# Thermotropic Side-Chain Liquid Crystalline Copolymers Containing Both Mono- and Bisazobenzene Mesogens: Synthesis and Properties

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Received July 5, 2005; Revised Manuscript Received September 13, 2005

ABSTRACT: The synthesis of a novel series of copolymers containing push-pull bisazobenzene (BAz) and monoazobenzene (MAz) groups with various N-alkyl donor groups and with spacers of two and four methylene units is presented, and the effects of the structural variables on the mesomorphic properties of the polymers are investigated. The copolymer with very short spacer (n = 2) and bulky N-ethyl group exhibits liquid crystalline (LC) properties when the BAz content is at least 30 mol %. Replacing the N-ethyl group with N-methyl increases the tendency toward smectic mesomorphism and expands the mesophases stability. If the flexible spacer is extended to four methylene units, the glass transition temperature ( $T_g$ ) decreases strongly, whereas the isotropization temperature ( $T_i$ ) is only slightly affected. X-ray diffraction investigations reveal an orthogonal partial bilayer smectic phase in which the mesogens are interdigitated. Annealing the BAz polymer films above  $T_g$  brings about the out-of-plane (homeotropic) orientation of chromophores and the formation of H-aggregates.

#### Introduction

The possibility of creating molecular oriented structures by light in azobenzene (Az)-containing polymer films has stimulated a considerable research activity from both fundamental and applied standpoints.<sup>1</sup> The photoresponsiveness of such systems is based on the readily induced and reversible isomerization between the trans and cis isomers of Az, which triggers significant changes in the physical and chemical properties of polymeric materials. For instance, irradiation with linearly polarized light (LPL) induces reversible birefringence and linear dichroism in initially isotropic polymer films as a result of the orientation of Az dipole axis perpendicular to the light polarization direction.<sup>2-5</sup> Also, massive displacement of the polymeric material, creating micrometer-deep surface relief gratings (SRG),<sup>6,7</sup> and photoinduced chirality in achiral azopolymer films<sup>8</sup> have been reported. All these properties are of great interest for photonic applications, making the Azcontaining polymers suitable for optical data storage applications, photoswitching, alignment of liquid crystals, optical elements, and other photonic devices.<sup>9</sup>

To fully understand the relationship between the structure and physical property, various systems with Az moieties either in the side or main chain have been synthesized, and their photoresponsive behavior in amorphous<sup>4,10,11</sup> or liquid crystalline<sup>3,5,12,13</sup> (LC) polymer films has been investigated. It was shown that the photoinduced order depends strongly on various factors such as the molecular structure of Az, the spacer length, the chromophore aggregation, and the content of photochromic groups in sample.<sup>1,10–16</sup> Recently, there has been a growing interest in the photochemical behavior of azo block copolymers<sup>17</sup> and dendrimers.<sup>18</sup>

Although chromophores having only one azo group in their chemical structure (monoazobenzenes (MAz)) have been primarily studied, systems with bisazobenzene moieties (BAz) have also been investigated for optical storage applications.<sup>19–21</sup> BAz chromophores are distinguished by high anisotropy of molecular polarizability that can lead to large photoinduced orders when compared to MAz-based materials. The birefringence per azo structural unit in a copolymer with 11 mol % BAz is 5 times larger than that corresponding to a MAz-based copolymer having similar azo content.<sup>19</sup> In a series of side-chain LC (SCLC) copolymers with 4-alky-loxy-BAz moieties, Stumpe et al.<sup>20</sup> observed the largest and the most stable anisotropy for the copolymer containing 40 mol % BAz. Furthermore, annealing the oriented films above  $T_{\rm g}$  amplified the photoinduced anisotropy.

The presence of both MAz and BAz chromophores in the polymer chemical structure is of considerable interest for the creation of new promising multifunctional materials.<sup>22</sup> In such systems, both chromophores can undergo photoisomerization and consequently orientation under polarized light exposure, thus increasing the efficiency of photoalignment. Moreover, the occurrence of LC order, expected as a result of highly anisotropic chromophores, could enhance the photoinduced anisotropy. In this respect, we report here the synthesis, thermotropic behavior, and optical properties of a novel series of copolymers having both MAz and BAz in their side chain (Chart 1). The properties of the corresponding BAz-homopolymers are also presented for the first time. The polymer's abbreviations  $(PnR)_x$  stand for the polymethacrylate backbone (P), the number *n* of methylene carbons in the side chain spacer, the specific alkylamino functionality R (E and M for ethyl and methyl, respectively), and the concentration of BAz units (x). The chromophores are substituted with electron-donor (amino) and electron-acceptor (nitro) groups, an important consideration in the development of large photoinduced anisotropy.<sup>11</sup> While detailed studies on the thermotropic properties of SCLC copolymers containing MAz mesogens of various chemical structures have been systematically reported,<sup>23–26</sup> to the best of our knowledge there is no such study concerning copolymers having both MAz and BAz mesogens in their side chains. The trends

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of the thermodynamic phase transition parameters of our polymers will be discussed with reference to the content of BAz units, the size of the amine function, and the length of the spacer. These parameters should influence the polymers optical storage capabilities. The potential of these materials as optical storage media was investigated by birefringence measurements and SRG formation and will constitute the subject of a forthcoming paper.<sup>27</sup>

# **Experimental Section**

**Materials.** Unless otherwise specified, the reagents were obtained from Aldrich. *N*-(2-Hydroxyethyl)-*N*-ethylaniline (99%), 2-chloroethanol (99%), 4-chloro-1-butanol ( $\geq$ 90%), 4-amino-4'-nitroazobenzene (Disperse Orange 3, 90%), sodium iodide (99.5%), sodium nitrite (99.99%), sodium hydrogen carbonate (Sigma, 99.5%), hydrochloric acid (EMD, 36–38%), and acetone

(Fluka, 99.9% anhydrous) were all used as received. Reagent grade tetrahydrofuran (THF) and 1,4-dioxane were dried by distillation from purple sodium benzophenone ketyl under argon. Triethylamine (Et<sub>3</sub>N) (99.5%) and *N*,*N*-dimethylformamide (DMF) were vacuum-distilled off from calcium hydride just prior to use. *N*-Methylaniline (98%) and methacryloyl chloride (Fluka, 97%) were distilled under reduced pressure and kept in sealed tubes under argon gas. 2,2'-Azobis(isobutyronitrile) (AIBN, 98%) was recrystallized twice from absolute methanol. All other reagents and solvents were commercially available and used as received.

