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Combined Type Liquid Crystalline Polymers Composed of Poly(*p*-phenylene terephthalate) Main Chain and Azobenzene Mesogenic Side Groups Attached through Polymethylene Spacers

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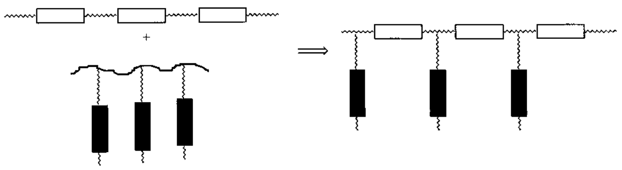
ABSTRACT: A series of combined main chain−side group thermotropic polyesters having varying lengths of oxypolymethyleneoxy spacers between the aromatic polyester main chain and the side azobenzene mesogenic unit have been synthesized and their liquid crystalline properties have been investigated. The thermal and liquid crystalline (LC) properties of the polymers were studied by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), optical microscopy, and X-ray diffractometry. The main chain is the poly(*p*-phenylene terephthalate) structure, and side mesogenic groups are attached through spacers onto terephthaloyl units. The spacer length was varied from oxytrimethyleneoxy (PAZO-3) to oxyhexamethyleneoxy (PAZO-6). A polymer with a longer spacer oxydecamethyleneoxy (PAZO-10), also was included in this investigation. The polymers with spacers up to the oxyhexamethyleneoxy spacer form nematic LC phases. In contrast, the polymer (PAZO-10) with the oxydecamethyleneoxy spacer was found to form a layered morphology in the mesophase. Moreover, a fiber spun from PAZO-10 revealed a biaxial molecular orientation where the side mesogenic groups including the spacer were oriented slightly tilted to the main chain. Other compositions produced only the fibers of the oriented nematic phases.

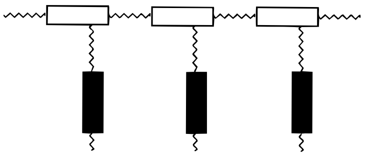
Introduction

A large variety of thermotropic liquid crystalline polymers (LCPs) have been reported for the past 20 years and they are classified as main chain, side chain or side group, and combined LCPs depending on the positions of the mesogenic structures in the molecular architecture.[1−3] The last group is the latest among the three groups of LCPs that was first reported by Ringsdorf et al.[4,5] followed by more intensive structural analysis by Zentel et al.[6−10] Most of the combined LCPs reported so far are combinations of main chain and side group LCPs, both of which contain so-called flexible spacers, as presented below.

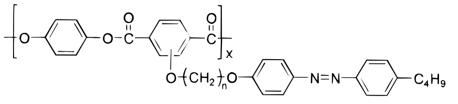


The mesophases formed by this type of combined LCPs are strongly dependent on the relative length of the main chain and side group spacers: comparable length favors the formation of smectic phases whereas different lengths induce the formation of nematic phases. In the smectic phases, the mesogenic groups in the main chain and side branches are more or less parallel to each other and form smectic layers.[11] The temperature range of the LC phases of those combined LCPs is strongly broadened by a synergistic interaction between the main chain and side group mesogenic structures.[6] However, there seem to be no clearly proven examples of combined LCPs containing flexible spacers in the main chain as well as in the side group that show a biaxial orientation with the pendent mesogenic groups oriented perpendicular or close to perpendicular to the main chain.

Another structure of combined LCPs is also possible where the pendent mesogenic groups are attached directly to the main chain mesogens[5,12] as shown below:



These combined LCPs tend to form only nematic phases, because formation of smectic layers consisting of main chain and pendent mesogenic groups becomes difficult in these structures. In addition to the structures mentioned above, chiral combined LCPs[13−15] and cross-linked combined LCPs[16−18] are also known. The former exhibit selective reflection of light when they are cholesteric or ferroelectric through the formation of the chiral S_C (S_C*) phase. In this investigation, we have prepared the following new combined LCPs, and mainly their LC properties and molecular organization in the LC phases have been studied.



