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### Synthesis and Properties of Polymers Containing Phosphatidylcholine Analogues in the Main Chains and Long Alkyl Groups in the Side Chains

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# **SYNTHESIS AND PROPERTIES OF POLYMERS CONTAINING PHOSPHATIDYLCHOLINE ANALOGUES IN THE MAIN CHAINS AND LONG ALKYL GROUPS IN THE SIDE CHAINS**

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## **ABSTRACT**

Several new polymers containing hydrophilic phosphatidylcholine analogues in the main chains and hydrophobic docosyl or stearyl groups in the side chains have been synthesized. The polymers exhibit thermotropic liquid crystalline behaviors from 65°C up to ca. 280°C as determined by polarizing microscopy. One of the polymers shows slight crystallinity as evidenced by wide-angle x-ray diffraction. The viscosity measurements show that some of the polymers have properties similar to usual polyelectrolytes. However, one polymer shows a linear increase of reduced viscosity.

## **INTRODUCTION**

There is considerable interest in phospholipids because they, together with proteins, are the main components of biomembranes. In addition, their self-organization and function are of great interest [1, 2]. Phospholipids are contained in all living organisms and are essential to life. However, phospholipid membranes are mechanically weak and unstable. Accordingly, it is very interesting to synthesize polymeric phospholipids to constitute artificial cells with biomimetic functions for a wide variety of practical applications.

During the past 20 years a great amount of our effort has been directed toward the synthesis and properties of polymers containing phosphatidylethanolamine [3, 4] or choline [5, 6] analogues in the side chains. In addition, we reported the syntheses and some properties of polymers containing phosphatidylcholine analogues in the main chains [7-9].

In previous work [10] we found that amphiphilic polyurethane, consisting of quaternary ammonium salt with long alkyl chains, exhibit thermotropic liquid-crystalline behavior. As an extension of our study in this series, our continuing interest in this type of ring-opening polymerization prompted us to design new polymers containing phosphatidylcholine analogues in the main chains as the hydrophilic part and long alkyl groups in the side chains as the hydrophobic part. The synthesized polymers, whose structures are comblike, are amphiphilic in nature and exhibit thermotropic liquid crystalline states as well as some crystallinity, based on the analysis of wide-angle x-ray diffraction (WXR) patterns combined with polarizing microscopy.

## EXPERIMENTAL

### Materials

1-Docosanol, stearyl chloride, thionyl chloride, thionyl bromide, 12 N hydrochloric acid, sodium hydroxide, anhydrous sodium sulfate, *N,N,N',N'*-tetramethylhexamethylenediamine, and dimethylamine hydrochloride were purchased commercially and used as received.

Ethylene glycol, phosphorus trichloride, triethylamine, diethanolamine, and 1-butanol were commercially available and purified by vacuum distillation. Methanol was distilled in the presence of magnesium methoxide to ensure dryness. Dichloromethane and benzene were dried by distillation from phosphorus pentoxide. THF was distilled from lithium aluminum hydride to ensure dryness. DMF was distilled in the presence of calcium hydride. Acetone was dried by distillation from anhydrous potassium carbonate. All solvents were dried over Molecular Sieves (Nakarai Chemicals, M4M7034).

2-Chloro-1,3,2-dioxaphospholane, bp 45.5-46.5°C/15 mbar (Ref. 11, 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. [11], and oxidized to 2-chloro-2-oxo-1,3,2-dioxaphospholane, bp 103.5-105.0°C/1 mbar (Ref. 12, bp 79°C/0.4 mbar), in 90% yield with oxygen, according to the procedure of Edmundson [12]. Dimethylamine was prepared by reaction of dimethylamine hydrochloride with 50% sodium hydroxide, following the procedure of Adams and Brown [13].

### Docosyl Chloride (1a)

A mixture of 25.0 g (0.0765 mol) 1-docosanol and 54.6 g (0.459 mol) thionyl chloride was heated at 60°C for 2 hours with stirring, and the excess thionyl chloride was distilled off under reduced pressure, recrystallized from methanol, affording product **1a** as a white solid: 24.0 g (91%).

