# Preparation and Characterization of Amphiphilic Acrylamidic Polymers with Lipid Side Chains

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*Received May 25, 1995; Revised Manuscript Received August 25, 1995*[⊗]

ABSTRACT: A phospholipid-like acrylamidic monomer with both a long alkyl chain as the hydrophobic group and a phosphatidylcholine analogue as the hydrophilic group was newly synthesized and characterized. The homopolymerization and copolymerization with acrylamide were carried out in the presence of a radical initiator. The obtained polymers were characterized by FT-NMR, IR, and melting points. From the X-ray diffraction measurements, the structures proposed for monomer, homopolymer, and copolymer are basically constructed from alternately stacked bilayers with hydrophilic and hydrophobic regions of the monomer or the side chain, the bilayer structures of which are similar to that found for lipid bilayers. The thermal properties of monomer and polymers were also studied by DSC measurements.

## Introduction

Phospholipids have been recently attracting much interest in fields such as chemistry and biochemistry.[1–4] It is because phospholipid, together with protein, is a main component of the biomembrane[5,6] and is physiologically active. The most characteristic property of phospholipid from a physicochemical point of view is its amphiphilic behavior, resulting from the presence of a water-repelling (hydrophobic) part and a water-attracting (hydrophilic) part of the molecule. Depending on this amphiphilic character, not only stable bilayer structure but also smectic liquid-crystalline order can be freely formed by itself, and then amphiphilic protein molecules can insert into the bilayer of phospholipid. Since energy, material, and information can be exchanged selectively and communicated high efficiently through the biomembrane, it is important for the study of molecular arrangements and phase behavior in the solid state of phospholipids and composed phospholipid analogues.

Since the first report in 1977, we have studied the syntheses and properties of a number of phospholipid analogue polymers containing phosphatidylethanolamine, phosphatidylcholine, and their analogous moieties in polymer main chains or in side chains.[7–15] Among them, most of the synthesized vinyl polymers containing the phosphatidylcholine group or analogue in side chains are based on methacrylic back bones. An interesting and important result was that some amphiphilic methacrylic copolymers with a phosphatidylcholine analogue in the hydrophilic side chains were found to exist as stacked bilayer structures similar to that found for lipid bilayers.[13] To obtain some phospholipid analogue polymers having more ordered arrangements, in this work, we synthesized a novel amphiphilic monomer which bears the eicosyl group in the hydrophobic part and the hydrophilic acrylamide group together with a phosphatidylcholine analogue in the polar head part. The monomer was homopolymerized and copolymerized with acrylamide (AAm) in the presence of α,α′-azobisisobutyronitrile (AIBN) as a radical initiator. The present paper is mainly concerned with the structures of the condensed phase and the thermal properties of such monomer and polymers.

## Experimental Section

**Characterization.** $^1$H NMR spectra were recorded with a JEOL α −400 (400 MHz) spectrometer. Proton chemical shifts, reported in parts per million, were referenced to tetramethylsilane directly as an internal standard. Multiplicities of resonance peaks are indicated as singlet s, double doublet dd, triplet t, broad singlet br s, multiplet m, broad multiplet br m. Infrared (IR) spectra (KBr disks) were obtained at room temperature by using a Jasco A-202 spectrometer and were reported in wavenumbers (4000−400 cm$^{-1}$). In the IR data presentation, bracketed s and vs indicate the extent of absorption as strong and very strong. The viscosity measurement was performed with a Ubbelohde-type viscometer by using a mixture of chlorobenzene and methanol in the absence (4:1, v/v) and presence (1:1, v/v) of 0.2 M sodium bromide at 25 °C. Phase transition temperatures were determined by differential scanning calorimetry (DSC), using a Rigaku Thermoflex apparatus DSC-8230B. The sample quantity was 5 mg with a 10 °C/min rate of heating. For an X-ray diffraction measurement, the specimen was completely sealed with mica in the sample holder. The specimen was stable during X-ray diffraction measurement as judged from the reproducibility of the diffraction pattern. The X-ray powder diagram was photographed with nickel-filtered Cu Kα radiation (37.5 kV, 20 mA), using a flat-plate camera of 7.21 cm passage at room temperature.

