Synthesis and Properties of Polyimides Containing Multiple Alkyl Side Chains

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ABSTRACT: A series of diamine monomers, i.e., 2,2′-bis{4-[3,4,5-tris(*n*-alkan-1-yloxy)benzoate]}-4,4′-biphenyldiamines containing multiple alkyl side chains, were synthesized in which the length of the alkyl side chains was varied from 5 to 18 carbon atoms. Polyimides were prepared from the diamines and pyromellitic dianhydride (PMDA), 3,3′4,4′-biphenyltetracarboxylic dianhydride (BPDA), 2,2′-dibromo-4,4′,5,5′-biphenyltetracarboxylic dianhydride (DBBPDA), and 2,2′-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA), respectively, using a one-step method in 1,2-dichlorobenzene or 1-chloronaphthalene. Most of the polymers had good solubility in chlorinated solvents. Several copolyimides were prepared: BPDA, 2,2′-bis(trifluoromethyl)benzidine (PFMB), and C14 and C16 diamines. The solubility of copolyimides was dramatically affected by different monomer addition sequences. The high-molecular-weight polyimides could be solution cast into flexible, tough films except for those based on PMDA. The side chains that contained at least 10 carbon atoms crystallized. The melting points of the crystalline regions increased as the length of the side chains increased. Variable-temperature (VT) solid state ^{13}C nuclear magnetic resonance (NMR) showed that the polyimide containing C18 side chains crystallized at room temperature. A wide-angle X-ray diffraction (WAXD) study showed that the spacing between the main chains increased as the number of carbon atoms in the side chains increased. The diameter of aggregated backbones was 2.14 nm, indicating several polyimide main chains stacked each other to form supermolecular, nanoscale structures. Three polyimides and one copolyimide were used to prepare alignment layers. The films generated liquid crystal pretilt angles of 6, 9, 90, and 90°, respectively.

Introduction

Rodlike polymers are of considerable interest because of their superior mechanical and high-temperature properties. However, they usually exhibit very low solubilities and melting points far above their thermal decomposition temperatures. Flexible alkyl side chains have been attached to rodlike polymers, such as aromatic polyesters, polyimides, polyamides, and polyphenylenes, to decrease their melting points and glass transition temperatures (T_gs) and to increase their solubilities.[1−13] The flexible alkyl side chains have been attached to phenylene rings with ether, ester and thio linkages with one, two or four substituents per phenylene ring. These types of polymers are referred to as "hairy-rod" polymers. In some cases, the attachment of alkyl side chains also results in changes in liquid crystalline behavior. For example, poly(1,4-phenylene 2,5-dialkoxyterephthalate)s with short side chains exhibit nematic mesophases, while longer side chains lead to novel layered mesophases.[1,2] A sanidic structure or layered structure has been proposed for the liquid crystal and crystal structures of polyamide containing alkyl side chains, based on WAXD studies.[8,9]

Polyimides containing alkyl side chains exhibit improved solubilties and lower T_gs, which make them easier to process.[5] Langmuir−Blodgett films have been prepared for the first time from soluble polyimides containing long alkyl side chains.[6] Polyimides contained two side chains per repeat unit have been prepared to increase the solubility of aromatic polymers and to maintain the rigidity of the backbone.[14,15] The attachment of alkyl side chains to polyimides has also recently been used in the development of alignment layers for liquid crystal displays (LCDs).[16] Alignment layers, which are mechanically robbed prior to use, align the liquid crystal molecules unidirectionally. Another important function of the alignment layers is to cause the liquid crystal molecules to position themselves at an angle to the film surface, which is called the pretilt angle. If the liquid crystals in a LCD cell have no pretilt angle, either end of the molecule may rise when the voltage is applied. The tilt also results in a faster response to the applied voltage.[17] The amount of pretilt angle required depends on the device. A small pretilt angle of 2−3° is sufficient for twisted nematic (TN) displays. However, in super twisted nematic (STN) displays, which have higher resolution, higher pretilt angles are required.[18]

The objectives of this research were to improve the solubility and processability of rigid-rod polyimides by attaching multiple alkyl side chains, i.e., six side chains per repeat unit, to their backbones, to investigate their morphologies due to the phase separation between aromatic and aliphatic components and to study the effect of lengths of alkyl side chains on pretilt angles for LCD applications.

Results and Discussion

Monomer Synthesis. 3,4,5-Tris(*n*-alkan-1-yloxy)benzoates (**3**) were prepared by coupling *n*-alkyl bromides (**1**) with methyl 3,4,5-trihydroxybenzoate (**2**) using Williamson conditions. These intermediates **3** were then hydrolyzed in potassium hydroxide solution to afford the 3,4,5-tris(*n*-alkan-1-yloxy)benzoic acids (**4a**−**g**) as shown in Scheme 1.

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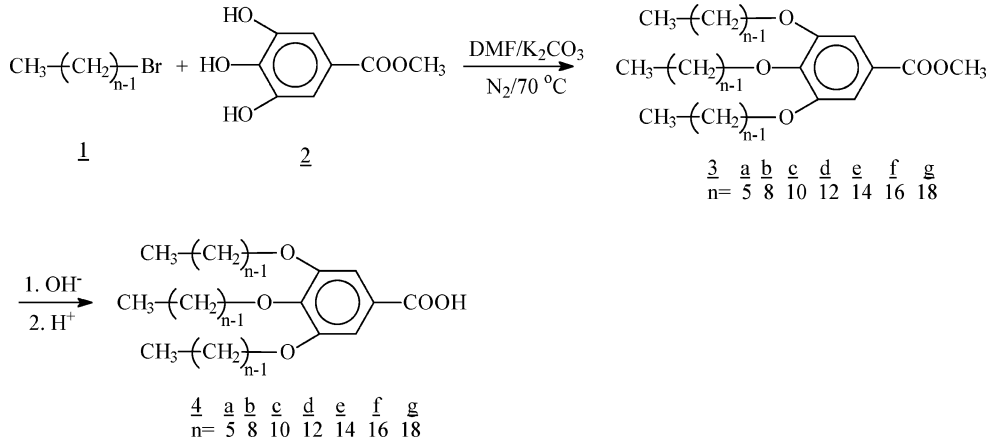
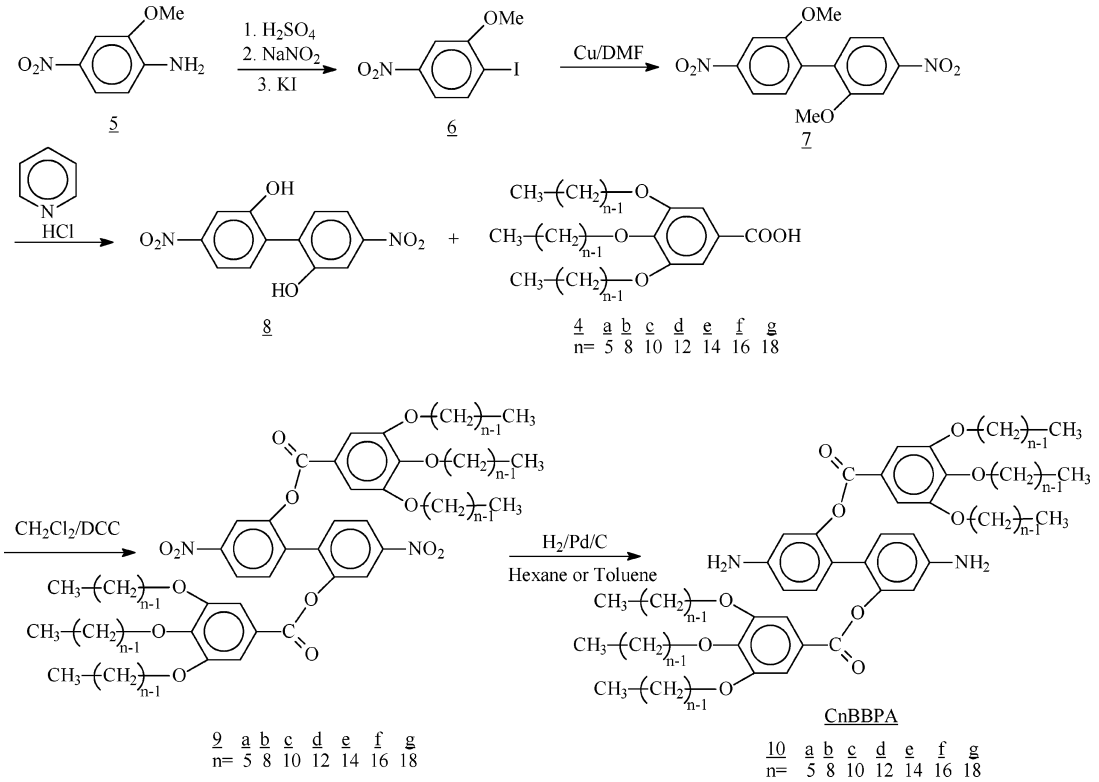
Scheme 1. Synthesis of Side Chains



Scheme 2. Synthesis of Diamines Containing Multiple Alkyl Side Chains



In Scheme 2, 2-methoxy-4-nitroaniline (**5**) was converted to 4-iodo-3-methoxynitrobenzene (**6**) using a Sandmeyer reaction. Ullmann conditions were then used to dimerize compound *6* to give 2,2′-dimethoxy-4,4′-dinitrobiphenyl (**7**). Demethylation of compound **7** in pyridine hydrochloride at 200 °C gave 4,4′-dinitro-2,2′-biphenyldiol (**8**). Compound **8** was esterified with the 3,4,5-tris(*n*-alkan-1-yloxy)benzoic acids **4a**−**g** to afford the alkyl-substituted dinitro compounds **9a**−**g** using dicyclohexylcarbodiimide (DCC) as the dehydration agent.

The next step in the reaction sequence required the selection of a suitable method to reduce the nitro groups to amino groups. The most common reducing agents are Zn, Sn, or Fe (or sometimes other metals) and acids, and catalytic hydrogenation. The use of acids as hydrogen sources was not feasible in the reduction of **9** because of the possibility of hydrolysis of the ester groups. $LiAlH_4$ could not be used because it could also reduce the ester groups to benzyl alcohol groups. The use of hydrazine monohydrate resulted in the cleavage of the ester groups. Reduction with stannous chloride and ethanol appeared to give the diamines. However, the diamines were very difficult to separate from the tin salts. Catalytic hydrogenation affords clean products in high yields when carried out in nonpolar solvents. The use of the polar solvents, such as ethyl acetate, resulted in the cleavage of the ester groups. Thus, the alkyl-substituted dinitro compounds **9** were successfully reduced to the alkyl-substituted diamines **10a**−**g** using palladium on activated carbon in hexane or toluene (Schemes 2). The ^{1}H NMR spectra of diamine **10d** (C12BBPA) and ^{13}C NMR spectra of diamine **10a** (C5BBPA) are shown in Figures 1 and 2, respectively.

Syntheses of Polyimides. The polyimides were prepared from four dianhydrides, i.e., PMDA, BPDA, 6FDA and 2,2′-dibromo-4,4′,5,5′-biphenyltetracarboxylic dianhydride (DBBPDA), and alkyl-substituted diamines (**10a**−**g**). The polyimides were prepared by the one-step method in 1-chloronaphthalene or *o*-dichlorobenzene at 180−200 °C (Scheme 3). Several copolyimides were also prepared from different ratios of C14 and C16 diamines, i.e., **10e** and **10f**, and PFMB and BPDA (Scheme 4).