IR (KBr): 3350  $\text{cm}^{-1}$  ( $-\text{OH}$ ) absorption band has disappeared; color test: green.

### **Bis(2-ethanol)docosylamine (2a) and Bis(2-ethanol)stearylamine (2b)**

A mixture of alkyl chloride (**1a** or **1b**) (0.260 mol) and diethanolamine (1.04 mol) in 100 mL 1-butanol was heated at 100°C with stirring for 4 hours. Then the solvent was removed by a rotary evaporator under vacuum. The crude products were extracted from 200 mL benzene and 200 mL of 25% aqueous sodium hydroxide. This procedure was repeated one more time, and the benzene layer was washed with pure water and dried with anhydrous sodium sulfate. After the sodium sulfate was filtered, the solvent was evaporated under vacuum, the residue was recrystallized from methanol, and gave **2a** and **2b**, respectively.

**2a**: Yield 68%; mp 68.5°C. IR (neat): 2925, 2850, 1460 ( $-\text{CH}_2-$ ), and 3400  $\text{cm}^{-1}$  ( $-\text{OH}$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 0.88 (t;  $-\text{CH}_3$ , 3H), 1.26 (s;  $-\text{CH}_2-$ , 40H), 2.25 (s;  $-\text{OH}$ , 2H), 2.6 (m;  $\text{N}-\text{CH}_2-$ , 6H), and 3.0 (t;  $-\text{CH}_2\text{O}-$ , 4H).  $\text{C}_{26}\text{H}_{55}\text{NO}_2$  (413.7): Calculated C 75.48, H 13.42; found C 75.01, H 13.65.

**2b**: Yield 78.5%; mp 54–54.5°C. IR (neat): 2925, 2850, 1460 ( $-\text{CH}_2-$ ), and 3400  $\text{cm}^{-1}$  ( $-\text{OH}$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 0.88 (t;  $-\text{CH}_3$ , 3H), 1.26 (s;  $-\text{CH}_2-$ , 32H), 2.38 (s;  $-\text{OH}$ , 2H), 2.6 (m;  $\text{N}-\text{CH}_2-$ , 6H), 3.0 (t;  $-\text{CH}_2\text{O}-$ , 4H).  $\text{C}_{22}\text{H}_{47}\text{NO}_2$  (357.6): Calculated C 73.87, H 13.25; found C 73.63, H 13.54.

### **Bis(2-hydroxyethyl) Stearylamine Hydrochloride (3b)**

After 35.76 g (0.10 mol) of bis(2-ethanol)stearylamine **2b** was dissolved in acetone, 10 mL of 12 N hydrochloric acid was slowly added into the solution with stirring. After addition, the mixture was stirred for 30 minutes to cool to room temperature and filtered by a glass filter. The solid was collected and washed with acetone three times, then dried under vacuum to obtain the product **3b**: 36.5 g (92.6%); mp 87°C; color test: green.

### **Bis(2-bromoethyl) Stearylamine Hydrochloride (4b)**

Bis(2-hydroxyethyl) stearylamine hydrochloride **3b** [23.7 g (0.06 mol)] was added to 75 g (0.361 mol) thionyl bromide. The mixture was heated at 60°C for 2 hours and the excess thionyl bromide was distilled off under reduced pressure to give the desired compound **4b** in quantitative yield.

### **Bis(2-bromoethyl) Stearylamine (5b)**

To a solution of 31.3 g (0.06 mol) bis(2-bromoethyl) stearylamine hydrochloride **4b** in 200 mL benzene was added 200 mL of 30% aqueous sodium hydroxide. The mixture was vigorously shaken and the organic layer was partitioned. This procedure was repeated one more time, and then it was washed successively with pure water. After drying over anhydrous sodium sulfate and removal of solvents under vacuum, the product was purified by recrystallization from methanol: 18.0 g (62.1%).

IR (neat): 2900, 2825, 1460 ( $-\text{CH}_2-$ ), and  $620\text{ cm}^{-1}$  ( $-\text{Br}$ ).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 0.88$  (t;  $-\text{CH}_3$ , 3H), 1.26 (s;  $-\text{CH}_2-$ , 32H), 2.9 (m;  $\text{N}-\text{CH}_2-$ , 6H), 3.2(m;  $-\text{CH}_2\text{Br}$ , 4H).

