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Synthesis and Properties of Polyazomethines Having Flexible (*n*-Alkyloxy)methyl Side Chains

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ABSTRACT: By solution condensation of 2,5-bis((*n*-alkyloxy)methyl)terephthalaldehydes with *p*-phenylenediamine a series of para-linked aromatic polyazomethines having (*n*-alkyloxy)methyl ($CH_2OC_nH_{2n+1}$, $n = 4, 6, 8, 12$) side chains were prepared and their structures and properties were investigated. The presence of the side chains played a role in improving the solubility of the polymers of not too high molecular weight, but the polyazomethines of very high molecular weight could not be made soluble even in trifluoroacetic acid. Thermal stability decreased with increasing side-chain length. The polyazomethines showed basically three thermal transitions: disordering of the side-chain crystal (T_s), solid-mesophase transition (T_m), and mesophase-isotropic transition (T_i). T_s could be observed in the polymers of $n \geq 6$ and T_i only in that of $n = 12$. As usual T_m decreased drastically with increasing side-chain length. UV-vis spectroscopic studies made in sulfuric acid showed that the main-chain azomethine bond has a quite low stability against acid-catalyzed hydrolysis, but the side-chain ether bond has a different hydrolytic stability, depending on the side chains. In the solid state the as-polymerized samples crystallized into a layered structure, and the layer spacing determined by X-ray diffraction increased linearly with increasing side-chain length, suggesting that the side chains are interdigitated.

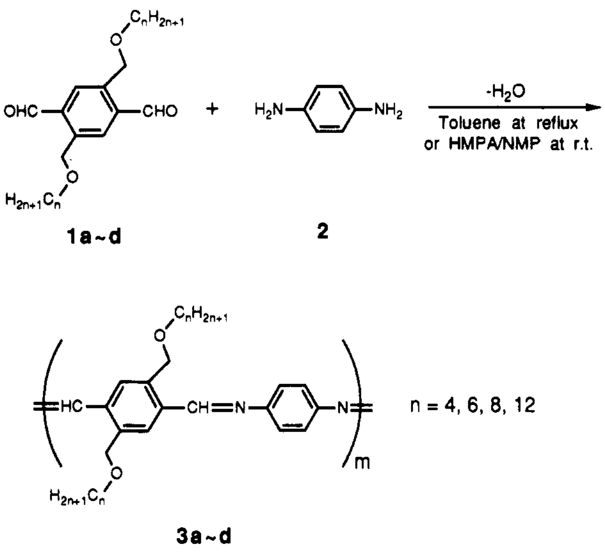
Introduction

In the past several years much interest has been devoted to the study of rigid chain polymers, mainly because of their superior mechanical properties.[1] Many of these materials form mesomorphic phases on heating or dissolving; however, their high melting points and low solubility make them inaccessible for processing by conventional methods. To improve the processibility of these materials, several approaches, such an introduction into the main chain of bent, crankshaft-shaped, laterally substituted, and flexible units, have been used.[1-3] Recently, systematic studies on rigid polymers, mainly on aromatic polyesters, containing flexible side chains have shown that the melting temperatures decrease as the length of the side chains increases and that these polymers are able to form a novel layered mesophase.[4-9] The flexible side chains are thought to act as a bound solvent for the rigid polymeric backbone.[10]

Aromatic polyazomethines, prepared for the first time by Adams and co-workers[11] from terephthalaldehyde and benzidine and dianisidine, were known to be insoluble and infusible. More recently, a variety of polyazomethines forming high-strength fibers have been synthesized by Morgan and co-workers[12] and Wojtkowski.[13] Tractability has been achieved by lowering the melting points through modification and selection of polymer structure in several ways, for example, by unsymmetrical substitution of main-chain aromatic ring units[12] or insertion of flexible units into the rigid backbone.[13]

In this paper we report a series of para-linked aromatic polyazomethines with flexible (*n*-alkyloxy)methyl side chains symmetrically disubstituted on a dialdehyde moiety. For this 2,5-bis((*n*-alkyloxy)methyl)terephthalaldehydes were condensed with *p*-phenylenediamine as shown in Scheme I. The key objective is to prepare and characterize new meltable and soluble polyazomethines.

Scheme I



n of $-CH_2OC_nH_{2n+1}$	Code of **3a~d**
n = 4	**C_4-PAM**
6	**C_6-PAM**
8	**C_8-PAM-A, C_8-PAM-B**
12	**C_{12}-PAM**

Results and Discussion

Monomer Preparation. The synthetic route to dialdehyde monomers is shown in Scheme II, in which the procedure and route to 2,5-bis((*n*-alkyloxy)methyl)-1,4-dicyanobezenes **4a** and **4c** have already been described elsewhere.[14] 2,5-Bis((*n*-alkyloxy)methyl)-1,4-benzenedicarboxylic acids **5a-d** were prepared by base hydrolysis[15] of **4a-d** without or with the aid of 15% hydrogen peroxide solution. The dicarboxylic acids could be purified via formation of their sodium salts. The sodium salts of **5a-d** were formed by treating dicarboxylic acids with Na metal in methanol at room temperature and recovered by precipitating from an excess of 1,4-dioxane. 2,5-Bis((*n*-alkyloxy)methyl)-1,4-benzenedimethanols **6a-d** were prepared by reduction of **5a-d** over $LiAlH_4$ in tetrahydrofuran (THF).[16] 2,5-Bis((*n*-alkyloxy)methyl)terephthalaldehydes