The main chain of the polymers is the poly(*p*-phenylene terephthalate) structure and the azobenzene type mesogenic groups are attached to the main chain through the oxypolymethyleneoxy spacers. The number

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Table 1. Results of Elemental Analysis[a]

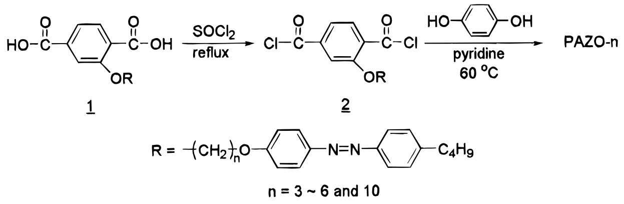
polymer	wt % C	wt % H	wt % N
PAZO-3	71.3 (72.0)	5.46 (5.49)	4.92 (5.09)
PAZO-4	72.0 (72.3)	5.54 (5.71)	4.91 (4.96)
PAZO-5	72.2 (72.6)	5.75 (5.92)	4.68 (4.84)
PAZO-6	72.5 (72.9)	6.22 (6.07)	4.67 (4.72)
PAZO-10	73.9 (74.1)	6.82 (6.84)	4.35 (4.32)

[a] Values in parentheses represent the calculated values for chemical formulaes neglecting terminal groups.

of methylene units in the spacer was varied from 3 to 6, and the decamethylene ($n = 10$) unit also was included in the present study. For convenience, these polymers are denoted as PAZO-*n*, where *n* describes the number of methylene units in the spacers.

Results and Discussion

Synthesis of Polymers. The substituted terephthalic acid monomers, 2-[ω-{4-(4-butylphenylazo)phenoxy}alkyloxy]terephthalic acids, were prepared following the synthetic method described by us recently.[19] These compounds were converted to the corresponding diacid dichlorides by refluxing in thionyl chloride. Dichlorides were polymerized at 60 °C with hydroquinone in the presence of pyridine using tetrahydrofuran (THF) as a solvent. The polymers were purified by Soxhlet extraction for 2 days using ethanol.



The structures of the polymers were confirmed by elemental analysis (Table 1) and IR, ^{1}H-NMR, and ^{13}C-NMR spectra. Polymers were soluble in trifluoroacetic acid and phenol/1,1,2,2-tetrachloroethane (TCE) mixtures. In general, the polymers with longer spacers exhibited better solubility in organic solvent. For example, PAZO-6 was soluble enough in $CDCl_3/C_2D_2Cl_4$ (1/5 by volume) to obtain its ^{13}C-NMR spectrum. Due to the presence of the azobenzene chromophore structures, all of the polymers are orange. Figure 1 shows the UV–vis spectrum of a representative polymer. The spectrum reveals a strong absorption in the visible region of 250–450 nm with its absorption maximum located at 343 nm. The solution viscosity values measured at 30 °C for the polymers range from 0.67 to 0.83 dL/g (Table 2), indicating that their molecular weights are reasonably high.

Thermal Properties. All of the polymers are semicrystalline and therefore exhibit clear melting transitions on DSC thermograms (Figure 2). DSC thermograms of PAZO-3 to PAZO-6 were obtained for the samples annealed at 150 °C for 1 h (PAZO-3), at 155 °C for 1 h (PAZO-4 and –5), or at 160 °C for 1 h (PAZO-6). The thermogram for PAZO-10 was obtained for the as-obtained sample. The melting transition temperatures (T_ms) range from about 166 to 188 °C. The melting transition temperatures shown in Table 2 are the temperatures where the endothermic peak maxima appeared on the first-heating DSC thermograms obtained at the heating rate of 10 °C/min. We do not find any correlation between the T_m values and the length of the spacers. However, it is very clear that the presence of large pendent structures has resulted in such low T_ms as observed in the present investigation.

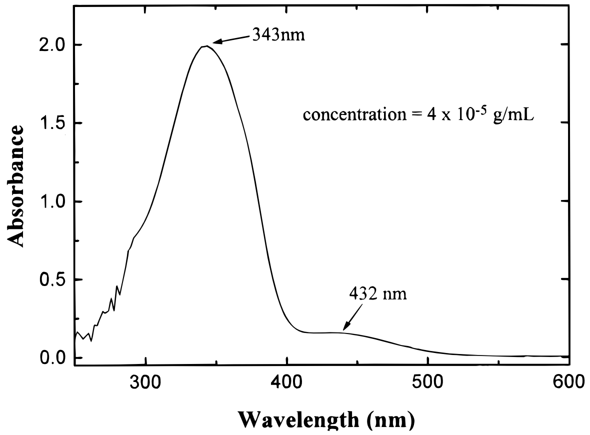


Figure 1. UV–vis spectrum of PAZO-6.