**Materials.** Acetonitrile, chloroform, chlorobenzene, and benzene were distilled over phosphorus pentoxide. Tetrahydrofuran (THF) was distilled from lithium aluminum hydride. Anhydrous methanol was obtained by distillation in the presence of magnesium and iodine. Acetone was dried by distillation from anhydrous potassium carbonate. [(*N*,*N*-Dimethylamino)propyl]acrylamide was obtained from Kohjin Co., Tokyo, Japan. 2-Chloro-2-oxo-1,3,2-dioxaphospholane (**1**), bp (1.0 mbar) 102.5−105.0 °C, was prepared according to the method of Lucas et al.[16] and Edmundson.[17] All other solvents and chemicals were guaranteed or extra pure reagent grade and were used without further purification. All reagents were purchased from Nacalai Chemical Co. unless otherwise noted.

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[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1995.

0024-9297/95/2228-7711$09.00/0 

**2-Eicosoxy-2-oxo-1,3,2-dioxaphospholane (2).** 2-Eicosoxy-2-oxo-1,3,2-dioxaphospholane was obtained by the following procedure. In a dry 300-mL three-necked flask equipped with a mechanical stirrer, a drying tube, and a dropping funnel were placed 15.0 g (0.05 mol) of 1-eicosanol, 6.06 g (0.06 mol) of triethylamine, and 150 mL of dry THF. After cooling at 0 °C by an ice–water bath, 7.1 g (0.05 mol) of **1** was slowly added in dropwise with stirring over a period of 1 h. During the reaction, triethylamine hydrochloride precipitated as a white solid. The reaction mixture was maintained at 0 °C during the addition, and then it was allowed to warm 20–25 °C. Following stirring at this temperature for 2 h, the reaction mixture was filtered, and then the residue was washed with 15 mL of THF. After evaporation of the solvent, the product as a white powder was obtained. Yield: 22.8 g (83.5%). IR (KBr): 2910 and 2850 (vs, $\nu_{C-H}$, $(CH_2)_{19}CH_3$); 1460 (s, $\delta_{C-H}$, $(CH_2)_{19}CH_3$); 1275 (s, $\nu_{C-O}$, OPO), 1050 $cm^{-1}$ (vs, $\nu_{P-O}$, POC). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 0.88 (t, 3H, $CH_3$); 1.17–1.35 (m, 34H, $CH_2CH_2(CH_2)_{17}CH_3$); 1.57 (br m, 2H, $OCH_2CH_2(CH_2)_{17}$) and 4.13–4.30 ppm (br m, 6H, $OCH_2CH_2O$ and $POCH_2(CH_2)_{18}$).

**2-[(3-Acrylamidopropyl)dimethylammonio]ethyl Eicosyl Phosphate (3).** After 22.8 g (0.04 mol) of **2** and 30 mL of dry acetonitrile were placed into a 300-mL glass pressure bottle, 12.5 g (0.08 mol) of [(*N,N*-dimethylamino)propyl]acrylamide dissolved in 30 mL of dry acetonitrile was quickly added into the same bottle. The pressure bottle was closed and then shaken in a thermostat maintained at 70 °C for 40 h. After the reaction, it was cooled to room temperature and then the pressure bottle was opened. The solution was concentrated to give a crude product as a yellow solid. The crude product was dissolved in the mixture of chloroform and methanol and then reprecipitated from dry acetone. This operation was repeated three times to afford pure **3** as a white solid. Yield: 14.9 g (66.5%). mp: 120–122 °C. IR (KBr): 2910 and 2850 (vs, $\nu_{C-H}$, $(CH_2)_{19}CH_3$); 1460 (s, $\delta_{C-H}$, $(CH_2)_{19}CH_3$); 1660 (vs, $\nu_{C=O}$, CONH); 1625 (vs, $\nu_{C=C}$, $CH_2$=CH); 1230 (vs, $\nu_{P-O}$, $O^-P$=O), and 1050–1080 $cm^{-1}$ (vs, $\nu_{C-O}$, POC). $^1H$ NMR (400 MHz, $CDCl_3$ and $CD_3OD$): $\delta$ 0.88 (t, 3H, $J$ = 6.83 Hz, $CH_3$); 1.17–1.35 (m, 34H, $CH_2CH_2(CH_2)_{17}CH_3$); 1.57 (br m, 2H, $OCH_2CH_2(CH_2)_{17}$); 2.09 (br m, 2H, $CONHCH_2CH_2$); 3.28 (s, 6H, $N^+(CH_3)_2$); 3.40 (br m, 2H, $CONHCH_2$); 3.60–3.87 (br m, 4H, $CH_2{}^+NCH_2$ and 2H, $POCH_2(CH_2)_{17}$); 4.24 (br m, 2H, $^+NCH_2CH_2OP$); 5.55 (dd, 1H, CH=CCONH, trans); 6.24 (dd, 1H, C=CHCONH); 6.42 (dd, 1H, $J$ = 17.07 and 10.24 Hz, CH=CCONH, cis); 9.11 ppm (br s, 1H, CONH). Anal. Calcd for $C_{30}H_{61}O_5N_2P\cdot H_2O$: C, 62.23; H, 10.97; N, 4.84. Found: C, 62.29; H, 11.10; N, 4.81.