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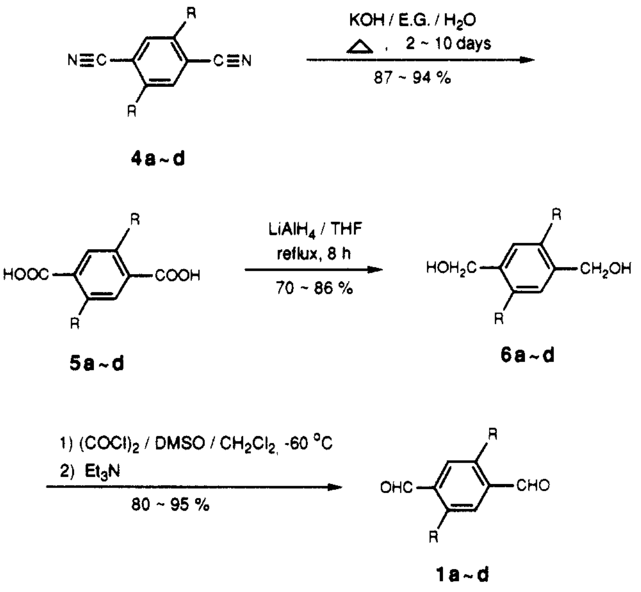
Scheme II



	$R = -CH_2OC_nH_{2n+1}$
4a, 5a, 6a, 7a	n = 4
4b, 5b, 6b, 7b	n = 6
4c, 5c, 6c, 7c	n = 8
4d, 5d, 6d, 7d	n = 12

1a–d were prepared by oxidation of **6a–d** with dimethyl sulfoxide (DMSO) activated by oxalyl chloride.[17,18] Exposure of **1a–d** to light and air changed the color from colorless to violet.

Polymer Preparation. By polycondensation without catalyst all polyazomethines C_n-PAM except C_8-PAM-B were prepared in toluene for removing the water azeotropically. C_8-PAM-B was obtained from a hexamethylphosphoramide (HMPA)/1-methyl-2-pyrrolidinone (NMP) mixture. Physical and thermal properties of the polyazomethines are summarized in Table I. All polymerization reactions proceeded in quantitative yields, and C_6-PAM and C_8-PAM-A were isolated in leaf form while the other polymers were isolated in the usual powder form.

The structure of the polyazomethines obtained was identified by elemental analyses and IR and ^{1}H-NMR spectroscopy. In IR spectra of all the samples showed strong absorption bands at 1607–1611 and 1094–1097 cm^{-1} attributable to C=N and C–O–C, respectively. C_8-PAM-B gave a noticeable absorption at 1691 cm^{-1} resulting from the terminal CHO group. This CHO end group could also be identified in the ^{1}H-NMR spectrum at $\delta = 10.32$. The identification of the terminal CHO group indicates that C_8-PAM-B has a lower molecular weight than the others.

Color and UV–vis Spectra. Polyazomethines C_n-PAM were orange to brown in color. When C_8-PAM-A of orange color was heat-treated at 175 °C, the color deepened with time. This change is related with the increase in molecular weight and hence with the extension of π-electron conjugation along the polymer chain. This could be observed also in FT-IR spectroscopy. The C=N absorption band of C_8-PAM-A in the as-polymerized state appeared at 1608 cm^{-1}, whereas that of C_8-PAM-A after heat-treatment at 175 °C for 80 min shifted to 1611 cm^{-1}.

The effect of side-chain substitution on UV–vis spectral behavior was studied in concentrated sulfuric acid. After a noticeable hydrolysis of the main chain, all the polyazomethines showed a π–π^* transition absorption band at about 300 nm, and the (n-butyloxy)methyl-substituted polymer exhibited an addition π–π^* transition at about 268 nm (K band). This indicates that there is practically no effect of side-chain substitution to observe.

Polyazomethines are known to undergo very facile hydrolysis[19] in the presence of acids, and in our polyazomethines the (n-alkyloxy)methyl group can also be hydrolyzed. The hydrolysis of both the main-chain C=N bond and the side-chain (n-alkyloxy)methyl group was investigated by UV–vis spectroscopy also in concentrated sulfuric acid. In Figure 1 are reproduced the UV–vis spectral curves of (n-octyloxy)methyl-substituted polyazomethine C_8-PAM-A measured in various time intervals. Figure 1 shows clearly that the conjugated C=N absorption band at 442 nm undergoes simultaneously a hypochromic effect and a hypsochromic shift as time passes. This means that the length of π-electron conjugation decreases with an increase in the degree of acid-catalyzed hydrolysis of the main chain. After a sufficiently long time, the hydrolysis reaction proceeds so far as to form the dialdehyde monomer, which can easily be detected by comparison of the monomer curve with the polymer curve taken after 70 h.

In Figure 1 additional broad and low-intensity bands around 510 nm are observable. These bands begin to appear after hydrolysis periods of longer than 10 h. They seem to result from hydroxymethyl groups formed by hydrolysis of the side-chain (n-octyloxy)methyl groups. These hydroxyl groups are known to form intramolecular hydrogen bonding with the C=N bond, and this hydrogen-bonded structure absorbs around 510 nm.[20]

From the above discussions concerning the results shown in Figure 1, it can be said that in concentrated sulfuric acid the rate of hydrolysis of the side-chain (n-octyloxy)methyl group is much lower than that of the main-chain azomethine group.