Table 2. General Properties of Polymers

n	η_{inh}[a] (dL/g)	T_{g1}[a] (°C)	T_{g2}[b] (°C)	T_m[b] (°C)	T_i[c] (°C)	T_d[i] (°C)
3	0.70	67	116	168	dec (>327)	327
4	0.78	63	113	172	dec (>329)	329
5	0.70	58	101	173	dec (>319)	319
6	0.83	38		188	dec (>315)	315
10	0.67	42[d]	114[d]	166[d]	dec (>307)	307

[a] Measured at 30 °C for 0.2 g/dL solutions in *p*-chlorophenol/1,1,2,2-tetrachloroethane (w/w = 6/4). [b] Estimated from DSC thermograms of annealed polymers obtained under a nitrogen atmosphere at the heating rate of 10 °C/min. [c] Observed by optical polarizing microscopy. [d] The value was obtained from the DSC thermogram of as-polymerized polymer.

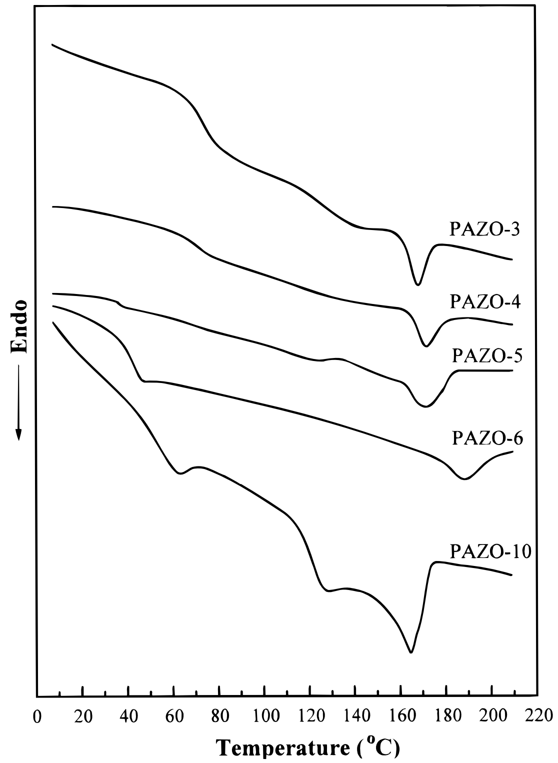


Figure 2. DSC thermograms of PAZO-*n* polymers obtained under a nitrogen atmosphere at the heating rate of 10 °C/min.

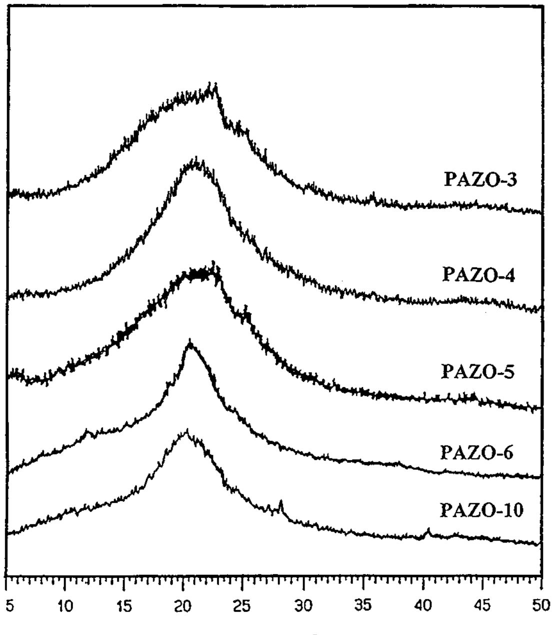
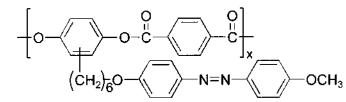
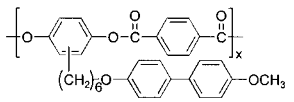


Figure 3. Wide-angle X-ray diffractograms of PAZO-*n* polymers.

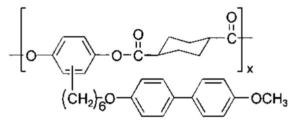
It should be noted that the T_m value of unsubstituted poly(*p*-phenylene terephthalate) is about 600 °C.[20] Not only the bulkiness of the side groups on the terephthaloyl units but also the unsymmetrical substitution that can lead to positional isomerism in the placement of the substituents along the polymer chain cause extra reduction in T_ms.[21,22] Such structural factors altogether are expected to give rise to irregularities in the structure of polymer chains, which would make the chains difficult to crystallize. Indeed, X-ray diffractograms (Figure 3) imply that the degrees of crystallinity of the present polymers are rather low. Annealing did not improve their degrees of crystallinity to any significant extent.