**Polymerization Procedure.** Homopolymerization of monomer **3** was carried out in a mixture of chlorobenzene and methanol (4:1, v/v), with AIBN (2% of monomer molar ratio) as an initiator in a sealed ampule by shaking at 70 °C for 15 h. After the ampule was opened, the solution was poured into anhydrous acetone (polymerized solution/acetone, 1:10, v/v) to precipitate the homopolymer. The crude product was purified by reprecipitation with the mixed solvent of acetone, methanol, and chloroform (10:1:1, v/v/v) three times, and the pure polymer **4** was obtained as a white solid. Yield: 72.7%. mp: >250 °C.

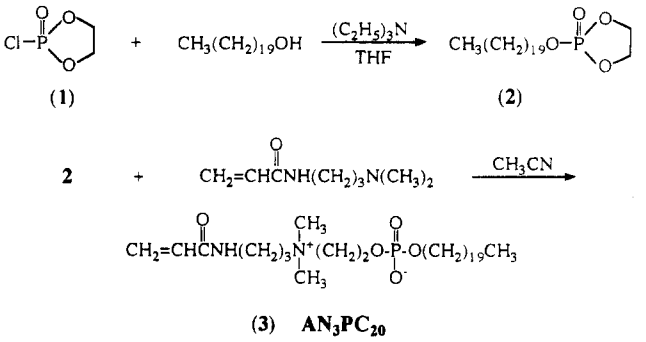
Using the same procedure, copolymerization of monomer **3** with acrylamide (AAm) was carried out, and the copolymer **5** was obtained as a white solid. The structure of copolymer **5** was investigated by IR (KBr) and $^1H$ NMR (in $CDCl_3$ and $CD_3OD$), while the composition was determined by elemental analysis. Yield: 74.6%. mp: >250 °C. Anal. Found: C, 61.93; H, 10.26; N, 7.31.

## Results and Discussion

2-[(3-Acrylamidopropyl)dimethylammonio]ethyl eicosyl phosphate (**3**) was synthesized according to Scheme 1.

2-Chloro-2-oxo-1,3,2-dioxaphospholane (**1**) was prepared according to the procedures described by Lucas et al.[16] and Edmundson.[17] 2-Eicosoxy-2-oxo-1,3,2-dioxaphospholane (**2**) was obtained by the reaction of **1** with

**Scheme 1. Synthesis for Monomer $AN_3PC_{20}$**




(3) $AN_3PC_{20}$

1-eicosanol. According to the method of Thoung and Chabrier,[18] the reaction of **2** with [(*N,N*-dimethylamino)propyl]acrylamide was carried out in anhydrous acetonitrile at 70 °C for 40 h to give 2-[(3-acrylamidopropyl)dimethylammonio]ethyl eicosyl phosphate (**3**) as a white solid in good yield. The monomer **3** was investigated by IR, $^1H$ NMR, and elemental analysis.

Monomer **3** was homopolymerized with AIBN (2% of monomer molar ratio) as an initiator by shaking at 70 °C for 15 h to give the corresponding homopolymer **4** in good yield. The homopolymer was purified by precipitation and reprecipitation from the mixed solvent of acetone, methanol, and chloroform (10:1:1, v/v/v). In this process, only the homopolymer **4** was precipitated, while the corresponding monomer and oligomer are still dissolved. The homopolymer was investigated by IR, $^1H$ NMR, and melting point. The IR spectrum showed that the absorption band of acrylic C=C double bond is inexistent, while the absorption bands of other groups appear as well as the monomer **3**. In the $^1H$ NMR spectrum, only the peaks of C=C double bonds cannot be observed, and the other peaks are similar to those of monomer **3**.

Using the same method, copolymerization of monomer **3** with AAm was performed, and then the obtained copolymer **5** was purified by reprecipitation in anhydrous acetone as was the homopolymer **4**. The pure copolymer **5** as a white solid was determined by IR, $^1H$ NMR, and elemental analysis. Its IR spectrum did not show the absorption band of C=C double bonds due to the acrylamide group, while it showed two characteristic absorption bands at 1640 and 1655 $cm^{-1}$, attributed to the stretching vibration of $CONH_2$ and CONHR groups, respectively. In the $^1H$ NMR spectrum of copolymer **5**, the peaks of the C=C double bond disappeared, while the others remained.

