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Synthesis of Novel Organopolysiloxanes Having a Phospholipid-like Structure

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Organopolysiloxanes containing various functional groups and processes for their preparation are known in the previous reports.[1,2] These methods generally consist of contacting an unsaturated organic compound containing a functional group such as polyoxyalkylene oxide, cyano, acetoxy groups, or the like, with an organohydrogenpolysiloxane, under the influence of a hydrosilylation catalyst. On the other hand, considerable attention has been paid to phospholipids because they are known to be the important building units of biological membranes.[3,4] From this point of view, it seemed to be very interesting to investigate the behavior of compounds containing the phospholipid analogues. During the past 20 years, a great amount of our effort has been directed toward the synthesis and properties of polymeric phospholipid analogues.[5–10]

Our continuing interest in the chemistry of the phospholipid prompted us to design new compounds containing phospholipid analogues; we now report the first synthesis of organopolysiloxanes containing a phospholipid-like structure.

Synthesis of Unsaturated Monomers. 22-Tricosenyl-2-(trimethylammonio)ethyl phosphate (**3a**) and 28-nonacosenyl-2-(trimethylammonio)ethyl phosphate (**3b**) were synthesized using methods similar to those reported previously by Nakaya and co-workers.[5–10]

22-Tricosenyl-2-(trimethylammonio)ethyl Phosphate (3a). 22-Tricosenyl alcohol (3.38 g, 0.010 mol) was dissolved in dry tetrahydrofuran (150 mL), triethylamine (1.21 g, 0.012 mol) was added, and after cooling to −5 °C, 2-chloro-2-oxo-1,3,2-dioxaphospholane (1.74 g, 0.012 mol) was added dropwise over 30 min with stirring. After the completion of addition, the reaction was continued at 5–10 °C with stirring for 2 h, the precipitated triethylamine hydrochloride was then filtered off, and the filtrate was concentrated under reduced pressure to remove the tetrahydrofuran. The residual liquid was combined with dimethylformamide (100 mL) and trimethylamine (2.95 g, 0.050 mol), and this was placed in a pressure-resistant glass bottle, sealed, and then reacted at 75 °C for 36 h with shaking. The dimethylformamide was then distilled off in vacuo. The product, a viscous liquid, was dissolved in methanol (5 mL), which was then poured into a large volume of diethyl ether to obtain a white precipitate. The white precipitate was collected on a glass filter and then dried in vacuo to obtain a white powder of **3a** (39% yield): IR (neat) 2925, 2850, 1450 (methylene), 1620 (vinyl), 1230 (P=O), 1040, 930 ($POCH_2-$) cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 1.3 ($-CH_2-$, 38H), 1.9 ($C{=}CCH_2-$, 2H), 3.4 (N^+CH_3, 9H), 3.8 (N^+CH_2-, 2H), 4.0 (OCH_2-, 4H), 4.9 (HC=C, trans, 1H), 5.6 (HC=C−, cis, 1H), 5.9 (C=C(H)C, 1H). Elem anal. Calcd for $C_{28}H_{58}NO_4P{\cdot}H_2O$: N, 2.6. Found: N, 2.4.

28-Nonacosenyl-2-(trimethylammonio)ethyl Phosphate (3b). Using the procedure similar to that for the preparation of **3a**, 28-nonacosenyl alcohol was reacted with 2-chloro-2-oxo-1,3,2-dioxaphospholane in the presence of triethylamine in THF. Successively, ring-opening reaction was carried out by trimethylamine in DMF. **3b**: IR (neat) 2925, 2850, 1450 (methylene), 1620 (vinyl), 1230 (P=O), 1040, 930 ($POCH_2-$) cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 1.3 ($-CH_2-$, 50H), 1.9 ($C{=}CCH_2-$, 2H), 3.4 (N^+CH_3, 9H), 3.8 (N^+CH_2-, 2H), 4.0 (OCH_2-, 4H), 4.9 (HC=C, trans, 1H), 5.6 (HC=C−, cis, 1H), 5.9 (C=C(H)C, 1H). Elem anal. Calcd for $C_{34}H_{70}NO_4P{\cdot}2H_2O$: N, 2.2. Found: N, 2.4.

