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Synthesis and properties of polyurethanes containing phosphatidylcholine analogues in the main chains and long-chain alkyl groups in the side chains

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Summary

New phospholipid polyurethanes containing phosphatidylcholine analogues in the main chains and octyl or oleyl groups in the side chains were synthesized by the addition polymerization of diols, bis[2-(2-hydroxyethyldimethylammonio)ethyl]2-octyl-1,3-propanediphosphate or bis[2-(2-hydroxyethyldimethylammonio)ethyl]2-oleyl-1,3-propanediphosphate, with diisocyanates such as 4,4'-diphenylmethane diisocyanate (MDI), hexamethylene diisocyanate (HDI), and 2,4-tolylene diisocyanate (TDI). The new phospholipid diols and polyurethanes were characterized by their IR and ^{1}H-NMR spectral data and elemental analysis. The new phospholipid polyurethanes exhibit common polyelectrolyte viscosity behaviours revealed by viscosity measurements. Moreover, π-A isotherms for these polyurethanes were also prepared.

Introduction

Segmented polyurethanes as biomaterials display certain favorable mechanical properties and biocompatibilities. However, some controversy still remains and limits their greater widespread application. In order to develop segmented polyurethanes with surfaces that will not activate the blood coagulation system, a number of surface modification approaches have been taken (1—3). Among them, an interesting and important observation is that albumin binds by hydrophobic bonds to molecules containing long alkyl chains suggested to synthesize different type of polymers normally containing alkyl chains of 16 or 18 carbon atoms (4—6) as side groups. These earlier studies suggest that improved blood compatibility might be attained by introducing hydrocarbon groups at the surface.

In recent approaches of our study on biocompatible phospholipid polymers, we reported a series of results on polyurethanes containing phospholipid moieties in the side chains (7—14). On the other hand, it also seemed to be very interesting to investigate the properties of polymers containing phospholipid analogues in the main chains (15). In our previous papers (16—19), we reported some polymers containing phosphatidylcholine analogues in the main chains. Recently, new polyurethanes bearing phosphatidylcholine analogues in the main chains (20, 21) have been synthesized in this laboratory. As a part of

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our general survey on biomembrane models, we now wish to report the synthesis and properties of some new polyurethanes containing phosphatidylcholine analogues in the main chains and long-chain alkyl groups in the side chains.

Experimental

General

Ethylene glycol, phosphorus trichloride, triethylamine (TEA), dichloromethane, benzene, toluene, acetonitrile, tetrahydrofuran (THF), diethyl ether, *N*,*N*-Dimethylformamide (DMF), acetone, methanol, ethanol, dimethyl sulfoxide (DMSO), 2-dimethylaminoethanol (*N*,*N*-dimethylethanolamine), hexamethylene diisocyanate (HDI), 4-methyl-1,3-phenylene diisocyanate (2,4-tolylene diisocyanate, TDI), and 4,4'-methylenediphenyl diisocyanate (MDI) were commercially obtained and purified by vacuum distillation. 1-Bromooctane, oleyl chloride, diethyl malonate, and lithium aluminum hydride were commercially obtained and used as received.

2-Chloro-1,3,2-dioxaphospholane [b.p. 45.5 - 46.5 °C (15 mbar); Lit. (22) : b.p. 45.5 - 47.0 °C (15 mbar)] was prepared in 66 % yield by the reaction of ethylene glycol with phosphorus trichloride in dichloromethane, according to the method of Lucas et al. (22), and oxidized to 2-chloro-2-oxo-1,3,2-dioxaphospholane [b.p. 103.5 - 105.0 °C (1 mbar); Lit. (23) : b.p. 79 °C (0,4 mbar)] in 90 % yield with oxygen, according to the procedure of Edmundson (23). IR spectra were recorded on a Jasco A 202 spectrometer and ^{1}H-NMR spectra on a 400 MHz α FT NMR spectrometer JNM-A 400 using tetramethylsilane (TMS) as an internal standard. The viscosity of polymers in DMSO at 25 °C was measured with an Ubbelohde viscometer. π-A isotherms were measured by the Film-Balance Measuring apparatus (Lauda).

