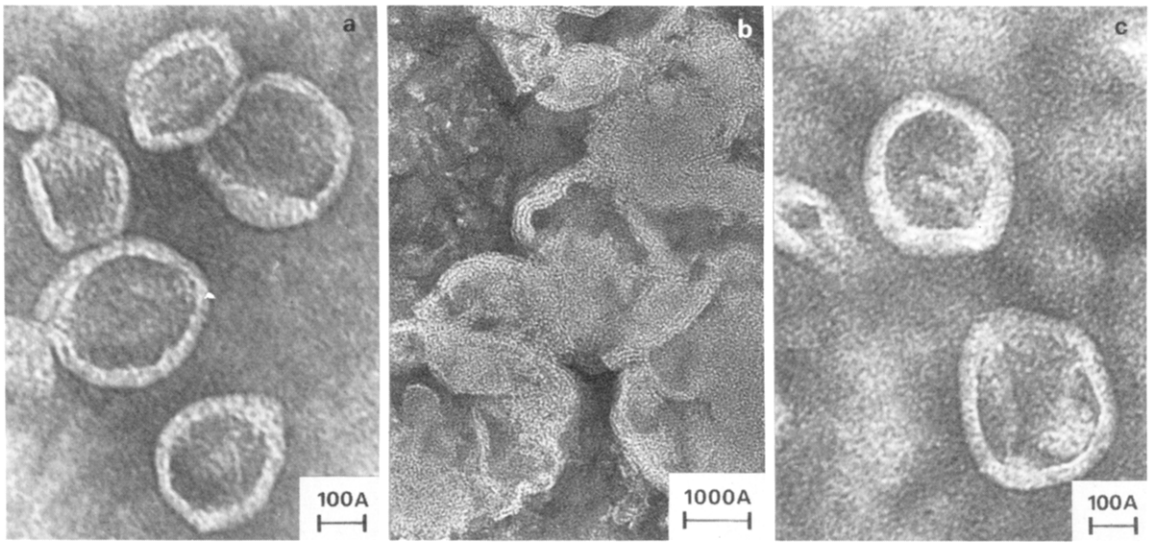
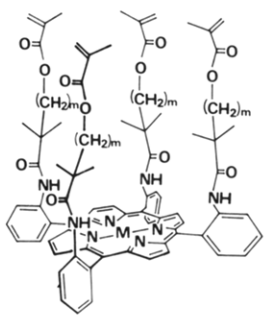
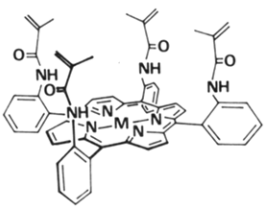


Figure 2. Transmission electron micrographs of the porphyrin/lipid liposomes before and after polymerization: a, porphyrin (1)/lipid before polymerization; b, porphyrin (4)/lipid; c, porphyrin (1)/lipid after polymerization.

5,10,15,20-tetrakis[$\alpha,\alpha,\alpha,\alpha$-*o*-(methacrylamido)phenyl]-porphyrin (**4g**),[14] were also synthesized from the reaction of **5** with methacryloyl chloride. Iron insertion gave the (porphinato)iron derivatives (**4d–f** and **4h**) (see Experimental Section).





		m = n − 2		
		6	12	18
M	2H	4a	4b	4c
	Fe	4d	4e	4f

		m
		0
M	2H	4g
	Fe	4h

Copolymerization of the Porphyrins with the Phospholipid in a Bilayer State. A bilayer membrane of the porphyrin (**1** or **2**) with the lipid (**3**) is prepared in an aqueous medium through the normal procedure[15] for liposome preparation (**1** or **2**/**3** = 1/20–50 (molar ratio), [**1** or **2**] = 50 μM). The porphyrins are efficiently taken into the lipid bilayer membrane of the liposome; only 20 mol of the lipid was enough to solublize 1 mol of the porphyrin completely in water.

Differential scanning calorimetry (DSC) was used to estimate the phase transition of the bilayer membrane for the liposomes of **3** containing **1** or **2**.[16] The **1** or **2**/**3** bilayer membranes showed an endothermic peak at 18 °C, which is assigned to the gel–liquid crystal phase transition temperature (T_c) of the bilayer membrane and agrees with that of the bilayer liposome **3**. This suggests that the compatibility of the porphyrins with the lipid is large enough to form a stable bilayer in an aqueous medium.

The bilayer liposomes of the porphyrin (**1** or **2**) with the lipid (**3**) were allowed to polymerize under UV irradiation. Complete copolymerization of the porphyrins with the lipid was confirmed by UV absorption and ^{13}C NMR spectroscopy: disappearance of absorption bands based on the diene (254 nm) or the vinylydene (228 nm) group of the porphyrin and the diene group (255 nm) of the lipid and disappearance of characteristic carbon signals based on the diene (127.9, 128.5, 140.7, 141.0 ppm), the vinylydene (122.2, 130.9 ppm) group, and the diene group (118.4, 128.2, 145.2, 146.0 ppm).

Incorporation of the porphyrins in the copolymerized liposome was confirmed by ultracentrifugation. After ultracentrifugation (45 000 rpm, 4 h, at 10 °C), the supernatants did not contain both the porphyrins and the lipid. The incorporation was also confirmed by gel permeation chromatography (GPC, Sepharose 4B column) monitored by absorptions at 418 and 255 nm based on the porphyrins and the lipid, respectively. The curves coincided with each other, which means the porphyrins are included in the bilayer membrane.

The freeze-dried powders of the **1** or **2**/**3** copolymerized liposomes could be resolubilized in water but not in organic solvents, while **1**, **2**, and **3** before the polymerization were soluble in chloroform. The copolymers were extracted with chloroform: the chloroform did not contain **1**, **2**, and **3**, and the compositions of **1** or **2**/**3** in the extracted copolymers agreed with the feed compositions. These results indicate the porphyrin is copolymerized with the lipid and covalently fixed in the polymerized lipid bilayer.