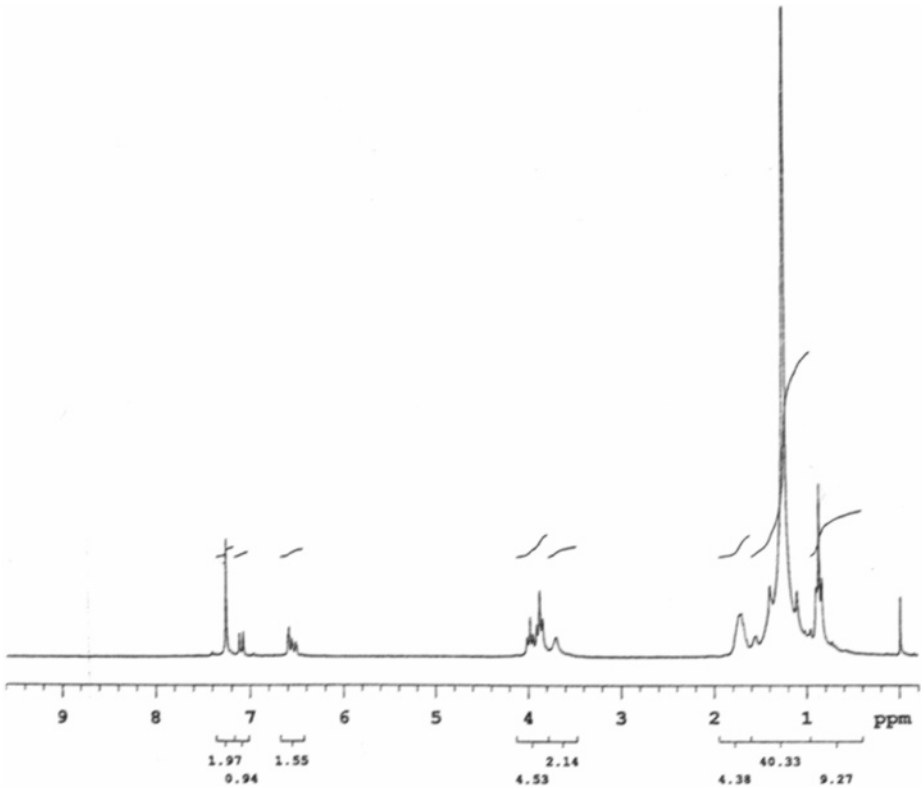


Figure 1. ^{1}H NMR spectrum of 2,2′-bis{4-[3,4,5-tris(*n*-dodecan-1-yloxy)benzoate]}-4,4′-biphenyldiamine (**10d**, C12BBPA) in $CDCl_3$.

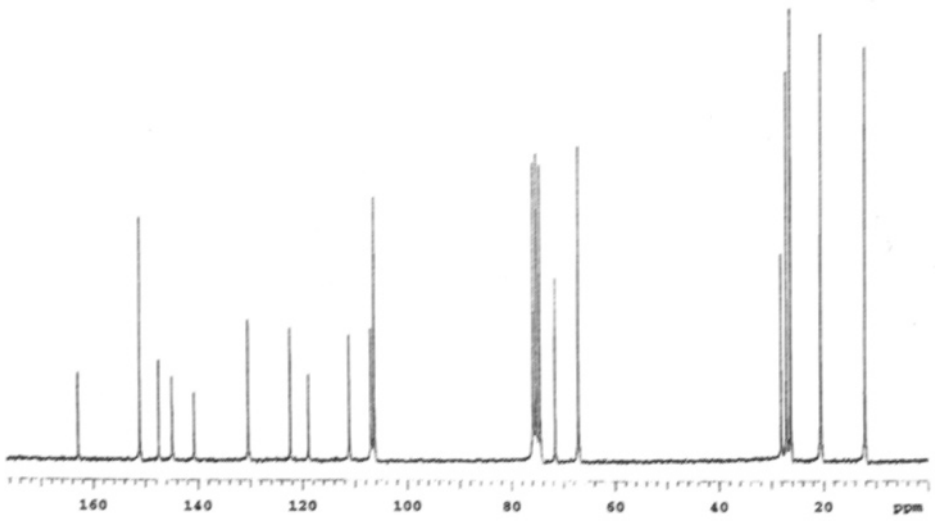


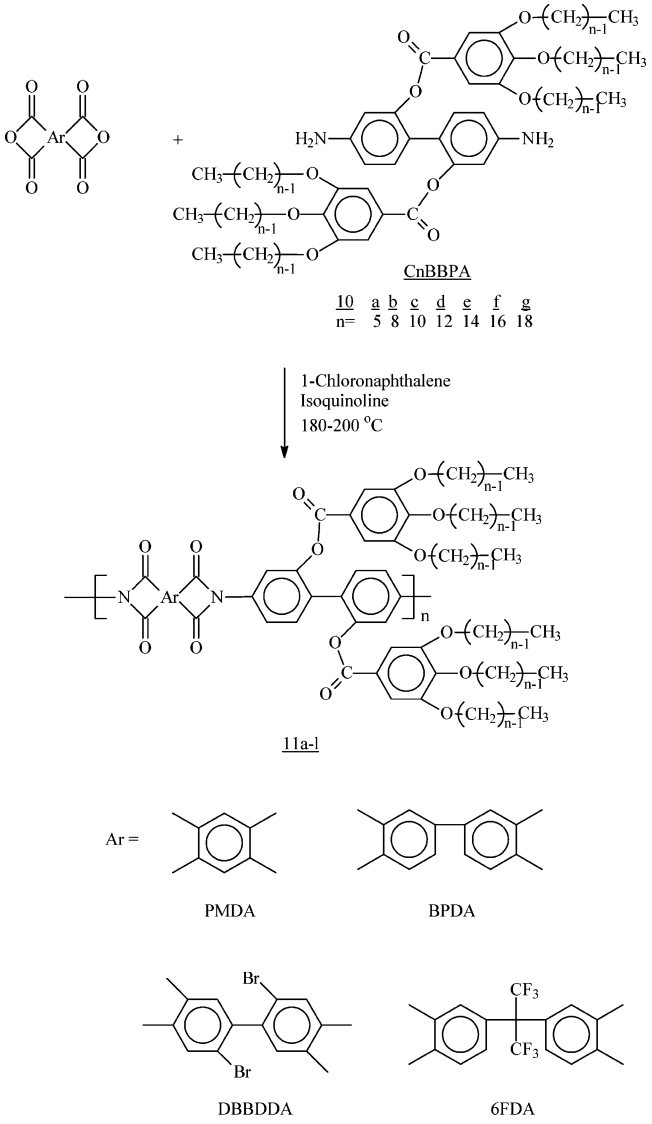
Figure 2. ^{13}C NMR spectrum of 2,2′-bis{4-[3,4,5-tris(*n*-pentan-1-yloxy)benzoate]}-4,4′ biphenyldiamine (**10a**, C5BBPA) in $CDCl_3$.

Initially, *m*-cresol was used as the polymerization solvent because it is the most commonly used solvent for the one-step method. However, when C12BBPA was polymerized with BPDA in *m*-cresol, the resulting polyimides precipitated during the polymerization. The precipitate was insoluble in common solvents. When C12BBPA was polymerized with 6FDA in *m*-cresol, the polyimides remained in solution throughout the polymerization. The polymers, which were isolated by precipitation in methanol, were soluble in acetone. However, the ^{1}H NMR spectra showed that all side chains had been cleaved from the polymer backbone. It was speculated that the *m*-cresol may have acted as a nucleophile at the elevated temperature and displaced the carboxylate group from the benzoate position. Thus, the less polar *o*-dichlorobenzene or 1-chloronaphthalene was used as the solvent in these two polymerizations. In both cases, the polyimides remained in solution and no side chain cleavage occurred.

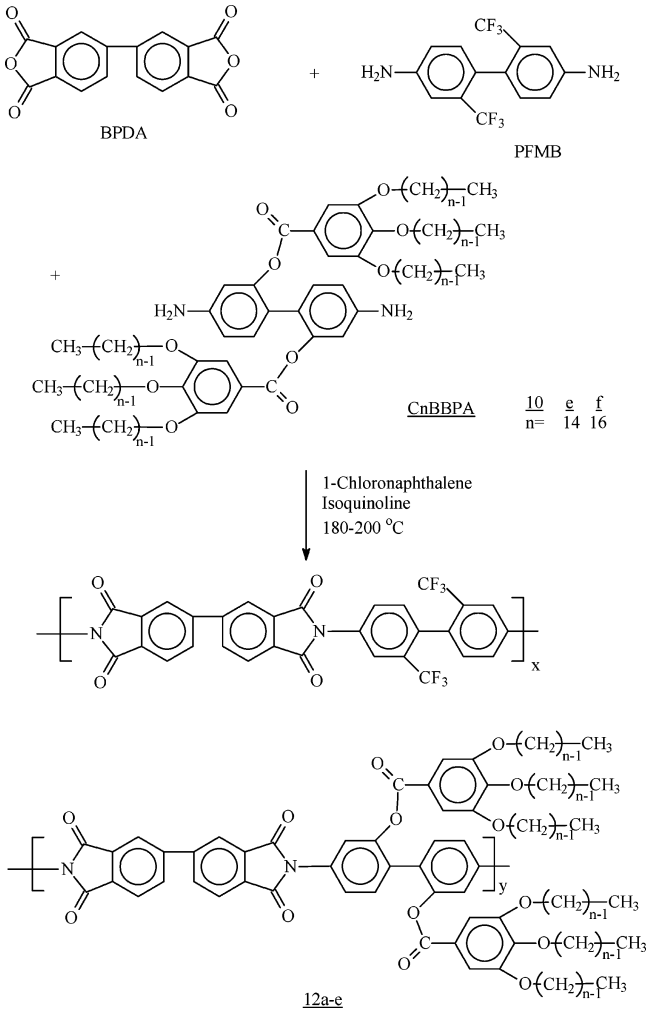
Solution Viscosities and Thermal Properties. The intrinsic viscosities and thermal properties of polyimides **11a**−**l** are shown in Table 1. The intrinsic viscosities of the polymers, which ranged from 0.30 to 7.60 g/dL, were measured at 30.0 ± 0.1 °C in chloroform. The intrinsic viscosities of the rigid-rod polyimides based on PMDA were higher than those of the polyimides prepared from the other dianhydrides.

The T_gs of polymers could not be detected due to the rigid polymer backbones and the presence of the side chains. As the side chains became longer, they crystallized. For the polymers **11** based on BPDA, the T_m increased from −56 to +39 °C as the number of carbon atoms in the side chains increased from 10 to 18.

Scheme 3. Synthesis of Polyimides Containing Multiple Alkyl Side Chains



Scheme 4. Synthesis of Copolyimides



Solubility and Molecular Weight. Six solvents, i.e., CH_2Cl_2, $CHCl_3$, TCE, *o*-dichlorobenzene, 1-chloronaphthalene, and toluene, were used to test the solubilities of polyimides **11**. The polymers were considered soluble if a solution containing 1 g/dL could be prepared. The results are shown in Tables 2.

The polyimides based on BPDA, DBBPDA, and 6FDA were soluble in the chlorinated solvents except for **11d** (BPDA/C5BBPA). The polyimides based on PMDA were insoluble in all of the solvents but 1-chloronaphthalene.

As mentioned before, the introduction of twisted-biphenyl structures is known to increase polymer solubility. The length of side chains and the dianhydrides used are also known to have an important effect on solubility. Since the side chains in polyimide **11d** were short (C5), the solubility was poor. Polyimides (**11e**−**j**) containing longer side chains were soluble in most of the solvents tested. The backbones of the polyimides based on PMDA (**11a**−**c**) were so rigid that the polymers were insoluble in most of the solvents tested. The polymers were more soluble than polyimide containing two side chains per repeat unit.[14,15] Thus, the increase in side chain density did improve the solubility.