Diethyl 2-octylmalonate (**1a**)

Into a thoroughly dried 300-cm^3 three-necked round-bottomed flask, equipped with a mechanical stirrer, drying tube, and dropping funnel, were placed 23.01 g (0.144 mol) of diethyl malonate and 150 cm^3 of dry ethanol in which 3.31 g (0.144 mol) of sodium was dissolved. 13.88 g (0.072 mol) of 1-bromooctane was added slowly to stirred solution over a period of 1 h. The reaction mixture was maintained at 80 °C for 15 h with stirring. After cooling to room temperature, ethanol was evaporated under vacuum. The residue was extracted with dry diethyl ether, washed with water three times, and dried over anhydrous sodium sulfate. After drying, diethyl ether was evaporated under vacuum and the product **1a** was distilled at 137 - 140 °C (6 mbar). Colorless liquid. Yield: 14.97 g (76.4 %). ^{1}H-NMR ($CDCl_3$) δ (ppm): 0.86-0.88 (t, 3H, $-CH_3$), 1.22-1.25 (m, 18H, $-(CH_2)_6-$, $-COOCH_2\underline{CH_3}$), 1.87 (m, 2H, $-\underline{CH_2}-CH<$), 3.30 (t, 1H, $-CH<$), 4.19 (m, 4H, $-COO\underline{CH_2}CH_3$). IR (neat): 2925, 2850, 1460, 720 ($-CH_2-$), and 1735 cm^{-1} (C=O).

Diethyl 2-oleylmalonate (**1b**)

In a similar manner, **1b** was prepared from oleyl chloride and diethyl malonate in ethanol in the presence of sodium ethoxide at 80 °C for 15 h. The product **1b** was distilled at 190 - 195 °C (10 mbar). Colorless liquid. Yield: 50.5 %. ^{1}H-NMR ($CDCl_3$) δ (ppm): 0.86-0.88 (t, 3H, $-CH_3$), 1.23-1.27 (m, 30H, $-CH_2-$, $-COOCH_2\underline{CH_3}$), 1.86 (m, 2H, $-\underline{CH_2}-CH<$), 1.99 (m, 4H, $-\underline{CH_2}-CH=CH-$), 3.31 (t, 1H, $-CH<$), 4.18 (m, 4H,

$-COOCH_2CH_3$), 5.32-5.36 (m, 2H, $-CH=CH-$). IR (neat): 2925, 2850, 1460, 720 ($-CH_2-$), and 1735 cm^{-1} (C=O).

2-Octyl-1,3-propanediol (**2a**)

Into a thoroughly dried 500-cm^3 three-necked round bottomed flask, equipped with a mechanical stirrer, drying tube, and dropping funnel, were placed 4.19 g (0.110 mol) of lithium aluminum hydride and 150 cm^3 of dry THF. After cooling with ice bath (0 °C), 14.97 g (0.055 mol) of **1a** was added slowly to the stirred suspension over a period of 1 h. After the addition was complete, the reaction mixture was stirred at 70 - 80 °C for 2 h and then cooled to room temperature. Furthermore, 1.04 g (0.028 mol) of $LiAlH_4$ was added to the stirred suspension and the mixture was stirred with refluxing for 2 h. Excess $LiAlH_4$ was reacted with THF/water. The resulting solution was treated with dilute hydrochloric acid and extracted with dry diethyl ether. The organic phase was washed with water three times and dried over anhydrous sodium sulfate. Diethyl ether was evaporated under vacuum to give a crude product. The crude product was dissolved in dry diethyl ether and recrystallized at -20 °C to give pure **2a** as white solid. Yield: 7.92 g (76.6 %). Anal. Calcd for $C_{11}H_{24}O_2$: C, 70.16 %; H, 12.85 %. Found: C, 70.06 %; H, 12.88 %. ^{1}H-NMR ($CDCl_3$) δ (ppm): 0.86-0.88 (t, 3H, $-CH_3$), 1.26 (s, 14H, $-CH_2-$), 1.78 (m, 1H, $-CH<$), 2.62 (s, 2H, $-OH$), 3.63-3.83 (m, 4H, $-CH_2OH$). IR (KBr): 3300, 1030 ($-OH$), 2900, 2850, 1455, and 720 cm^{-1} ($-CH_2-$).