The copolymerization of the porphyrins with the lipid was also confirmed by the GPC measurement (Sepharose LH-60, methanol) of the half-polymerized samples,[17] as shown in Figure 1 for **1**/**3**. As mentioned above, the completely copolymerized liposome was insoluble in any organic solvents. On the other hand, the **1**/**3** copolymerized liposome with ca. 50% polymerization was soluble in methanol. The elution peak of the **1**/**3** copolymer situates at lower elution volume or higher molecular weight in comparison with those of the polymerized **3** without **1** and of the **1**/**3** mixture before the polymerization. This means that the molecular weight of the **1**/**3** copolymer is higher than that of the **3** homopolymer even at half-polymerization time, probably because of the four-functionality of the porphyrins.

Stability of the Porphyrin/Lipid Copolymerized Liposomes. Structure of the bilayer liposomes was estimated by transmission electron microscopy (TEM, Figure 2) of porphyrin **1** or **2** with the lipid **3** (molar ratio **1**/**3** = 1/50), their copolymer, and the reference sample of **4** with **3**. The mixture of **1** (or **2**) with **3** looks like a small unilamellar vesicle (SUV) with a particle size of ca. 300 Å

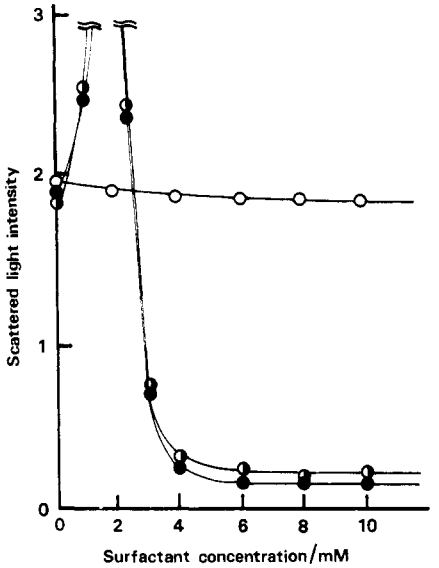


Figure 3. Relationship of the light-scattering intensity with the concentration of surfactant (Triton X-100) in the porphyrin/lipid copolymerized liposome solution. Evaluation of the stability of the liposome: ○, 1/3 copolymerized liposome solution; ◑, 1/3 liposome (before polymerization); ●, 3 liposome (before polymerization).

(Figure 2a), while the reference sample of **4h** with **3** looks like a plated and multilamellar structure (Figure 2b). This indicates that the porphyrins **1** and **2** form a stable bilayer with a phospholipid.[18] After the copolymerization, the SUV structure of the porphyrin with the lipid is maintained (particle size ca. 300 Å, Figure 1c), and the **1** (or **2**/**3**) copolymer gives a very stable SUV liposome, as mentioned below.

Stability of the **1** or **2**/**3** copolymerized liposomes was estimated as follows. Surfactants such as polyethylene glycol mono-*p*-octylphenyl ether (Triton X-100) are known as the reagents to destroy a bilayer structure. In Figure 3, a light scattering based on the bilayer liposome is plotted by using the example of **1**/**3**. The light-scattering intensity decreases with the addition of Triton X-100 to the **3** liposome solution and to the **1**/**3** solution before the polymerization, which means that their bilayer liposomes are easily destroyed and are solublized with the surfactant. On the contrary, the light-scattering intensity of the **1**/**3** copolymerized liposome is not influence by the Triton X-100 addition. Furthermore, the **1**/**3** copolymerized liposome solution could be stocked for months without phase separation or precipitation. It is concluded that the bilayer structure of copolymerized liposome is stabilized by a cross-linking due to the four functional groups of the porphyrin monomer.

Next, the stability of the **1** or **2**/**3** copolymerized liposome was checked by GPC. The liposome solutions before and after the polymerization were mixed with a surfactant (sodium cholate) and were developed on a GPC column (TOYO Pearl HW-40), as shown for **1**/**3** in Figure 4. The elution curve of the liposome before the polymerization shows two peaks, the small fraction with shorter retention time and the large one with longer retention time, which are assigned to the SUV liposome and the surfactant micelle, respectively. On the other hand, the elution curve of the **1**/**3** copolymerized liposome shows a single peak assigned to that of SUV. This result also indicates that the copolymerized liposome is stabilized by the crossing polymerization through the porphyrin monomer.

The metal-free porphyrin derivatives **1a–c** and **2a–c** are fluorescent active and are used as a fluorescent probe to

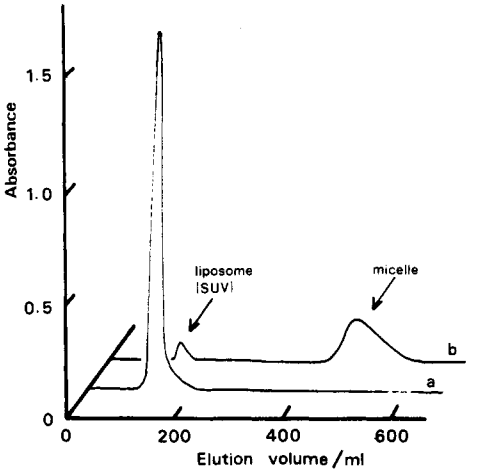


Figure 4. GPC elution curve of the porphyrin/lipid copolymerized liposome mixed with surfactant (sodium cholate): a, **1**/**3** copolymerized liposome; b, **1**/**3** liposome (before polymerization).