Solubility and Viscosity. Improvement in the solubility of aromatic polyazomethines having alkyloxy side chains has recently been reported.[21,22] Lee et al.[21] reported that sufficiently long alkyloxy side chains (C_8–C_{18}) improved the solubility so greatly that all their polyazomethines were completely soluble in common organic solvents, whereas Reinhardt and Unroe[22] reported that the polyazomethine with a decyloxy side chain (C_{10}) could not be dissolved completely in any organic solvent. This discrepancy brought us to a belief that the solubility of the side-chain pendant polyazomethines can depend not only on the presence of the side chain but also on the molecular weight. For this study aromatic polyazomethines with various (n-alkyloxy)methyl side-chain lengths were prepared in toluene for attaining high molecular weights by removing the water azeotropically and one sample, C_8-PAM-B, was synthesized in HMPA/NMP mixture to keep the molecular weight reasonably low.

In Table I are summarized solubilities and inherent viscosity values which were measured in trifluoroacetic acid to reduce the possibility of hydrolysis of the main-chain azomethine bonds and the side-chain (n-alkyloxy)methyl groups, though, as already discussed, the latter are not readily hydrolyzed even in concentrated sulfuric acid. Table I shows that the inherent viscosity values lie in the range of 0.12–0.17 dL/g and that the polymers have a good solubility in m-cresol, which may be effected from the presence of the (n-alkyloxy)methyl side chains, because unsubstituted polyazomethine of comparable structure is soluble only in strong acids.[12]

Table I shows also that the polymer C_8-PAM-B obtained from condensation in HMPA/NMP mixture has a lower

Table I
Pyrolysis and Solubility Behaviors of C_n-PAM

		thermal stability in nitrogen		solubility[c]				
polymer code	η_{inh}[b] (dL/g)	temp of 5% weight loss (°C)	residual weight at 700 °C (%)	HMPA	THF	toluene	$CHCl_3$	*m*-cresol
C_4-PAM	0.16	339	45	+	–	–	+	+++
C_6-PAM	0.17	333	40	+	–	–	+	+++
C_8-PAM-A	0.16	332	34	++	–	–	+	+++
C_8-PAM-B[a]	0.12	332	32	+++	+	++	+++	+++
C_{12}-PAM	0.12	302	32	++	–	–	+	+++

[a] Prepared from polycondensation in HMPA/NMP mixture. [b] Determined at 25 °C in CF_3COOH (0.5 g/dL). [c] +++, soluble at room temperature; ++, partly soluble; +, slightly soluble or swellable; –, insoluble.

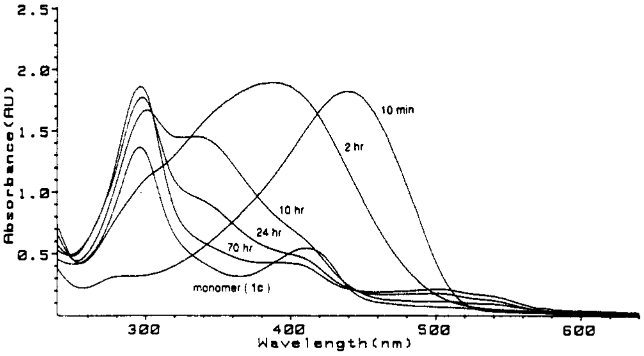


Figure 1. UV–vis spectra of polyazomethine C_8-PMA-A taken at various time intervals after dissolution in concentrated sulfuric acid.

inherent viscosity value (0.12 dL/g) than C_8-PAM-A obtained from polymerization in toluene (0.16 dL/g). The former polymer also shows good solubility in HMPA and chloroform, whereas the latter shows only limited solubility in both solvents, even though both polymers have the same side-chain length ($n = 8$). This fact may indicate the effect of molecular weight on the solubility. To confirm this, C_8-PAM-A was further polycondensed by heating at 175 °C for 80 min. This heat-treated sample had too high a molecular weight to be soluble even in trifluoroacetic acid. Thus, introduction of (*n*-alkyloxy)methyl side chains improves the solubility of rigid polyazomethines with limited molecular weight, but the role of the side chains is not enough in too high molecular weight polyazomethines.

Thermal Stability and Phase Transitions. Table I shows the thermal stabilities of polyazomethines C_n-PAM evaluated by the temperature of 5% weight loss and residual weights at 700 °C. It reveals that both values decrease as the length of the side chain increases. This behavior results from the fact that the volume fraction of side chains acting as internal plasticizer increases with increasing side-chain length.

When a sample of polyazomethine is heated for a DSC scan, it naturally has an increase in molecular weight due to thermal polycondensation. This increase in molecular weights results in a dramatically different thermogram in the next scan of the same sample. Figure 2 shows three DSC thermocurves of sample C_{12}-PAM. Curve 1 was obtained from a scan from 50 to 300 °C. Here phase transitions at 100, 125, and 255 °C can be observed. In analogy to comblike polymers[23] as well as to wholly aromatic polymers having pendant *n*-alkoxy side chains[2,9,10] with similar lengths, the transitions at 107 °C could be assigned to melting of the side-chain crystal (T_s), and the endotherm at 127 °C to the solid–mesophase transition (T_m). The small and broad endotherm at 255 °C had to be ascribed to the mesophase–isotropic melt transition (T_i), because the presence of the mesophase was confirmed by cross-polarized microscopic photographs taken at temperatures between T_m and T_i.

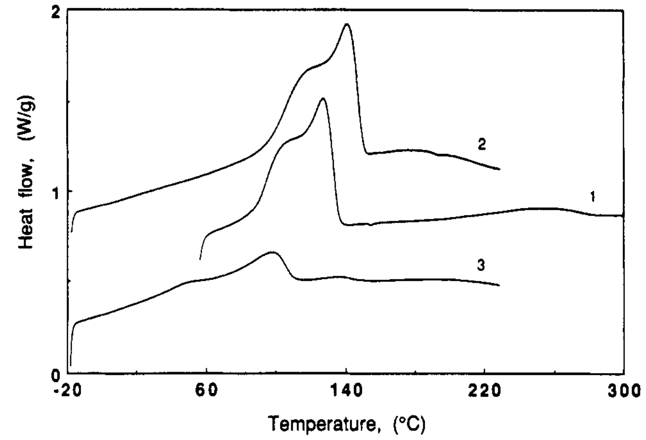


Figure 2. Normalized DSC thermograms of polyazomethine C_{12}-PAM at 20 °C/min scan rate.