2-Oleyl-1,3-propanediol (**2b**)

This was synthesized in the similar manner as **2a**. White solid. Yield: 76.6 %. Anal. Calcd for $C_{21}H_{42}O_2$: C, 77.24 %; H, 12.96 %. Found: C, 77.15 %; H, 13.01 %. ^{1}H-NMR ($CDCl_3$) δ (ppm): 0.86-0.88 (t, 3H, $-CH_3$), 1.26 (s, 26H, $-CH_2-$), 1.77 (m, 1H, $-CH<$), 1.97-2.02 (m, 4H, $-CH_2-CH=$), 3.62-3.83 (m, 4H, $-CH_2OH$), 5.35-5.47 (m, 2H, $-CH=CH-$). IR (KBr): 3300, 1030 ($-OH$), 2925, 2850, 1460, and 720 cm^{-1} ($-CH_2-$).

1,3-Bis(2-oxo-1,3,2-dioxaphospholan-2-yloxy)2-octylpropane (**3a**)

Into a thoroughly dried 300-cm^3 three-necked round-bottomed flask, equipped with a mechanical stirrer, drying tube, and dropping funnel, were placed 3.75 g (0.02 mol) of **2a** and 4.44 g (0.04 mol) of triethylamine in 150 cm^3 of dry THF. After cooling with dry-ice/methanol bath (-20 °C), 5.68 g (0.04 mol) of 2-chloro-2-oxo-1,3,2-dioxaphospholane was added slowly to the stirred solution over a period of 1 h, by which procedure triethylamine hydrochloride began to precipitate. The reaction mixture was maintained at -20 to -15 °C for 1 h with stirring and then allowed to warm to 0 °C. After being kept at this temperature for 1.5 h, the precipitate formed was filtered off and washed with 30 cm^3 of dry THF. The filtrate and the THF solution were evaporated under vacuum for 1 h to give product **3a** as pale yellow viscous liquid. Yield: 7.81 g (98 %). ^{1}H-NMR ($CDCl_3$) δ (ppm): 0.86-0.88 (t, 3H, $-CH_3$), 1.26 (s, 14H, $-CH_2-$), 2.30 (m, 1H, $-CH<$), 3.71-3.84 (m, 4H, $-PO-CH_2-CH<$), 4.04-4.50 (m, 8H, $-OCH_2CH_2OP-$). IR (neat): 2925, 2850, 1460, 720 ($-CH_2-$), 1260 (P=O), and 1020 cm^{-1} ($PO-CH_2-$).

1,3-Bis(2-oxo-1,3,2-dioxaphospholan-2-yloxy)2-oleylpropane (**3b**)

In the similar manner, **3b** was prepared from **2b** and 2-chloro-2-oxo-1,3,2-

dioxaphospholane in THF in the presence of triethylamine at -20 to -15 °C. The product **3b** was pale yellow viscous liquid in 98 % yield. ^{1}H-NMR ($CDCl_3$) δ (ppm): 0.86-0.88 (t, 3H, $-CH_3$), 1.27 (s, 26H, $-CH_2-$), 2.0 (m, 4H, $-C\underline{H}_2-CH=$), 2.28 (m, 1H, $-CH<$), 3.79-3.87 (m, 4H, $-PO-C\underline{H}_2-CH<$), 4.06-4.36 (m, 8H, $-OCH_2CH_2OP-$), 5.35-5.38 (m, 2H, $-CH=CH-$). IR (neat): 2925, 2850, 1470, 720 ($-CH_2-$), 1290 (P=O), and 1040 cm^{-1} ($PO-CH_2-$).

Bis[2-(2-hydroxyethyldimethylammonio)ethyl]2-octyl-1,3-propanediphosphate (**4a**)
Into a 300-cm^3 glass pressure bottle (Top Model E 1435, Type A) were placed 7.81 g (0.02 mol) of **3a** and 60 cm^3 of dry acetonitrile. 5.33 g (0.06 mol) of 2-dimethylaminoethanol were rapidly added to the solution. The pressure bottle was closed and then shaken in a thermostat maintained at 70 °C for 20 h. After the bottle was opened, the solvent was evaporated under vacuum. The residue was washed with dry acetone, the solvent was discarded by decantation. This procedure was repeated three times, then the residue was collected and dried under vacuum to give a crude product. The crude product was dissolved in dry methanol and reprecipitated from dry acetone. The reprecipitation procedure was repeated three times to give pure product **4a** as yellow viscous liquid. Yield: 7.83 g (69.4 %). Anal. Calcd for $C_{23}H_{52}N_2O_{10}P_2 \cdot 2H_2O$: C, 44.94 %; H, 9.18 %; N, 4.56 %. Found: C, 45.11 %; H, 9.15 %; N, 4.54 %. ^{1}H-NMR ($CDCl_3$) δ (ppm): 0.86-0.88 (t, 3H, $-CH_3$), 1.26 (s, 14H, $-CH_2-$), 2.89 (s, 12H, N^+-CH_3), 3.20 (m, 1H, $-CH<$), 3.4-4.2 (m, 20H, $-OCH_2$, N^+-CH_2-). IR (neat): 3350 ($-OH$), 2925, 2850, 1480, 790 ($-CH_2-$), 1220 (P=O), and 1040 cm^{-1} ($PO-CH_2-$).