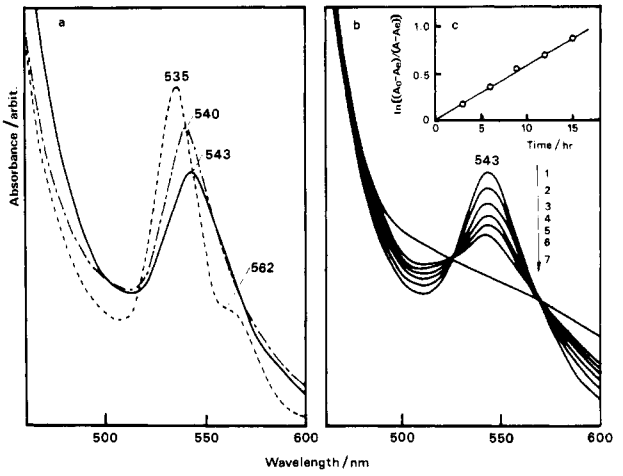


Figure 5. UV–vis absorption spectrum of the heme/lipid copolymerized liposome (a), spectral change of the oxygen adduct with time (b), and a plot of the first-order kinetics (c). a: (—) oxy, (- - -) deoxy, (-·-) carboxy. b: time = 0 (1), 3 (2), 6 (3), 9 (4), 12 (5), 15 (6) (hours) and 1 week (7).

estimate the position of the porphyrin in the bilayer membrane. For example, the fluorescence spectrum of **1** copolymerized with **3** with maxima at 585 and 650 nm agrees with those in aprotic and organic solvents, and its fluorescence intensity situates at the intermediate between those in benzene and dichloromethane. Before and after polymerization, the fluorescence spectrum and intensity were not changed. These results indicates that the porphyrin is molecularly dispersed in the bilayer and surrounded by an environment similar to that in aprotic and organic solvents.

Oxygen-Binding Property of the (Porphinato)iron (Heme)/Lipid Copolymerized Liposomes. The UV–vis absorption spectrum of the (porphinato)iron (heme)/lipid (**1e**/**3**) copolymerized liposome is shown in Figure 5a. The spectrum assigned to the deoxyheme complex (λ_{max} = 430, 535, and 562 (shoulder) nm) changed to that assigned to the heme–oxygen adduct (λ_{max} = 422 and 543 nm) on exposure to oxygen gas, through isosbestic points (516 and 544 nm). The spectrum of the oxygen adduct changed to that of the heme–carbon monoxide (CO) adduct (λ_{max} = 424 and 540 nm) on bubbling through CO and returned to that of the deoxyheme on bubbling through nitrogen gas. The oxy–deoxy cycle was repeated more than 100 times. The **2f**/**3** copolymerized liposome showed the same

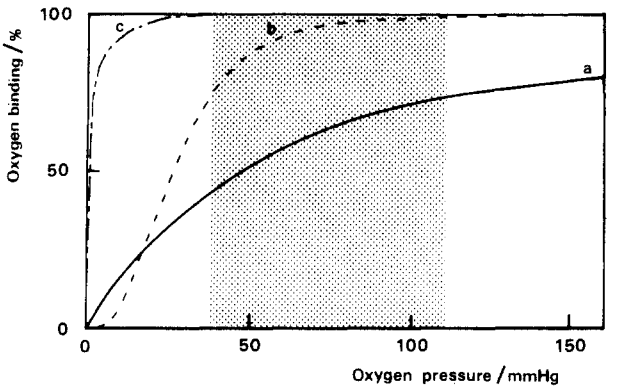


Figure 6. Oxygen-binding and dissociation equilibrium curve of the (porphinato)iron (heme)/lipid copolymerized liposome under physiological conditions: a, heme/lipid copolymerized liposome; b, hemoglobin in red blood cell; c, myoglobin.

Table I
Oxygen-Binding Ability of the Heme/Lipid Copolymerized Liposome[a]

heme	k_{on}, M^{-1} s^{-1}	$p_{1/2}$, mmHg
heme (1e)/lipid liposome copolymerized	1.7×10^4	46
nonpolymerized	2.4×10^4	28
heme (2f)/lipid liposome copolymerized	1.8×10^4	48
nonpolymerized	2.5×10^4	30
hemoglobin in red blood cell	1.1×10^4	27

[a] In pH 7.0 aqueous solution at 37 °C.

spectral features. The heme/lipid copolymerized liposome acted as an effective oxygen carrier.

The oxygen adduct was slowly degraded to a (porphinato)iron(III) (hemin) complex (Figure 5b), and this degradation obeyed first-order kinetics (Figure 5c). This indicates that the oxygen adduct of the heme copolymerized with **3** degrades via proton-driven oxidation and not via a bimolecular μ-dioxo (porphinato)iron dimer and that the (porphinato)iron (heme) is molecularly dispersed and covalently fixed in the bilayer of liposome.

The lifetime of the oxygen adduct was measured for the heme/lipid (**1e** or **2f**/**3**) copolymerized liposomes under physiological conditions in physiological salt solution at 37 °C, and the half-life (τ) was ca. 0.5 day. This lifetime for the copolymerized liposome was longer than that of the nonpolymerized ones (τ = ca. 4 h). Even when the copolymerized liposome was rapidly flowed through a capillary tube, the lifetime of its oxygen adduct was not affected, which was in contrast to the lifetime (τ = ca. 1.2 h) for the nonpolymerized ones under the same flowing condition. The copolymerization not only brings about physical or mechanical stability of the liposome but it also prolongs its lifetime as the oxygen carrier under physiological conditions.

The oxygen-binding and -dissociation equilibrium curve of the heme/lipid copolymerized liposome is shown in Figure 6, and the oxygen-binding affinity ($p_{1/2}$) is given in Table I. The $p_{1/2}$ value is ca. 50 mmHg, which is close to that of hemoglobin in a red blood cell but considerably different from that of myoglobin. The oxygen-binding rate constant (k_{on}) was measured with stopped-flow and flash-photolysis methods (Table I). The rate parameter for the oxygen binding is ca. 10^4 M^{-1} s^{-1}, which is similar to that of a red blood cell suspension. These suggest that the heme/lipid copolymerized liposome has a potential to act as the oxygen carrier under physiological conditions, that transports oxygen from the lungs (oxygen pressure $p(O_2)$ = ca. 110 mmHg) to myoglobin in muscle tissue ($p(O_2)$ = ca. 40 mmHg) as does hemoglobin in a red blood cell.