**Monomer Synthesis.** The MAz monomers 4'-{(2-methacryloyloxyethyl)methylamino}-4-nitroazobenzene,<sup>14</sup> 4'-{(2methacryloyloxyethyl)ethylamino}-4-nitroazobenzene,<sup>4</sup> and 4'-{(4-methacryloyloxy butyl)methylamino}-4-nitroazobenzene<sup>14</sup> were prepared as previously reported. The synthetic route for the target BAz monomers is shown Scheme 1.

Synthesis of N-(n-Hydroxyalkyl)-N-methylaniline (1-n, n = 2, 4). These compounds were prepared by a modified literature procedure<sup>28</sup> as follows: 2-chloro-1-ethanol (8.05 g, 100 mmol) and sodium iodide (45.0 g, 300 mmol) were dissolved in acetone (60 mL) and refluxed for 8 h under argon. The resulting mixture was evaporated to dryness, and the solid was dissolved in 60 mL of DMF. Freshly distilled N-methylaniline (21.5 g, 200 mmol) and NAHCO<sub>3</sub> (16.8 g, 200 mmol) were added to this solution, and the mixture was stirred at 70 °C for 20 h. The reaction mixture was cooled to room temperature, poured into water, and extracted several times with ethyl ether. After the organic layer was dried over anhydrous MgSO<sub>4</sub>, the solvent was evaporated off and the residue oil was purified over silica gel column chromatography using a mixture of ethyl acetate:hexane (2:1 v/v) as eluent. Yield: 68%.

**N-(2-Hydroxyethyl)-N-methylaniline** (1–2). <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ (ppm): 7.32 (m, 2H, Ph–H), 6.90 (m, 3H, Ph–H), 3.80 (t, 2H, CH<sub>2</sub>OH), 3.49 (t, 2H, NCH<sub>2</sub>), 3.00 (s, 3H, CH<sub>3</sub>), 2.6 (broad t, 1H, OH). <sup>13</sup>C NMR (CDCl<sub>3</sub>), δ (ppm): 149.6 (Ph: C1), 129.0 (Ph: C3, C5), 116.8 (Ph: C4), 112.6 (Ph: C2, C6), 59.2 (CH<sub>2</sub>OH), 55.0 (NCH<sub>2</sub>), 38.5(NCH<sub>3</sub>).

**N-(4-Hydroxybutyl)-N-methylaniline (1–4).** Yield: 30%. <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 7.26 (m, 2H, Ph–H), 6.75 (m, 3H, Ph–H), 3.68 (t, 2H, CH<sub>2</sub>OH), 3.36 (t, 2H, NCH<sub>2</sub>), 2.95 (s, 3H, CH<sub>3</sub>), 1.85 (broad t, 1H, OH), 1.65 (m, 4H, CH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 148.7 (Ph: C1), 130.1 (Ph: C3, C5), 116.2



(Ph: C4), 112.2 (Ph: C2, C6), 61.5 (CH<sub>2</sub>OH), 57.3 (NCH<sub>2</sub>), 41.7 (NCH<sub>3</sub>), 29.8 (CH<sub>2</sub>), 26.7 (CH<sub>2</sub>).

Synthesis of 4-{N-Methyl-N-(n-hydroxyalkyl)amino}-4'-(4-nitrophenylazo)azobenzene (2-n, n = 2, 4) and 4-{N-Ethyl-N-(2-hydroxyethyl)amino}-4'-(4-nitrophenylazo)azobenzene (3-2). The alcohols were prepared in 50-60% yield as in the following example: 4-amino-4'-nitroazobenzene (5.00 g, 20.6 mmol) was dissolved in a solution of concentrated hydrochloric acid (10 mL) in DMF (40 mL). The mixture was cooled to 0 °C in an ice-water bath, and then sodium nitrite (1.45 g, 21.0 mmol) dissolved in a small amount of water was added dropwise. The reaction mixture was stirred for 2 h, and then  $1{-}2\ (3.50$  g, 23.1 mmol) in 15 mL of acetic acid was added slowly. The resultant purple solution was vigorously stirred for 4 h at 0-5 °C and for an additional 16 h at room temperature. The precipitate formed was collected by vacuum filtration, washed with saturated NaCO<sub>3</sub>, and finally dried. The crude product was purified by silica gel chromatography using toluene: acetone (1:1 v/v), followed by recrystallization from THF:hexane to yield 4.67 g of purple 2-2 crystals. Yield: 56%.

**4**-{*N*-Methyl-*N*-(2-hydroxyethyl)amino}-4'-(4-nitrophenylazo)azobenzene (2–2). Mp 207 °C (by DSC). <sup>1</sup>H NMR (DMSO- $d_6$ ),  $\delta$  (ppm): 8.46 (d, 2H, Ph-**H** ortho to NO<sub>2</sub>), 8.18–7.80 (3d, 8H, Ph-**H**), 6.89 (d, 2H, Ph-**H** ortho to NR<sub>2</sub>), 4.82 (t, 1H, OH), 3.60 (m, 4H, NCH<sub>2</sub> and CH<sub>2</sub>OH), 3.11 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (DMSO- $d_6$ ),  $\delta$  (ppm): 155.2, 154.7, 152.4 (Ph: C1',C4',C1'' linked to -N=N-), 151.5 (Ph: C4'' linked to NO<sub>2</sub>), 148.3 (Ph: C1 linked to NR<sub>2</sub>), 142.8 (Ph: C4 linked to -N=N-), 125.2, 124.7, 124.0, 123.2 (8C, ortho to -N=N-), 122.6 (2C, ortho to NO<sub>2</sub>), 111.4 (2C, ortho to NR<sub>2</sub>), 58.1 (CH<sub>2</sub>-OH), 53.9 (NCH<sub>2</sub>), 38.6 (NCH<sub>3</sub>). UV-vis (THF),  $\lambda_{max}$ : 348, 514 nm.