To make distinctive the small and very broad endotherm T_i, C_{12}-PAM was annealed at various temperatures. The annealing did not help at all, but instead the T_i disappeared upon annealing, presumably because the molecular weight of the sample increases greatly on heat treatment. Currently, wide-angle X-ray diffraction studies as a function of temperature are under way for the better characterization of this T_i. The formation of a thermotropic mesophase could be detected in all polyazomethines C_n-PAM. C_4-PAM gave no T_s, presumably because the volume fraction of the relatively shorter (butyloxy)methyl group is too small to form a side-chain crystalline state.

To determine T_g of the polymers, a separate sample had to be scanned not from 50 °C but instead from –20 °C to about +230 °C (curve 2, Figure 2), cooled to –20 °C, and finally reheated to 230 °C (curve 3, Figure 2). By this means T_g of C_{12}-PAM could be determined to be 39 °C and T_g of C_4-PAM to be 51 °C. When thermocurve 3 in Figure 2 is compared with thermocurve 1, we can clearly see that T_m cannot be observed anymore. This is because through heating once the molecular weight of C_{12}-PAM has been increased to such a degree that the rate of crystallization is so lowered that practically no crystals are formed.

The change in the DSC thermogram with increase in molecular weight[24] by thermal polycondensation is reproduced in Figure 3 for C_4-PAM, whose T_m measured from the first heating scan lay at 247 °C. If C_4-PAM is repeatedly cooled and rescanned, the T_m shifts, as Figure 3 shows, to lower temperature and at the same time the intensity decreases considerably; after the sixth scan the T_m is not observable anymore. Under the same conditions of scan rate and range, this behavior becomes more remarkable the longer the side chain is, as discussed already.

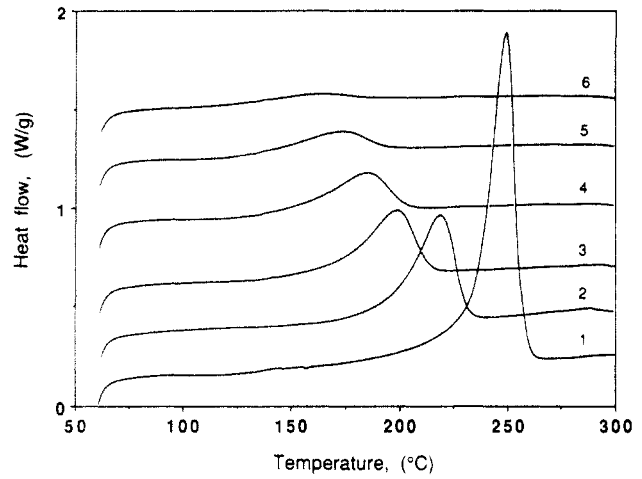


Figure 3. Normalized DSC responses of polyazomethine C_4-PAM to the repeated cyclic scanning at a rate of 40 °C/min. Number on curve denotes nth heating scan.

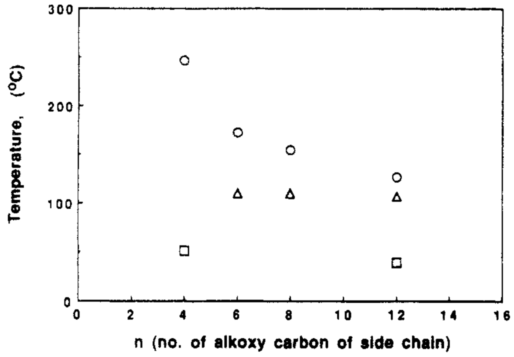


Figure 4. Changes in the transition temperatures of polyazomethines C_n-PAM as a function of n (carbon number of alkoxy side chain): T_g (□), T_s (△), and T_m (○).

The side-chain length affects naturally the thermal transition behavior of the polyazomethines. This effect is presented in Figure 4, in which phase transition temperatures of as-polymerized samples obtained from polycondensation in toluene are plotted against number of carbon atoms of the alkyloxy side chain. Figure 4 shows that with increasing (n-alkyloxy)methyl side-chain length, T_m decreases rapidly and T_g decreases slightly, whereas T_s remains practically unaffected. The reason for the fast decrease of T_m and the slight decrease of T_g comes from the increase in volume fraction of the side chain acting as internal plasticizer and having lower T_g values than the main chain, respectively.

Crystalline Structure. It is generally known that rigid-rod polymers having long flexible side chains crystallize into layered structures,[2,4-9] in which the rigid backbones come together to form backbone layers and the side chains to form a separate crystal region. In Figure 5 are reproduced X-ray diffractograms obtained from the as-polymerized sample powders of C_n-PAM in a reflection mode at room temperature. Exact assignments of all the reflections cannot be made at the moment, and hence detailed structural studies are now under way.