Experimental Section

Syntheses of Porphyrins. 1a–f and **2a–f** were synthesized as follows.

5,10,15,20-Tetrakis[$\alpha,\alpha,\alpha,\alpha$-*o*-(*n*'-[((4''-carboxybutadienyl)carbonyl)oxy]-2',2'-dimethylalkan(*n*)amido)phenyl]porphyrin (*n* = 8, 1a; *n* = 14, 1b; *n* = 20, 1c) and Its (Porphinato)iron Derivatives (*n* = 8, 1d; *n* = 14, 1e; *n* = 20, 1f). Muconic acid chloride was prepared by refluxing muconic acid with excess dry thionyl chloride under nitrogen for 3 h. 5,10,15,20-Tetrakis[$\alpha,\alpha,\alpha,\alpha$-*o*-(*n*'-hydroxy-2',2'-dimethylalkan-(*n*)amido)phenyl]porphyrin synthesized as in our previous paper[13] (0.12 mmol: **5a**, 200 mg; **5b**, 245 mg; **5c**, 290 mg) was reacted with the muconic acid chloride in chloroform for 2 days. The mixture was added to ice water (1 L) and extracted with chloroform. The chloroform solution was washed with water and dried over anhydrous sodium sulfate. The concentrated solution was developed on a silica gel column (Merck silica gel 60, 5 cm × 20 cm) with chloroform and chloroform/methanol (10/1) to give 5,10,15,20-tetrakis[$\alpha,\alpha,\alpha,\alpha$-*o*-(*n*-[((4''-carboxybutadienyl)carbonyl)oxy]-2',2'-dimethylalkan(*n*)amido)phenyl]porphyrin. Yield: **1a**, 180 mg (67%); **1b**, 130 mg (43%); **1c**, 110 mg (32%).

1a. ^{1}H NMR δ_H ($CDCl_3$, TMS standard, ppm) −2.30 (s, 2 H, inner pyrrole proton (H) of porphyrin ring (P)), −0.21 (s, 24 H, 2',2'-dimethyl H, P-Ph-*o*-NHCOC(CH_3)$_3$$CH_2$), 0.20–2.00 (m, 40 H, alkyl chain H, P-(*meso*-Ph)-*o*-NHCOC(CH_3)$_2$(CH_2)$_5$$CH_2$O), 3.90 (t, 8 H, alkyl chain H, P-(*meso*-Ph)-*o*-NHCOC(CH_3)$_2$(CH_2)$_5$$CH_2$O), 6.10–6.30 (d, d, 8 H, outer diene H, *CH*=CHCH=*CH*), 7.00–7.20 (m, 8 H, inner diene H, CH=*CHCH*=CH), 7.10–7.90 (m, 24 H, phenyl H of porphyrin ring), 8.70 (s, 4 H, β-H or porphyrin ring); ^{13}C NMR δ_C ($CDCl_3$, TMS standard, ppm) 24.3 (2',2'dimethyl carbon (C), P-(*meso*-Ph)-*o*-NHCOC(CH_3)$_2$$CH_2$), 24.8 (alkyl chain C (P-(*meso*-Ph)NHCOC(CH_3)$_2$$CH_2$$CH_2$), 28.6–29.6 (alkyl chain C, P-(*meso*-Ph)-*o*-NHCOC-(CH_3)$_2$$CH_2$$CH_2$($CH_2$)$_3$), 41.0 (alkyl chain C, P-(*meso*-Ph)-NHCOC(CH_3)$_2$$CH_2$), 42.3 (*t*-C of pivaloyl group, P-(*meso*-Ph)-*o*-NHCOC(CH_3)$_2$), 64.8 (alkyl chain C, P-(*meso*-Ph)NHCOC-(CH_3)$_2$$CH_2$$CH_2$($CH_2$)$_3$$CH_2$), 114.9 (*meso*-C of porphyrin ring), 120.8, 123.2, 130.1, 130.7, 134.4, 138.5 (3-, 5-, 4-, 1-, 6-, 2-carbon of phenyl C of porphyrin ring, respectively), 127.9, 128.5 (outer diene (4- and 1-) carbon of muconic acid group, respectively), 131.8 (β-C of porphyrin ring), 140.7, 141.0 (inner diene (3- and 2-) carbon of muconic acid group), 146.2 (α-C of porphyrin ring), 165.8 (top carbonyl C of muconic acid group), 166.2 (inner carbonyl C of muconic acid group), 174.6 (carbonyl C of pivaloyl group, P-(*meso*-Ph)-*o*-NH*CO*); IR (KBr pellet, cm^{-1}) 1620 ($\nu_{C=C}$); UV–vis (chloroform, nm) 254, 418, 513, 545, 589, 645. Anal. Calcd for $C_{108}H_{122}N_8O_{20}$: C, 84.7; H, 8.0; N, 7.3. Found: C, 85.0; H, 7.6; N, 7.4.