4-{*N*-Methyl-*N*-(4-hydroxybutyl)amino}-4'-(4-nitrophenylazo)azobenzene (2–4). Mp 169 °C (by DSC). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>), δ (ppm): 8.46 (d, 2H, Ph–H ortho to NO<sub>2</sub>), 8.12–7.76 (3d, 8 H, Ph–H), 6.88 (d, 2H, Ph–H ortho to NR<sub>2</sub>), 4.27 (t, 1H, OH), 3.48 (m, 4H, NCH<sub>2</sub> and CH<sub>2</sub>OH), 3.07 (s, 3H, CH<sub>3</sub>), 1.49–1.64 (m, 4H, CH<sub>3</sub>). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>), δ (ppm): 155.2, 154.8, 152.1 (Ph: C1',C4',C1" linked to -N=N-), 151.6 (Ph: C4" linked to NO<sub>2</sub>), 148.4 (Ph: C1 linked to NR<sub>2</sub>), 142.8 (Ph: C4 linked to -N=N-), 125.3, 124.7, 124.1, 123.3 (8C, ortho to -N=N-), 122.6 (2C, ortho to NO<sub>2</sub>), 111.3 (2C, ortho to NR<sub>2</sub>), 60.4 (CH<sub>2</sub>OH), 51.4 (NCH<sub>2</sub>), 37.9 (NCH<sub>3</sub>), 29.4 (CH<sub>2</sub>CH<sub>2</sub>OH), 23.1 (NCH<sub>2</sub>CH<sub>2</sub>). UV–vis (THF), λ<sub>max</sub>: 350, 512 nm.

4-{*N*-Ethyl-*N*-(2-hydroxyethyl)amino}-4'-(4-nitrophenylazo)azobenzene (3–2). Mp 227 °C (lit. 171 °C).<sup>19</sup> <sup>1</sup>H NMR (DMSO- $d_6$ ), δ (ppm): 8.46 (d, 2H, Ph–H ortho to NO<sub>2</sub>), 8.13–7.81 (3d, 8H, Ph–H), 6.89 (d, 2H, Ph–H ortho to NR<sub>2</sub>), 4.85 (t, 1H, OH), 3.60 (m, 4H, CH<sub>2</sub>), 1.16 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (DMSO- $d_6$ ), δ (ppm): 155.4, 155.0 (Ph: C1', C4' linked to -N=N-), 151.5 (Ph: C1'', C4''), 148.6 (Ph: C1 linked to NR<sub>2</sub>), 142.8 (Ph: C4 linked to -N=N-), 125.8, 124.5, 123.6 (8C, ortho to -N=N-), 122.9 (2C, ortho to NO<sub>2</sub>), 111.5 (2C, ortho to NR<sub>2</sub>), 58.5 (CH<sub>2</sub>OH), 52.3 (NCH<sub>2</sub>CH<sub>2</sub>), 45.3 (NCH<sub>2</sub>CH<sub>3</sub>), 12.3 (CH<sub>3</sub>). UV–vis (THF)  $\lambda_{max}$ : 346, 502 nm.

Synthesis of BAz Monomers. The synthesis of 4-{(2methacryloyloxyethyl)methylamino}-4'-(4-nitrophenylazo)azobenzene (4-2), as an example, is given below: 2-2 (1.62 g, 4.00 mmol) was dissolved in 25 mL of anhydrous THF, and freshly distilled triethylamine (1.12 mL, 8.04 mmol) was added to this solution. The reaction mixture was then cooled to 0-5°C. Methacryloyl chloride (0.80 mL, 8.1 mmol) in THF (5 mL) was injected gradually to the above solution via a glass syringe while the solution temperature was kept below 5 °C. The formation of precipitate of triethylammonium salt was observed immediately after the methacryloyl chloride addition. The reaction mixture was stirred overnight at room temperature. The resulting precipitate was filtered off, and the filtrate was evaporated to dryness. The remaining purple solid was then dissolved in CHCl<sub>3</sub>, washed with 5% aqueous NaHCO<sub>3</sub> and water to neutrality, and finally dried over MgSO4. Purification was performed by column chromatography using chloroform as eluent followed by recrystallization from 50:50 toluene:ethanol.

**4-{(2-Methacryloyloxyethyl)methylamino}-4'-(4-nitrophenylazo)azobenzene (4–2).** Dark red crystals; yield 69%; mp 173 °C (by DSC). <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 8.42 (d, 2H, Ph–H ortho to NO<sub>2</sub>), 8.20–7.80 (m, 8H, Ph–H), 6.86 (d, 2H, Ph–H ortho to NR<sub>2</sub>), 6.10 (s, 1H, C=CH<sub>2</sub>, cis), 5.59 (s, 1H, C=CH<sub>2</sub>, trans), 4.42 (t, 2H, CH<sub>2</sub>O), 3.82 (t, 2H, NCH<sub>2</sub>), 3.18 (s, 3H, NCH<sub>3</sub>), 1.94 (s, 3H, =C-CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 167.2 (C=O), 155.8 (Ph: C1',C4',C1'' linked to -N=N-), 152.3 (Ph: C4'' linked to NO<sub>2</sub>), 148.7 (Ph: C1 linked to NR<sub>2</sub>), 143.7 (Ph: C4 linked to -N=N-), 135.8 (C=CH<sub>2</sub>), 126.6, 124.8, 124.5, 123.5 (8C, ortho to NR<sub>2</sub>), 61.6 (CH<sub>2</sub>O), 51.0 (NCH<sub>2</sub>), 39.2 (NCH<sub>3</sub>), 18.3 (=CCH<sub>3</sub>). UV– vis (THF)  $\lambda_{max}$ : 346, 496 nm. Elem. Anal. Calcd for C<sub>25</sub>H<sub>24</sub>N<sub>6</sub>O<sub>4</sub>: C, 63.54%; H, 5.11%; N, 17.78%. Found: C, 63.19%; H, 5.06%; N, 17.15%.