Synthesis of Organopolysiloxanes. The organopolysiloxanes **5** and **7a–d** were synthesized by hydrosilylation reaction of the alkylhydrogenpolysiloxane (**4**, **6a** or **6b**)[11] and **3a** or **3b** in the presence of chloroplatinic acid in toluene.

Organopolysiloxane 5. Dimethyl[[[(trimethylammonio)ethyl]phosphatidyl]tricosyl]siloxy-Terminated Dimethylpolysiloxane (5). Methylhydrogenpolysiloxane **4** (0.347 g, 3.97×10^{-4} mol) and 22-tricosenyl-2-(trimethylammonio)ethyl phosphate **3a** (0.400 g, 7.94×10^{-4} mol) was dissolved in warm toluene (30 mL), and chloroplatinic acid (220–275 μmol/L) was also added to and dissolved in this toluene solution. The resulting solution was placed in a pressure-resistant glass bottle, which was then sealed and immersed in a water bath at 80 °C for 24 h in order to carry out a hydrosilylation reaction. After completion of the reaction, the contents were removed and poured into a large excess of acetone for reprecipitation. The precipitate was filtered off and then dried. The product was a white, very slightly hygroscopic solid. IR analysis of this product provided the following results: disappearance of vinyl (1670) and hydrosilyl (2200); presence of methylene (2925, 2850, and 1460), $SiCH_3$ (1260), P=O (1200), and $POCH_2-$, SiOSi (1060) cm^{-1}.

Organopolysiloxanes 7a–d. Trimethylsiloxy-terminated methyl[[[(trimethylammonio)ethyl]phosphatidyl]tricosyl]polysiloxane (**7a**), trimethylsiloxy-terminated methyl[[[(trimethylammonio)ethyl]phosphatidyl]nonacosyl]polysiloxane (**7b**), trimethylsiloxy-terminated methyl[[[(trimethylammonio)ethyl]phosphatidyl]tricosyl]siloxane–dimethylsiloxane copolymer (**7c**), and trimethylsiloxy-terminated methyl[[[(trimethylammonio)ethyl]phosphatidyl]nonacosyl]siloxane–dimethylsiloxane copolymer (**7d**) were synthesized using a procedure similar to that described for the preparation of organopolysiloxane **5**. Methylhydrogenpolysiloxane **6a** or **6b** was reacted with 22-tricosenyl-2-(trimethylammonio)ethyl phosphate (**3a**) or 28-nonacosenyl-2-(trimethylammonio)ethyl phosphate (**3b**) in the presence of chloroplatinic acid in toluene, affording corresponding organopolysiloxanes **7a**, **7b**, **7c**, and **7d**, respectively. All of them were white, very slight hygroscopic solids, and IR analysis of these products provided the following results: disappearance of vinyl (1670) and hydrosilyl (2200); presence of methylene (2925, 2850, and 1460), $SiCH_3$ (1260), P=O (1200), and $POCH_2-$, SiOSi (1060) cm^{-1}. Elemental analyses of organopolysiloxanes **7a–d** were in good agreement with theory. Molecular weights were determined using TSK-GEL-4000PW columns based on poly(ethylene glycol)s as standard. GP analysis was carried out with a Waters Model GPC-244. Molecular weights for **7a–d** are 3600, 3700, 6900, and 7000, respectively.