The polymerization procedure for the polymers is shown in Scheme 2.

The structures of the condensed phases of monomer and polymers were investigated by X-ray diffraction (XRD) method at room temperature. In the XRD pattern of monomer **3**, a strong ring at 50.5 $Å^{-1}$ together with a weak ring at 15.9 $Å^{-1}$, which was taken to be the third-order reflection of that at 50.5 $Å^{-1}$ in the small-angle region, and a strong ring at 4.24 $Å^{-1}$ in the wide-angle region were observed as shown in Figure 1. On the basis of the XRD results, it can be proposed that the condensed phase of monomer **3** is constructed from stacked layers and the hydrocarbon chain part of it is in a crystalline state within the layer.

This monomer has only one hydrocarbon chain for one bulky polar head group. The rough theoretical value of the whole length of the monomer and that of the planar zig-zag hydrocarbon chain are about 39 and 26

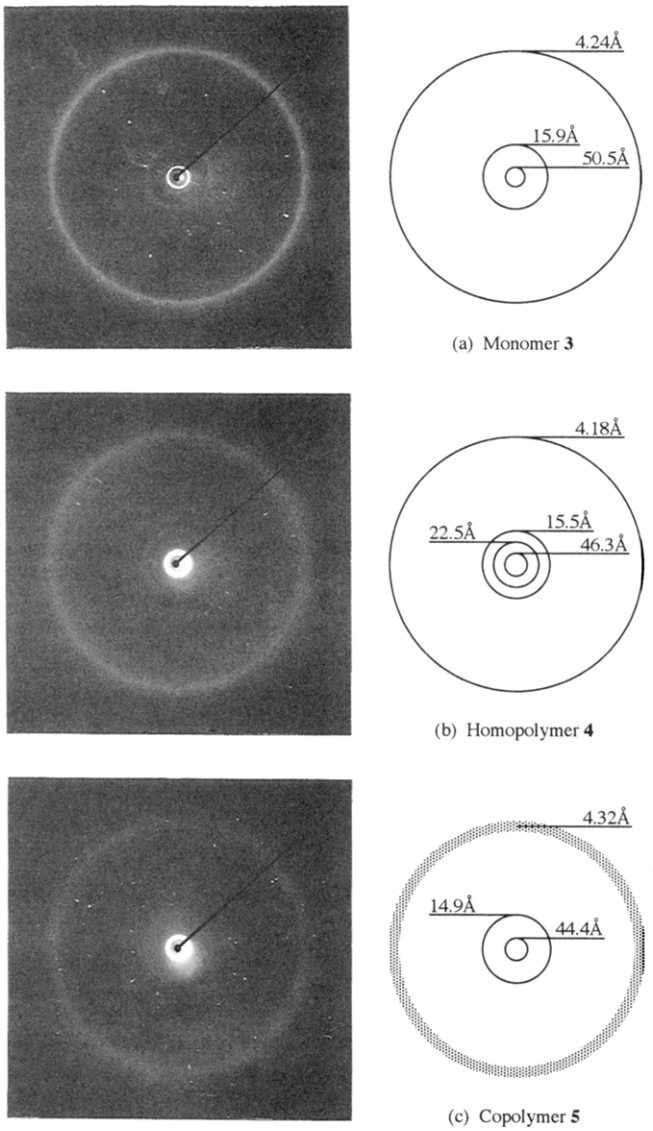
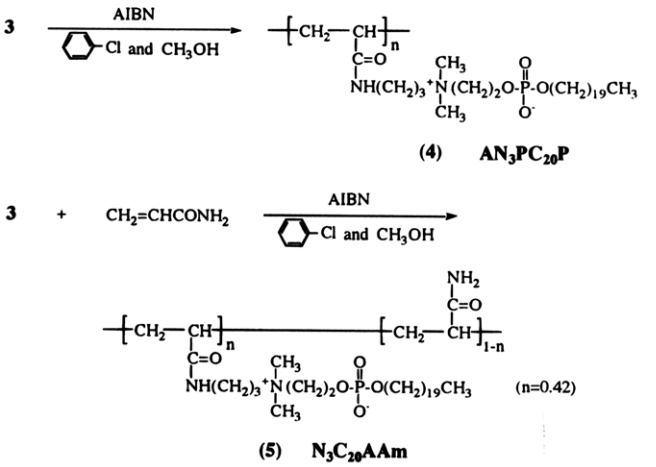



**Figure 1.** X-ray diffraction patterns for (a) monomer **3**, (b) homopolymer **4**, and (c) copolymer **5** obtained with a flat camera by Ni-filtered X-rays of Cu Kα (camera length 72.1 mm).