Although the polyimides based on PMDA had very low solubility (<1 g/dL) in most of solvents, very viscous gels could be formed at higher concentrations (>1 g/dL). Flexible films could not be made from the polyimide solutions or gels. The polyimides based BPDA, DBBPDA and 6FDA could be cast into flexible, tough films from tetrachloroethane solutions.

It is surprising that polyimides **11i**−**j**, which were prepared from BPDA and the C16 and C18 diamines, were soluble in the nonpolar-solvent toluene. Both polyimides became insoluble in polar solvents such as methylene chloride. These observations can be attributed to the high aliphatic content of the polymers. These facts also led to speculation that these polyimides may associate in polar solvents. This would also explain the gels that formed in these solvents at high concentrations at room temperature.

The number-average molecular weights ($\bar{M}_n$), weight-average molecular weights ($\bar{M}_w$), and molecular weight distributions (MWD) of polyimides **11g**, **11k**, and **11l** were determined with gel permeation chromatography (GPC) with chloroform as the eluent (Table 3). The molecular weights were much higher than expected possibly due to the fact that the polyimides have more rigid backbones than the coil-shape polystyrenes that were used as standards. The aggregation nature of the polyimides was probably contributed to the high molecular weights for **11g**, **11k**, and **11l** and narrow MWDs (<2) for **11g** and **11l**, too.

Variable-Temperature Solid State ^{13}C NMR Analysis. Variable temperature solid state ^{13}C NMR is a good method to investigate the relaxation and transition behavior of hairy-rod polymers.[19−22] In this work, the ratios of the *gauche* to *trans* conformations in the alkyl side chains at different temperatures

Table 1. Intrinsic Viscosities and Thermal Properties of Polyimides 11a−l

PI	dianhydride/diamine	$[\eta]^a$ (dL/g)	T_d (°C) in N_2[b]	T_g (°C)[c]	T_m (°C)[d]
11a	PMDA/C10BBPA	4.12	373	ND[e]	ND
11b	PMDA/C12BBPA	7.60	366	ND	−17
11c	PMDA/C18BBPA	1.42	351	ND	39
11d	BPDA/C5BBPA		351	ND	ND
11e	BPDA/C8BBPA	1.41	345	ND	ND
11f	BPDA/C10BBPA	0.75	316	ND	−56
11g	BPDA/C12BBPA	1.05	388	ND	−33
11h	BPDA/C14BBPA	0.76	335	ND	−4
11i	BPDA/C16BBPA	0.78	324	ND	20
11j	BPDA/c18BBPA	0.99	375	ND	39
11k	DBBPDA/C12BBPA	0.93	358	ND	ND
11l	6FDA/C12BBPA	0.46	364	ND	ND

[a] Intrinsic viscosity determined in chloroform at 30.0 ± 0.1 °C. [b] Temperature at which a 5% weight loss occurred when subjected to TGA with a heating rate of 10 °C/min. [c] Midpoint of change in slope on DSC thermogram obtained with a heating rate of 10 °C/min. [d] Minimum of melting point endotherm on DSC thermogram obtained with a heating rate of 10 °C/min. [e] ND: No detected.

were determined with this technique. This was possible because the chemical shifts of hydrocarbon chains in *gauche* and *trans* conformations are different. For example, for polyethylene the peak at 32 ppm is due to the chains in the amorphous regions that are in *gauche* conformations. The peak observed at 34 ppm results from the crystalline regions of the chains, which are in extended *trans* conformations.

As state earlier, the side chains of polyimide **11c**, which was prepared from PMDA and C18BBPA, were crystalline with a T_m of 39 °C. Solid state ^{13}C NMR showed that the side chains were almost amorphous at 50 °C (Figure 3). Most of side chains were in *gauche* conformations. As the temperature was decreased, the side chains started to crystallize and the corresponding peak at 34 ppm appeared. At 40 °C, which was the T_m of the side chains, the ratio of the *gauche* to *trans* conformations was 1:1, i.e., the areas under the peaks at 31 and 34 ppm were almost the same. Most of the side chains became crystalline at 30 °C. There was very little change in the absorption peak of the methyl groups at 15 ppm during the cooling process, which shows that the groups were not involved in the crystallization process. The absorption peak due to the methylene groups next to the methyl groups disappeared at 30 °C, which indicates that these groups were incorporated in the crystal structure.

Wide-Angle X-ray Diffraction (WAXD) Analysis. The WAXD powder patterns of polyimide **11j** (BPDA/C18BBPA) obtained at different temperatures during heating are shown in Figure 4. The T_m of polyimide **11j** is 39 °C. In the pattern obtained at 29 °C, the small peak at about 21°, can be attributed

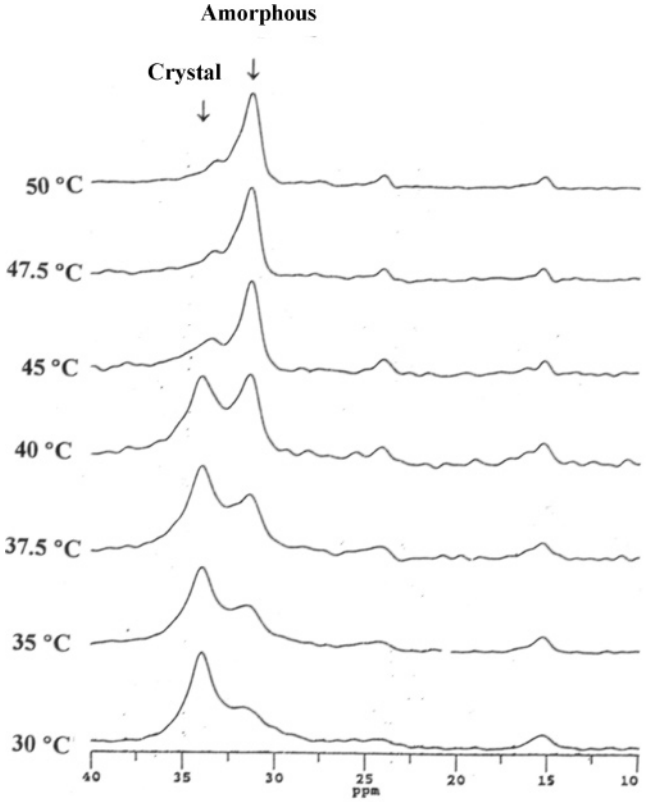


Figure 3. Variable temperature solid state ^{13}C NMR of polyimide **11c** (PMDA/C18BBPA, T_m = 39 °C) during cooling.

to the side chain crystalline regions. As temperature was increased, this peak decreased and disappeared at 43 °C. This indicates that all of the side chain crystals had melted.

Hairy-rod polymers exhibit characteristic layer structures, which can be characterized using WAXD. The layer structures have discrete distances separating the main chains, which are governed by the length of the side chains. The strong reflection at about 3° indicates that the backbones have undergone lateral packing and formed layered structures. The reflection at about 3° became sharp during heating after the side chain crystals had melted, which indicates the lateral packing became more ordered. Since the side chains can move relatively freely in the amorphous state, the main chains can be arranged in a more orderly state. Several small peaks in the 2θ range from 7 to 10° indicate that there are several kinds of layered structures present. These peaks did not change during heating.

The WAXD pattern of a fiber of polyimide **11e** (BPDA/C8BBPA) is shown in Figure 5. The two strong reflections in the low angle region along the equatorial direction give a *d*

Table 2. Solubility of Polyimides 11a−l[a]

PI	dianhydride/diamine	CH_2Cl_2	$CHCl_3$	TCE	DCB	CN	toluene
11a	PMDA/C10BBPA	−	−	−	−	+	−
11b	PMDA/C12BBPA	−	−	−	−	+	−
11c	PMDA/C18BBPA	−	−	−	−	+	−
11d	BPDA/C5BBPA	−	−	−	−	−	−
11e	BPDA/C8BBPA	+	+	+	+	+	−
11f	BPDA/C10BBPA	+	+	+	+	+	−
11g	BPDA/C12BBPA	+	+	+	+	+	−
11h	BPDA/C14BBPA	+	+	+	+	+	−
11i	BPDA/C16BBPA	−	+	+	+	+	+
11j	BPDA/C18BBPA	−	+	+	+	+	+
11k	DBBPDA/C12BBPA	+	+	+	+	+	−
11l	6FDA/C12BBPA	+	+	+	+	+	−

[a] Key: (+) minimum solubility of 1 g/dL at room temperature; (−) solubility less than 1 g/dL at room temperature. TCE: tetrachloroethane. DCB: *o*-dichlorobenzene. CN: 1-chloronaphthalene.

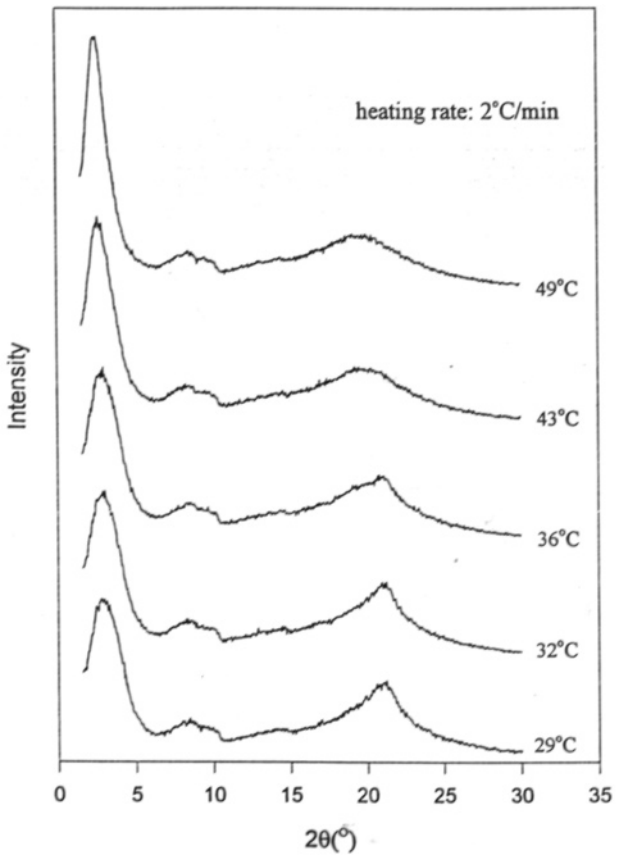


Figure 4. WAXD powder patterns of polyimides **11j** (BPDA/C18BBPA, T_m = 39 °C) at different temperatures during heating.

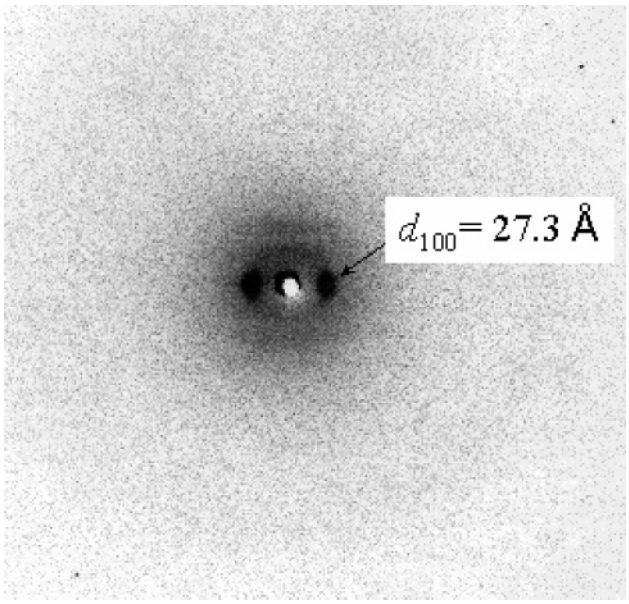


Figure 5. WAXD fiber pattern of polyimide **11e** (BPDA/C8BBPA).

spacing of 27.3 Å, which reflects the distance between two backbones. This pattern can be attributed to the hexagonal packing of the rigid backbones. Since the *d* spacing is much less than twice the side chain length, disordered side chains must fill in the space between the rigid backbones in a partially interdigitated manner.