4-{(4-Methacryloyloxybutyl)methylamino}-4'-(4-nitrophenylazo)azobenzene (4-4). Purple crystals; yield 81%; mp 168 °C (by DSC). <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 8.40 (d, 2H, Ph-H ortho to NO<sub>2</sub>), 8.15-7.90 (m, 8H, Ph-H), 6.80 (d, 2H, Ph-H ortho to NR<sub>2</sub>), 6.12 (s, 1H, C=CH<sub>2</sub> cis), 5.58 (s, 1H,  $C=CH_2$  trans), 4.23 (t, 2H, CH<sub>2</sub>O), 3.52 (t, 2H, NCH<sub>2</sub>), 3.11 (s, 3H, NCH<sub>3</sub>), 1.97 (s, 3H, =CCH<sub>3</sub>), 1.78 (m, 4H, CH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>), δ (ppm): 167.4 (**C=**O), 155.9, 155.2, 152.4 (Ph: C1',C4',C1" linked to -N=N-), 152.1 (Ph: C4" linked to NO<sub>2</sub>), 148.7 (Ph: C1 linked to NR<sub>2</sub>), 143.9 (Ph: C4 linked to -N=N-), 136.4 ( $-C=CH_2$ ), 125.5 ( $-C=CH_2$ ), 126.2, 124.8, 124.5, 123.5 (8C, ortho to -N=N-), 123.1 (2C, ortho to NO<sub>2</sub>), 111.7 (2C, ortho to NR<sub>2</sub>), 64.1 (CH<sub>2</sub>O), 52.4 (NCH<sub>2</sub>), 38.8 (NCH<sub>3</sub>), 26.3 (NCH<sub>2</sub>CH<sub>2</sub>), 23.7 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 18.3 (=CCH<sub>3</sub>). UV-vis (THF)  $\lambda_{max}$ : 348, 510 nm. Elem. Anal. Calcd for C<sub>27</sub>H<sub>28</sub>N<sub>6</sub>O<sub>4</sub>: C, 64.78%; H, 5.63%; N, 16.79%. Found: C, 64.49%; H, 5.68%; N, 16.68%.

4-{(2-Methacryloyloxyethyl)ethylamino}-4'-(4-nitrophenylazo)azobenzene (5-2). Red crystals; yield 56%; mp 162 °C (lit. 198 °C).<sup>19</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ (ppm): 8.40 (d, 2H, Ph-H ortho to NO<sub>2</sub>), 8.12-7.92 (m, 8H, Ph-H), 6.85 (d, 2H, Ph-H ortho to NR<sub>2</sub>), 6.12 (s, 1H, C=CH<sub>2</sub> cis), 5.61 (s, 1H, C=CH<sub>2</sub> trans), 4.39 (t, 2H, CH<sub>2</sub>O), 3.75 (t, 2H, NCH<sub>2</sub>), 3.56 (q, 2H, NCH<sub>2</sub>CH<sub>3</sub>), 1.96 (s, 3H,  $=C-CH_3$ ), 1.28 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>), δ (ppm): 168.2 (C=O), 156.7, 155.5, 153.3 (Ph: C1',C4',C1" linked to -N=N-), 152.0 (Ph: C4" linked to NO<sub>2</sub>), 149.6 ((Ph: C1 linked to NR<sub>2</sub>), 144.7 (Ph: C4 linked to -N=N-), 136.8 ( $-C=CH_2$ ), 127.2 ( $-C=CH_2$ ), 127.4, 125.7, 125.4, 124.4 (8C, ortho to -N=N-), 124.0 (2C, ortho to NO<sub>2</sub>), 112.7 (2C, ortho to NR<sub>2</sub>), 62.6 (CH<sub>2</sub>O), 49.8 (NCH<sub>2</sub>), 46.7(NCH<sub>2</sub>-CH<sub>3</sub>), 19.3 (=CCH<sub>3</sub>), 13.2 (CH<sub>2</sub>CH<sub>3</sub>). UV-vis (THF),  $\lambda_{max}$ : 340, 502 nm. Elem. Anal. Calcd for C<sub>26</sub>H<sub>26</sub>N<sub>6</sub>O<sub>4</sub>: C, 64.18%; H, 5.38%; N, 17.27%. Found: C, 64.01%; H, 5.61%; N, 17.34%.

**Polymerization.** The synthesis of  $(P2M)_{30}$  (Table 1), as a typical polymerization procedure, is discussed below.

Into a baked 100 mL two-necked round-bottom flask were placed 1.12 g (2.37 mmol) of 4-2, 0.88 g (2.4 mmol) of 4'-{(2methacryloyloxyethyl)methylamino}-4-nitroazobenzene, and 39 mL of distilled 1.4-dioxane. After stirring under argon for 30 min at 40 °C, the reaction mixture was transfer to a baked Pyrex ampule using a dry cannula. A solution of 0.16 g of AIBN (0.97 mmol) in 1 mL of THF was added, and immediately the mixture was frozen in liquid nitrogen and vacuum was applied. Following three freeze-pump-thaw cycles, the ampule was sealed under argon and placed in an oil bath preheated at 80 °C; the reaction lasted 72 h. The polymerization mixture was poured into vigorously stirred hot ethanol. The solid precipitate was filtered, dissolved in DMF, and reprecipitated into a mixture of hot ethanol-acetone (10% acetone). This procedure was repeated several times until the unreacted monomers were completely removed. Finally, the polymer was dried in a vacuum oven at 80 °C for 2 days. Yield: 46%.