The glass transition behaviors of the polymers are rather complex. They reveal two weak endothermic transitions before melting (Figure 2). The lower temperature transition for PAZO-3 is 67 °C, while the one at the higher temperature is 116 °C. As one can see from Table 2, the lower transition temperature decreases from 67 °C for PAZO-3 to 38 °C for PAZO-6. It's value for PAZO-10 is 42 °C. The slightly higher T_g value of PAZO-10 compared with that of PAZO-6 seems to relate to the conformational differences of the spacers as will be discussed later. In other words, it decreases as the length of the spacer increases. This indicates that the low-temperature transition must be related to the motion of the spacers. In contrast, the higher transition temperatures are somewhat higher, ranging from 101 to 116 °C, and do not show any regular dependence on the length of the spacers. We believe that these transitions correspond to the usual glass transition temperatures (T_gs or α-transitions) of the main chain. Those glass transitions are sometimes so weak that their detection becomes very difficult as in the case of PAZO-6, whose glass transition could not be detected by DSC analysis. In order to study more closely the motion of the spacers and the main chain, we[23] previously examined the temperature dependence of the solid-state CP/MAS ^{13}C-NMR spectra of PAZO-6 and PAZO-10. We found that the ratio of the peak intensity of the first-order sideband to the center peak of the protonated aromatic peak clearly shows a strong temperature dependence and, at the same time, demonstrated the existence of two distinct transitions that appear at temperatures which are practically the same as the T_{g1} and T_{g2} values given in Table 2. Reck and Ringsdorf[5,12] reported about the same T_g values of 64–67 °C for the following polymers:





T_g ; 67 ℃[5] 65 ℃[5]



T_g ; 65 ℃ for cyclohexane unit of 97 % trans[12]
64 ℃ for cyclohexane unit of 77 % trans[12]

Comparison of the structures of the main chains and the pendent mesogenic groups in these polymers indicates that the T_g values reported by Reck and Ringsdorf are more likely associated with the motion of the oxyhexamethylene spacer than that of the main chain. Otherwise, the T_g values of the first and the last polymers should be further apart due to the higher flexibility of the main chain of the latter. Another point to be noted is that the T_g values of the above reported polymers lie in between the values of PAZO-3 and PAZO-6. Therefore, it is very reasonable to believe that the transition values in the lower temperature region observed for the present PAZO polymers correspond to secondary relaxations. It also is pointed out that the T_g values of various substituted aromatic polyesters are usually higher than 100 °C.[24–32]

Table 2 shows the initial decomposition temperatures ($T_D{}^i$) of the present series of polymers. They are not much different and occur at about 320 °C. This is understandable because the $T_D{}^i$ values are the temperatures where the same diazo group in the polymers undergoes thermal decomposition.

Liquid Crystallinity. Recently, Zentel and Brehmer[33] critically reviewed the relationship between the structure of combined LC polymers and the LC phases therefrom. Most of the combined LCPs subjected to a review by the same authors, however, contain spacers in the main chain as well as in the side chain. These polymers tend to form a smectic or nematic phase depending on the relative length of the spacers in the main and side chains, when the side group mesogenic structure is attached to the spacer part of the main chain through a flexible spacer. However, the combined LCPs in which the pendent mesogens are attached to the mesogenic part of the main chain tend to form nematic phases.

In the present combined LCPs, the main chains do not contain any spacer but, instead, are of the wholly aromatic polyester type. Therefore, the possibility for these polymers to form smectic phases must be rather slim. They, however, may be able to form layered LC phases where the side groups form separate layers oriented more or less perpendicular to the main chains. We have studied the nature of the mesophases formed by these polymers by observing their optical textures and the x-ray diffraction patterns of their melts. The polymers from PAZO-3 to PAZO-6 exhibited schlieren textures typical for a nematic phase (Figure 4a). The