### Bis(2-dimethylaminoethyl) Stearylamine (6b)

Into a 300-mL glass pressure bottle (Top Model E 1435, Type A) were placed 9.66 g (0.010 mol) bis(2-bromoethyl) stearylamine **5b**, 75 mL dry methanol, and 75 mL dry benzene. After the pressure bottle was cooled in cold water, 9.0 g (0.20 mol) dimethylamine was rapidly added to the cold solution. The pressure bottle was closed and then shaken in a thermostat maintained at  $30^\circ\text{C}$  for 4 days. After the reaction was completed, it was cooled down in cold water to  $10^\circ\text{C}$ , the bottle was opened, and the solvents were evaporated off under vacuum in a stream of nitrogen for 2 hours. To the residue, 200 mL dry benzene and 200 mL of 30% aqueous sodium hydroxide were added. After the mixture was vigorously shaken for 15 minutes, the organic layer was separated. This procedure was repeated three times. The organic layer was washed successively with 200 mL pure water. After drying over anhydrous sodium sulfate, the solvent was removed under vacuum. The product was purified by recrystallization from methanol: 3.5 g (19.5%).

IR (neat): 2825, 2770 [ $-\text{CH}_2\text{N}(\text{CH}_3)_2$ ], and 2925, 2825,  $1460\text{ cm}^{-1}$  ( $-\text{CH}_2-$ ).

### Bis[2-(2'-oxy-2'-oxo-1',3',2'-dioxaphospholane) Ethyl] Docosylamine (7a) and Bis[2-(2'-oxy-2'-oxo-1',3',2'-dioxaphospholane) Ethyl] Stearylamine (7b)

Into a thoroughly dried 500 mL three-necked round bottom flask, equipped with a mechanical stirrer, drying tube, and dropping funnel, were placed **2a** or **2b** (0.010 mol) and 2.29 g (0.022 mol) triethylamine in 150 mL dry THF. After cooling with dry-ice/methanol ( $-15^\circ\text{C}$ ), 2.85 g (0.020 mol) 2-chloro-2-oxo-1,3,2-dioxaphospholane was added slowly to the stirred solution over a period of 30 minutes; triethylamine hydrochloride began to precipitate. The reaction mixture was maintained at  $-20$  to  $-15^\circ\text{C}$  for 30 minutes with stirring and then allowed to warm to  $0^\circ\text{C}$ . The mixture was kept at this temperature for 2 hours, and the precipitate that formed was filtered off and washed with 30 mL dry THF. The filtrate and the THF solution were evaporated under vacuum in a stream of nitrogen. To the residue, 50 mL dry THF were added. The mixture was shaken for 30 seconds and then filtered with a glass filter to remove a small amount of triethylamine hydrochloride. The filtrate was evaporated under vacuum in a stream of nitrogen for about 1.5 hours to give products **7a** and **7b** in quantitative yield.

IR (neat): 2900, 2825, 1460 ( $-\text{CH}_2-$ ), 1280 ( $\text{P}=\text{O}$ ), and 1080,  $980\text{ cm}^{-1}$  ( $\text{PO}-\text{CH}_2-$ ). There are no important differences between the IR spectra of **7a** and **7b**.

### Polymers 8a and 8b

Into a 300 mL-glass pressure bottle (Top Model E 1435, Type A) were placed **7a** or **7b** (0.01 mol) and 75 mL dry DMF. *N,N,N',N'*-Tetramethylhexamethylene-

diamine [1.72 g (0.01 mol)] was rapidly added to the solution. The pressure bottle was closed and then shaken in a thermostat maintained at 75°C for 36 hours. After the bottle was opened, the solvent was evaporated under vacuum in a stream of nitrogen. To the residue, 100 mL dry acetone were added. After the mixture was shaken for 1 minute, the solvent was discarded by decantation. The solid mass was collected and dried under vacuum to give a caramel product. The crude product was dissolved in dry methanol and reprecipitated from dry acetone. The reprecipitation procedure was repeated three times to give pure polymers **8a** and **8b**. Yields for **8a** and **8b** were 82 and 74%, respectively.  $T_m$  and  $T_i$  of these polymers are listed in Table 1.