Å, respectively. If the layer is constructed of a bilayer structure, 39 Å is too big to explain the observed value of the bilayer thickness of 50.5 Å. Therefore, in the proposed model, hydrocarbon chains of top and bottom monomers are interdigitated with each other, giving a stable bilayer structure as shown in Figure 2, which is just the same structure as that of lysophosphatidylcholine.[19] Thus, the observed long spacing, i.e., the bilayer thickness of 50.5 Å, roughly corresponds to the sum of ~26 Å of the interdigitated hydrocarbon chain part and the two bilayered polar head parts with ~10 Å each in their length along the layer normal. As for the length of polar head part of 10 Å, the estimation was made based on the reported values for the length of the glycerophosphorylcholine group[20] and the polar head group of phospholipid.[21,22] The orientation of the hydrocarbon chains is normal to the bilayer plane.

**Scheme 2. Homopolymerization Route of Monomer 3 and Copolymerization Route of Monomer 3 with AAm**




The difference between the observed value of layer thickness and the theoretical one would be reduced if we know the real length of the interdigitated region of the hydrocarbon chain and the precise conformation of the polar head group. The second- and fourth-order reflections from the general lipid bilayer, e.g., phosphatidylcholine and phosphatidylethanolamine in a crystalline state, are usually stronger than the third-order one. This intensity distribution comes probably from a specific electron density profile along the normal bilayer, i.e., a profile with a very low electron density at the center of the bilayer which is a crevice between both ends of the hydrocarbon chains facing each other and with a slightly lower electron density between two polar head groups of adjacent bilayers.[12]

For the case of monomer **3**, however, hydrocarbon chains are interdigitated and there is no crevice at the central part of the electron density profile along the normal bilayer. This electron density profile results in a weaker second-order reflection than the third-order one.

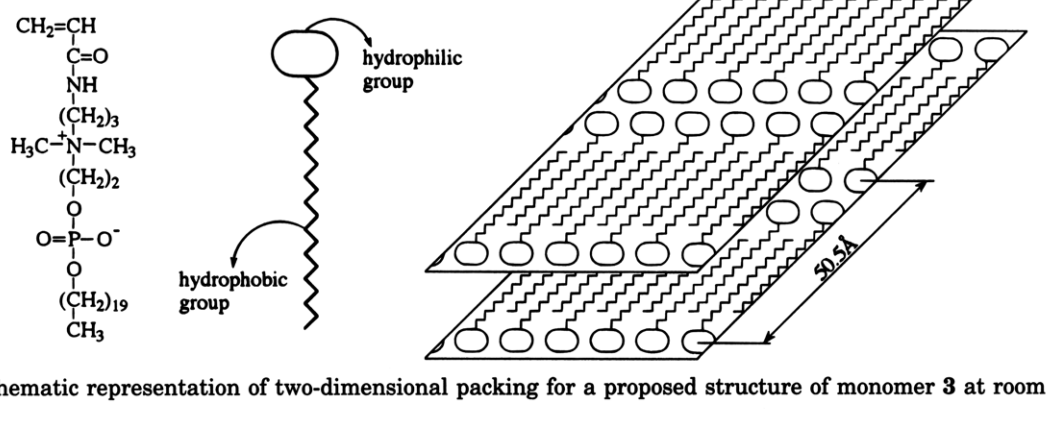



**Figure 2.** Schematic representation of two-dimensional packing for a proposed structure of monomer **3** at room temperature.