Bis[2-(2-hydroxyethyldimethylammonio)ethyl]2-oleyl-1,3-propanediphosphate (**4b**)
This was synthesized in the similar manner as **4a**. Yield: 38.0%. Anal. Calcd for $C_{33}H_{70}N_2O_{10}P_2 \cdot 2H_2O$: C, 52.64 %; H, 9.91 %; N, 3.72 %. Found: C, 52.55 %; H, 9.88 %; N, 3.68 %. ^{1}H-NMR ($CDCl_3$) δ (ppm): 0.86-0.88 (t, 3H, $-CH_3$), 1.26 (s, 26H, $-CH_2-$), 1.97-2.01 (m, 4H, $-C\underline{H}_2-CH=$), 2.80 (s, 12H, N^+-CH_3), 3.07 (m, 1H, $-CH<$), 3.37-4.24 (m, 20H, $-OCH_2$, N^+-CH_2-), 5.33-5.38 (m, 2H, $-CH=CH-$). IR (neat): 3350 ($-OH$), 2925, 2850, 1465, 780 ($-CH_2-$), 1220 (P=O), and 1040 cm^{-1} ($PO-CH_2-$).

Polyurethanes
Polyurethane **5a**: Into a 300-cm^3 round-bottomed flask, equipped with a reflux condenser with a drying tube and mechanical stirrer, were placed 2.00 g (3.46 mmol) of **4a**, 0.87 g (3.46 mmol) of MDI in 100 cm^3 of DMF under a nitrogen atmosphere. The mixture was stirred at 95 to 115 °C for 4 h. At the end of reaction, the mixture was concentrated to one third of its original volume. The concentrate was poured into 200 cm^3 of diethyl ether by which polymer **5a** precipitated. It was purified three times by reprecipitation from methanol with diethyl ether. Reddish brown solid. Yield: 0.87 g (30.3 %). Anal. Calcd for $(C_{38}H_{62}N_4O_{12}P_2 \cdot 2H_2O)_n$: C, 52.77 %; H, 7.69 %; N, 6.48 %. Found: C, 52.93 %; H, 7.65 %; N, 6.43 %. ^{1}H-NMR ($CDCl_3$) δ (ppm): 0.86-0.88 (t, 3H, $-CH_3$), 1.25 (s, 14H, $-CH_2-$), 2.82 (s, 12H, N^+-CH_3), 3.06 (m, 1H, $-CH<$), 3.46-4.27 (m, 22H, $-OCH_2$, N^+-CH_2-, arom.$-CH_2-$arom.), 6.90-7.08 (m, 8H, arom.). IR (neat) : 2925, 2850, 1460, 770 ($-CH_2-$), 1720 ($-NHCOO-$), 1600 (arom.), 1220 (P=O), and 1040 cm^{-1} ($PO-CH_2-$).

Polyurethanes **5b**, **6a**, **6b**, **7a**, *and* **7b**

The same procedure was applied for the preparation of polyurethanes **5b**, **6a**, **6b**, **7a**, and **7b**. **4b** was reacted with MDI by a 1 : 1 mole ratio in dry DMF at 95 - 115 °C for 4 h to afford polyurethane **5b**. **4a** and **4b** were reacted with HDI and TDI by a 1 : 1 mole ratio in dry DMF at 95-115 °C for 4 h to afford polyurethanes **6a**, **6b**, **7a**, and **7b**, respectively.

5b: Yellow solid. Yield: 30.3 %. ^{1}H-NMR ($CDCl_3$) δ (ppm): 0.86-0.88 (t, 3H, $-CH_3$), 1.22-1.27 (s, 26H, $-CH_2-$), 1.94-2.05 (m, 4H, $-C\underline{H}_2-CH=$), 2.89 (s, 12H, N^+-CH_3), 3.19 (m, 1H, $-CH<$), 3.49-4.25 (m, 22H, $-OCH_2$, N^+-CH_2-, arom.$-CH_2-$arom.), 6.9-7.0 (m, 8H, arom.). IR (neat) : 2925, 2850, 1460, 780 ($-CH_2-$), 1720 ($-NHCOO-$), 1600 (arom.), 1220 (P=O), and 1040 cm^{-1} ($PO-CH_2-$).