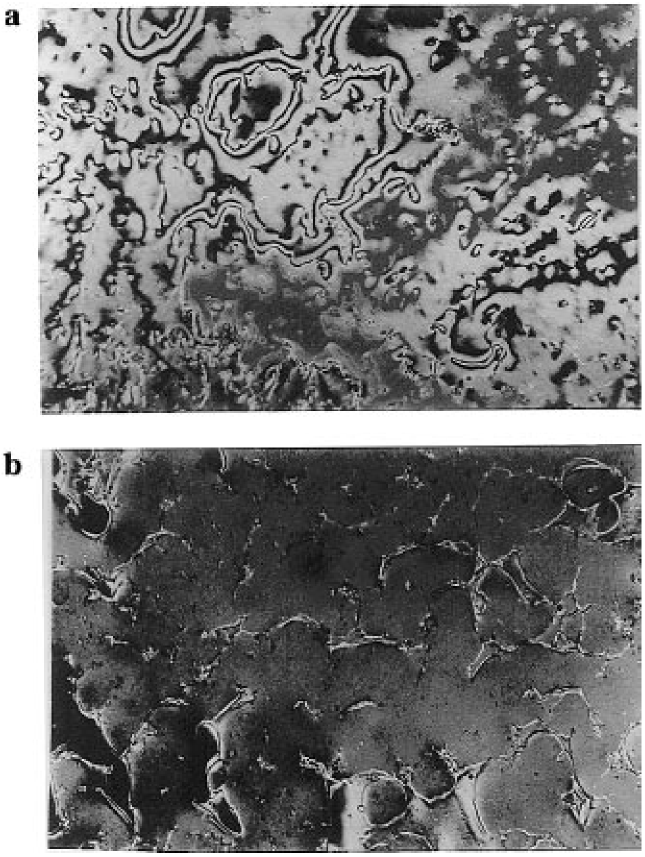


Figure 4. Optical photomicrographs of (a) PAZO-6 (220 °C) and (b) PAZO-10 (181 °C) (magnification 200x).

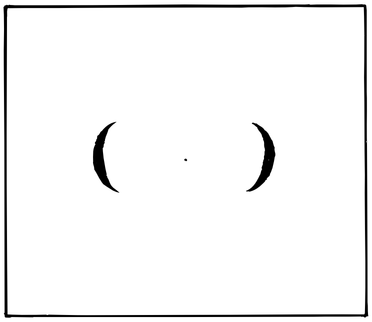
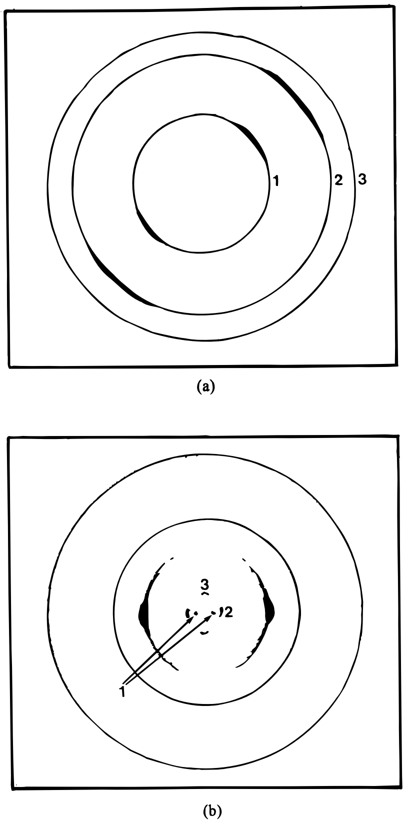


Figure 5. Schematic representation of the X-ray pattern of PAZO-6 melt-spun fibers drawn at 200 °C (fiber axis vertical).

optical texture of PAZO-10 (Figure 4b), however, is not so clear. Since all of the present polymers undergo thermal decomposition before reaching isotropization temperatures, it is impossible to correlate their mesophase temperature range with the length of the spacers in the pendent structures. However, according to the optical observation, they formed only one mesophase before decomposition.