However, the sharp, strong reflection of C_{12}-PAM in the small-angle region, for example, in Figure 5 corresponds to a spacing of 20.77 Å, and this could be assigned for the spacing of the crystal domain filled with (n-dodecyloxy)methyl groups. If we consider the one O atom as one C atom, because the O content is low and the C–O bond length and the C–O–C bond angle are eventually the same as C–C and C–C–C, respectively, we should be able to calculate the spacing of the side-chain crystal domain; in the extended zigzag structure of polymethylene an increase of one C atom results in an increase of 1.25-Å spacing, and hence the spacing of the side-chain crystal domain should be 1.25 Å × 2 × 14 = 35 Å, if the C_{14} side chains were not interdigitated. Because the measured value, 20.77 Å, is much smaller than the calculated value, 35 Å, we naturally come to know that the (n-dodecyloxy)methylene side chains are strongly interdigitated.

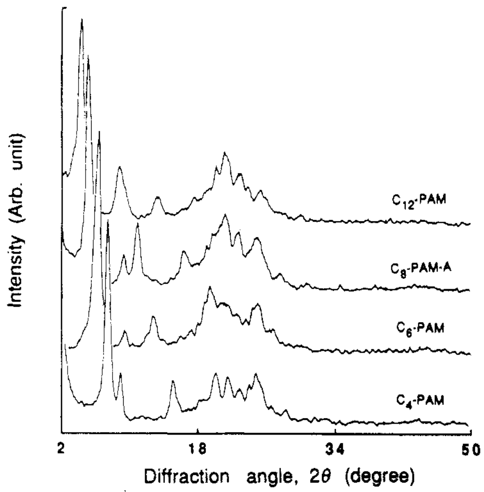


Figure 5. X-ray diffractograms of as-polymerized samples C_n-PAM.

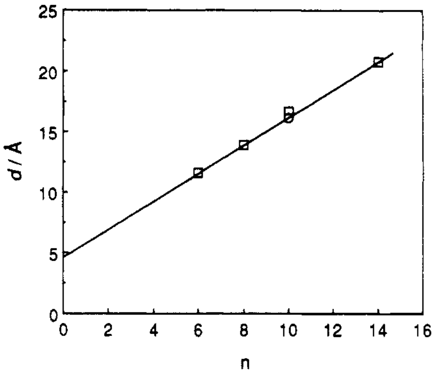


Figure 6. Plot of the Bragg distance d calculated from the sharp reflections in the small-angle region of Figure 5 (□) including that from C_8-PAM-B (○) versus n, the number of backbone atoms on the (n-alkyloxy)methyl side chain.

Figure 5 shows also that the sharp reflections in the small-angle region shift to lower angles as the side chains become longer. This means that the corresponding spacings increase with increasing side-chain length. In Figure 6 these spacings are plotted against n, the number of skeletal atoms in the side chains. Figure 6 shows a good linearity, having a slope of 1.14 Å/atom and an intercept of 4.76 Å. The value of increment 1.14 Å per atom should be similar to the increment 1.25 Å per C atom, if the side chains would have extended perpendicularly to the rigid backbone axis with no tilting with respect to the backbone layer. The difference in the increment leads to the inference that the side chains are arrayed not perpendicularly, but tilted with an angle of 66.3° (or 23.7° from 90°) with respect either to the backbone layer or to the backbone axis.

The intercept value 4.76 Å is ascribed to the width of the rigid backbone. When this width was calculated by using structural data of benzylideneaniline, whose crystal structure has been well characterized,[25] a value of 4.44 Å was obtained. This calculated value coincides quite well with the measured value within experimental error and the suitability of the model compound.

The reflections at $2\theta = 23.5°$ corresponding to 3.5-Å spacing are assignable to the spacings between rigid backbone axes.

Experimental Section

Materials and Measurements. Tetrahydrofuran (THF) (Mallinckrodt) and dichloromethane (Mallinckrodt) were purified under standard conditions. Toluene (Mallinckrodt) was used right after purification by fractional distillation over CaH_2. Dimethyl sulfoxide (DMSO) (Mallinckrodt), HMPA (Aldrich), and NMP (Aldrich) were used after being stored over 4-Å molecular sieves. *p*-Phenylenediamine (Aldrich) was purified by distillation under reduced pressure followed by sublimation. Other reagents (Aldrich) were used as received.

Melting points of monomeric compounds were determined using a Haake-Büchler apparatus without correction. Microanalyses were made using a Carlo Erba EA 1108 microanalyzer. Mass spectra were obtained using a Kratos 25-RFA spectrometer. Infrared spectra (KBr pellets) were recorded on a Shimadzu FT-IR 4300 spectrophotometer. ^{1}H-NMR and ^{1}H-decoupled ^{13}C-NMR spectra were obtained using a Bruker AM 300 (300 MHz) at room temperature (except for **5d**, recorded at 65 °C in DMSO-d_6). Thermal analyses of polymers were carried out under N_2 using a Perkin-Elmer Delta Seires TGA 7 thermogravimetric analyzer at a heating rate of 10 °C/min and a Perkin-Elmer PEPC Series DSC 7 thermal analyzer at various heating rates. Wide-angle X-ray diffractograms were obtained in a reflection mode using Ni-filtered Cu Kα radiation on a Rigaku Geiger Flex D-Max X-ray diffractometer. A Zeiss MC 100 cross-polarizing microscope with a Leitz hot stage was employed to identify the development of the optical texture of the polymers at the mesophase. The UV-vis spectra were obtained on a Hewlett-Packard 8452A diode array spectrophotometer. Inherent viscosities were measured using an Ubbelohde type viscometer at 25 °C for a 0.5 g/dL solution in trifluoroacetic acid. The determination of viscosity was conducted as quickly as possible; the polymer sample was dissolved by stirring with a spin bar in a volumetric flask wrapped with aluminum foil to retard degradation by light, and the polymer solution was transferred to the viscometer as soon as the polymer sample dissolved (30 min to 2 h).