6a: Pale yellow semisolid. Yield: 35.1 %. ^{1}H-NMR ($CDCl_3$) δ (ppm): 0.86-0.88 (t, 3H, $-CH_3$), 1.25-1.32 (m, 18H, $-CH_2-$, $-(C\underline{H}_2)_2(CH_2)_2NHCOO-$), 1.49 (s, 4H, $-C\underline{H}_2CH_2NHCOO-$), 2.88 (s, 12H, N^+-CH_3), 3.14 (m, 1H, $-CH<$), 3.46-4.26 (m, 24H, $-OCH_2$, N^+-CH_2-, $-CH_2C\underline{H}_2NHCOO-$). IR (neat) : 2925, 2850, 1460, 780 ($-CH_2-$), 1710 ($-NHCOO-$), 1230 (P=O), and 1050 cm^{-1} ($PO-CH_2-$).

6b: Pale yellow solid. Yield: 52.3 %. ^{1}H-NMR ($CDCl_3$) δ (ppm): 0.86-0.88 (t, 3H, $-CH_3$), 1.26-1.35 (m, 30H, $-CH_2-$, $-(C\underline{H}_2)_2(CH_2)_2NHCOO-$), 1.51 (s, 4H, $-C\underline{H}_2CH_2NHCOO-$), 2.0 (m, 4H, $-C\underline{H}_2-CH=$), 2.86 (s, 12H, N^+-CH_3), 3.10 (m, 1H, $-CH<$), 3.38-4.27 (m, 24H, $-OCH_2$, N^+-CH_2-, $-CH_2C\underline{H}_2NHCOO-$), 5.35 (m, 2H, $-CH=CH-$). IR (neat) : 2925, 2850, 1460, 780 ($-CH_2-$), 1710 ($-NHCOO-$), 1220 (P=O), and 1040 cm^{-1} ($PO-CH_2-$).

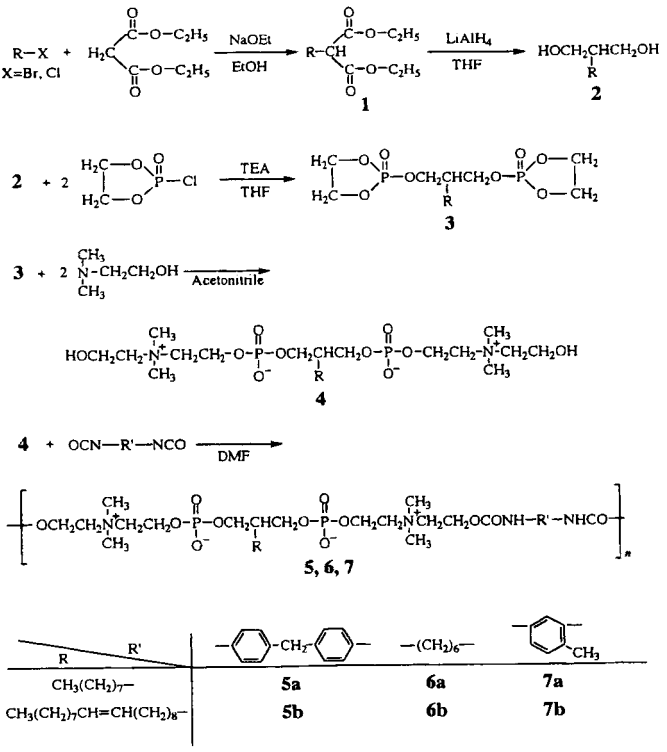
7a: Brown solid. Yield: 78.0 %. ^{1}H-NMR ($CDCl_3$) δ (ppm): 0.86-0.88 (t, 3H, $-CH_3$), 1.25 (s, 14H, $-CH_2-$), 2.18 (s, 3H, arom.$-CH_3$), 2.89 (s, 12H, N^+-CH_3), 3.10 (m, 1H, $-CH<$), 3.46-4.27 (m, 20H, $-OCH_2$, N^+-CH_2-), 7.0-7.1 (m, 3H, arom.). IR (neat) : 2925, 2850, 1460, 780 ($-CH_2-$), 1720 ($-NHCOO-$), 1600 (arom.), 1220 (P=O), and 1040 cm^{-1} ($PO-CH_2-$).