1b. ^{1}H NMR δ_H ($CDCl_3$, TMS standard, ppm) −2.50 (s, 2 H, inner pyrrole proton (H) of porphyrin ring (P)), −0.22 (s, 24 H, 2',2'-dimethyl H, P-Ph-*o*-NHCOC(CH_3)$_3$$CH_2$), 0.18–2.00 (m, 88 H, alkyl chain H, P-(*meso*-Ph)-*o*-NHCOC(CH_3)$_2$(CH_2)$_{11}$$CH_2$O), 4.10 (t, 8 H, alkyl chain H, P-(*meso*-Ph)-*o*-NHCOC(CH_3)$_2$-(CH_2)$_5$$CH_2$O), 6.10–6.30 (d, d, 8 H, outer diene H, *CH*=CHCH=*CH*), 7.05–7.20 (m, 8 H, inner diene H, CH=*CHCH*=CH), 7.10–7.90 (m, 24 H, phenyl H of porphyrin ring), 8.80 (s, 4 H, β-H of porphyrin ring), ^{13}C NMR δ_C ($CDCl_3$, TMS standard, ppm) 24.4 (2',2'-dimethyl carbon (C), P-(*meso*-Ph)-*o*-NHCOC-(CH_3)$_2$$CH_2$), 24.9 (alkyl chain C (P-(*meso*-Ph)NHCOC-(CH_3)$_2$$CH_2$$CH_2$), 28.6–29.5 (alkyl chain C, P-(*meso*-Ph)-*o*-NHCOC(CH_3)$_2$$CH_2$$CH_2$($CH_2$)$_9$, 40.8 (alkyl chain C, P-(*meso*-Ph)NHCOC(CH_3)$_2$$CH_2$), 42.4 (*t*-C of pivaloyl group, P-(*meso*-Ph)-*o*-NHCOC(CH_3)$_2$), 64.8 (alkyl chain C, P-(*meso*-Ph)-NHCoC(CH_3)$_2$$CH_2$$CH_2$($CH_2$)$_3$$CH_2$), 114.9 (*meso*-C of porphyrin ring), 120.9, 123.0, 130.0, 130.7, 134.3, 138.6 (3-, 5-, 4-, 1-, 6-, 2-carbon of phenyl C of porphyrin ring, respectively), 127.8, 128.4 (outer diene (4- and 1-) carbon of muconic acid group, respectively), 131.8 (β-C of porphyrin ring), 140.7, 141.0 (inner diene (3- and 2-) carbon of muconic acid group), 146.5 (α-C of porphyrin ring), 165.8 (top carbonyl C of muconic acid group), 165.8 (inner carbonyl C of muconic acid group), 174.7 (carbonyl C of pivaloyl group, P-(*meso*-Ph)-*o*-NH*CO*); IR (KBr pellet, cm^{-1}) 1620 ($\nu_{C=C}$); UV–vis (chloroform, nm) 255, 418, 514, 546, 589, 646.

1c. ^{1}H NMR δ_H ($CDCl_3$, TMS standard, ppm) −2.28 (s, 2 H, inner pyrrole proton (H) of porphyrin ring (P)), −0.21 (s, 24 H, 2′,2′-dimethyl H, P-Ph-*o*-NHCOC(CH_3)$_3$CH$_2$), 0.20–2.00 (m, 136 H, alkyl chain H, P-(*meso*-Ph)-*o*-NHCOC(CH$_3$)$_2$(CH_2)$_{17}$CH$_2$O), 3.90 (t, 8 H, alkyl chain H, P-(*meso*-Ph)-*o*-NHCOC(CH$_3$)$_2$-(CH$_2$)$_5$$CH_2$O), 6.10–6.30 (d, d, 8 H, outer diene H, *CH*=CHC*H*), 7.00–7.20 (m, 8 H, inner diene H, CH=*CHCH*=CH), 7.10–7.90 (m, 24 H, phenyl H of porphyrin ring), 8.70 (s, 4 H, amido H, P-(*meso*-Ph)-*o*-*NHCO*), 8.80 (s, 4 H, β-H of porphyrin ring); IR (KBr pellet, cm^{-1}) 1620 ($\nu_{C=C}$); UV–vis (chloroform, nm) 254, 418, 513, 545, 589, 645.

The porphyrins were reacted with $FeBr_2$ (0.5 g) in dimethylformamide under nitrogen atmosphere for 12 h. The resultants were evaporated and purified by chromatography (alumina column, chloroform). The products were resolved and added to chloroform containing hydrobromic acid (0.1 mL), and the solutions were evaporated to give the corresponding (porphinato)iron(III) bromides.

5,10,15,20-Tetrakis[α,α,α,α-*o*-(*n*′-[(2″-carboxypropenyl)-carbonyl)oxy]-2′,2′-dimethylalkan(*n*)amido)phenyl]-porphyrin (*n* = 8, 2a; *n* = 14, 2b; *n* = 20, 2c) and Its (Porphinato)iron Derivatives (*n* = 8, 2d; *n* = 14, 2e; *n* = 20, 2f). Anhydrous itaconic acid (2.5 g) was reacted with 5,10,15,20-tetrakis[α,α,α,α-*o*-(*n*′-hydroxy-2′,2′-dimethylalkan(*n*)amidophenyl]porphyrin (0.12 mmol: **5a**, 200 mg; **5b**, 245 mg; **5c**, 290 mg) in dry tetrahydrofuran under nitrogen atmosphere for 3–4 days. The resultant solution was evaporated, diluted with chloroform, and washed with water. The resultants were purified by column chromatography (5 cm φ × 20 cm, silicagel, chloroform and chloroform/methanol (20/1–5/1)) to give 5,10,15,20-tetrakis[α,α,α,α-*o*-(*n*′-[(2″-carboxypropenyl)carbonyl)oxy]-2′,2′-dimethylalkan(*n*)amido)phenyl]porphyrin (**2a**, 180 mg (70); **2b**, 140 mg (47%); **2c**, 120 mg (35%)).

2a. ^{1}H NMR δ_H ($CDCl_3$, TMS standard, ppm) −2.28 (s, 2 H, inner pyrrole proton (H) of porphyrin ring (P)), −0.20 (s, 24 H, 2′,2′-dimethyl H, P-Ph-*o*-NHCOC(CH_3)$_3$CH$_2$), 0.21–2.02 (m, 40 H, alkyl chain H, P-(*meso*-Ph)-*o*-NHCOC(CH$_3$)$_2$(CH_2)$_{17}$CH$_2$O), 2.24 (methylene H of itaconic acid group), 3.51 (t, 8 H, alkyl chain H, P-(*meso*-Ph)-*o*-NHCOC(CH$_3$)$_2$(CH$_2$)$_5$$CH_2$O), 5.90 (s, 8 H, side chain CH_2 of itaconic acid group, P-(*meso*-Ph)NHCOC(CH$_3$)$_2$-(CH$_2$)$_{17}$CH$_2$OCOCH$_2$C(=CH_2)COOH), 7.13–7.90 (m, 24 H, phenyl H of porphyrin ring), 8.71 (s, 4 H, amido H, P-(*meso*-Ph)-*o*-*NHCO*), 8.81 (s, 4 H, β-H of porphyrin ring); IR (KBr pellet, cm^{-1}) 1640 ($\nu_{C=C}$); UV–vis (chloroform, nm) 228, 418, 513, 544, 588, 644.

