

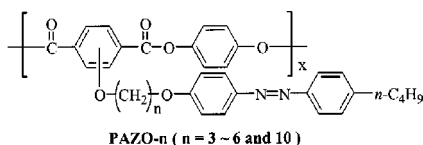
# Revisit to Mesophase Structure of Combined Type Liquid Crystalline Polymers Consisting of Poly(*p*-phenyleneterephthalate) Backbone and Azobenzene Type Chromophores Attached Through Long Alkylene Spacers

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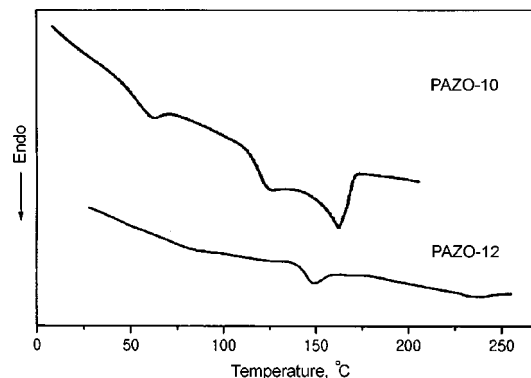
Relative orientation of pendant mesogenic units with respect to the backbone in combined type liquid crystalline polymers (LCPs)<sup>1-6</sup> has been a subject of the recent interests. One of our earlier publications reported<sup>7</sup> that, among the following polymers, only the one with the decamethylene ( $n = 10$ ) spacer, *i.e.*, PAZO-10, formed a layered structure in the mesophase while the rest exhibited nematic LC phases in melt.



Surprisingly enough, replacement of the *n*-butyl tail of the pendant mesogens with the phenyl group, however, deprived the polymers even with long spacers such as deca- and dodecamethylene groups of their ability to form layered morphology in their mesophases.<sup>8</sup> Instead, they formed only the nematic phase.

Observation of this unexpected contrasting behavior prompted us to prepare a PAZO polymer with the decamethylene ( $n = 12$ ) spacer, *i.e.*, PAZO-12, and examine the morphological structure, or relative orientation of the backbone and pendants, in the mesophase of this polymer in order to see if the mesophase morphology observed earlier for PAZO-10 was only an isolated instance or was originated from an experimental artifact. Therefore, we also reexamined of the mesophase morphology of PAZO-10. PAZO-12 was prepared as described earlier by us.<sup>7</sup> The inherent solution viscosity value of this polymer was 0.62 g/dL. This polymer and PAZO-10 were subjected to X-ray analysis especially in its mesophase.

Figure 1 shows thermograms of PAZO-10 and -12. Both polymers are semicrystalline and their respective crystalline melting temperatures are 166 and 150 °C. The optical textures of polymer melts observed through a polarizing microscope did not provide us with a clear clue as to the nature of the mesophase. Another important behavior of these polymers to be noted is the fact that they show two relaxational transitions at 42 and 114 °C for PAZO-10 and at 49 and 84 °C for PAZO-12 before melting (Table 1). The first ones correspond to the  $\hat{\alpha}$ -relaxations originated from the motions of the pendants and the seconds to the segmental motions of the backbones, *i.e.*, glass transitions. The exactly same thermal behavior was observed earlier by us for PAZO series with shorter spacers<sup>7</sup> and also in other similar LC polymer.<sup>8</sup>



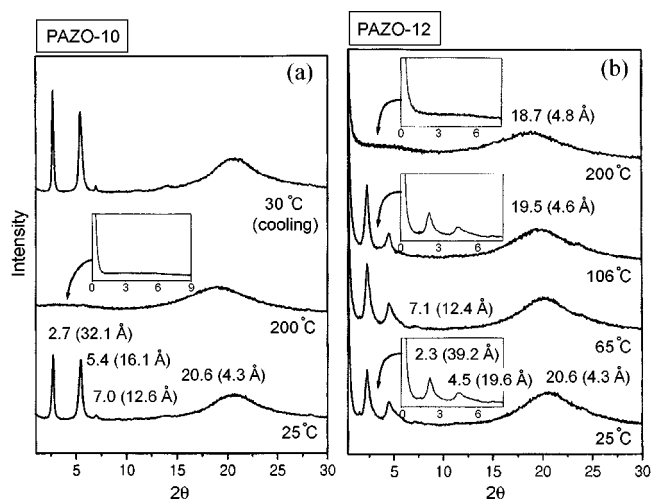
**Figure 1.** DSC thermograms of PAZO-10 and PAZO-12 (nitrogen atmosphere, heating rate: 10 °C/min.)