The <sup>1</sup>H NMR spectrum of  $(P2M)_{30}$  is presented in Figure 1 together with the monomers spectra. Table 1 summarizes the reaction conditions and the characterization of the polymers. We should add that BAz homopolymers purification was carried out from pyridine/ethanol-acetone mixtures.

**Characterization Methods.** <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were recorded on a Bruker AVANCE

Table 1. Synthesis and Characterization of the Polymers Used in This Study

			BAz (mol %)				
sample	n	R	in feed	in copolym <sup>c</sup>	$10^{-3}M_{ m n}{}^d$	$M_{ m w}\!/\!M_{ m n}{}^d$	yield (%)
PDR1M <sup>a</sup>	2	$C_2H_5$	0	0	6.0	1.90	68
(P2E) <sub>10</sub>	2	$C_2H_5$	17	10	5.6	1.76	53
(P2E) <sub>30</sub>	2	$C_2H_5$	50	32	4.5	1.32	46
(P2E) <sub>50</sub>	2	$C_2H_5$	66	49	4.0	1.48	40
(P2E) <sub>100</sub>	2	$C_2H_5$	100	100	е	е	31
$P2MAN^b$	2	$CH_3$	0	0	5.0	1.40	60
(P2M) <sub>30</sub>	2	$CH_3$	50	30	4.3	1.27	48
(P2M) <sub>50</sub>	2	$CH_3$	66	50	3.8	1.42	37
(P2M) <sub>100</sub>	2	$CH_3$	100	100	е	е	28
$P4MAN^b$	4	$CH_3$	0	0	4.4	1.60	77
(P4M) <sub>50</sub>	4	$CH_3$	67	50	3.6	1.34	46
(P4M)100	4	$CH_3$	100	100	е	е	36

<sup>*a*</sup> PDR1M is the MAz homopolymer with n = 2 and  $R = C_2H_5$  (Chart 1); synthesis reported in ref 4. <sup>*b*</sup> P2MAN and P4MAN are the MAz homopolymers with  $R = CH_3$  and n = 2 and n = 4, respectively (Chart 1); synthesis reported in ref 14. <sup>*c*</sup> Determined from <sup>1</sup>H NMR spectra. <sup>*d*</sup> By GPC in THF. <sup>*e*</sup> Not measured; the polymer is not soluble in THF.

400 spectrometer using  $\text{CDCl}_3$ ,  $\text{DMSO-}d_6$ , or trifluoroacetic acid as solvents. Chemical shifts are in ppm from the internal standard tetramethylsilane (TMS).

UV-vis measurements in the 700-300 nm spectral region were performed at room temperature in solutions (for monomers) or in films (for polymers) with a Shimadzu TR-280 spectrometer. Films were prepared by spin-coating solutions of polymers in pyridine onto glass microscope slides and subsequently dried in a vacuum oven. To evaluate the out-ofplane orientation of the azochromophores in polymer films, polarized absorption spectra were taken at different incident angles  $(\theta_i)$  of the probe light. s- and p-linearly polarized light were obtained by passing the spectrometer light through a calcite Glan-Taylor prism that was mounted in a rotating holder and placed in front of the film sample. Reference spectra at various incident angles were subtracted from sample spectra at different  $\theta_i$  to discard the effect of the additional multiple reflection on polymer films. To account for the difference in optical path length at each incident angle, the observed absorbance  $(A_{obs})$  was corrected  $(A_{corr})$  according to eq 1:<sup>16</sup>

$$A_{\rm corr} = A_{\rm obs} \cos[\sin^{-1}(\sin\theta_{\rm i}/n_{\rm f})] \tag{1}$$

where  $n_{\rm f}$  is the refractive index of the polymer film.

The out-of-plane order parameter,  $S_{\rm h}$ ,<sup>15</sup> was derived from the absorbance of the initial as-cast film and the absorbance of the annealed film to

$$S_{\rm h} = 1 - P \quad \text{with } P = A_{\rm annealed} / A_{\rm initial}$$
 (2)

The average molecular weights and polydispersity indices of the polymers were determined by gel permeation chromatography (GPC) using a Waters system equipped with six 5 $\mu$ -Styragel columns (100, 500, 10<sup>3</sup>,10<sup>4</sup>, 10<sup>5</sup>, and 10<sup>6</sup> Å pore sizes), a Waters 440 UV/vis detector, and a Waters 410 differential refractometer. The measurements were made at 35 °C with THF as eluent at a flow rate of 1.0 mL/min. GPC columns were calibrated using monodisperse polystyrene standards. Elemental analyses of monomer and copolymer samples were performed by Elemental Analysis Service (Montreal University) using the dynamic flash combustion method and a Fisons EA 1108 analyzer.

Differential scanning calorimetry (DSC) measurements were performed with a Perkin-Elmer DSC 6 instrument under nitrogen at a heating/cooling rate of 10 °C/min. Indium was used as calibration standard. First-order transition temperatures are given by the peak maximum value and glass transitions by the midpoint of the heat capacity jump.

Optical microscopy observations were performed on polymer films between glass slides by means of a Nikon Labophot-2 POL polarized optical microscope equipped with an Instec HS1-I programmable hot stage and a Nikon FX-35 color camera. X-ray diffraction analysis was carried out with Cu Ka radiation ( $\lambda = 0.15406$  nm) on a Scintag X1 Advanced Diffraction system equipped with a  $\theta - \theta$  wide-angle goniometer. The measurements were performed at room temperature on thick polymer films (about 8  $\mu$ m). The samples for XRD measurements were prepared as follows: first, the polymer films were annealed at their texture forming temperature for several days and then rapidly placed on a cooled metal surface to freeze the molecular arrangements in the liquid crystalline states. The layer spacing d was determined according to Bragg's relation:  $d = \lambda/(2 \sin \theta)$ .

The calculated length  $(l_c)$  of a hypothetical single-layer period was estimated using Hyperchem 3 (Hypercube Inc.) for the lowest energy conformation of the side-chain with *all-trans* methylene units.

# **Results and Discussion**

**Monomers Synthesis and Characterization.** The general strategy for the synthesis of push-pull substituted BAZ monomers is outlined in Scheme 1 and involves three main steps that will be discussed successively.