A plot of the *d* spacings of BPDA/CnBBPA polyimides as a function of the number of carbon atoms in the side chains is shown in Figure 6. The *d* spacings increase linearly as the length of the side chains increases. The slope of the curve is 0.71 Å

Table 3. Polyimide Molecular Weights and Molecular Weight Distributions

PI	dianhydride/diamine	$\bar{M}_n$ ($\times 10^3$)[a]	$\bar{M}_w$ ($\times 10^3$)[a]	MWD[a]
11g	BPDA/C12BBPA	91.6	135	1.48
11k	DBBPDA/C12BBPA	382	974	2.55
11l	6FDA/C12BBPA	79.8	139	1.74

[a] Number-average, weight-average molecular weight and molecular weight distribution determined using GPC with a light scattering detector in chloroform at 40.0 ± 0.1 °C with polystyrene standard.

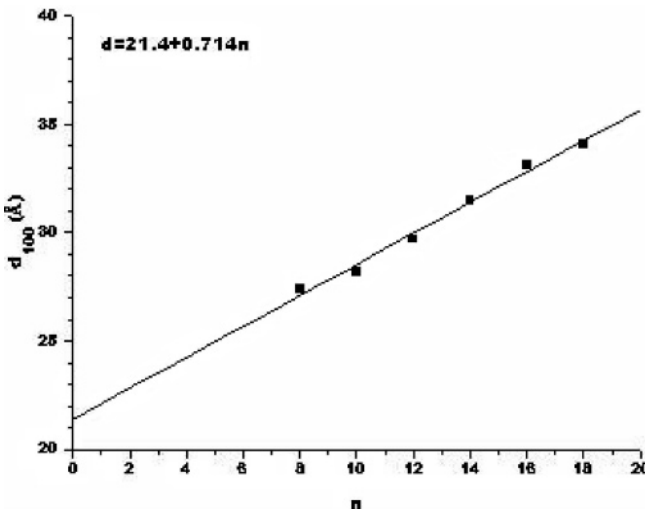


Figure 6. d_{100} spacing in BPDA/CnBBPA fibers as a function of the number of carbon atoms in the side chains.

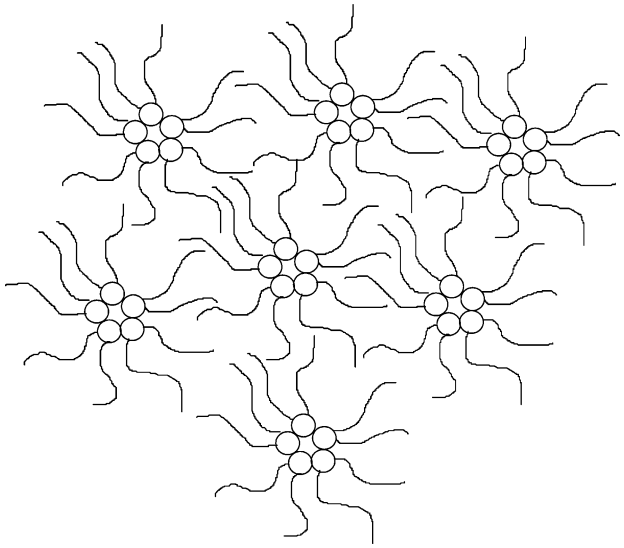


Figure 7. Microstructures of BPDA/CnBBPA polyimides.

per CH_2 unit, which is much less than the theoretical value of 1.27 Å for an extended hydrocarbon chain. This indicates that the side chains are somewhat disordered. Extrapolation to n = 0 leads to an intercept of 2.14 nm, which represents the diameter of the aggregated backbones. Since the diameter of single polyimide backbone is only about 0.40 nm, the actual diameter (2.14 nm) indicated that several polyimide main chains stacked each other, probably via intermolecular charge transfer interaction, to form supermolecular, nanosize aggregates inside while the aliphatic side chains extended out to form an amorphous (C5−12) or crystalline (C14−18) cylinder outside as shown in Figure 7.

Copolyimides. Copolyimides **12a[1]**−**e[1]** were prepared from BPDA, PFMB and diamines **10e** and **10f** (C14BBPA and C16BBPA) as shown in Scheme 4. The amount of PFMB in

Table 4. Intrinsic Viscosities and Thermal Properties of Copolyimides 12a^1−e^1 and 12d^2

CPI	dianhydride/diamines (ratio)	$[\eta]^a$ (dL/g)	T_d (°C) in N_2[b]	T_g (°C)[c]
12a^1	BPDA/PFMB:C14BBPA (1/0.5:0.5)	0.97	351	ND[d]
12b^1	BPDA/PFMB:C14BBPA (1/0.75:0.25)	1.10	345	ND
12c^1	BPDA/PFMB:C16BBPA (1/0.25:0.75)	0.81	342	ND
12d^1	BPDA/PFMB:C16BBPA (1/0.5:0.5)	0.87	367	ND
12d^2	BPDA/PFMB:C16BBPA (1/0.5:0.5)	*e*	358	ND
12e^1	BPDA/PFMB:C16BBPA (1/0.75:0.25)	1.02	343	ND

[a] Intrinsic viscosity determined in chloroform at 30.0 ± 0.1 °C. [b] Temperature at which a 5% weight loss occurred when subjected to TGA with a heating rate of 10 °C/min. [c] Midpoint of change in slope on DSC thermogram obtained with a heating rate of 10 °C/min. [d] ND: No detected. [e] **12d^2** was insoluble in chloroform.

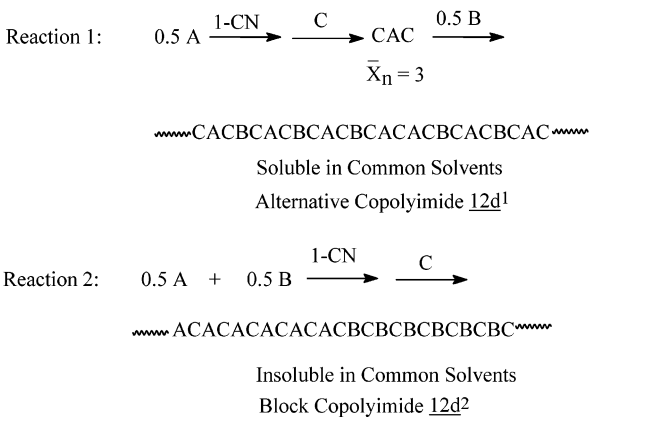
Table 5. Solubility of Copolyimides 12a−e[a]

CPI	dianhydride/diamines (ratio)	$CHCl_3$	TCE	DCB	CN	CP
12a^1	BPDA/PFMB:C14BBPA (1/0.5:0.5)	+	+	+	+	+
12b^1	BPDA/PFMB:C14BBPA (1/0.75:0.25)	+	+	+	+	−
12c^1	BPDA/PFMB:C16BBPA (1/0.25:0.75)	+	+	+	+	−
12d^1	BPDA/PFMB:C16BBPA (1/0.5:0.5)	+	+	+	+	+
12e^1	BPDA/PFMB:C16BBPA (1/0.75:0.25)	+	+	+	+	−

[a] Key: (+) minimum solubility of 1g/dL at room temperature; (−) solubility less than 1g/dL at room temperature. TCE: tetrachloroethane. DCB: *o*-dichlorobenzene. CN: 1-chloronaphthalene. CP: cyclopentanone.

Scheme 5. Two Addition Sequences for Copolyimide Synthesis

A = C16BBPA B = PFMB C = BPDA 1-CN = 1-Chloronaphthalene



the copolyimides was varied from 25% to 75%. The intrinsic viscosities and thermal properties of the copolyimides **12a^1−e^1** are shown in Table 4. The intrinsic viscosities ranged from 0.81 to 1.10 dL/g. Similarly to the homopolymers, the T_gs of the copolyimides **12** could not be detected due to the rigid backbones and the side chains.

All of copolyimides were soluble in common solvents, such as chloroform, TCE, *o*-dichlorobenzene, and 1-chloronaphthalene (Table 5). Unlike the homopolymers, copolyimides **12a^1** and **12d^1** were also soluble in cyclopentanone.

During preparation the copolyimides, it was determined that the solubility of the copolymers could be affected dramatically by different monomer addition sequences. For example, when copolyimide **12d^1** was prepared by first dissolving C16BBPA (0.5 mol) in 1-chloronaphthalene followed by the addition of BPDA (1 mol), followed by addition of PFMB (0.5 mol), it could be dissolved in common solvents (reaction 1, Scheme 5). However, when C16BBPA (0.5 mol) and PFMB (0.5 mol) were dissolved in 1-chloronaphthalene at the same time followed by addition of BPDA (1 mol), the resulting copolymer **12d^2** was not soluble in any common solvent (reaction 2, Scheme 5). Copolyimides **12d^1** and **12d^2** had almost the same elemental compositions (Table 6). However, in reaction 1, a copolyimide with a relatively high degree of alternation was formed. In reaction 2, it is likely that the copolymer had a block structure due to the different reactivities of the diamines. C16BBPA is considerably more reactive than PFMB. Aromatic alternating copolyimides have been prepared from the diamines, such as *p*-phenylenediamine, and *m*-phenylenediamine, and dianhydrides, such as PMDA, BPDA, and 6FDA.[23,24] The alternating copolyimides exhibited much better solubility in NMP, DMSO, and DMAc than the corresponding random isomers, which were insoluble or partially soluble in NMP and DMSO, and insoluble in DMAc. Copolyimides **12d^1** and **12d^2** also show similar thermal stability (Table 4). However, the viscosity of **12d^2** was unable to be measured due to its insolubility in chloroform.

Table 6. Elemental Analysis of Copolyimides BPDA/PFMB:C16BBPA (50:50)

	CPI	C (%)	H (%)	F (%)
calcd	**12d**	76.01	8.79	4.40
found[a]	**12d^1**	74.24	8.76	4.20
found[b]	**12d^2**	74.11	8.85	4.35

[a] Prepared by reaction 1, Scheme 5. [b] Prepared by reaction 2, Scheme 5.

Table 7. Pretilt Angles Generated by Polyimide Films

polyimides	pretilt angle (deg)	LC
11k	6[a]	E7
12c^1	9[a]	E7
11h	90[b]	E7
11j	90[b]	E7

[a] Determined by the crystal rotation method. [b] Determined by optical microscopy.

Pretilt Angles Generated by Polyimide Films. Pretilt angles generated by films of on polyimides **11k**, **12c^1**, **11h**, and **11i** were determined either by the crystal rotation method or with optical microscopy in a preliminary test (Table 7). Antiparallel liquid crystal cells were first prepared in the clean room at the Kent State University Liquid Crystal Institute. Thus, *o*-dichlorobenzene solutions of the polyimides (1 wt %) were spin-coated on ITO glass followed by heating to 180 °C. Each polyimide film was rubbed twice in one direction. The cells were then assembled in an antiparrallel configuration using a ultraviolet (UV) adhesive, leaving a small gap for liquid crystal molecules. After the cells were cured in a UV cure station, they were filled with the liquid crystal (E7) using a vertical vacuum fill station. After the LC cells were pressed to a uniform thickness, the fill hole was sealed.

At first, it was thought that the multiple alkyl side chains would increase not only the solubility but also the pretilt angles generated by the polyimide films. As stated earlier, the polyimides containing multiple side chains were soluble in common solvents. However, the pretilt angle generated by a film of the polyimide prepared from C12BBPA (**11k**) was only 6°. When the length of the side chain was increased to C14 and C16, the corresponding films generated pretilt angles of 90°, i.e., the liquid crystal molecules were homoetropically

aligned. When PFMB was included in one of these systems in copolyimide **12c**, the film pretilt angle fell to 9°. This indicates that the perfluoromethyl groups counteracted the effect of the long pendent alkyl groups.