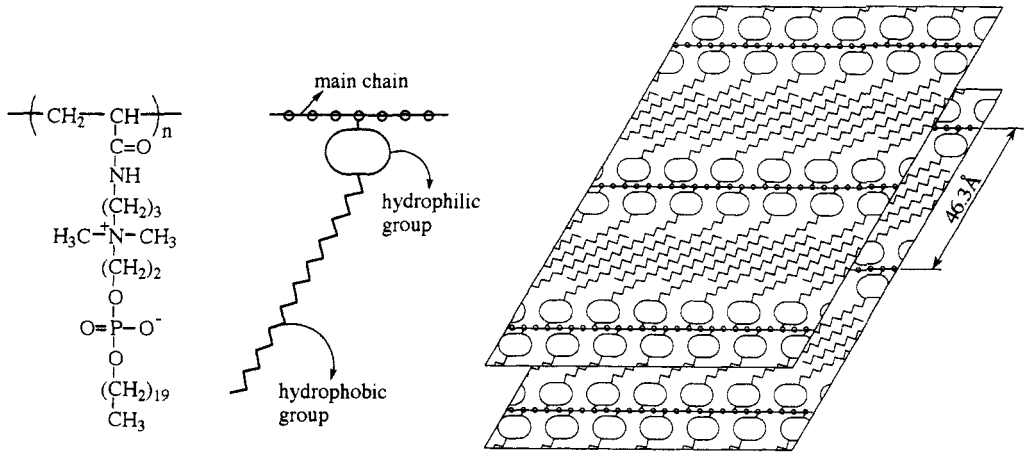



**Figure 3.** Schematic representation of two-dimensional packing for a proposed structure of homopolymer **4** at room temperature.

The structure of homopolymer **4** was estimated by analyzing XRD data as shown in Figure 1. In the small-angle region, we could observe a strong ring at 46.3 $Å^{-1}$ together with two weak rings at 22.5 $Å^{-1}$ and at 15.5 $Å^{-1}$ which were the second and the third reflections of that at 46.3 $Å^{-1}$, respectively, and a strong ring at 4.18 $Å^{-1}$ in wide-angle region. Almost overlapped with the strong ring at the spacing of 46.3 Å, an additional strong reflection seemed to exist just at the inside of the former one. It is thought to come from another condensed phase of this homopolymer due to a lyotropic phase transition during the XRD measurement. In the case of homopolymer **4** with the same side chain as monomer **3**, weak second- and third-order reflections were observed. The differences in the intensity distribution in XRD data of monomer **3** and homopolymer **4** would come from whether the main chain exists and connects side chains. Based on the XRD result, the structure is proposed to be constructed from stacked layers and hydrocarbon chain part in the layer is in a crystalline state. The side chain, i.e., monomer **3**, is connected to the main chain syndiotactically. The rough theoretical values of the whole length of the side chain and hydrocarbon chain are ~39 and ~26 Å, respectively, as is the case with monomer **3**. A length of 39 Å × 2 is also too big to explain the observed value of bilayer thickness of 46.3 Å, and the side chain has only one hydrocarbon chain for one bulky polar head group. Therefore, in the proposed model, hydrocarbon chains of the top and bottom main chains should be interdigitated with each other. The observed value of the bilayer thickness of homopolymer **4** is 46.3 Å, which is shorter than that of monomer **3**. For the case of the homopolymer, there should be an additional contribution of the main chain part to the whole thickness. Therefore, it is proposed that the side chains of the homopolymer are slightly tilted from the normal of the bilayer plane as shown in Figure 3. The tilting angle is not clear but may be small.

For copolymer **5**, a strong ring with spacing of 44.4 Å and a weak ring at 14.9 $Å^{-1}$, which was taken to be the third-order reflection of that at 44.4 $Å^{-1}$ in the small-angle region, and a diffuse ring with spacing of 4.32 Å in the wide-angle region were observed by XRD method. The XRD result shows the existence of an ordered structure with a spatial repeating period of ~44.4 Å, which seems to correspond to the thickness of stacked layer structure, and also shows hydrocarbon chains are nearly in an amorphous state. For copolymer **5**, a stacked bilayer structure with longer side chains and main chain could be presumed from the XRD results. As for shorter side chains, no conclusion was possible from the present data. XRD results, therefore, imply that the copolymer contains a part with longer side chains and that with shorter ones, hence, a block copolymer. In this case, information from the XRD measurement is too little to analyze the structure of the condensed phase in more detail.