The first step comprises the nucleophilic displacement of the halide of an *n*-haloalkanol with *N*-methylaniline to yield the tertiary amines 1-n. Although the preparation of tertiary amines by direct alkylation of alkyl halides with secondary amines is rarely a useful synthetic procedure, due to of the polyalkylation reactions, Robello<sup>28</sup> reported high yields of tertiary amines by reacting alkyl chlorides or bromides with N-methylaniline. The reaction was carried out in refluxing butanol in the presence of K<sub>2</sub>CO<sub>3</sub> and KI as acid absorbent and catalyst, respectively. The main drawback of this procedure is that it is too slow to be practical: it requires 4-5 days for completion. We therefore employed a slightly modified approach to prepare 1-n. First, to increase the nucleophilicity of alkyl halides, 2-chloro-1-ethanol and 4-chloro-1-butanol were converted to their iodine analogues. Second, the alkylation with N-methylaniline was carried out in DMF at 70 °C in the presence of NaHCO<sub>3</sub>. Under these conditions, the reaction was completed after 20 h as indicated by thin-layer chromatography. This modified procedure was particularly useful in the preparation of 1-4 because the milder conditions used reduced the intermolecular cyclization of 4-chloro-1-butanol to form THF, thus increasing the amine yield.

The second step involves the coupling reaction between the diazonium salt of 4-amino-4'-nitroazobenzene, which was prepared in situ, and 1-n or the com-



Figure 1. <sup>1</sup>H NMR spectra of (P2M)<sub>30</sub> in DMSO-d<sub>6</sub> and its corresponding comonomers.

mercially available *N*-(2-hydroxyethyl)-*N*-ethylaniline to afford the mesogenic azo alcohols 2-n and 3-2, respectively. In the last step, the methacrylate monomers 4-nand 5-2 were obtained in 55–80% yields by reacting the azo alcohols with methacryloyl chloride in THF in the presence of triethylamine as nucleophilic catalyst and hydrochloric acid acceptor. <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy as well as the elemental analysis confirmed the chemical structure and purity of the monomers. All monomers are easily soluble at ambient temperature in organic solvents such as chloroform, THF, DMF, and DMSO.

DSC measurements revealed for **4**–**2**, **4**–**4**, and **5**–**2** only a single endothermic transition in the heating scan

Table 2. Elemen	ntal Analysis	of BAz (	Copolymers
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			С		Н		N	
sample	formula	mol wt	calcd	found	calcd	found	calcd	found
(P2E) <sub>10</sub>	$(C_{20.6}H_{22.4}N_{4.2}O_4)_n$	$(392.8)_n$	62.98	62.56	5.74	5.50	14.97	15.31
$(P2E)_{30}$ $(P2E)_{50}$	$(C_{21.9}H_{23.3}N_{4.6}O_4)_n$ $(C_{22.9}H_{23.9}N_5O_4)_n$	$(415.7)_n$ $(433.2)_n$	63.27 63.48	$63.11 \\ 64.25$	$5.65 \\ 5.56$	$5.84 \\ 5.45$	$15.50 \\ 16.17$	15.67 16.35
$(P2M)_{30}$	$(C_{20.8}H_{21.2}N_{4.6}O_4)_n$	$(399.6)_n$	62.51	63.12	5.35	5.58	16.12	15.87
$\begin{array}{c} (P2M)_{50} \\ (P4M)_{50} \end{array}$	$\begin{array}{c} ({\rm C}_{22}{\rm H}_{22}{\rm N}_5{\rm O}_4)_n \\ ({\rm C}_{24}{\rm H}_{26}{\rm N}_5{\rm O}_4)_n \end{array}$	$(420.4)_n$ $(448.5)_n$	$62.84 \\ 64.26$	$62.26 \\ 65.10$	$5.27 \\ 5.84$	$5.34 \\ 5.63$	$\begin{array}{c} 16.66\\ 15.61 \end{array}$	$\begin{array}{c} 16.31\\ 15.24\end{array}$

at 173 °C ( $\Delta H = 98 \text{ J g}^{-1}$ ), 168 °C ( $\Delta H = 116 \text{ J g}^{-1}$ ), and 162 °C ( $\Delta H = 76$  J g<sup>-1</sup>), respectively. The large enthalpy changes are typical of a transition between a crystalline phase and an isotropic phase. POM observations confirmed that the monomers melt directly into the isotropic phase. The crystalline forms obtained from the melt are less stable than those from solution. However, the most thermodynamically stable crystalline forms can also be obtained from the melt by annealing at the appropriate temperature. There is little dependence of the transition temperatures on alkyl spacer length (in comparison, the precursors have melting points that do depend on the spacer length: 207 and 169 °C for 2-2 and 2-4). This suggests that the monomer melting point is dominated by thermodynamic changes involving interactions of the rigid BAz cores and not the alkyl chains.

Synthesis and Structural Characterization of the Polymers. The homopolymerization of 4-n and 5-2 as well as the copolymerization with the corresponding MAz monomers<sup>4,14</sup> were carried out in 1,4dioxane at 80 °C with AIBN as radical initiator. Methacrylic monomers with pendant Az moieties that also contain polar groups such as -NO<sub>2</sub> are weakly reactive in free radical polymerization because both the Az moiety and the nitrobenzene group can act as retarders.<sup>29</sup> Consequently, large amounts of initiator  $(\geq 2 \text{ wt } \%)$  and long reaction times are usually needed to prepare MAz polymers in high yields. Since the retardation effect is expected to be even more pronounced when BAz monomers are involved in polymerization, we used about 8 wt % initiator and stopped the polymerization reaction after 72 h. Despite these conditions, the polymerization yields were rather moderate ranging from 28% to 53%. The yields decrease with increasing BAz content in reaction mixture likely due to the stronger retardation effect of these moieties. The results of polymerization are summarized in Table 1. For comparison, the MAz homopolymers, the so-called PDR1M, P2MAN, and P4MAN, were prepared as previously described.4,14