7b: Brown solid. Yield: 44.0 %. ^{1}H-NMR ($CDCl_3$) δ (ppm): 0.88-0.92 (t, 3H, $-CH_3$), 1.21-1.26 (s, 26H, $-CH_2-$), 1.85 (m, 4H, $-C\underline{H}_2-CH=$), 2.1 (s, 3H, arom.$-CH_3$), 2.86 (s, 12H, N^+-CH_3), 3.10 (m, 1H, $-CH<$), 3.45-4.27 (m, 20H, $-OCH_2$, N^+-CH_2-), 5.35 (m, 2H, $-CH=CH-$), 6.9-7.0 (m, 3H, arom.). IR (neat) : 2925, 2850, 1460, 780 ($-CH_2-$), 1720 ($-NHCOO-$), 1600 (arom.), 1210 (P=O), and 1040 cm^{-1} ($PO-CH_2-$).

Results and discussion

The synthetic procedure is outlined in Scheme 1. According to the method of Hsu and Percec (24), compounds **1a** and **1b** were obtained by the reaction of 1-bromooctane or oleyl chloride with diethyl malonate in ethanol in the presence of sodium ethoxide. **2a** and **2b** were obtained by reduction of **1a** and **1b** in THF in the presence of $LiAlH_4$. The characterization of **1a**, **1b**, **2a**, and **2b** was based on their IR and ^{1}H-NMR spectral data and elemental analyses. The bifunctional intermediates **3a** and **3b** were obtained by the reaction of **2a** or **2b** with 2-chloro-2-oxo-1,3,2-dioxaphospholane in THF in the presence of triethylamine in nearly quantitative yields. They were characterized by IR and ^{1}H-NMR spectral data. According to the method of Thuong and Chabrier (25), the ring-opening

Scheme 1



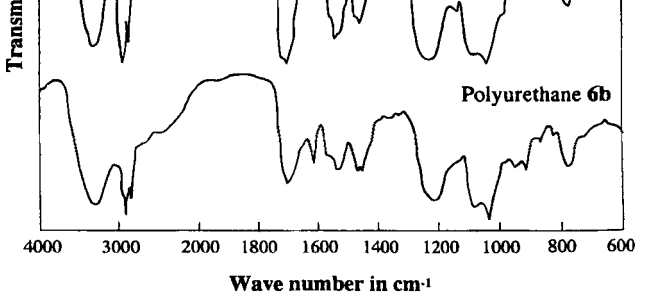


Fig. 1. IR spectra of polyurethanes **6a** and **6b**.

reaction of **3a** and **3b** was performed with 2-dimethylaminoethanol in acetonitrile at 70 °C for 20 h to afford new diols **4a** and **4b** as pale yellow viscous liquid in good yields. The characterization of the new diols **4a** and **4b** was based on their IR and ^{1}H-NMR spectral data and elemental analyses. Both diols were very hygroscopic and soluble in DMF at 70 °C, but almost insoluble in acetone and diethyl ether at room temperature.

Polyurethanes **5a**, **5b**, **6a**, **6b**, **7a**, and **7b** were synthesized by reaction of diols **4a** or **4b** with diisocyanates such as 4,4'-methylenediphenyl diisocyanate (MDI), hexamethylene diisocyanate (HDI), and 2,4-tolylene diisocyanate (TDI), respectively. Polyurethanes were obtained at 95-115 °C in DMF. The characterization of the synthesized polyurethanes was based on their IR and ^{1}H-NMR spectral data and elemental analyses. The IR spectra of polyurethanes showed absorption bands due to —NHCOO— at 1720, —P=O at 1220 and —PO—CH_2— at 1080 cm^{-1}, respectively. Moreover, because synthesized polyurethanes were very hygroscopic, absorption bands due to H_2O at 3300 cm^{-1} also

appeared in their IR spectra. As an example, Fig. 1 shows the IR spectra of polyurethanes **6a** and **6b**.

All of the polyurethanes were soluble in DMSO and DMF but insoluble in acetone and diethyl ether. Viscosity measurements on these polyurethanes were performed at 25 °C in DMSO. Fig. 2(A) and (B) show the values of the reduced viscosity of these polyurethanes.