Organopolysiloxanes containing a phospholipid-like structure were synthesized according to the reaction in Scheme 1. The reaction of 22-tricosenyl alcohol (**1a**) or 28-nonacosenyl alcohol (**1b**) with 2-chloro-2-oxo-1,3,2-

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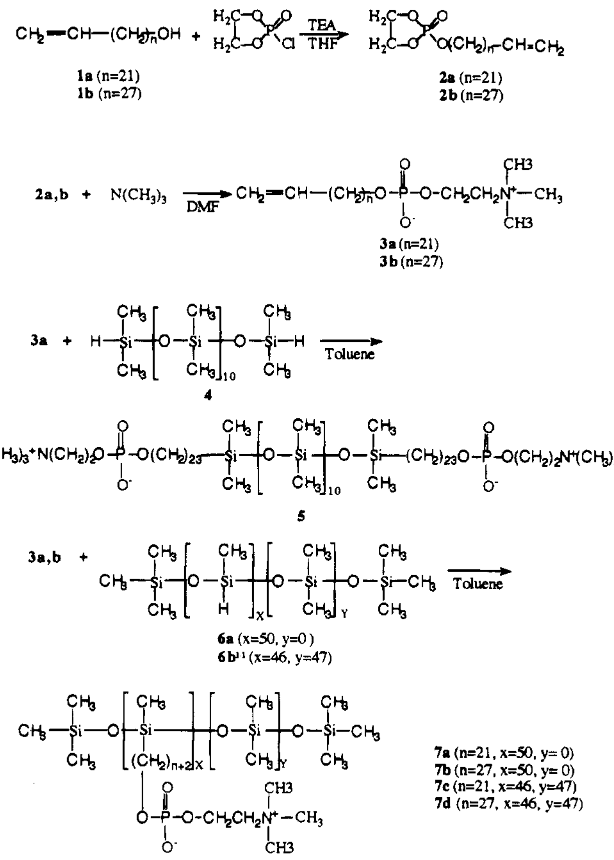
Scheme 1



dioxaphospholane[12,13] was carried out in THF in the presence of triethylamine to give 2-(22-tricosenyloxy)-2-oxo-1,3,2-dioxaphospholane (**2a**) or 2-(28-nonacosenyloxy)-2-oxo-1,3,2-dioxaphospholane (**2b**), respectively. Successively, the ring-opening reaction of **2a** and **2b** was carried out by trimethylamine[14] in DMF to obtain **3a** and **3b**, respectively. The characterization of **3a** and **3b** was based on their IR and ^{1}H NMR spectral data and elemental analyses.

In order to obtain the desired organopolysiloxanes containing a phospholipid-like structure, a hydrosilylation catalyst is required to carry out the hydrosilylation reaction between the alkylhydrogenpolysiloxane (**4**, **6a**, **6b**) and **3a** or **3b**. We chose chloroplatinic acid as a hydrosilylation catalyst and toluene as the solvent to synthesize the target organopolysiloxanes.

The synthesized organopolysiloxanes **7a–d** are generally solids and occasionally liquids at room temperature. When the unsaturated monomers and products' thermal changes were examined under a polarizing microscope, they were found to be nematic liquid crystals. As shown in Table 1, monomers **3a** and **3b** show transition temperatures from the solid to the mesophase at 77 and 85 °C, and transition temperature to the isotropic phase at 89 and 193 °C, respectively. The synthesized organopolysiloxanes **7a–d** show transition temperatures from the solid to the mesophase at 83, 80, 83, and 75 °C and transition temperature to the isotropic phase at 195, 209, 185, and 198 °C, respectively.

Table 1. Thermal Data of the Monomers 3a and 3b and Organopolysiloxanes 7a–d[a]

monomers and organopolysiloxanes	T_m/°C	T_i/°C
3a	77	89
3b	85	193
7a	83	195
7b	80	209
7c	83	185
7d	75	198

[a] T_m: phase transition temperatures, crystalline to liquid crystalline. T_i: phase transition temperatures, liquid crystalline to isotropic melt.

They also show hygroscopicity and hydrophilicity when their concentration is high. The presence of the phospholipid-like structure organic group also confers biocompatibility. The present synthesized organopolysiloxane containing a phospholipid-like structure is very useful in a wide range of applications, such as liquid crystal displays, artificial visceral organs, ion-exchange membranes, humidity sensors, gas sensors, biosensors, etc.

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