Monomer Synthesis. 2,5-Bis((*n*-alkyloxy)methyl)-1,4-dicyanobenzenes **4b–d** were prepared from the corresponding 2,5-bis((*n*-alkyloxy)methyl)-1,4-dibromobenzenes according to our previous paper.[14] The following are some data of new materials which have not described in that paper.

2,5-Bis((*n*-hexyloxy)methyl)-1,4-dibromobenzene: yield 94%; mp (EtOH) 74–76 °C; MS (EI) (70 eV) *m/e* (relative intensity, %) 467 (M^+, 2), 466 (M^+, 5), 465 (M^+, 2), 464 (M^+, 8), 462 (M^+, 5), 43 (100); ^{1}H-NMR ($CDCl_3$) δ 0.86–4.48 (H in the (*n*-hexyloxy)methyl group), 7.62 (s, H_{arom}). Anal. Calcd for $C_{20}H_{32}Br_2O_2$: C, 51.74; H, 6.95. Found: C, 51.62; H, 6.49.

2,5-Bis((*n*-dodecyloxy)methyl)-1,4-dibromobenzene: yield 90–93%; mp (EtOH) 86–88 °C; MS (EI) (70 eV) *m/e* (relative intensity, %) 634 (M^+, 3), 633 (M^+, 3), 632 (M^+, 7), 630 (M^+, 5), 262 (100); ^{1}H-NMR ($CDCl_3$) δ 0.85–4.49 (H in the (*n*-dodecyloxy)methyl group), 7.63 (s, H_{arom}). Anal. Calcd for $C_{32}H_{56}Br_2O_2$: C, 60.76; H, 8.92. Found: C, 60.63; H, 9.38.

2,5-Bis((*n*-hexyloxy)methyl)-1,4-dicyanobenzene (4b): yield 88%; mp (EtOH) 65.5–66.5 °C; MS (EI) (70 eV) *m/e* (relative intensity, %) 358 ($(M + 2)^+$, 1), 357 ($(M + 1)^+$, 1), 356 (M^+, 3), 43 (100); ^{1}H-NMR ($CDCl_3$) δ 0.86–4.66 (H in the (*n*-hexyloxy)methyl group), 7.85 (s, H_{arom}). Anal. Calcd for $C_{22}H_{32}N_2O_2$: C, 74.12; H, 9.05; N, 7.86. Found: C, 73.97; H, 9.51; N, 7.92.

2,5-Bis((*n*-dodecyloxy)methyl)-1,4-dicyanobenzene (4d): yield 94–96%; mp (2-butanone) 86–87 °C; MS (EI) (70 eV) *m/e* (relative intensity, %) 526 ($(M + 2)^+$, 2), 525 ($(M + 1)^+$, 15), 524 (M^+, 34), 97 (100); ^{1}H-NMR ($CDCl_3$) δ 0.85–4.67 (H in the (*n*-dodecyloxy)methyl group), 7.86 (s, H_{arom}). Anal. Calcd for $C_{34}H_{56}N_2O_2$: C, 77.81; H, 10.76; N, 5.34. Found: C, 76.49; H, 11.32; N, 5.03.

2,5-Bis((*n*-alkyloxy)methyl)-1,4-benzenedicarboxylic Acids 5a–d. Method A (for 5a–c). Potassium hydroxide (0.51 mol) was dissolved in hydrogen peroxide solution (15%, 104 mL), and then ethylene glycol (500 mL) was added. 2,5-Bis((*n*-alkyloxy)methyl)-1,4-dicyanobenzenes **4a–c** (0.05 mol) were added to the solution, and the mixture was boiled at 122–125 °C for about 2–8 days until the evolution of ammonia ceased. The light brown solution was cooled to room temperature, filtered, and poured into cold 50% aqueous sulfuric acid (1200 mL). The precipitate formed was filtered, washed with water thoroughly, recrystallized (**5a,b**: acetone/H_2O mixture; **5c**: acetone), and dried at 100 °C for 2 days in a vacuum oven: yield 89–92% (**5a**), 87% (**5b**), 87–94% (**5c**); mp 217–222 (**5a**), 201–205 (**5b**), 183–186 °C (**5c**); MS (EI) for **5a** (70 eV) *m/e* (relative intensity, %) 339 ($(M + 1)^+$, 1), 338 (M^+, 3), 281 (42), 263 (100), 57 (15); ^{1}H-NMR (DMSO-d_6) for **5a** δ 0.85–4.79 (H in the (*n*-butyloxy)methyl group), 8.05 (s, H_{arom}), 13.17 (br s, COO*H*). Anal. Calcd for **5a** ($C_{18}H_{26}O_6$): C, 63.89; H, 7.74; O, 28.37. Found: C, 64.01; H, 8.02; O, 28.01.

Method B (for 5d). A mixture of potassium hydroxide (0.51 mol), ethylene glycol (500 mL), and 2,5-bis((*n*-dodecyloxy)methyl)-1,4-dicyanobenzene (**4d**) (26.2 g, 0.05 mol) was heated to 180 °C. On addition of distilled water (100 mL) after about 8 days, the temperature of the mixture was lowered to 125 °C. The mixture was heated at that temperature for an additional 2 days until the evolution of ammonia ceased. The light brown solution was allowed to cool and was stirred overnight at room temperature. The precipitate formed was filtered, dissolved in water (400 mL), and filtered directly into an evacuated, stirred flask containing 50% aqueous sulfuric acid (1200 mL). The white precipitate was filtered, washed with water thoroughly, recrystallized from 2-butanone, and dried at 70 °C for 2 days in a vacuum oven: yield 88–92%; mp 175–176 °C. Anal. Calcd for $C_{34}H_{58}O_6$: C, 72.56; H, 10.39. Found: C, 72.09; H, 10.31.