IR (neat): 2925, 2850, 1460 ( $-\text{CH}_2-$ ), 1240 ( $\text{P}=\text{O}$ ), and 1080, 980  $\text{cm}^{-1}$  ( $\text{PO}-\text{CH}_2-$ ). There are no important differences between the IR spectra of **8a** and **8b**.

**8a**: ( $\text{C}_{40}\text{H}_{85}\text{N}_3\text{O}_8\text{P}_2 \cdot 2\text{H}_2\text{O}$ )<sub>n</sub> (834.1)<sub>n</sub>: Calculated C 57.60, H 10.75, N 5.04; Found C 57.31, H 10.48, N 4.96.

**8b**: ( $\text{C}_{36}\text{H}_{77}\text{N}_3\text{O}_8\text{P}_2 \cdot 2\text{H}_2\text{O}$ )<sub>n</sub> (778.0)<sub>n</sub>: Calculated C 55.58, H 10.49, N 5.40; Found: C 55.10, H 10.20, N 5.19.

### Polymer 9

Using a similar procedure as described for the preparation of polymers **8a** and **8b**, **7b** was reacted with **6b** in dry DMF and afforded a corresponding polymer **9** in a yield of 76%.  $T_m$  and  $T_i$  are shown in Table 1.

IR (neat): 2925, 2850, 1460 ( $-\text{CH}_2-$ ), 1240 ( $\text{P}=\text{O}$ ), and 1080, 980  $\text{cm}^{-1}$  ( $\text{PO}-\text{CH}_2-$ ).

**9**: ( $\text{C}_{52}\text{H}_{110}\text{N}_4\text{O}_8\text{P}_2 \cdot 2\text{H}_2\text{O}$ )<sub>n</sub> (1017.4)<sub>n</sub>: Calculated C 61.39, H 11.29, N 5.51; Found C 61.61, H 11.54, N 5.31.

TABLE 1. Thermal Data of the Diols **2a** and **2b**, Monomers **7a** and **7b**, and Polymers **8a**, **8b**, and **9**

Samples	$T_m$ , °C <sup>a</sup>	$T_i$ , °C <sup>b</sup>
<b>2a</b>	66	—
<b>2b</b>	42	—
<b>7a</b>	70	190
<b>7b</b>	62	170
<b>8a</b>	96	206
<b>8b</b>	65	170
<b>9</b>	76	274

<sup>a</sup> $T_m$ : phase transition temperatures, crystalline → liquid crystalline.

<sup>b</sup> $T_i$ : phase transition temperatures, liquid crystalline → isotropic melt.