Conclusions

One series of alkyl substituted diamines was synthesized, i.e., 2,2′-bis{4-[3,4,5-tris(*n*-alkan-1-yloxy)benzoate]}-4,4′-biphenyldiamines. The *n*-alkyl chains contained from 5 to 18 carbon atoms. The diamines, which contained twisted biphenyl structures, were polymerized with PMDA, BPDA, DBBPDA, and 6FDA. The polyimides were prepared using the one-step polymerization method. Most of the polyimides could be dissolved in chlorinated solvents, such as chloroform and TCE. The polyimides could be solution cast into flexible, tough films, except for those based on PMDA. The $\bar{M}_n$s of the polyimides as determined with GPC ranged from 79 800 and 382 000. The side chains that contained at least 10 carbon atoms crystallized. The T_ms of the crystalline regions increased as the length of the side chains increased. The crystallization of C_{18} side chains was studied with variable temperature, solid state ^{13}C NMR. A WAXD study showed that the spacing between the main chains increased as the number of carbon atoms in the side chains increased. The backbone diameter was 2.14 nm, indicating several polyimide main chains stacked each other to form supermolecular, nanoscale structures. Four polyimides were used to prepare alignment layers. The films generated liquid crystal pretilt angles of 6, 9, 90, and 90°, respectively.

Experimental Section

Materials. Pyromellitic dianhydride (PMDA) (Chriskev Co.), 3,3′,4,4′-biphenyltetracarboxylicdianhydride (BPDA) (Chriskev Co.) and 2,2′-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) (Chriskev Co.) were sublimated prior to use (mp 246−248 °C). 2,2′-Dibromo-4,4′,5,5′-biphenyltetracarboxylic dianhydride (DBBPDA) and 2,2′-bis(trifluoromethyl)benzidine (PFMB) were synthesized according to the previous publications in Harris's group.[25] Dichlorobenzene (DCB) and 1-chloronaphthalene (Aldrich) were distilled under reduced pressure after drying with calcium hydride. Copper (Cu) (Aldrich Chemical Co.) was activated with a 2% iodine/acetone solution and washed first with hydrochloric acid/acetone (1:1) and then acetone. All the other reagents and solvents were used as received.

Instrumentation. Proton and carbon nuclear magnetic ($^1H-$ and ^{13}C NMR) spectra were measured at 200 MHz on a Varian Gemini-200 spectrometer. Variable temperature (VT) solid state ^{13}C NMR measurements were carried out using a Chemagnetics CMX-200. Infrared (IR) spectra were obtained with an ATI Mattson Genesis Series Fourier transform infrared spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. All melting points were determined on a Mel-Temp melting point apparatus and were uncorrected. Intrinsic viscosities were determined with a Cannon Ubbelohde No. 50 viscometer using chloroform as the solvent at 30.0 ± 0.1 °C. Thermogravimetric analyses (TGA) were performed in nitrogen and air with a TA Hi-Res TGA 2950 thermogravimetric analyzer using a heating rate of 10 °C/min. Gel permeation chromatography (GPC) analyses were carried out using a Waters 510 HPLC pump, a Waters 410 differential refractometer, and a series of UltraStyragel columns (50, 10^2, 10^3, 10^4, and 10^5 nm) with tetrahydrofuran as the eluent at 35 °C. In some cases, HT UltraStyragel columns (10^2, 10^3, 10^4 and 10^5 nm) were used with chloroform as the eluent at 40 °C. All the analyses were carried out with a flow rate of 1 mm/min using UV, RI and light scattering detectors. Molecular weights and molecular weight distributions of polymers were determined using a universal calibration curve, which was obtained by plotting ln($[\eta]M_n$) as a function of elution volume, after calibration with polystyrene standards (Polymer Laboratories). Differential scanning calorimetry (DSC) analyses were carried out on a DuPont 9900 thermal analysis system and a Perkin-Elmer DSC-2 using a heating rate of 10 °C/min. A Rigaku X-ray generator with a 12 kW rotating anode was used for wide-angle X-ray diffraction analysis. The point-focus beam was monochromatized to Cu Kα (1.54 A) with a graphite crystal. X-ray diffraction data were obtained on a Rigaku diffractometer. A thermal controller was added to the X-ray apparatus for thermal measurements. The temperature accuracy was ±1 °C and the heating and cooling rates were 2 °C/min. Polymer thin films were solution cast from 10 to 15 wt % of 1,1,2,2-tetrachloroethane solutions. The pretilt angles of the liquid crystals on polyimide films were determined using crystal rotation measurements, which were carried out using a LCD Parameter Tester (LCD-5016).

Methyl 3,4,5-Tris(*n*-pentan-l-yloxy)benzoate (3a). To a 500 mL, three-necked flask equipped with condenser and a mechanical stirrer were added 1-bromopentane (27.0 g, 0.180 mol) and DMF (250 mL). The mixture was sparged with N_2, and then potassium carbonate (51.0 g, 0.360 mol) and methyl 3,4,5-trihydroxybenzoate (11.1 g, 0.0600 mol) were added. The reaction mixture was heated at 70 °C for 12 h with stirring under N_2. After the mixture was allowed to cool to room temperature, the filtrate obtained by filtration was diluted with ethyl ether (400 mL) and transferred to a separator funnel. The organic phase was washed three times with water (500 mL), once with dilute hydrochloric acid, once with water (200 mL), and then with a saturated sodium chloride aqueous solution (50 mL). The organic phase was separated and dried with magnesium sulfate. The mixture was filtered, and the solvent was removed under reduced pressure. The liquid residue was passed through a short column of basic aluminum oxide using methylene chloride as the eluent to yield 18.2 g (77%) of a colorless liquid; (lit.[26] bp not reported). IR (KBr): 2953, 2920, 2952, 1721 (C═O), 1613, 1585, 1515, 1465, 1433, 1332, 1248, 1203, 1127, 821, and 762 cm^{-1}. ^1H NMR ($CDC1_3$): δ 0.88 (t, 9H, CH_3), 1.27 (m, 12H, $(CH_2)_2$), 1.78 (m, 6H, CH_2CH_2OPh), 3.89 (s, 3H, CO_2CH_3), 4.01 (m, 6H, CH_2CH_2OPh), and 7.25 ppm (s, 2H, Ar−H).

Methyl 3,4,5-Tris(*n*-octan-l-yloxy)benzoate (3b). Compound **3b** was synthesized from 1-bromooctane (69.5 g, 0.360 mol) and methyl 3,4,5-trihydroxybenzoate (22.2 g, 0.120 mol) using the same procedure used for compound **3a** to afford 52.0 g (83%) of a colorless liquid: (lit.[27] bp not reported). ^1H NMR ($CDC1_3$): δ 0.88 (t, 9H, CH_3), 1.27 (m, 30H, $(CH_2)_5$), 1.78 (m, 6H, CH_2CH_2OPh), 3.89 (s, 3H, CO_2CH_3), 4.01 (m, 6H, CH_2CH_2OPh), and 7.25 ppm (s, 2H, Ar−H).

Methyl 3,4,5-Tris(*n*-decan-l-yloxy)benzoate (3c). Compound **3c** was synthesized from 1-bromodecane (79.6 g, 0.360 mol) and methyl 3,4,5-trihydroxybenzoate (22.2 g, 0.120 mol) using the same procedure used for compound *3a* with following modification: the product was recrystallized from ethanol to afford 59.0 g (82%) of white crystals: mp 28−29 °C (lit.[28] 29 °C). IR (KBr): 2920, 2850, 1716 (C═O), 1614, 1516, 1332, 1248, 1101, 821, 762 cm^{-1}. ^1H NMR ($CDC1_3$): δ 0.88 (t, 9H, CH_3), 1.27 (m, 42H, $(CH_2)_7$), 1.78 (m, 6H, CH_2CH_2OPh), 3.89 (s, 3H, CO_2CH_3), 4.01 (m, 6H, CH_2CH_2OPh), and 7.25 ppm (s, 2H, Ar−H).

Methyl 3,4,5-Tris(*n*-dodecan-l-yloxy)benzoate (3d). Compound **3d** was synthesized from 1-bromododecane (90.5 g, 0.360 mol) and methyl 3,4,5-trihydroxybenzoate (22.2 g, 0.120 mol) using the same procedure used for compound **3a** with the following modification: the product was recrystallized from acetone to afford 71.1 g (86%) of a white solid: mp 42−44 °C (lit.[29] 39−42.5 °C). IR (KBr): 2953, 2919, 2849, 1717, 1613, 1587, 1515, 1466, 1433, 1332, 1246, 1204, 1175, 1127, 978, 821, and 762 cm^{-1}. ^1H NMR ($CDC1_3$): δ 0.88 (t, 9H, CH_3), 1.27 (m, 54H, $(CH_2)_9$), 1.78 (m, 6H, CH_2CH_2OPh), 3.89 (s, 3H, CO_2CH_3), 4.01 (m, 6H, CH_2CH_2OPh), and 7.25 ppm (s, 2H, Ar−H). ^{13}C NMR ($CDC1_3$): δ 14.18, 22.83, 26.26, 29.51, 29.55, 29.73,29.79, 29.85,30.54, 32.08, 52.16, 69.54, 73.72, 108.60, 125.00, 143.01, 153.21, and 167.21 ppm.

Methyl 3,4,5-Tris(*n*-tetradecan-l-yloxy)benzoate (3e). Compound **3e** was synthesized from 1-bromotetradecane (149.7 g, 0.5400 mol) and methyl 3,4,5-trihydroxybenzoate (33.3 g, 0.180

mol) using the same procedure used for compound **3a** with the following modification: the product was recrystallized from acetone to afford 103.6 g (75%) of a white solid: mp 54−55 °C (lit.[30] mp not reported). ^{1}H NMR ($CDC1_3$): δ 0.88 (t, 9H, CH_3), 1.27 (m, 66H, $(CH_2)_n$), 1.78 (m, 6H, CH_2CH$_2$OPh), 3.89 (s, 3H, CO_2CH_3), 4.01 (m, 6H, CH$_2$CH_2OPh), and 7.25 ppm (s, 2H, Ar−H).

Methyl 3,4,5-Tris(*n*-hexadecan-l-yloxy)benzoate (3f). Compound **3f** was synthesized from 1-bromohexadecane (90.9 g, 0.300 mol) and methyl 3,4,5-trihydroxybenzoate (18.5 g, 0.100 mol) using the same procedure used for compound **3a** with the following modification: the product was recrystallized from acetone to afford 60.0 g (86%) of a white solid: mp 63−64 °C (lit.[31] mp not reported). ^{1}H NMR ($CDC1_3$): δ 0.88 (t, 9H, CH_3), 1.27 (m, 78H, $(CH_2)_{13}$), 1.78 (m, 6H, CH_2CH$_2$OPh), 3.89 (s, 3H, CO_2CH_3), 4.01 (m, 6H, CH$_2$CH_2OPh), and 7.25 ppm (s, 2H, Ar−H).

Methyl 3,4,5-Tris(*n*-octadecan-l-yloxy)benzoate (3g). Compound **3g** was synthesized from 1-bromooctadecane (45.0 g, 0.180 mol) and methyl-3,4,5-trihydroxybenzoate (11.1 g, 0.060 mol) according to the same procedure used for compound **3a** with following modification: the product was recrystallized from acetone to afford 29.5 g (53%) of a white solid: mp 68−69 °C (lit[32] 61−63 °C). ^{1}H NMR ($CDC1_3$): δ 0.88 (t, 9H, CH_3), 1.27 (m, 90H, $(CH_2)_{15}$), 1.78 (m, 6H, CH_2CH$_2$OPh), 3.89 (s, 3H, CO_2CH_3), 4.01 (m, 6H, CH$_2$CH_2OPh), 7.25 ppm (s, 2H, Ar−H).