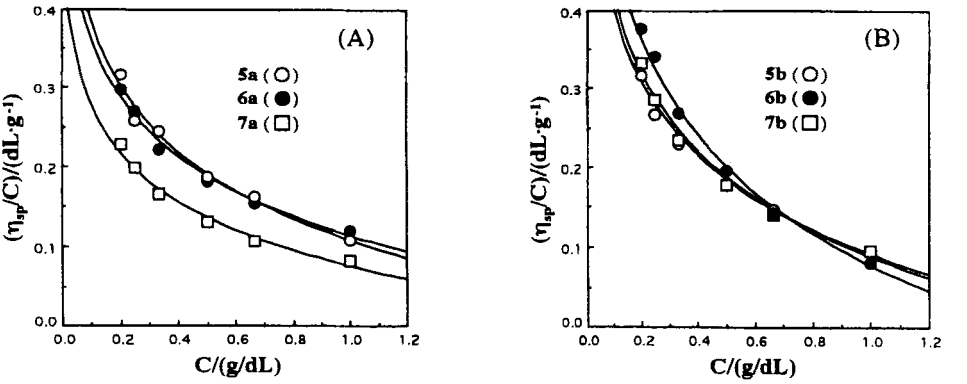


Fig. 2. Reduced viscosity (η_{sp}/C) vs. concentration (C) for polyurethanes in DMSO at 25°C. (A) for **5a**, **6a**, and **7a**; (B) for **5b**, **6b**, and **7b**.

As can be seen, the reduced viscosities of these polyurethanes have the tendency to increase rapidly upon dilution. These findings suggest that polyurethanes containing phosphatidylcholine analogues in the polymer backbones show similar properties as usual polyelectrolytes. These results agree with our previous reports on the viscosity of the phospholipid polyurethanes (7—9, 20).

The monolayers of these polyurethanes were prepared by spreading samples on clean water surface from the mixture of toluene and methanol, and then the π-A isotherms were measured. All polyurethanes show solid analogous phase with relatively high collapse pressures (ca. 34-46 mN/m) at collapse areas of ca. 7-12 Å^2/repeat unit. The π-A isotherms of polyurethane **6b** at different temperatures are shown in Fig. 3(A). The π-A isotherms

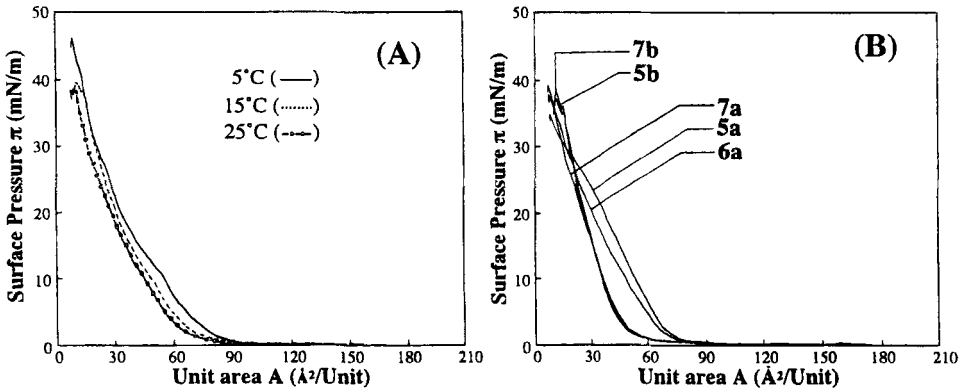


Fig. 3. π-A isotherms of polyurethanes. (A) for **6b** at 5°C (——), 15°C (----), and 25°C (-·-·-); (B) for **5a**, **5b**, **6a**, **7a**, and **7b** at 25 °C.
(from toluene and methanol mixture (**5b** for 9.5:0.5, v/v; others for 8:2, v/v)).

were found to reduce gradually as temperature increased. These findings suggest that polyurethane **6b** shows the property of collapse pressure depending on temperature. The π-A isotherms of other polyurethanes at 25 °C are shown in Fig. 3(B). As can be seen, all polyurethanes show the monotonic increase excepting that of polyurethane **5a**. Moreover, the surface pressures of polyurethanes **5a** and **6a** rise earlier than those of others. These results are perhaps due to the relative length and saturation degree of polymer side chains, as well as the difference between aromatic and aliphatic polymer main chains.

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