It has been reported that natural or synthetic lipids and phospholipids display a polymorphic phase transition in aqueous systems,[23,24] solid states,[25] and monolayers[26] with variation of temperature. In order to study the thermal properties of the synthesized monomer and polymers, DSC measurements were carried out to monitor the phase transition behavior from 0 to 250 °C with heating at 10 °C/min. All the DSC traces for monomer and polymers are shown in Figure 4, and the results are summarized in Table 1. As can be seen from Figure 4a, three endothermic peaks (around 44.6, 56.1, and 82.2 °C) and an unclear endothermic peak (from 125.1 to 198.0 °C) were observed on heating for monomer **3**. The four endothermic peaks overlapped, so that the latent heat for each peak could not be obtained. Depending on the XRD results in the wide-angle region at room temperature, polarizing microscopy observation (i.e., monomer **3** displays liquid-crystalline behavior from about 30 to 80 °C), it can be suggested that the arrangement of hydrocarbon chains is transformed from a crystalline state to a more or less disordered liquid-crystalline state by the polymorphic phase transition, giving rise to two endothermic peaks around 44.6 and 56.1 °C. The bigger endothermic peak at ~82.2 °C may correspond to the disordering of the stacked layer structure by hydrocarbon chains. Furthermore, according to the results of Kishore et al.[27,28] and melting point measurement (i.e., monomer **3** melts at 120–122 °C), the unclear endothermic peak observed from 125.1 to 198.0 °C indicates the melting process for monomer **3** and the following process of pyrolysis of phosphates.

A sharp endothermic peak was observed in the low-temperature region of a DSC plot for the polymers examined (Figure 4b,c). The location of the endothermic peak is at ~59.1 °C for homopolymer **4** and at ~53.4 °C for copolymer **5**. According to the results of X-ray analysis as discussed above and the observations of polarizing microscopy (i.e., both the polymers display liquid-crystalline behavior in the range of about 50–200 °C, but the liquid-crystalline behavior is observed clearly for homopolymer **4** and unclearly for copolymer **5**), the arrangement of hydrophobic groups for both

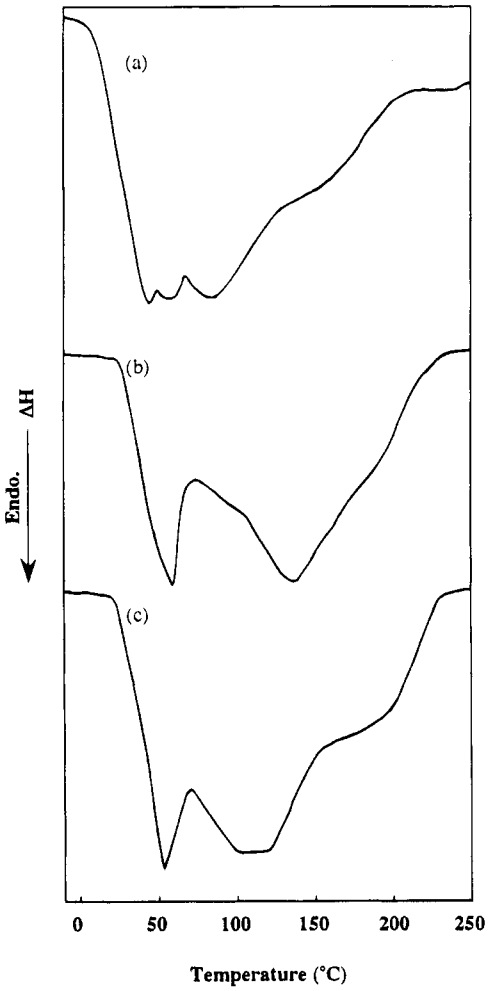



**Figure 4.** DSC curves of (a) monomer **3**, (b) homopolymer **4**, and (c) copolymer **5**.

**Table 1. Summary of the Results of XRD and DSC Measurements**

| | monomer **3** | homopolymer **4** | copolymer **5** |
|---|---|---|---|
| intensity at the small angle | sharp rings<br>50.5 Å<br>15.9 Å | sharp rings<br>46.3 Å<br>22.5 Å<br>15.5 Å | sharp rings<br>44.4 Å<br>14.9 Å |
| intensity at the wide angle | sharp ring<br>4.24 Å | sharp ring<br>4.18 Å | halo<br>4.32 Å |
| DSC data | ~44.6 °C<br>~56.1 °C<br>~82.2 °C<br>125.1–198.0 °C | at 59.1 °C<br>~136.7 °C<br>~200.0 °C | at 53.4 °C<br>99.7–162.5 °C<br>~200.0 °C |

polymers **4** and **5** in their side chains is transformed from a crystalline state to a liquid-crystalline state as well as monomer **3**. Furthermore, the polymers give only sharp endothermic peaks because the hydrocarbon chains are pinned by their main chains at one end. A similar phase transition is observed at 38.1 °C for a polymeric phospholipid analogue with a stearyl group as the hydrophobic side chains, as shown by our early work.[12] The shifts of the phase transition temperature to a higher temperature may come partly from the characteristic structure of the present polymers which contain the longer alkyl groups in their side chains.