3,4,5-Tris(*n*-pentan-l-yloxy)benzoic Acid (4a). To a 125 mL Erlenmeyer flask containing a Teflon-coated magnetic stir bar were added methyl 3,4,5-tris(*n*-pentan-l-yloxy)benzoate (6.1 g, 0.015 mol), 95% ethanol (50 mL) and potassium hydroxide (5.8 g, 0.10 mol). The mixture was heated at 78 °C for 2 h with stirring and allowed to cool to room temperature. The solution was acidified with dilute hydrochloric acid and added to water (ca. 100 mL). The solid that precipitated was collected by filtration to yield 5.4 g (95%) of a white solid: mp 46−48 °C (lit.[26] mp 51 °C, DSC, 20 °C/min). IR (KBr): 3078, 2920, 2850, 2640 (br, COOH), 1685 (C═O), 1587,1505, 1466, 1433, 1391, 1333, 1231, 865, 765 cm^{-1}. ^{1}H NMR ($CDC1_3$): δ 0.88 (t, 9H, CH_3), 1.27 (m, 12H, $(CH_2)_2$), 1.78 (m, 6H, CH_2CH$_2$OPh), 4.01 (m, 6H, CH$_2$CH_2OPh), and 7.24 ppm (s, 2H, Ar−H).

3,4,5-Tris(*n*-octan-l-yloxy)benzoic Acid (4b). Compound **4b** was synthesized from methyl 3,4,5-tris(*n*-octan-l-yloxy)benzoate (26.0 g, 0.0500 mol) using the same procedure used for compound **4a** to afford 25.3 g (96%) of a white solid: mp 59−61 °C (lit.[27] mp 53 °C). ^{1}H NMR ($CDC1_3$): δ 0.94 (t, 9H, CH_3), 1.40 (m, 30H, $(CH_2)_5$), 1.78 (m, 6H, CH_2CH$_2$OPh), 4.01 (m, 6H, CH$_2$CH_2OPh), and 7.24 ppm (s, 2H, Ar−H).

3,4,5-Tris(*n*-decan-l-yloxy)benzoic Acid (4c). Compound **4c** was synthesized from methyl 3,4,5-tris(*n*-decan-l-yloxy)benzoate (25.4 g, 0.0422 mol) using the same procedure used for compound **4a** with the following modification: the product was recrystallized from acetone to afford 23.1 g (93%) of a white solid: mp 52−53 °C (lit.[28] 53−54 °C). ^{1}H NMR ($CDC1_3$): δ 0.88 (t, 9H, CH_3), 1.27 (m, 42H, $(CH_2)_7$), 1.78 (m, 6H, CH_2CH$_2$OPh), 4.01 (m, 6H, CH$_2$CH_2OPh), and 7.24 ppm (s, 2H, Ar−H).

3,4,5-Tris(*n*-dodecan-l-yloxy)benzoic acid (4d). To a 500 mL Erlenmeyer flask containing a Teflon-coated magnetic stir bar were added methyl 3,4,5-tris(*n*-dodecan-l-yloxy)benzoate (20.4 g, 0.0294 mol), 95% ethanol (160 mL), and potassium hydroxide (14.5 g, 0.204 mol). The mixture was heated at 78 °C for 2 h with stirring and then allowed to cool to room temperature. The resulting solid was collected by filtration, transferred to a 500 mL Erlenmeyer flask, and then dissolved in THF (300 mL). The solution was acidified with dilute hydrochloric acid to pH = l and then added into water (ca. 500 mL). The precipitate that formed was collected by filtration and recrystallized from acetone to yield 17.8 g (90%) of a white solid: mp 59−60 °C (lit.[26] 64 °C, DSC, 20 °C/min). IR (KBr) 2955, 2919, 1850, 2643 (br, COOH), 1683 (C═O), 1586, 1504, 1468, 1431, 1383, 1333, 1275, 1226, 1121, 994, and 767 cm^{-1}. ^{1}H NMR ($CDC1_3$): δ 0.88 (t, 9H, CH_3), 1.27 (m, 54H, $(CH_2)_9$), 1.78 (m, 6H, CH_2CH$_2$OPh), 4.01 (m, 6H, CH$_2$CH_2OPh), and 7.24 ppm (s, 2H, Ar−H). ^{13}C NMR ($CDC1_3$): δ 14.18, 22.83, 26.26, 29.51, 29.55, 29.73,29.79, 29.85,30.54, 32.08, 69.64, 73.88, 109.30, 125.11, 142.95, 153.29, and 172.62 ppm.

3,4,5-Tris(*n*-tetradecan-l-yloxy)benzoic Acid (4e). Compound **4e** was synthesized from methyl 3,4,5-tris(*n*-tetradecan-l-yloxy)-benzoate (30.9 g, 0.0300 mol) using the same procedure used for compound **4d** to afford 29.0 g (96%) of a white solid: mp 74−76 °C (lit[30] mp 69−70 °C). ^{1}H NMR ($CDC1_3$): δ 0.88 (t, 9H, CH_3), 1.27 (m, 66H, $(CH_2)_{11}$), 1.78 (m, 6H, CH_2CH$_2$OPh), 4.01 (m, 6H, CH$_2$CH_2OPh), and 7.24 ppm (s, 2H, Ar−H).

3,4,5-Tris(*n*-hexadecan-l-yloxy)benzoic Acid (4f). Compound **4f** was synthesized from methyl 3,4,5-tris(*n*-hexadecan-l-yloxy)-benzoate (26.0 g, 0.0300 mol) using the same procedure as compound **4d** to afford 24.0 g (95%) of a white solid: mp 78−80 °C (lit.[31] mp 78−80 °C). ^{1}H NMR ($CDC1_3$): δ 0.88 (t, 9H, CH_3), 1.27 (m, 78H, $(CH_2)_{13}$), 1.78 (m, 6H, CH_2CH$_2$OPh), 4.01 (m, 6H, CH$_2$CH_2OPh), and 7.24 ppm (s, 2H, Ar−H).

3.4,5-Tris(*n*-octadecan-l-yloxy)benzoic acid (4g). Compound **4g** was synthesized from methyl 3,4,5-tris(*n*-octadecan-l-yloxy)-benzoate (9.4 g, 0.010 mol) using the same procedure used for compound **4d** was obtained 8.3 g (93%) of a white solid: mp 85−86 °C (lit.[33] 83−85 °C). ^{1}H NMR ($CDC1_3$): δ 0.88 (t, 9H, CH_3), 1.27 (m, 90H, $(CH_2)_{15}$), 1.78 (m, 6H, CH_2CH$_2$OPh), 4.01 (m, 6H, CH$_2$CH_2OPh), and 7.24 ppm (s, 2H, Ar−H).

4-Iodo-3-methoxynitrobenzene (6). Concentrated sulfuric acid (200 mL) was added slowly to a mixture of 2-methoxy-4-nitroaniline (100.8 g, 0.3000 mol) and water (400 mL). The solution was heated until all the solids dissolved and then cooled to 0 °C in an ice bath. A solution of sodium nitrite (49.2 g, 0.720 mol) in water (160 mL) was added dropwise, so that the mixture was maintained between 0 and 5 °C. After the addition was complete, the solution was stirred for 30 min at 0 °C and then filtered. The filtrate was added slowly to a vigorously stirred solution of potassium iodide (199.2 g, 1.200 mol) in the water (2000 mL). The solid was collected by filtration and washed first with a dilute aqueous sodium bisulfite solution and then with water. The product was recrystallized from acetone/methanol to afford 128.0 g (77%) of brown crystals: mp 133−135 °C (lit.[34] mp 127−128 °C). ^{1}H NMR ($CDC1_3$): 8 3.96 (s, 3H, CH_3), 7.54−7.61 (m, 2H, Ar−H), and 7.91 ppm (d, 1H, Ar−H).

2,2′-Dimethoxy-4,4′-dinitrobiphenyl (7). To a 250 mL, three-necked flask equipped with a condenser and a mechanical stirrer were added 4-iodo-3-methoxynitrobenzene (33.4 g, 0.120 mol), activated copper (38.1 g, 0.600 mol), and DMF (80 mL). After the solution was stirred and heated at reflux for 16 h, DMF (80 mL) was added. The resulting solution was heated to reflux and then filtered while hot. The filtrate was stored in a freezer (−10 °C) overnight. The solid that formed was collected by filtrated and washed with methanol to afford 10.8 g (61%) of yellow crystals: mp 255−257 °C (lit.[35] mp 253−254 °C). ^{1}H NMR ($CDC1_3$): δ 3.86 (s, 6H, CH_3), 7.34 (d, 2H, Ar−H), 7.82 (d, 2H, Ar−H), and 7.88 ppm (dd, 2H, Ar−H).

4,4′-Dinitro-2,2′-biphenyldiol (8). 2,2′-Dimethoxy-4,4′-dinitrobiphenyl (10.0 g, 0.0333 mol) and pyridine hydrochloride (100 g) were stirred and heated at 210 °C for 2 h and then poured into water (800 mL). The solid that formed was collected by filtration and recrystallized from acetone/water to give 8.24 g (90%) of yellow crystals: mp 254−255 °C (lit.[35] mp 253−254 °C). ^{1}H NMR (DMSO-d_6): δ 7.44 (dd, 2H, Ar−H), and 7.69−7.75 ppm (m, 4H, Ar−H).

2,2′-Bis{4-[3,4,5-tris(*n*-pentan-l-yloxy)benzoate]}-4,4′-dinitrobiphenyl (9a). 4,4′-Dinitro-2,2′-biphenyldiol (0.80 g, 0.0030 mol), 3,4,5-tris(*n*-pentan-l-yloxy)benzoic acid (2.28 g, 0.00600 mol), dicyclohexylcarbodiimide (1.24 g, 0.00600 mol), 4-dimethylaminipyridine (0.22 g), and methylene chloride (50 mL) were stirred at room temperature for 24 h. The resulting precipitate was filtered, and the methylene chloride was evaporated on a rotary evaporator. The residue was dispersed in hexane (50 mL) and then filtered. The filtrate was evaporated to dryness under reduced pressure. THF (25 mL) was added, and the solution was poured into water (200 mL) that was slightly acidified with hydrochloric acid. After the mixture was stirred for 24 h, methylene chloride (75 mL) was added.

The organic layer was separated, dried over magnesium sulfate, and the methylene chloride was evaporated. The solid was recrystallized from ethanol to yield 2.3 g (77%) of a white solid: mp 77−78 °C. IR (KBr): 2917, 2850, 1738(C═O), 1337, and 1123 cm^{-1} (C−O−Ph). ^1H NMR ($CDCl_3$): δ 0.85 (t, 18H, CH_3), 0.95−1.43 (m, 24H, $(CH_2)_2$), 1.69 (m, 12H, CH_2CH_2O), 3.80−4.01 (overlapped t, 12H, CH_2O), 7.12 (s, 4H, Ar−H *ortho* to C═O), 7.58 (d, 2H, Ar−H *meta* to O−C═O), 8.20 (dd, 2H, Ar−H para to O−C═O), and 8.26 ppm (d, 2H, Ar−H *ortho* to O−C═O). ^{13}C NMR ($CDCl_3$): δ 14.09, 14.15, 22.51, 22.60, 28.24, 28.30, 29.04, 30.10, 69.23, 73.75, 108.56, 118.64, 121.11, 122.25, 131.83, 135.77, 143.94, 148.90, 153.30, and 163.91 ppm. Anal. Calcd for $C_{62}H_{76}N_2O_{14}$: C, 67.18; H, 7.65%. Found: C, 67.34; H, 7.86.