2,5-Bis((*n*-alkyloxy)methyl)-1,4-benzenedimethanols 6a–d. To a 1-L flask equipped with a mechanical stirrer and nitrogen inlet were placed $LiAlH_4$ powder (4.8 g, 0.12 mol) and THF (480 mL). The mixture was stirred vigrously at room temperature for 1 h, and then 2,5-bis((*n*-alkyloxy)methyl)-1,4-benzenedicarboxylic acids **5a–d** (0.04 mol) were added slowly in a solid state to the mixture. The reaction mixture was refluxed for 8 h, allowed to cool, and stirred overnight at room temperature, and then ethylene glycol (40 mL) was dropped into the mixture. The mixture was filtered (after warming the mixture in the case of **6d** due to its lower solubility in THF), and the filtrate was evaporated at room temperature. Concentrated filtrate (about 100 mL) was poured into an excess of distilled water. The precipitated white solids were washed with water thoroughly, recrystallized (**6a,b**: *n*-hexane/EtOH mixture; **6c,d**: EtOH), and dried at 40 °C for 2 days in a vacuum oven: yield 70–73% (**6a**), 75% (**6b**), 83–86% (**6c**), 75–77% (**6d**); mp 86–87.5 (**6a**), 92–93.5 (**6b**), 98–99.5 (**6c**), 106–107.5 °C (**6d**); MS (EI) for **6a** (70 eV) *m/e* (relative intensity, %) 293 ($(M + 1 - H_2O)^+$, 4), 292 ($(M - H_2O)^+$, 12), 162 (100), 57 (32); ^{1}H-NMR ($CDCl_3$) for **6a** δ 0.86–4.56 (H in the (*n*-butyloxy)methyl group), 3.19–3.23 (t, CH_2OH), 4.62–4.64 (d, CH_2OH), 7.32 (s, H_{arom}). Anal. Calcd for **6a** ($C_{18}H_{30}O_4$): C, 69.65; H, 9.74; O, 20.62. Found: C, 68.49; H, 11.18; O, 21.12.

2,5-Bis((*n*-alkyloxy)methyl)-1,4-benzenedialdehydes 1a–d. **1a–d** were prepared according to a modified literature procedure.[17] Oxalyl chloride (0.031 mol) dissolved in dichloromethane (70 mL) was placed in a four-neck flask equipped with a thermometer and two pressure-equalizing addition funnels protected by drying tubes. One addition funnel contained DMSO (0.068 mol) dissolved in dichloromethane (14 mL) and the other *p*-dimethylolbenzene **6a–d** (0.014 mol) dissolved in a dichloromethane (48 mL)/DMSO (20 mL) mixture. The contents of the flask were cooled to −60 °C, and the DMSO solution was added dropwise over 10 min. Stirring was continued at −60 °C for 10 min followed by addition of the *p*-dimethylolbenzene solution in 10 min (for **6d**, the *p*-dimethylolbenzene solution was kept warm during the addition due to the lower solubility of **6d** in the dichloromethane/DMSO mixture). The reaction mixture was stirred for 15 min, and triethylamine (14.3 g) was added in 5 min with stirring at −60 °C. The cooling bath was removed, and water (85 mL) was added at room temperature. Stirring was continued for 10 min, and the organic layer was separated. The aqueous phase was reextracted with dichloromethane (80 mL), and the organic layer was combined and washed successively with dilute HCl (ca. 5%), water, dilute Na_2CO_3 (ca. 5%), and water. The washed organic layer was dried with anhydrous $MgSO_4$ and evaporated at room temperature to give a white solid. The solid was recrystallized (**1a**,**b**: *n*-hexane/*n*-pentane mixture; **1c–d**; *n*-hexane) and dried at 40 °C for 2 days in vacuum.

1a: yield 80–82%; mp 68–69 °C; MS (EI) (70 eV) *m/e* (relative intensity, %) 308 ($(M + 2)^+$, 2), 307 ($(M + 1)^+$, 7), 306 (M^+, 36), 249 (100); IR (KBr): ν 2793/2739 (C(=O)–H), 1695 (C=O), 1103 cm^{-1} (C–O–C); ^{1}H-NMR ($CDCl_3$) δ 0.89–4.90 (H in the (*n*-butyloxy)methyl group), 8.10 (s, H_{arom}), 10.28 (s, C*H*O); ^{13}C-NMR ($CDCl_3$) δ 13.87, 19.39, 31.78, 69.48, 71.07, 131.82, 136.31, 140.70, 192.37. Anal. Calcd for $C_{18}H_{26}O_4$: C, 70.56; H, 8.55; O, 20.89. Found: C, 69.98; H, 9.01; O, 21.76.

1b: yield 90–91%; mp 72–74 °C; MS (EI) (70 eV) *m/e* (relative intensity, %) 364 ($(M + 2)^+$, 2), 363 ($(M + 1)^+$, 10), 362 (M^+, 39), 277 (90), 43 (100); ^{13}C-NMR ($CDCl_3$) δ 13.98, 22.57, 25.86, 29.66, 31.63, 69.47, 71.39, 131.84, 136.30, 140.69, 192.37.

1c: yield 90–95%; mp 81–82 °C; MS (EI) (70 eV) *m/e* (relative intensity, %) 420 ($(M + 2)^+$, 2), 419 ($(M + 1)^+$, 8), 418 (M^+, 23), 305 (83), 43 (100); ^{13}C-NMR ($CDCl_3$) δ 14.05, 22.62, 26.20, 29.22, 29.40, 29.70, 31.81, 69.47, 71.40, 131.84, 136.29, 140.69, 192.35.