**Table 1.** Thermal Properties of PAZO-10 and PAZO-12\*

| Polymer | Relaxational Transitions |            | $T_m$ , °C | $T_i$ , °C       |
|---------|--------------------------|------------|------------|------------------|
|         | $T_1$ , °C               | $T_2$ , °C |            |                  |
| PAZO-10 | 42                       | 114        | 166        | dec (> 307)      |
| PAZO-12 | 49                       | 84         | 150        | 272 <sup>a</sup> |

\*All estimated from DSC thermograms under a nitrogen atmosphere at the heating rate of 10 °C/min. <sup>a</sup>Observed by optical polarizing microscopy.

Figure 2a and 2b compares X-ray diffractograms of PAZO-10 and -12 obtained at the room temperature and also at 200 °C which is within their mesophase temperature range. At room temperature PAZO-10 exhibits three sharp diffraction peaks ( $2\theta = 2.7^\circ$  (32.1 Å),  $5.4^\circ$  (16.1 Å) and  $7.0^\circ$  (12.6 Å)), one broad peak at  $2\theta = 15-25^\circ$  and a very weak and broad peak centered at  $2\theta = 20.6^\circ$  (4.3 Å). The first two sharp and strong peaks in the small angle region are the 1st and 2nd order peaks, respectively. The spacing estimated from 1st peak is 32.1 Å, which happens to be equal to the interchain distance assuming the trans anti conformation for the decamethylene spacer. The third diffraction peak at  $2\theta = 7.0^\circ$  corresponds to the length of the repeating unit of the backbone. The broad peaks in the wide angle region arise from various interchain spacings in the amorphous part of the polymer. When the polymer was heated to 200 °C, all of the sharp peaks in the small angle side disappear, and we observed only one broad peak centered around  $2\theta = 19.0^\circ$  (4.7 Å). Such diffraction is typical to the nematic mesophase.<sup>9</sup> When the melt is cooled to the room temperature, the original diffraction pattern is recovered. Basically a similar diffraction is observed also for PAZO-12. At room temperature the first



**Figure 2.** X-ray diffractograms for (a) PAZO-10 and (b) PAZO-12 at varying temperatures.

sharp peak appearing at  $2\theta = 2.3^\circ$  (39.2 Å) again corresponds to the interchain distance and the second one at  $2\theta = 4.5^\circ$  is originated from the second order diffraction. The spacing corresponding to the length of the repeating unit is observed at  $2\theta = 7.1^\circ$  (12.4 Å), which disappears even before reaching the crystalline melting point (150 °C). In the mesophase, the polymer exhibits only a very broad diffraction peak at  $2\theta = 13$ -25 centered at  $2\theta = 18.7^\circ$  (4.8 Å). The interchain distances, or short spacings in the mesophase are a little larger for both polymers than in the solid state. Therefore we would like to conclude that PAZO-10 and -12 both form nematic phases in melt, not the layered structures. One of our earlier reports<sup>7</sup> alluded that PAZO-10 may form a layered structures in the mesophase that is of interdigitated morphology. Such an erroneous result was derived from the analysis of X-ray diffraction patterns obtained for a quenched melt. Evidently, the melt was not effectively frozen in the mesophase and, thus, must have undergone crystallization to a minor extent. This artifact led us to a misinterpretation as to the morphology of the polymers in the mesophase.