2,2′-Bis{4-[3,4,5-tris(*n*-octan-l-yloxv)benzoate]}-4,4′-dinitrobiphenyl (9b). Compound **9b** was synthesized from 4,4′-dinitro-2,2′-biphenyldiol (3.45 g, 0.0125 mol), and 3,4,5-tris(*n*-octan-l-yloxy)benzoic acid (12.7 g, 0.0250 mol) using the same procedure used for compound **9a** to afford 12.4 g (77%) of a white solid: mp 49−51 °C. IR (KBr): 2917, 2850, 1738(C═O), 1337, and 1123 cm^{-1} (C−O−Ph). ^1H NMR ($CDCl_3$): δ 0.85 (t, 18H, CH_3), 0.95−1.43 (m, 60H, $(CH_2)_5$), 1.69 (m, 12H, CH_2CH_2O), 3.80−4.01 (overlapped t, 12H, CH_2O), 7.12 (s, 4H, Ar−H *ortho* to C═O), 7.58 (d, 2H, Ar−H *meta* to O−C═O), 8.20 (dd, 2H, Ar−H para to O−C═O), and 8.26 ppm (d, 2H, Ar−H *ortho* to O−C═O). Anal. Calcd for $C_{74}H_{112}N_2O_{14}$: C, 70.90; H, 9.00. Found: C, 71.01; H, 8.96.

2,2′-Bis{4-[3,4,5-tris(*n*-decan-1-yloxylbenzoate]}-4,4′-dinitrobiphenyl (9c). Compound **9c** was synthesized from 4,4′-dinitro-2,2′-biphenyldiol (1.65 g, 0.00600 mol) and 3,4,5-tris(*n*-decan-l-yloxy)benzoic acid (7.08 g, 0.0120 mol) using the same procedure used for compound **9a** with the following modification: the product was recrystallized from acetone to afford 7.2 g (90%) of a white solid: mp 32−34 °C. IR (KBr): 2917, 2850, 1738(C═O), 1337, and 1123 cm^{-1} (C−O−Ph). ^1H NMR ($CDCl_3$): δ 0.85 (t, 18H, CH_3), 0.95−1.43 (m, 84H, CH_2s), 1.69 (m, 12H, CH_2CH_2O), 3.80−4.01 (overlapped t, 12H, CH_2O), 7.12 (s, 4H, Ar−H *ortho* to C═O), 7.58 (d, 2H, Ar−H *meta* to O−C═O), 8.20 (dd, 2H, Ar−H *para* to O−C═O), and 8.26 ppm (d, 2H, Ar−H *ortho* to O−C═O). Anal. Calcd for $C_{86}H_{136}N_2O_{14}$: C, 72.64; H, 9.64. Found: C, 72.64; H, 9.69.

2,2′-Bis{4-[3,4,5-tris(*n*-dodecan-l-yloxv)benzoate]}-4,4′-dinitrobiphenyl (9d). Compound **9d** was synthesized from 4,4′-dinitro-2,2′-biphenyldiol (1.1 g, 0.0040 mol) and 3,4,5-tris(*n*-dodecan-l-yloxy)benzoic acid (5.4 g, 0.0080 mol) using the same procedure used for compound **9a** with the following modification: the product was recrystallized from acetone to afford 5.91 g (91%) of a white solid: mp 58−59 °C. IR (KBr): 3084, 2955, 2919, 2850, 1711-(C═O), 1586, 1529, 1501, 1467, 1437, 1345, 1284, 1238, 1148, 1105 (C−O−Ph), 961, and 721 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.85 (t, 18H, CH_3), 0.95−1.43 (m, 108H, CH_2s), 1.69 (m, 12H, CH_2-CH_2O), 3.80−4.01 (overlapped t, 12H, CH_2O), 7.12 (s, 4H, Ar−H *ortho* to C═O), 7.58 (d, 2H, Ar−H *meta* to O−C═O), 8.20 (dd, 2H, *Ar−H para* to O−C═O), and 8.26 ppm (d, 2H, Ar−H *ortho* to O−C═O). Anal. Calcd for $C_{98}H_{160}N_2O_{14}$: C, 74.01; H, 10.14. Found: C, 74.37; H, 10.25.

2,2′-Bis{4-[3,4,5-tris(*n*-tetradecan-l-yloxy)benzoate]}-4,4′-dinitrobiphenyl (9e). 4,4′-Dinitro-2,2′-biphenyldiol (2.76 g, 0.0100 mmol), 3,4,5-tris(*n*-tetradecan-l-yloxy)benzoic acid (15.4 g, 0.0200 mmol), dicyclohexylcarbodiimide (4.20 g, 0.0200 mol), 4-dimethylaminipyridine (0.40 g), and methylene chloride (300 mL) were stirred at room temperature for 6 h, and then heated at reflux for 24 h. The mixture was filtered while hot. After the solution was allowed to cool to room temperature, a precipitate formed. The precipitate was removed by filtration and the filtrate was stored in a refrigerator (0 °C). The solid that formed was collected by filtration, and recrystallized from acetone to give 15.6 g (86%) of a white powder: mp 66−68 °C. IR (KBr): 2917, 2850, 1738(C═O), 1337, and 1123 cm^{-1} (C−O−Ph). ^1H NMR ($CDCl_3$): δ 0.85 (t, 18H, CH_3), 0.95−1.43 (m, 132H, CH_2s), 1.69 (m, 12H, CH_2-CH_2O), 3.80−4.01 (overlapped t, 12H, CH_2O), 7.12 (s, 4H, Ar−H *ortho* to C═O), 7.58 (d, 2H, Ar−H *meta* to O−C═O), 8.20 (dd, 2H, Ar−H *para* to O−C═O), and 8.26 (d, 2H, Ar−H *ortho* to O−C═O). Anal. Calcd for $C_{110}H_{184}N_2O_{14}$: C, 75.13%; H, 10.55. Found: C, 75.06; H, 10.44.

2,2′-Bis{4-[3,4,5-tris(*n*-hexadecan-l-yloxy)benzoate]}-4,4′-dinitrobiphenyl (9f). Compound **9f** was synthesized from 4,4′-dinitro-2,2′-biphenyldiol (2.76 g, 0.0100 mol) and 3,4,5-tris(*n*-hexadecan-l-yloxy)benzoic acid (16.8 g, 0.0200 mol) using the same procedure used for compound **9e** to afford 16.90 g (88%) of a white powder: mp 77−79 °C. IR (KBr): 3069, 2955, 2918, 2850, 1723(C═O), 1586, 1524, 1467, 1438, 1349, 1281, 1243, 1116 (C−O−Ph), 966, 833, and 720 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.85 (t, 18H, CH_3), 0.95−1.43 (m, 156H, CH_2s), 1.69 (m, 12H, CH_2CH_2O), 3.80−4.01 (overlapped t, 12H, CH_2O), 7.12 (s, 4H, Ar-*H ortho* to O−C═O), 7.58 (d, 2H, Ar−H *meta* to O−C═O), 8.20 (dd, 2H, Ar−H *para* to O−C═O), and 8.26 ppm (d, 2H, Ar−H *ortho* to O−C═O). Anal. Calcd for $C_{122}H_{208}N_2O_{14}$: C, 75.87; H, 11.04. Found: C, 76.04; H, 10.88.

2,2′-Bis{4-[3,4,5-tris(*n*-octadecan-l-yloxy)benzoate]}-4,4′-dinitrobiphenyl (9g). Compound **9g** was synthesized from 4,4′-dinitro-2,2′-biphenyldiol (1.22 g, 0.00440 mol) and 3,4,5-tris(*n*-octadecan-l-yloxy)benzoic acid (8.20 g, 0.00887 mol) using the same procedure used for compound **9e** to afford 8.10 g (86%) of a white powder: mp 61−62 °C. IR(KBr): 2917, 2850, 1738(C═O), 1337, and 1123 cm^{-1} (C−O−Ph). ^1H NMR ($CDCl_3$): δ 0.85 (t, 18H, CH_3), 0.95−1.43 (m, 180H, CH_2s), 1.69 (m, 12H, CH_2CH_2O), 3.80−4.01 (overlapped t, 12H, CH_2O), 7.12 (s, 4H, Ar−H *ortho* to C═O), 7.58 (d, 2H, Ar−H *meta* to O−C═O), 8.20 (dd, 2H, Ar−H *para* to O−C═O), and 8.26 ppm (d, 2H, Ar−H *ortho* to O−C═O). Anal. Calcd for $C_{134}H_{232}N_2O_{14}$: C, 76.81; H, 11.16. Found: C, 76.91; H, 11.11.

2,2′-Bis{4-[3,4,5-tris(*n*-pentan-l-yloxy)benzoate]}-4,4′-biphenyldiamine (10a, C5BBPA). 2,2′-Bis{4-[3,4,5-tris(*n*-pentan-l-yloxy)benzoate]}-4,4′-dinitrobiphenyl (5.5 g, 0.0055 mol), hexane (150 mL), and 5% palladium on activated carbon (0.70 g) were added to a hydrogenation bottle. The bottle was secured on a Parr hydrogenation apparatus, flushed three times with hydrogen, and then pressurized to 16 psi. After the mixture was agitated at room temperature for 12 h under the hydrogen pressure of 16 psi, it was filtered through Celite. The filter cake was washed with hexane, and then the filtrate was evaporated to dryness under reduced pressure on a rotary evaporator. The yellow residue was recrystallized from ethanol/water, which was stored in a freezer, to give 4.20 g (76%) of yellow crystals: mp 90−92 °C. IR (KBr) 3455-(NH_2), 3371 (NH_2), 2923, 2853, 1723 (C═O), 1625, 1586, 1496, 1430, 1336,1201, and 1117 cm^{-1} (C−O−Ph). ^1H NMR ($CDCl_3$): δ 0.88 (t, 18H, CH_3), 1.15−1.35 (m, 24H, $(CH_2)_2$), 1.72 (m, 12H, CH_2CH_2O), 3.74 (br s, 4H, NH_2), 3.89−3.99 (overlapped t, 12H, CH_2O), 6.56 (dd, 2H, Ar−H *para* to O−C═O), 6.60 (d, 2H, Ar−H *ortho* to O−C═O), 7.08 (d, 2H, Ar−H *meta* to O−C═O), and 7.27 ppm (s, 4H, Ar−H *ortho* to C═O). ^{13}C NMR ($CDCl_3$): δ 14.15, 14.18, 22.54, 22.64, 28.29, 28.33, 29.10, 30.11, 69.13, 73.61, 108.37, 108.96, 113.13, 120.88, 124.36, 132.43, 142.71, 146.90, 149.50, 153.07, and 164.91 ppm. Anal. Calcd for $C_{56}H_{80}N_2O_{10}$: C, 71.87; H, 8.73; N, 2.89. Found: C, 71.48; H, 8.45; N, 2.97.