The copolymer structures and compositions were determined by <sup>1</sup>H NMR spectroscopy and confirmed by elemental analysis. Figure 1 displays the <sup>1</sup>H NMR spectrum for one of the copolymer samples (i.e.,  $(P2M)_{30}$ )) along with that of its corresponding comonomers. The spectral assignments clearly support the proposed structure: the sharp and clearly separated proton resonances of monomers disappear after copolymerization, while broad and overlapped resonances of azochromophores bound to polymeric chains appeared at nearly the same positions. Furthermore, the vinylidene protons, which resonate in the 6.3-5.6 ppm region for monomers, disappear in the  $(P2M)_{30}$  spectrum, whereas the  $\alpha$ --methyl resonances are shifted upon polymerization from  $\sim$ 1.90 ppm to higher field (1.15 ppm). All of these confirm the consumption of the double bond in copolymerization. The copolymer composition can be readily determined from the ratio of the integrated peak areas of the protons *ortho* to amino group (g, g') resonating at ~6.7 ppm and the total number of aromatic protons resonating in the 7.5–8.6 ppm range (h–j and h'–l'). The results are listed in Table 1. Elemental analysis of the copolymers closely matched the values calculated from NMR data (Table 2). Although one should exercise caution in interpreting copolymer composition at relatively high conversions, it appears that BAz monomers are less reactive than the MAz monomers on the basis of the fact that their content is smaller in copolymers than in the corresponding feeds.

The resulting number-average molecular weight  $(M_n)$ values of the copolymers, as evaluated by GPC analysis, range from 3600 to 5600 g/mol, with polydispersity indices between 1.27 and 1.76. Compared to  $M_{\rm n}$  of other BAz polymers,<sup>30</sup> for which values of 9100 up to 45 000 were reported, the  $M_{\rm n}$  of our samples are yet low. This might be attributed to the presence of nitrobenzene, a well-known chain transfer agent. Moreover, an increased extent of termination reactions, as a result of high concentration of growing chain radicals (due to the high AIBN/monomer ratio used), should also be taken into account. The molecular weight of BAz homopolymers  $(P2E)_{100}$ ,  $(P2M)_{100}$ , and  $(P4M)_{100}$  could not be determined by GPC because these samples are insoluble in THF. Actually, in terms of solubility, the homopolymers are readily soluble only in pyridine, strong acid solvents (i.e., trichloroacetic acid, methanesulfonic acid), and mixtures of hexafluoro-2-propanol:chloroform. Conversely, the copolymers are easily soluble in conventional laboratory solvents as THF, DMSO, DMF, and NMP. It is very likely that the "dilution" of polymer chains with the less polar MAz groups diminishes the strong dipole-dipole interactions among the BAz side chains sufficiently to increase the solubility in common organic solvents.

**Mesomorphic Properties of the Polymers.** Phase transition temperatures and relevant thermodynamic parameters of the polymers were determined by a combination of DSC measurements and POM observations. As previously mentioned, the monomers 4-2, 4-4, and 5-2 melt directly into the isotropic phase with no indication of LC character. The same holds for MAz monomers.  $^{4,14}$  However, the BAz homopolymers and the copolymers with MAz, with few exceptions, exhibit thermotropic LC properties. The thermograms of most samples display a LC phase melting endotherm on heating and a LC phase formation exotherm on cooling from the isotropic phase. Thus, as observed for other systems,<sup>14,28,31</sup> the "polymer effect" is functioning: the macromolecular chains string the mesogenic pendants together in a comblike fashion, correlating their movements and stabilizing them in LC mesophases.

Figure 2 displays the second DSC heating curves for the copolymer series with a very short spacer (n = 2)and ethylamino functionality. At this point we should



**Figure 2.** DSC heating curves (second scan) for the PDR1M- $(P2E)_x$  series.

note that the rather low molecular weights of the investigated polymers might place the polymers thermal behavior in the regime in which the transition temperatures are strongly molecular weight dependent.<sup>32</sup> This, however, does not prevent a comparison of the transitional properties of the polymers here as being directly related to the different structural features of the samples because the polymers have similar molecular weights (see Table 2). From a structural standpoint, both homopolymers of this particular series, namely PDR1M and (P2E)<sub>100</sub>, possess the typical features of SCLC polymers, i.e., a linear backbone containing the rigid-rod-like mesogenic groups, the principles of which have been reviewed elsewhere.<sup>32</sup> However, because of the bulky *N*-ethyl group, which reduces the axial-to-diameter ratio (A/D) of MAz mesogen and accordingly its anisometry, and the short alkyl spacer, which restricts the mobility of side groups, the occurrence of LC phase is impeded in the former homopolymer. As a result, its DSC thermogram reveals only a second-order transition corresponding to the glass transition at 120 °C. In the case of  $(P2E)_{100}$ , however, the effect of bulky N-ethyl substituent on the A/D ratio of the more elongated BAz mesogen is less pronounced; therefore, the tendency to form LC phases is not suppressed. Besides, it is known that three-ring mesogens are more favored in a LC environment.<sup>32</sup> Accordingly, (P2E)<sub>100</sub> does exhibit on heating a first-order transition at 159 °C, in addition to the glass transition at 114 °C (Figure 2).