2b. ^{1}H NMR δ_H ($CDCl_3$, TMS standard, ppm) −2.28 (s, 2 H, inner pyrrole proton (H) of porphyrin ring (P)), −0.21 (s, 24 H, 2′,2′-dimethyl H, P-Ph-*o*-NHCO(CH_3)$_3$CH$_2$), 0.20–2.00 (m, 72 H, alkyl chain H, P-(*meso*-Ph)-*o*-NHCOC(CH$_3$)$_2$(CH_2)$_{17}$CH$_2$O), 2.21 (methylene H of itaconic acid group), 3.49 (t, 8 H, alkyl chain H, P-(*meso*-Ph)-*o*-NHCoC(CH$_3$)$_2$(CH$_2$)$_5$$CH_2$O), 5.93 (s, 8 H, side chain CH_2 of itaconic acid group, P-(*meso*-Ph)NHCOC(CH$_3$)$_2$-(CH$_2$)$_{17}$CH$_2$OCOCH$_2$C(=CH_2)COOH), 7.10–7.90 (m, 24 H, phenyl H of porphyrin ring), 8.70 (s, 4 H, amido H, P-(*meso*-Ph)-*o*-*NHCO*), 8.80 (s, 4 H, β-H of porphyrin ring); IR (KBr pellet, cm^{-1}) 1640 ($\nu_{C=C}$); UV–vis (chloroform, nm) 228, 418, 513, 544, 588, 644.

2c. ^{1}H NMR δ_H ($CDCl_3$, TMS standard, ppm) −2.28 (s, 2 H, inner pyrrole proton (H) of porphyrin ring (P)), −0.21 (s, 24 H, 2′,2′-dimethyl H, P-Ph-*o*-NHCOC(CH_3)$_3$CH$_2$), 0.20–2.00 (m, 136 H, alkyl chain H, P-(*meso*-Ph)-*o*-NHCOC(CH$_3$)$_2$(CH_2)$_{17}$CH$_2$O), 3.50 (t, 8 H, alkyl chain H, P-(*meso*-Ph)-*o*-NHCOC(CH$_3$)$_2$-(CH$_2$)$_5$$CH_2$O), 5.90 (s, 8 H, side chain CH_2 of itaconic acid group, P-(*meso*-Ph)NHCOC(CH$_3$)$_2$(CH$_2$)$_{17}$CH$_2$OCOCH$_2$C(=CH_2)-COOH), 7.10–7.90 (m, 24 H, phenyl H of porphyrin ring), 8.70 (s, 4 H, amido H, P-(*meso*-Ph)-*o*-*NHCO*), 8.80 (s, 4 H, β-H of porphyrin ring); ^{13}C NMR δ_C ($CDCl_3$, TMS standard, ppm) 24.2 (2′,2′-dimethyl carbon (C), P-(*meso*-Ph)-*o*-NHCOC(CH_3)$_2$CH$_2$), 24.8 (alkyl chain C (P-(*meso*-Ph)NHCOC(CH$_3$)$_2$CH$_2$$CH_2$), 29.2–31.6 (alkyl chain C, P-(*meso*-Ph)-*o*-NHCOC-(CH$_3$)$_2$CH$_2$CH$_2$(CH_2)$_9$), 40.5 (alkyl chain C, P-(*meso*-Ph)-NHCOC(CH$_3$)$_2$$CH_2$), 42.4 (*t*-C of pivaloyl group, P-(*meso*-Ph)-*o*-NHCOC(CH$_3$)$_2$), 62.4 (alkyl chain C of itaconic acid group, P-(*meso*-Ph)NHCOC(CH$_3$)$_2$CH$_2$CH$_2$(CH$_2$)$_{15}$CH$_2$OCOCH_2), 65.5 (alkyl chain C, P-(*meso*-Ph)NHCoC(CH$_3$)$_2$CH$_2$CH$_2$(CH$_2$)$_3$$CH_2$), 114.9 (*meso*-C of porphyrin ring), 121.3, 123.6, 130.2, 131.3, 134.1, 138.5 (3-, 5-, 4-, 1-, 6-, 2-carbon of phenyl C of porphyrin ring, respectively), 122.2 (side-chain vinyl C of itaconic acid group, P-(*meso*-Ph)-NHCOC(CH$_3$)$_2$CH$_2$CH$_2$(CH$_2$)$_{15}$CH$_2$OCOCH$_2$C(=CH_2)COOh), 130.9 (inner vinyl C of itaconic acid group, P-(*meso*-Ph)NHCOC(CH$_3$)$_2$CH$_2$CH$_2$(CH$_2$)$_{15}$CH$_2$OCOCH$_2$C(=CH$_2$)COOH), 131.8 (β-C of porphyrin ring), 146.2 (α-C of porphyrin ring), 167.9 (top carbonyl C of itaconic acid group), 168.9 (inner carbonyl C of itaconic acid group), 175.5 (carbonyl C of pivaloyl group, P-(*meso*-Ph)-*o*-NH*CO*); IR (KBr pellet, cm^{-1}) 1640 ($\nu_{C=C}$); UV–vis (chloroform, nm) 228, 417, 512, 544, 588, 643. Anal. Calcd. for $C_{152}H_{214}N_8O_{20}$: C, 84.8; H, 10.0; N, 5.2. Found: C, 84.5; H, 9.8; N 5.7.

The iron insertion into the porphyrin was carried out as mentioned above.