In summary, this investigation leads us to the conclusion that the layered mesophase morphology observed earlier by us for PAZO-10 was derived from an artifact and that all of the PAZO series, regardless the length of spacers, form only the nematic phase, which implies that the side pendant groups orient themselves more or less parallel to the backbone. At the same time multiple relaxational transitions occurring before crystalline melting temperature appear to be common for the combined type LCPs whose structure characteristics are described in this investigation.

### Experimental Section

**Synthesis of Monomer and Polymer.** All of intermediate compounds, monomers, and polymers were prepared in the same manner as described in previous reports.<sup>7,10</sup>

**4-(12-Bromododecyloxy)-4'-butylazobenzene.** The product yield was 6.5 g (77%), mp 63 °C. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>, ppm): δ 0.9 (t, 3H, CH<sub>3</sub>), 1.3-1.5 (m, 2H, -CH<sub>2</sub>-), 1.5-1.8 (m,

22H, Ar-CH<sub>2</sub>CH<sub>2</sub>- and OCH<sub>2</sub>(CH<sub>2</sub>)<sub>10</sub>CH<sub>2</sub>Br), 2.7-2.8 (t, 2H, Ar-CH<sub>2</sub>-), 3.5-3.7 (t, 2H, -CH<sub>2</sub>Br), 4.1-4.3 (t, 2H, -OCH<sub>2</sub>-) and 7.0-8.0 (m, 8H, Ar). Elemental analysis, calc. for C<sub>28</sub>H<sub>41</sub>BrN<sub>2</sub>O: C 67.05, H 8.24, N 5.59; found C 67.06, H 8.31, N 5.61%.

**2-[12-{4-(4-Butylphenylazo)phenoxy}dodecyloxy]terephthalic acid.** The product yield was 3.9 g (76% for the last two steps), mp 187 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, ppm): δ 0.9 (t, 3H, -CH<sub>3</sub>), 1.25-1.5 (m, 2H, -CH<sub>2</sub>-), 1.4-2.0 (m, 22H, Ar-CH<sub>2</sub>CH<sub>2</sub>- and OCH<sub>2</sub>(CH<sub>2</sub>)<sub>10</sub>CH<sub>2</sub>Br), 2.6-2.8 (t, 2H, Ar-CH<sub>2</sub>-), 4.2-4.5 (t, 4H, -OCH<sub>2</sub>-) and 7.1-8.0 (m, 11H, Ar). Elemental analysis, calc. for C<sub>36</sub>H<sub>46</sub>N<sub>2</sub>O<sub>6</sub>: C 71.74, H 7.69, N 4.64; found C 71.69, H 7.74, N 4.63%.

**Poly[oxy-1,4-phenyleneoxy-[2-5-{4-(butylphenylazo)phenoxy}dodecyloxy]terephthaloyl], PAZO-12.** The yield was 1.4 g (83%). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, ppm): δ 0.9 (t, 3H, -CH<sub>3</sub>), 1.3-1.5 (m, 2H, -CH<sub>2</sub>-), 1.5-1.8 (m, 22H, Ar-CH<sub>2</sub>CH<sub>2</sub>- and OCH<sub>2</sub>(CH<sub>2</sub>)<sub>10</sub>CH<sub>2</sub>Br), 2.7-2.8 (t, 2H, Ar-CH<sub>2</sub>-), 3.5-3.7 (t, 2H, -CH<sub>2</sub>Br), 4.1-4.3 (t, 2H, -OCH<sub>2</sub>-) and 6.8-8.0 (m, 15H, Ar). Elemental analysis, calc. for C<sub>42</sub>H<sub>48</sub>N<sub>2</sub>O<sub>6</sub>: C 74.42, H 7.29, N 4.13; found C 74.35, H 7.47, N 4.12%.

### Characterization of Polymer

PAZO-12 was characterized in the same manner as described in the previous reports.<sup>7,10</sup> The X-ray analysis was conducted at the Pohang Laboratory of Synchrotron using a radiation (1.542 Å). The powder sample holder was equipped with a heating and cooling thermostat.

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