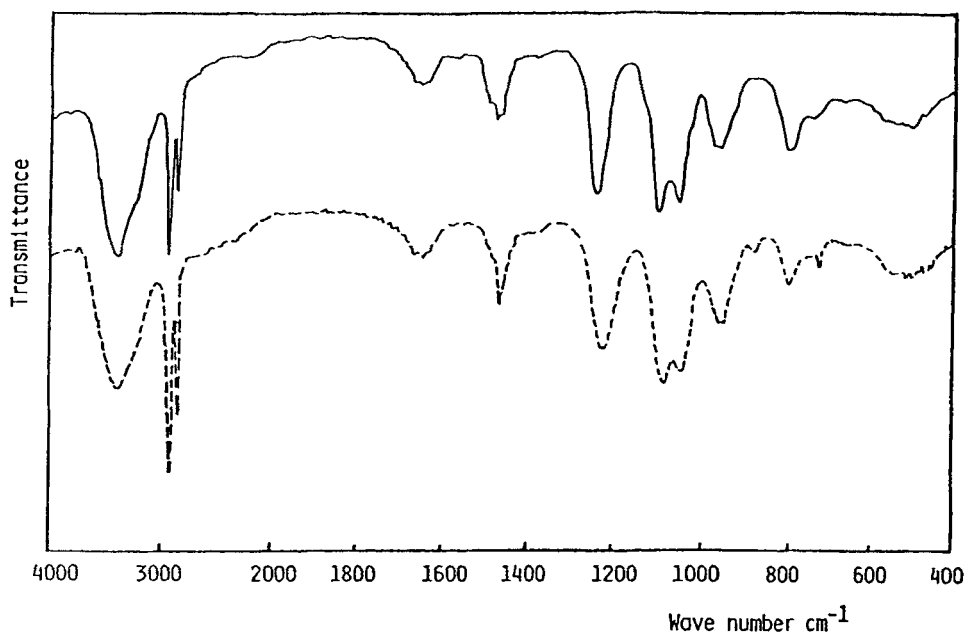


FIG. 1. IR spectra of polymers **8b** (—) and **9** (---).

### Physical Measurements

The infrared measurements were recorded on a Jasco A 202 spectrometer, <sup>1</sup>H-NMR spectra were performed on a 60-MHz Hitachi-Perkin-Elmer Model R-20 NMR spectrometer using tetramethylsilane as an internal reference. Molecular weight was determined by GPC (Jasco model TRI ROTER, Type 1) in a 2-amino-2,2-bis(hydroxymethyl)ethanol buffer solution (pH 7.9) with TSK-GEL-G4000PW columns and narrowly distributed poly(ethylene glycol)s as standards. The viscosity of polymers in methanol at 25°C was measured using an Ubbelohde dilution viscometer. The wide-angle x-ray diffraction patterns were recorded on powder using the JEOL Model DX-GE-2F.

## RESULTS AND DISCUSSION

The new polymers **8a**, **8b**, and **9** were prepared according to the reaction Scheme 1.

The starting materials, 1-docosanol and thionyl chloride, were heated at 60°C for 2 hours to give docosyl chloride (**1a**) in good yield. It was characterized by its IR spectrum as well as color reaction. A mixture of **1a** or stearyl chloride (**1b**) with diethanolamine in 1-butanol was heated at 100°C for 4 hours to afford the diols bis(2-ethanol)docosylamine (**2a**) or bis(2-ethanol)stearylamine (**2b**) in good yield, respectively. The products **2a** and **2b** were characterized by their IR, <sup>1</sup>H-NMR spectral data, and elemental analyses. To obtain the new ring-opening reagent bis(2-dimethylaminoethyl) stearylamine (**6b**), **2b** was reacted with 12 N hydrochloric acid



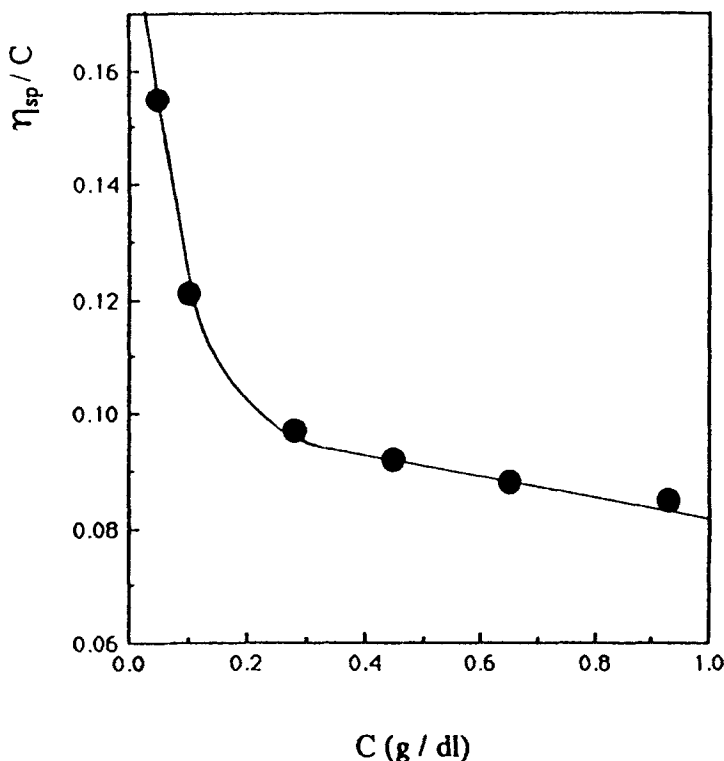


FIG. 2. Reduced viscosity of polymer **8b** in methanol at 25°C.