5,10,15,20-Tetrakis[α,α,α,α-*o*-(*n*′-[(methyacrylcarbonyl)-oxy]-2′,2′-dimethylalkan(*n*)amido)phenyl]porphyrin (*n* = 8, 4a, *n* = 14, 4b, *n* = 20, 4c) and Its (Porphinato)iron Derivatives (*n* = 8, 4d; *n* = 14, 4e; *n* = 20, 4f). 5,10,15,20-Tetrakis[α,α,α,α-*o*-[(*n*′-(methacrylcarbonyl)oxy]-2′,2′-dimethylalkan-(*n*)amido)phenyl]porphyrin (*n* = 8, **4a**; *n* = 14, **4b**; *n* = 20, **4c**) was obtained by the reaction of 5,10,15,20-tetrakis[α,α,α,α-*o*-(*n*′-hydroxyalkan(*n*)amido)phenyl]porphyrin (**5**) with methacrylic acid chloride.

4a. ^{1}H NMR δ_H ($CDCl_3$, TMS standard, ppm) −2.27 (s, 2 H, inner pyrrole proton (H) of porphyrin ring (P)), −0.21 (s, 24 H, 2′,2′-dimethyl H, P-Ph-*o*-NHCOC(CH_3)$_3$CH$_2$), 0.21–2.00 (m, 36 H, alkyl chain H, P-(*meso*-Ph)-*o*-NHCOC(CH$_3$)$_2$(CH_2)$_{17}$CH$_2$O) and methyl H of methacryl acid group), 3.51 (t, 8 H, alkyl chain H, P-(*meso*-Ph)-*o*-NHCOC(CH$_3$)$_2$(CH$_2$)$_5$$CH_2$O), 4.41 (s, 8 H, vinyl H of methacryl acid, OCOC(CH$_3$)=CH_2), 7.10–7.91 (m, 16 H, phenyl H of porphyrin ring), 8.71 (s, 4 H, amido H, P-(*meso*-Ph)-*o*-*NHCO*), 8.83 (s, 4 H, β-H of porphyrin ring).

4b. ^{1}H NMR δ_H ($CDCl_3$, TMS standard, ppm) −2.27 (s, 2 H, inner pyrrole proton (H) of porphyrin ring (P)), −0.21 (s, 24 H, 2′,2′dimethyl H, P-Ph-*o*-NHCOC(CH_3)$_3$CH$_2$), 0.20–2.00 (m, 100 H, alkyl chain H, P-(*meso*-Ph)-*o*-NHCOC(CH$_3$)$_2$(CH_2)$_{17}$CH$_2$O and methyl H of methacryl acid group), 3.50 (t, 8 H, alkyl chain H, P-(*meso*-Ph)-*o*-NHCOC(CH$_3$)$_2$(CH$_2$)$_5$$CH_2$O), 4.43 (s, 8 H, vinyl H of methacryl acid, OCOC(CH$_3$)=CH_2), 7.10–7.93 (m, 16 H, phenyl H of porphyrin ring), 8.71 (s, 4 H, amido H, P-(*meso*-Ph)-*o*-*NHCO*), 8.83 (s, 4 H, β-H of porphyrin ring).

4c. ^{1}H NMR δ_H ($CDCl_3$, TMS standard, ppm) −2.28 (s, 2 H, inner pyrrole proton (H) of porphyrin ring (P)), −0.21 (s, 24 H, 2′,2′-dimethyl H, P-Ph-*o*-NHCOC(CH_3)$_3$CH$_2$), 0.20–2.00 (m, 148 H, alkyl chain H, *p*-(*meso*-Ph)-*o*-NHCOC(nCH$_3$)$_2$(CH_2)$_{17}$CH$_2$O and methyl H of methacryl acid group), 3.52 (t, 8 H, alkyl chain H, P-(*meso*-Ph)-*o*-NHCOC(CH$_3$)$_2$(CH$_2$)$_5$$CH_2$O), 4.41 (s, 8 H, vinyl H of methacryl acid, OCOC(CH$_3$)=CH_2), 7.10–7.90 (m, 16 H, phenyl H of porphyrin ring), 8.70 (s, 4 H, amido H, P-(*meso*-Ph)-*o*-*NHCO*), 8.80 (s, 4 H, β-H of porphyrin ring); ^{13}C NMR δ_C ($CDCl_3$, TMS standard, ppm) 17.3 (methyl C of methacryl acid group), 24.2 (2′,2′-dimethyl carbon (C), P-(*meso*-Ph)-*o*-NHCOC-(CH$_3$)$_2$CH$_2$), 24.6 (alkyl chain C (P-(*meso*-Ph)NHCOC-(CH$_3$)$_2$CH$_2$$CH_2$), 29.1–30.6 (alkyl chain C, P-(*meso*-Ph)-*o*-NHCOC(CH$_3$)$_2$CH$_2$CH$_2$(CH_2)$_9$), 41.5 (alkyl chain C, P-(*meso*-Ph)NHCOC(CH$_3$)$_2$$CH_2$), 42.3 (*t*-C of pivaloyl group, P-(*meso*-Ph)-*o*-NHCOC(CH$_3$)$_2$), 65.4 (alkyl chain C, P-(*meso*-Ph)-NHCOC(CH$_3$)$_2$CH$_2$CH$_2$(CH$_2$)$_3$$CH_2$), 115.2 (*meso*-C of porphyrin ring), 120.4, 123.1, 129.6, 131.9, 134.7, 137.8 (3-, 5-, 4-, 1-, 6-, 2-carbon of phenyl C of porphyrin ring, respectively), 139.7 (vinyl C of methacryl acid group, CO*C*(CH$_3$)=CH$_2$), 148.1 (α-C of porphyrin ring), 165.4 (carbonyl C of methacryl acid group, *C*OC(CH$_3$)=CH$_2$), 174.5 (carbonyl C pivaloyl group, P-(*meso*-Ph)-*o*-NH*CO*).