1d: yield 93%; mp 90–91.5 °C; MS (EI) (70 eV) *m/e* (relative intensity, %) 533 ($(M + 2)^+$, 2), 532 ($(M + 1)^+$, 6), 531 (M^+, 14), 530 ($(M - 1)^+$, 38), 361 (78), 43 (100); ^{13}C-NMR ($CDCl_3$) δ 14.08, 22.67, 26.21, 29.33, 29.46, 29.58, 29.62, 29.71, 31.91, 69.48, 71.42, 131.86, 136.29, 140.70, 192.38.

Polymer Synthesis. Polymerization in Toluene (Method A). In a 500-mL round-bottomed flask equipped with a nitrogen inlet, Dean–Stark trap, condenser, and drying tube were placed *p*-phenylenediamine (0.015 mol, 1.622 g) and anhydrous toluene (150 mL). The mixture was warmed to dissolve the *p*-phenylenediamine, and then an equivalent weight of dialdehyde **1a–d** was added quickly to the solution at room temperature and the mixture was stirred under a N_2 atmosphere. The reaction mixture was heated to reflux for 6 h while the water was separated azeotropically. During the reaction time, C_4-PAM underwent gelation while the other polyazomethines were almost soluble at reflux temperature. On cooling, gelation occurred. The gel was allowed to stand overnight, powdered, washed with acetone, and filtered. The product was washed with acetone once again and dried at 60 °C under reduced pressure for 2 days. Anal. Calcd for the repeat unit of C_8-PAM-A: C, 78.32; H, 9.45; N, 5.71; O, 6.52. Found: C, 78.86; H, 9.45; N, 5.47; O, 6.78.

Polymerization in Amide Mixture Solvent (Method B). *p*-Phenylenediamine (5 mmol) was dissolved in an equal volume of HMPA/NMP mixture (20 mL) under a N_2 atmosphere. To this solution was added an equivalent weight of 2,5-bis((*n*-octyloxy)methyl)-1,4-benzenedialdehyde (**1c**) with stirring. In about 1 h at room temperature, the reaction mixture was unstirrable due to gelation. After standing overnight, the gel was isolated and treated under the same conditions as described above.

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References and Notes

(1) Preston, J. *Angew. Makromol. Chem.* **1982**, 1.
(2) Ballauff, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 253.
(3) Majnusz, J.; Catala, J. M.; Lenz, R. W. *Eur. Polym. J.* **1983**, *19*, 1043. Krigbaum, W. R.; Hakemi, H.; Kotek, R. *Macromolecules* **1985**, *18*, 965.
(4) Ballauff, M. *Makromol. Chem., Rapid Commun.* **1986**, *7*, 407.
(5) Ballauff, M.; Schmidt, G. F. *Makomol. Chem., Rapid Commun.* **1987**, *8*, 93; *Mol. Cryst. Liq. Cryst.* **1987**, *147*, 163.
(6) Berger, K.; Ballauff, M. *Mol. Cryst. Liq. Cryst.* **1988**, *157*, 109.
(7) Ballauff, M.; Rosenau-Eichin, R.; Fischer, E. W. *Mol. Cryst. Liq. Cryst.* **1988**, *155*, 211.
(8) Rodriguez-Parada, J. M.; Duran, R.; Wegner, G. *Macromolecules* **1989**, *22*, 2507.
(9) Stern, R.; Ballauff, M.; Lieser, G.; Wegner, G. *Polymer* **1991**, *32* (11), 2096.
(10) Ballauff, M. *Macromolecules* **1986**, *19*, 1366.
(11) Adams, R.; Bullock, J. E.; Wilson, W. C. *J. Am. Chem. Soc.* **1923**, *45*, 521.
(12) Morgan, P. W.; Kwolek, S. L.; Pletcher, T. C. *Macromolecules* **1987**, *20*, 729.
(13) Wojtkowski, P. W. *Macromolecules* **1987**, *20*, 740.
(14) Park, S.-B.; Jung, J. C. *Makromol. Chem.*, in press.
(15) Wolfe, J. F.; Arnold, F. E. *Macromolecules* **1981**, *14*, 909. Rehahn, M.; Schlüter, A.-D.; Feast, W. J. *Synth. Commun.* **1988**, 386.
(16) Brown, H. C.; Weissman, P. M.; Yoon, N. M. *J. Am. Chem. Soc.* **1966**, *88*, 1458.
(17) Omura, K.; Swern, D. *Tetrahedron* **1978**, *34*, 1651.
(18) Mancuso, A. J.; Swern, D. *Synthesis* **1981**, 165.
(19) Millaud, B.; Strazielle, C.; Weill, G. *Polymer* **1980**, *21*, 639.
(20) Yang, C.-J.; Jenekhe, S. A. *Chem. Mater.* **1991**, *3*, 878.
(21) Lee, K.-S.; Won, J. C.; Jung, J. C. *Makromol. Chem.* **1989**, *190*, 1547.
(22) Reinhardt, B. A.; Unroe, M. R. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1990**, *31* (1), 620.
(23) Platé, N. A.; Shibaev, V. P. *J. Polym. Sci., Macromol. Rev.* **1974**, *8*, 117.
(24) Suematsu, K.; Nakamura, K.; Takeda, J. *Polym. J.* **1983**, *15*, 71.
(25) Bürgi, H. B.; Dunitz, J. D. *Helv. Chim. Acta* **1970**, *53*, 1747.