in acetone to afford the corresponding bis(2-hydroxyethyl) stearylamine hydrochloride (**3b**) in good yield. Product **3b** was characterized by its color test. **3b** was reacted with thionyl bromide in methanol/benzene (volume ratio 1/1) to obtain bis(2-bromoethyl) stearylamine hydrochloride (**4b**) in quantitative yield. To the solution of **4b** in benzene, aqueous sodium hydroxide was added. After completely removing the sodium chloride salt formed, pure compound bis(2-bromoethyl) stearylamine (**5b**) was obtained. The characterization of **5b** was based on its IR and  $^1\text{H-NMR}$  spectral data. The new ring-opening compound **6b** was prepared from **5b** and dimethylamine in methanol/benzene (volume ratio 1/1) and characterized by its IR spectrum data. Diols **2a** or **2b** were reacted with 2-chloro-1,3,2-dioxaphospholane in THF in the presence of triethylamine to give bis[2-(2'-oxy-2'-oxo-1',3',2'-dioxaphospholane) ethyl] docosylamine (**7a**) or bis[2-(2'-oxy-2'-oxo-1',3',2'-dioxaphospholane) ethyl] stearylamine (**7b**) in nearly quantitative yield. They were characterized by their IR spectral data according to the method of Nguyen Thanh and Chabrier [14]. The ring-opening reaction of **7a** and **7b** with  $N,N,N',N'$ -tetramethylhexamethylenediamine in polar aprotic solvents such as acetonitrile, DMF, and DMSO at 75°C for 36 hours afforded new polymers **8a** and **8b** in good yield, respectively. Polymers **8a** and **8b** were very hygroscopic. Polymer **9** was synthesized by reaction of **7b** with **6b**. Polymer **9** was also obtained at 75°C in

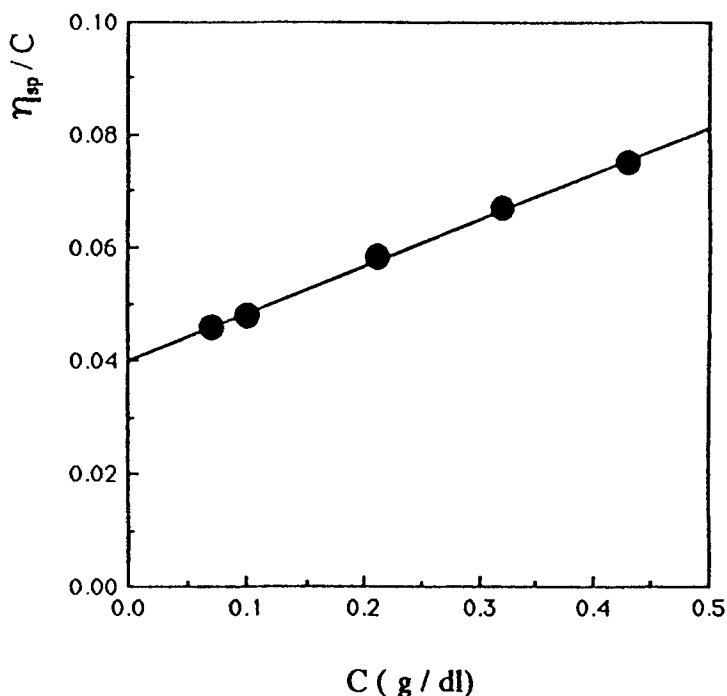


FIG. 3. Reduced viscosity of polymer **9** in methanol at 25°C.

DMF. The characterizations of polymers **8a**, **8b**, and **9** were based on their IR spectral data and elemental analyses. The IR spectra of polymers **8a**, **8b**, and **9** showed adsorption bands due to  $-\text{CH}_2-$  at 2850,  $-\text{P}=\text{O}$  at 1240, and  $-\text{PO}-\text{CH}_2-$  at  $1080\text{ cm}^{-1}$ , respectively. Figure 1 shows the IR spectra of polymers **8b** and **9**.