The porphyrins were iron-inserted to give the (porphinato)iron derivatives. 5,10,15,20-Tetrakis[α,α,α,α-*o*-(methacrylamido)-phenyl]porphyrin (**4g**) and its (porphinato)iron derivative (**4h**) were prepared according to a procedure in the literature.[14]

Other Materials. 1,2-Bis(2′,4′-octadecadienoyl)-*sn*-glycero-3-phosphocholine (lipid monomer, **3**) was synthesized according to a procedure in the literature.[10] Triton X-100 and sodium cholate of special grade were used without further purification.

Preparation of Porphyrin/Lipid Copolymerized Liposome. The porphyrin/lipid copolymerized liposome was prepared by modifying the normal method[15] of liposome preparation and photopolymerization.[13,19] By evaporation of the chloroform solution of the mixture of the porphyrin and the lipid (molar ratio porphyrin/lipid = 1/20–50) under reduced pressure, a thin film

was prepared on the glass wall of a round flask. Oxygen-free water was added to this, and the mixture was then mixed in a Vortex mixer. It was ultrasonicated and homogenized in an ice water bath under nitrogen atmosphere. Thus prepared porphyrin/lipid liposome solution was incubated at room temperature for a few hours and then was allowed under nitrogen atmosphere to polymerize under ultraviolet irradiation for 1–4 h to give the porphyrin/lipid copolymerized liposome. Complete polymerization was confirmed by UV and ^{13}C NMR spectroscopical measurements: disappearance of the absorption peak (muconyl type, **1a–f** 254 nm; itaconyl type, **2a–f** 228 nm) and the characteristic NMR signal (muconyl type (diene, 1), δ_C 127.9, 128.5, 140.7, 141.0 ppm; itaconyl type (vinylydene, 2) 122.2, 130.9 ppm; double-bond carbon of the lipid (**3**) 118.4, 128.2, 145.2–146.0 (d) ppm).

Physicochemical Measurements. The porphyrin/lipid copolymerized liposome was separated from the aqueous medium by ultracentrifugation (45 000 rpm, 4 h, at 10 °C, ultracentrifuge Hitachi 65p-7). A GPC elution curve was measured with a Sepharose 4B (aqueous type) and Sepharose LH-60 (methanol type) (Pharmacia Fine Chemical, 20 mm ϕ × 700–2000 mm, solvent water and methanol), respectively, and a TOYO Pearl HW-60 (water type) (Toyosoda, 20 mm ϕ × 700–1500 mm, water). The transmission electron microscopy (Hitachi H-500) of the porphyrin/lipid copolymerized liposome was carried out by a negative staining method using uranyl acetate. A fluorescence spectrum of the porphyrin/lipid copolymerized liposome was measured by using excitation at 430 nm with a fluorescence spectrophotometer (Japan Spectroscopic JASC FP-550). The relative light intensity of the porphyrin/lipid copolymerized liposome solution was measured with a static light-scattering apparatus (Union-Giken, LS-1000).

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Registry No. **1a**, 117179-15-4; **1a/3** (copolymer), 117248-10-9; **1b**, 117097-89-9; **1b/3** (copolymer), 117097-90-2; **1c**, 117098-01-8; **1c/3** (copolymer), 117180-35-5; **1d**, 117179-13-2; **1d/3** (copolymer), 117248-15-4; **1e**, 117097-93-5; **1e/3** (copolymer), 117182-16-8; **1f**, 117097-94-6; **1f/3** (copolymer), 117180-36-6; **2a**, 117179-16-5; **2a/3** (copolymer), 117248-11-0; **2b**, 117097-91-3; **2b/3** (copolymer), 117097-92-4; **2c**, 106252-35-1; **2c/3** (copolymer), 106252-36-2; **2d**, 117097-95-7; **2d/3** (copolymer), 117180-37-7; **2e**, 117097-96-8; **2e/3**, 117182-17-9; **2f**, 106252-37-3; **2f/3**, 106252-38-4; **3**, 76282-07-0; **4a**, 117098-02-9; **4b**, 117098-03-0; **4c**, 117098-04-1; **4d**, 117097-97-9; **4e**, 117097-98-0; **4f**, 117097-99-1; **5a**, 106252-43-1; **5b**, 117098-00-7; **5c**, 88088-83-9; muconic acid chloride, 20578-72-7; muconic acid, 505-70-4; itaconic acid, 97-65-4; methacrylic acid chloride, 920-46-7; oxygen, 7782-44-7.

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Alcohol Derivatives of Poly(methylphenylphosphazene)

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ABSTRACT: A series of polyphosphazenes with alcohol functional groups attached to the backbone phosphorus by two-carbon spacer groups were prepared by deprotonation/substitution reactions at the pendant methyl groups in poly(methylphenylphosphazene). The polymeric anion, prepared in THF at −78 °C by using *n*-BuLi, was treated with aldehydes and ketones and subsequently quenched with aqueous ammonium chloride, to give $[Ph(Me)P{=}N]_x\{Ph[CH_2C(OH)RR']P{=}N\}_y$ where R = H, Me; R′ = Me, H, Ph, $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$ (ferrocene), or C═CHCH═CH-S (thiophene); and *x*:*y* ranges from 1:1 to 1:2. These new polymers were characterized by elemental analysis; size-exclusion chromatography; IR spectroscopy; thermal analysis (DSC); and ^1H, ^{31}P, and ^{13}C NMR spectroscopy.

Introduction

The synthesis of polyphosphazenes has most generally been accomplished by substitution of poly(halophosphazenes) which are prepared by ring opening of the cyclic halogenated phosphazenes.[1] This ring-opening/substitution process has been used to prepare a large variety of alkoxy-, aryloxy-, and amino-substituted polymers. A variation of this involves ring opening of cyclic phosphazenes with both halo and organo substituents.[2] More recently, a condensation polymerization method[3] has been developed which produces poly(alkyl/arylphosphazenes) with all substituents attached to the backbone by direct

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