Detailed X-ray analysis of PAZO-6 and PAZO-10 was performed for the samples in the mesophase and melt-spun fibers prepared from LC melts. PAZO-6 did not exhibit any diffraction in the small-angle region, but a diffraction in the wide-angle region centered around $2\theta = 21°$, which corresponds to a short spacing of 4.2 Å. This spacing corresponds to the interchain distance. The X-ray diffraction pattern (Figure 5) obtained for PAZO-6 fibers spun at 200 °C shows only one crescent equatorial scattering at $2\theta = 21.0°$ (4.2 Å), again indicating nematic order. The situation for PAZO-10, however, is completely different. The X-ray diffraction pattern (Figure 6a) of PAZO-10 in the LC phase showed three rings at $2\theta = 7.2$, 5.7, and 2.9°, which correspond to spacings of 12.3, 15.5, and 30.4 Å, respectively. The crescent-like diffraction patterns observed in Figure 6a are believed to originate from flowing of the polymer melt in the mesophase before quenching with a dry ice/acetone mixture, which has resulted in partial orientation of mesogenic units. Fibers of PAZO-10 spun at 200 °C showed the X-ray pattern schematically represented in Figure 6b. The meridional scattering and two equatorial scatterings in the small-angle region in Figure 6b exactly match those in the powder pattern of Figure 6a as indicated by the same designated numbers 1, 2, and 3. A crescent scattering appears at $2\theta = 22.6°$ (3.9 Å) in the wide-angle region that corresponds to the short spacing, i.e., interchain distance. These X-ray data are indicative of a layered structure for the LC phase of PAZO-10. Figure 7 illustrates the proposed structure; the aromatic polyester main chains in the extended form are packed parallel to each other, and the side spacer and mesogenic groups occupy the space between the layer. The tilt angle of the pendent group is 13°. Although the figure illustrates a regular orientation of the side groups, in reality they should be positioned in either directions below and above the main chain. Moreover, they are not positioned regioregularly. Therefore, the actual structure is not like the smectic C mesophase, where side groups are more or less regularly spaced and oriented. In other words, the structure shown in Figure 7 simply emphasizes the layered morphology of PAZO-10 in which the main chain and side groups are biaxially oriented. A similar structure was proposed by Watanabe et al.[34,35] for the LC phase of polyesters prepared from 1,4-dialkyl esters of pyromellitic acid and hydroquinone or 4,4′-biphenol. Reck and Ringsdorf[12] also reported a biaxial orientation of



(a)

(b)

Figure 6. Schematic representation of (a) the small-angle X-ray pattern of PAZO-10 powder (quenched at 250 °C) and (b) the wide-angle X-ray pattern of melt-spun PAZO-10 fibers drawn at 200 °C (fiber axis vertical).

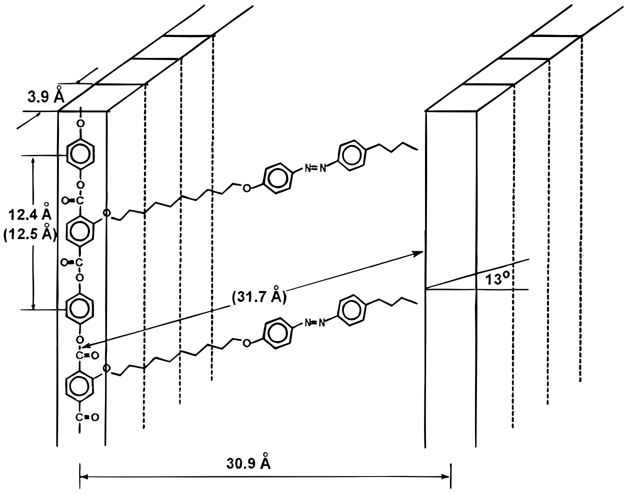


Figure 7. Proposed mesophase layered structure of melt-spun PAZO-10 fibers.

the mesogenic moieties and smectic layers in a combined LCP derived from a polymalonate.

It is concluded from the observations described up to this point that shorter spacers favor the formation of nematic phases, whereas longer spacers favor the formation of biaxially oriented layered mesophases. We, however, do not know yet the critical spacer length that is long enough to promote the biaxial orientation of main chains and pendent mesogenic groups. One can propose a conjecture that shorter spacers favor a more or less parallel orientation between the main chain and the pendent group through intramolecular interactions between them,[23] which leads to a nematic ordering in the melt. The longer spacers, however, tend to decouple the interactions and, thus, result in a layered morphology in the melt. According to the proposed model, the spacer in PAZO-10 appears to be of trans conformation, whereas those in PAZO-3 to PAZO-6 should have at least a partially gauche conformation. This could have resulted in a higher secondary transition temperature for PAZO-10 than, for example, PAZO-6, as mentioned earlier. Conformational analyses of the spacers in the present polymers can give better insight concerning the mesophase structure. The presence of the *n*-butyl tail in the side mesogenic group, however, makes such a study difficult. Therefore, we are presently in the process of synthesizing similar combined type LCPs with a slightly modified side mesogenic structure, which is expected to make conformational analyses of spacers by spectroscopic methods easier.