According to GPC, the weight-average molecular weights of polymers **8a**, **8b**, and **9** were 17,500, 14,700, and 25,600, respectively.

Viscosity measurements of the polymers were performed at 25°C in methanol. Examples of the reduced viscosity of polymers **8b** and **9** are shown in Figs. 2 and 3, respectively. As can be seen, Fig. 2 shows a tendency of the reduced viscosity,  $\eta_{sp}/C$ , vs the concentration,  $C$ , to increase rapidly upon dilution for polymer **8b**. Polymer **8a** displays a similar behavior. However, Fig. 3 shows a linear increase of the reduced viscosity,  $\eta_{sp}/C$ , vs the concentration,  $C$ , for polymer **9**.

These findings suggest that synthesized polymers **8a** and **8b** containing phosphatidylcholine analogues in the main chain and one long alkyl group in the side chain per molecular unit show properties similar to the usual polyelectrolytes. These results agree with those obtained from various polyelectrolytes such as vinyl polymers containing phosphatidylethanolamines [15] or phosphatidylcholines [16] in the side chain and poly(phosphatidylcholine) analogues [9]. On the other hand, the result of polymer **9** containing phosphatidylcholine analogues in the main chain and two long alkyl groups in the side chains per molecular unit agrees with those which

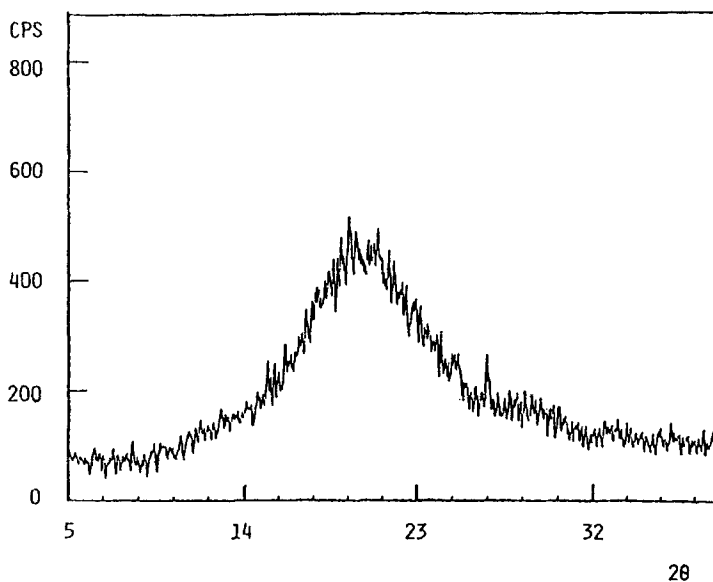


FIG. 4. The wide-angle x-ray diffraction patterns of polymer **8b**.

have been reported by Ehrlich and Doty [17] for isoionic polyampholytes of copolymers of methacrylic acid and 2-dimethylaminoethyl methacrylate. These results may be attributed to the fact that the hydrophobic properties of polymer **9** have been greatly increased due to the introduction of two long alkyl groups into every molecular unit.

The thermal properties of diols **2a** and **2b**, monomers **7a** and **7b**, and polymers **8a**, **8b**, and **9** were determined by polarizing microscopy. As shown in Table 1, diols **2a** and **2b** show transition temperatures from the solid to the mesophase at 66 and 42°C, respectively, but no transition temperature to the isotropic phase is observed because of their pyrolysis. Monomers **7a** and **7b** show a transition temperature from the solid to the mesophase at 70 and 62°C, and transition temperatures to the isotropic phase at 190 and 170°C, respectively. Polymers **8a**, **8b**, and **9** exhibit a thermotropic liquid-crystalline state from 65°C to ca. 280°C.

The wide-angle x-ray diffraction pattern of polymer **8b** is shown in Fig. 4. The polymer does not show a distinctive peak. Nevertheless, the existence of slight crystallinity is suggested by a few small peaks in the range of  $2\theta = 18\text{--}21^\circ$ .

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