2,2′-Bis{4-[3,4,5-tris(*n*-octan-l-yloxy)benzoate]}-4,4′-biphenyldiamine (10b, C8BBPA). Compound **10b** was synthesized from 2,2′-bis{4-[3,4,5-tri(*n*-octan-l-yloxy)benzoate]}-4,4′-dinitrobiphenyl (2.5 g, 0.0020 mol) using the same procedure used for compound **10a** with the following modification: the product was recrystallized from ethanol to afford 2.2 g (89%) of yellow crystals: mp 88−89 °C. IR (KBr) 3465(NH_2), 3372 (NH_2), 2926, 2855, 1726 (C═O), 1626, 1586, 1496, 1430, 1336,1199, and 1115 cm^{-1} (C−O−Ph). ^1H NMR ($CDCl_3$): δ 0.88 (t, 18H, CH_3), 1.15−1.35 (m, 60H, $(CH_2)_5$), 1.72 (m, 12H, CH_2CH_2O), 3.74 (br s, 4H, NH_2), 3.89−3.99 (overlapped t, 12H, CH_2O), 6.56 (dd, 2H, Ar−H *para* to O−C═O), 6.60 (d, 2H, Ar−H *ortho* to O−C═O), 7.08 (d, 2H, Ar−H *meta* to O−C═O), and 7.27 ppm (s, 4H, Ar−H *ortho* to C═O). Anal. Calcd for $C_{74}H_{116}N_2O_{10}$: C, 74.46; H, 9.79; N, 2.35. Found: C, 74.68; H, 9.80; N, 2.30.

2,2′-Bis{4-[3,4,5-tri(*n*-decan-l-yloxy)benzoate]}-4,4′-biphenyldiamine (10c, C10BBPA). Compound **10c** was synthesized from

2,2′-bis{4-[3,4,5-tris(*n*-octan-l-yloxy)benzoate]}-4,4′-dinitrobiphenyl (2.5 g, 0.0020 mol) using the same procedure used for compound **10a** with the following modification: the product was recrystallized from ethanol to afford 2.2 g (91%) of a yellow solid: mp 52 °C (DSC). IR (KBr) 3455(NH_2), 3371 (NH_2), 2923, 2853, 1723 (C═O), 1625, 1586, 1496, 1430, 1336,1201, and 1117 cm^{-1} (C−O−Ph). ^1H NMR ($CDC1_3$): δ 0.88 (t, 18H, CH_3), 1.15−1.35 (m, 84H, $(CH_2)_7$), 1.72 (m, 12H, CH_2CH_2O), 3.74 (br s, 4H, NH_2), 3.89−3.99 (overlapped t, 12H, CH_2O), 6.56 (dd, 2H, Ar−H *para* to O−C═O), 6.60 (d, 2H, Ar−H *ortho* to O−C═O), 7.08 (d, 2H, Ar−H *meta* to O−C═O), and 7.27 ppm (s, 4H, Ar−H *ortho* to C═O). Anal. Calcd for $C_{86}H_{140}N_2O_{10}$: C, 75.84; H, 10.36; N, 2.06. Found: C, 76.28; H, 10.27; N, 1.93.

2,2′-Bis{4-[3,4,5-tri(*n*-dodecan-l-yloxy)benzoate]}-4,4′-biphenyldiamine (10d, C12BBPA). 2,2′-Bis{4-[3,4,5-tris(*n*-dodecan-l-yloxy)benzoate]}-4,4′-dinitrobiphenyl (5.0 g, 0.0031 mol), hexane/ethyl acetate (150/45 mL), and 5% palladium on activated carbon (0.40 g) were added to a hydrogenation bottle. The bottle was secured on a Parr hydrogenation apparatus, flushed three times with hydrogen, and then pressurized to 16 psi. After the mixture was agitated at room temperature for 12 h under the hydrogen pressure of 16 psi, it was filtered through Celite. The filter cake was washed with ethyl acetate, and then the filtrate was evaporated to dryness under reduced pressure on a rotary evaporator. The residue was recrystallized from acetone, which was stored in a in freezer, to afford 3.50 g (71%) of a white powder: mp −14 and 44 °C (DSC). IR (KBr) 3453(NH_2), 3366 (NH_2), 2957, 2920, 2854, 1715 (C═O), 1622, 1592, 1496, 1465, 1440, 1375, 1331,1230, 1114 (C−O−Ph), 825 and 721 cm^{-1}. ^1H NMR ($CDC1_3$): δ 0.88 (t, 18H, CH_3), 1.15−1.35 (m, 108H, $(CH_2)_9$), 1.72 (m, 12H, CH_2CH_2O), 3.74 (br s, 4H, NH_2), 3.89−3.99 (overlapped t, 12H, CH_2O), 6.56 (dd, 2H, Ar−H *para* to O−C═O), 6.60 (d, 2H, Ar−H *ortho* to O−C═O), 7.08 (d, 2H, Ar−H *meta* to O−C═O), and 7.27 ppm (s, 4H, Ar−H *ortho* to C═O). Anal. Calcd for $C_{98}H_{168}N_2O_{10}$: C, 76.91; H, 10.80; N, 1.83. Found: C, 77.32; H, 10.66; N, 1.75.

2,2′-Bis{4-[3,4,5-tris(*n*-tetradecan-l-yloxy)benzoate]}-4,4′-biphenyldiamine (10e, C14BBPA). 2,2′-Bis{4-[3,4,5-tris(*n*-tetradecan-l-yloxy)benzoate]}-4,4′-dinitrobiphenyl (2.5 g, 0.0014 mol), toluene (150 mL), and 5% palladium on activated carbon (0.40 g) were added to a hydrogenation bottle. The bottle was secured on a Parr hydrogenation apparatus, flushed three times with hydrogen, and then pressurized to 16 psi. After the mixture was agitated at room temperature for 12 h under the hydrogen pressure of 16 psi, it was filtered through Celite. The filter cake was washed with toluene, and then the filtrate was evaporated to dryness under reduced pressure on a rotary evaporator. The solid was recrystallized from acetone to give 2.3 g (95%) of a white powder: mp 35 and 55 °C (DSC). IR(KBr) 3455 (NH_2), 3371 (NH_2), 2923, 2853, 1723 (C═O), 1625, 1586, 1496, 1430, 1336,1201, and 1117 cm^{-1} (C−O−Ph). ^1H NMR ($CDC1_3$): δ 0.88 (t, 18H, CH_3), 1.15−1.35 (m, 132H, (CH_2)n), 1.72 (m, 12H, CH_2CH_2O), 3.74 (br s, 4H, NH_2), 3.89−3.99 (overlapped t, 12H, CH_2O), 6.56 (dd, 2H, Ar−H *para* to O−C═O), 6.60 (d, 2H, Ar−H *ortho* to O−C−O), 7.08 (d, 2H, Ar−H *meta* to O−C═O), and 7.27 ppm (s, 4H, Ar−H *ortho* to C═O). Anal. Calcd for $C_{110}H_{188}N_2O_{10}$: C, 77.78; H, 11.15; N, 1.65. Found: C, 77.76; H, 11.39; N, 1.63.

2,2′-Bis{4-[3,4,5-tris(*n*-hexadecan-l-yloxy)benzoate]}-4,4′-biphenyldiamine (10f, C16BBPA). Compound **10f** was synthesized from 2,2′-bis{4-[3,4,5-tris(*n*-hexadecan-l-yloxy)benzoate]}-4,4′-dinitrobiphenyl (2.5 g, 0.0013 mol) according to the same procedure used for compound **10e** to afford 2.34 (95%) of a white powder: mp 59 °C (DSC). IR (KBr) 3455 (NH_2), 3371 (NH_2), 2923, 2853, 1723 (C═O), 1625, 1586, 1496, 1430, 1336,1201, and 1117 cm^{-1} (C−O−Ph). ^1H NMR ($CDC1_3$) 5 0.88 (t, 18H, CH_3), 1.15−1.35 (m, 156H, $(CH_2)i_3$), 1.72 (m, 12H, CH_2CH_2O), 3.74 (br s, 4H, NH_2), 3.89−3.99 (overlapped t, 12H, CH_2O), 6.56 (dd, 2H, Ar−H *para* to O−C═O), 6.60 (d, 2H, Ar−H *ortho* to O−C═O), 7.08 (d, 2H, Ar−H *meta* to O−C═O), and 7.27 ppm (s, 4H, Ar−H *ortho* to O−C═O). Anal. Calcd for $C_{122}H_{212}N_2O_{10}$: C, 78.49; H, 11.44; N, 1.56. Found: C, 78.74; H, 11.16; N, 1.56.

2,2′-Bis{4-[3,4,5-tris(*n*-octadecan-l-yloxy)benzoate]}-4,4′-biphenyldiamine (10g, C18BBPA). Compound **10g** was synthesized from 2,2′-bis{4-[3,4,5-tris(*n*-octadecan-l-yloxy)benzoate]}-4,4′-dinitrobiphenyl (2.68 g, 0.00128 mol) using the same procedure used for the compound **10e** to afford 2.46 (95%) of a white powder: mp 62 °C (DSC). IR (KBr) 3455 (NH_2), 3371 (NH_2), 2923, 2853, 1723 (C═O), 1625, 1586, 1496, 1430, 1336,1201, and 1117 cm^{-1} (C−O−Ph). ^1H NMR ($CDC1_3$): δ 0.88 (t, 18H, CH_3), 1.15−1.35 (m, 180H, $(CH_2)_{15}$), 1.72 (m, 12H, CH_2CH_2O), 3.74 (br s, 4H, NH_2), 3.89−3.99 (overlapped t, 12H, CH_2O), 6.56 (dd, 2H, Ar−H *para* to O−C═O), 6.60 (d, 2H, Ar−H *ortho* to O−C═O), 7.08 (d, 2H, Ar−H *meta* to O−C═O), and 7.27 ppm (s, 4H, Ar−H *ortho* to O−C═O). Anal. Calcd for $C_{134}H_{236}N_2O_{10}$: C, 79.08; H, 11.69; N, 1.38. Found: C, 79.12; H, 11.77; N, 1.30.

General Procedure for the Preparation of Polyimides (11a—l). The diamine with alkyl side chains (0.001000 mol), the dianhydride (0.001000 mol), and 1,2-dichlorobenzene or 1-chloronaphthalene (20−30 mL) were added to a three-necked resin kettle equipped with a mechanical stirrer, a nitrogen inlet, and a distillation head. Isoquinoline (5 drops) was added to the resin kettle. After the mixture was stirred and heated at 80 °C for 1 h, it was heated to 180−200 °C for 24 h. Water was continuously distilled from the reaction mixture. The solution was poured into a methanol (1 L). The polymer that precipitated was collected by filtration and dried under reduced pressure at 200 °C for 6−8 h.

Representative Procedure for the Preparation of Alternative Copolyimides (12d[1]). The diamine **10f** (0.001000 mol), BPDA (0.002000 mol) and 1-chloronaphthalene (20−30 mL) were added to a three-necked resin kettle equipped with a mechanical stirrer, a nitrogen inlet, and a distillation head. Isoquinoline (5 drops) was added to the resin kettle. The mixture was heated to 80 °C for 1 h and 180 °C for 2 h. After the mixture was allowed to cool to room temperature, PFMB (0.001000 mol) was added. The mixture was stirred and heated at 80 °C for 1 h, and then heated to 180−200 °C for 24 h. Water was continuously distilled from the reaction mixture. The solution was poured into a methanol (1 L). The polymer that precipitated was collected by filtration and dried under reduced pressure at 200 °C for 6−8 h. The yields of polyimides were 90−95%.

Procedure for the Preparation of Block Copolyimide (12d[2]). The diamine **10f** (0.001000 mol), PFMB (0.001000 mol), BPDA (0.002000 mol), and 1-chloronaphthalene (20−30 mL) were added to a three-necked resin kettle equipped with a mechanical stirrer, a nitrogen inlet, and a distillation head. Isoquinoline (5 drops) was added to the resin kettle. The mixture was heated to 80 °C for 1 h and 180 °C for 2 h. After the mixture was allowed to cool to room temperature, was added. The mixture was stirred and heated at 80 °C for 1 h, and then heated to 180−200 °C for 24 h. Water was continuously distilled from the reaction mixture. The solution was poured into a methanol (1 L). The polymer that precipitated was collected by filtration and dried under reduced pressure at 200 °C for 6−8 h. The yields of polyimides were 90−95%.

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