The DSC traces for both polymers show a broad endothermic peak at the higher temperature (Figure 4b,c). Namely, for homopolymer **4** a phase transition occurred around 136.7 °C, and for copolymer **5** it occurred from 99.7 to 162.5 °C. Referring to their melting points (neither homopolymer **4** nor copolymer **5** melted until heated to 250 °C), these broad endothermic peaks may correspond to the disordering of the stacked layer structure constructed from main chains and side chains. The broadening of these peaks can partly come from the distribution of the main chain length. For copolymer **5**, the peak is more broad than that of homopolymer **4**, it may correspond to the multicomponent of the side chains. Furthermore, an unclear endothermic peak at ~200.0 °C is also shown in the DSC curve of homopolymer **4** and copolymer **5**, respectively. They correspond to the pyrolysis of phosphates as well as monomer **3**.

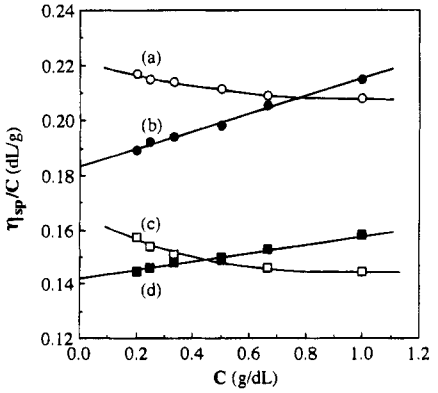



**Figure 5.** Reduced viscosity of homopolymer **4** and copolymer **5** at 25 °C: (a) homopolymer **4** in chlorobenzene and methanol (4:1, v/v); (b) homopolymer **4** in chlorobenzene and methanol (1:1, v/v) in the presence of 0.2 M sodium bromide; (c) copolymer **5** in chlorobenzene and methanol (4:1, v/v); (d) copolymer **5** in chlorobenzene and methanol (1:1, v/v) in the presence of 0.2 M sodium bromide.

In previous work,[10] we found that vinyl polymers having a phosphatidylcholine group in the side chains show the properties of polyelectrolytes in their viscosity behavior in polar solvents. It is because that the $PO_4^-$ group dissociates as a weak acid and the $N^+(CH_3)_3$ group dissociates as a strong base.[15] In this study, the viscosity measurements of homopolymer **4** and copolymer **5** were performed first in chlorobenzene and methanol (4:1 v/v) at 25 °C. As shown in Figure 5a and c, both the $\eta_{sp}/C$ of homopolymer and copolymer were found to increase with the dilution of concentration. This result suggests that these polymers containing phosphatidylcholine-like moieties show properties similar to usual polyelectrolytes. These phenomena may result from the mutual repulsion between $N^+$ and $N^+$, particularly the possible chain expansion at low concentrations. We measured the inherent viscosities for these polymers in the mixed chlorobenzene and methanol solvent (1:1, v/v) in the presence of 0.2 M sodium bromide. The reduced viscosities decreased linearly with a decrease in polymer concentrations (Figure 5b,d), and their $[\eta]$ at 25 °C were 0.142 for homopolymer **4** and 0.183 for copolymer **5**.

The present work may be useful for designing and constructing synthetic phospholipid membranes. Namely, the monomer, homopolymer, and copolymer could be considered as a fluid model system, a stable model system, and a modifiable model system of biological membranes, respectively. In addition, the charged monomer and polymers with stacked bilayer structure of hydrophilic and hydrophobic regions and a display of liquid-crystalline behavior within a wide temperature range could be applied widely in pharmaceutical chemistry, such as for carrying and delivery of drugs.

## Conclusion

Amphiphilic phospholipid-like acrylamidic monomer, homopolymer and copolymer were prepared and characterized. From the results of X-ray diffraction and DSC measurements, it is suggested that the synthesized monomer, homopolymer, and copolymer not only be constructed basically from alternately stacked bilayer structures, which are similar to that found for lipid bilayers, but also exhibit polymorphic phase transition in solid states with variation in temperature. Especially, homopolymer **4** was observed to exist as a more stable stacked bilayer structure than the monomer due to the restriction imposed by the main chains, and its crystallinity in the condensed phase is higher than that in the corresponding phase of the block copolymer **5**. Furthermore, both the polymers with cations and anions in their side chains are polyelectrolytes. The synthesized amphiphilic monomer and polymer could be expected to find application in LB film devices because of their excellent balance of hydrophilicity and hydrophobicity and ease of synthesis. Such investigations are underway.

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MA9507204