Experimental Section

Synthesis of Polymers. Since all of the polymers were prepared in the same manner, a representative synthetic procedure is given only for the preparation of PAZO-6. One[19] of our earlier papers describes the synthetic procedure for two substituted monomers, 2-[6-{4-(4-butylphenylazo)phenoxy}hexyloxy]terephthalic acid and 2-[10-{4-(4-butylphenylazo)phenoxy}decyloxy]terephthalic acid. The rest of the dicarboxylic acid monomers utilized in the synthesis of PAZO-3, -4, and -5 also were prepared exactly the same way, and their melting points are 238, 246, and 214 °C, respectively.

Compound **1** ($n = 6$; 5.00 g, 9.64 mmol) was refluxed for 3 h in 20 mL of thionyl chloride. After excess thionyl chloride was distilled off under reduced pressure, the residue (**2**) was dissolved in 18 mL of a dry mixture of pyridine[36]:tetrahydrofuran (THF)[37] = 1:5 (v/v). To the solution was added dropwise hydroquinone (1.06 g, 9.64 mmol) dissolved in 5 mL of THF. The whole mixture was stirred vigorously at 60 °C for 12 h under a nitrogen atmosphere. The reaction mixture was poured into excess methanol. The precipitate was collected on a filter and then was dissolved in 1,1,2,2-tetrachloroethane (TCE). The solution was again mixed with excess methanol, precipitating polymer. After being washed with acetone, the recovered polymer was subjected to Soxhlet extraction for 2 days using ethanol and dried at 60 °C in a vacuum oven. IR (KBr, cm^{-1}): 3040 (aromatic C−H stretching), 2925 and 2858 (aliphatic C−H stretching), 1732 (C=O stretching), 1600, 1578, 1500, and 1468 (aromatic C=C stretching), 1290 and 1238 (C−O stretching). ^{1}H-NMR ($CDCl_3$:$C_2Cl_4D_2$ = 1:5 (v:v), δ): 1.0 (CH_3, 3H), 1.45−2.0 (CH_2, 12H), 2.65 ($ArCH_2$, 2H), 3.9 (Ar-(terephthaloyl)−OCH_2, 2H), 4.15 (Ar(azo)−OCH_2, 2H), 6.8−7.9 (aromatic, 15H). ^{13}C-NMR ($CDCl_3$:$C_2Cl_4D_2$ = 1:5 (v:v), δ): 15.0 (CH_3), 23.7, 27.0, 30.2, and 34.9 (CH_2), 36.8 ($ArCH_2$), 69.8 and 70.7 ($ArOCH_2$), 116.2, 124.1, 126.2, 130.5, 148.5, and 150 (ArN=NAr), 114.8, 117.8, 123.5, 133.9, 135.8, and 152.5 (terephthaloyl Ar), 124.3 and 163.4 (hydroquinone Ar), 166.0 and 166.6 (C=O).

Characterization of Polymers. The solution viscosity values were measured at 30 °C on 0.2 g/dL solutions in a mixed solvent of *p*-chlorophenol/TCE = 60/40 (w/w) or of *p*-chlorophenol/TCE/phenol = 40/35/25 (w/w/w). Thermal properties were examined on a differential scanning calorimeter (Mettler DSC 821^e) at a heating and cooling rate of 10 °C/min. All the measurements were made under a nitrogen atmosphere. The initial inflection point on the DSC thermograms was taken as the glass transition temperature, whereas the peak maximum or minimum temperature was taken for the melting transition temperature (T_m). Thermogravimetric analysis (TGA) was performed under a nitrogen atmosphere at the heating rate of 10 °C/min on a DuPont 9900 thermogravimetric analyzer. The initial inflection points on TGA thermograms were taken as T_D^is. Optical textures of the polymer melts were observed on a hot stage (Mettler FP-82) attached to a polarizing microscope (Olympus BH-2). Wide-angle X-ray diffractograms were obtained on a Rigaku Geiger Flex D-Max IIIa instrument using nickel-filtered Cu Kα radiation (1.542 Å). Diffraction patterns were recorded on a fine collimated Philips PW 1729 X-ray camera equipped with an Aton-Paar vacuum chamber.

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