The copolymers propensity toward thermotropic selforganization increases, as expected, with increasing the proportion of BAz side groups. In fact, a relatively low proportion of such units (about 30%) proves to be enough to overcome the energetically preferred random coil conformation of the polymethacrylate backbone and allow the mesogens to pack in the parallel arrangement needed to form a LC phase. Thus, (P2E)10 is completely amorphous, as indicated by the lack of first-order transitions in DSC and the lack of birefringence in POM, whereas the remaining copolymers  $(P2E)_{30}$  and  $(P2E)_{50}$  form mesophases above  $T_{\rm g}$ . The phase transition temperatures and the enthaply changes  $(\Delta H)$  associated with the LC-isotropic phase transition are collected in Table 3. Several observations are worth mentioning. First, one notices a significant depression of  $T_{\rm g}$  from 120 °C (PDR1M) to 103 °C when 10 mol % BAz groups are introduced in the macromolecular chain. Such decrease could be ascribed to the plasticization effect of polymer backbone by the elongated BAz mesogen. Interestingly, a further increase in BAz content does not continue to diminish  $T_{\rm g}$ , but rather enhances it so that, at 100 mol % BAZ, the sample show a  $T_{\rm g}$  at 114 °C. As the increase

Table 3. Thermodynamic Parameters of the Polymers

		-	
sample	BAz (mol %)	MAz (mol %)	phase transitions <sup><i>a</i></sup> (°C) (corresponding enthalpy changes, $J g^{-1}$ ) heating/cooling
PDR1M	0	100	g 120 i
(P2E) <sub>10</sub>	10	90	g 103 i
(P2E) <sub>30</sub>	32	68	g 105 n 125 <sup>b</sup> i/i 98 g
(P2E) <sub>50</sub>	49	51	g 108 s 146 (4.2) i/i 140 (- 4.0) s 101 g
(P2E) <sub>100</sub>	100	0	g 114 s 159 (5.9) i/i 154 (- 5.5) s 110 g
P2MAN	0	100	g 110 s 134 (2.1) n 166 (2.6) i
(P2M) <sub>30</sub>	30	70	g 97 s 128 (3.6) i/i 123 (3.1) s 93 g
(P2M) <sub>50</sub>	50	50	g 100 s 159 (5.8) i/i 153 (5.4) g 96
(P2M) <sub>100</sub>	100	0	g 102 s 174 (7.2) i/i 167 (6.9) g 95
P4MAN	0	100	g 85 s 170 <sup>c</sup> (3.6) i
(P4M) <sub>50</sub>	50	50	g 79 (6.2) s 156 i/i 149 (5.7) g 73
(P4M) <sub>100</sub>	100	0	g 77 s 171 (7.6) i/i 163 (7.3) g 70

<sup>*a*</sup> Data from second heating and first cooling scans. <sup>*b*</sup> Determined by POM. <sup>*c*</sup> With thermal decomposition. Abbreviations: g = glass; n = nematic; s = smectic; PDR1M is the MAz homopolymer with n = 2 and  $R = C_2H_5$ ; P2MAN and P4MAN are MAz homopolymers with  $R = CH_3$  and n = 2 and 4, respectively (Chart 1).

in  $T_{\rm g}$  is concurrent with the observation of liquid crystallinity in the copolymer series, one could rationalize this behavior in terms of the reduction in the specific free volume on passing from the isotropic glass phase to the LC phase. Hence, the stabilization of mesogens in LC phases compensates to some extent the plasticization effect of BAz groups on  $T_{\rm g}$ .

By copolymerization of mesogenic groups with nonmesogenic units, the distance between the side mesogens increases, which in turn causes a reduction of the mesophase stability and the extent of mesophase structural order.<sup>32</sup> As compared to (P2E)<sub>100</sub>, the decrease of isotropization temperatures ( $T_i$ ) and enthaply changes with increasing the proportion of MAz comonomer in copolymers is in accord with this view (Table 3). In fact, the dilution with a very large fraction of MAz units as in (P2E)<sub>30</sub> renders the arrangement of BAz cores more difficult to develop so that the endothermic transition cannot be detected in DSC. However, a  $T_i$  at 125 °C was determined by optical microscopy observations.

In POM, freshly cast films of (P2E)<sub>30</sub>, (P2E)<sub>50</sub>, and (P2E)<sub>100</sub> are dark at ambient temperature, indicative of a glassy state, but display birefringent domains when heated above T<sub>g</sub>. To promote formation and identification of optical textures typical of low molar mass LC the samples were brought into the isotropic phase and cooled very slowly (0.1 °C/min) into their mesophases, where they were annealed for long times (24-72 h). Generally, the lower the BAz content the longer the annealing period. The homopolymer  $(P2E)_{100}$  and the copolymer with 50% BAz developed an optical pattern consisting of very fine grained, confocal textures (Figure 3a), which are closely reminiscent of the smectic A phases illustrated in refs 23 and 33. Such fine grain textures can be interpreted as the result of a relatively high nucleation density that results in ordered domains of very small direction. Attempts to enlarge the birefringent domains either by increasing the annealing time or by reducing the cooling rate from the isotropic phase were unsuccessful, possibly because the bulky N-ethyl group partially distorts the lateral packing arrangement of the mesogens and impedes the growth of LC domains. Yet, after several heating to/cooling from melt cycles, large and diffuse zones of homeotropic alignment were developed, a result implying an orthogonal arrangement of the director with respect to the layer planes and which points to the existence of a



**Figure 3.** Polarizing optical micrographs of (a) (P2E)<sub>50</sub> at 120 °C and (b) (P2E)<sub>30</sub> at 115 °C (magnification  $400 \times$ ).

smectic A mesophase. This view is also supported by X-ray diffraction data analysis (see the following) as well as by the order of magnitude of the isotropization enthalpies (i.e., 4.2 J g<sup>-1</sup> for (P2E)<sub>50</sub> and 5.9 J g<sup>-1</sup> for (P2E)<sub>100</sub>, which are typical of smectic A phases).<sup>23,34,35</sup>

Generally, the nature of the mesophase is not influenced by the addition of nonmesogenic comonomers.<sup>23,32</sup> However, changes have been reported.<sup>36,37</sup> In a copolymer series containing biphenyl and MAz mesogens, Ikeda et al.<sup>37</sup> observed that the copolymers with high fraction of azo groups display smectic phases similar to homopolymers. By contrast, the copolymers with low content of azo groups (i.e., 6, 15, and 35 mol %) exhibit nematic phases. A mesophase change occurs as well in our system. When the concentration of BAz units is reduced to 30 mol %, because of the backbone dilution with many non-LC comonomers, the stabilizing effect of the polymer backbone is no longer strong enough to promote the ordered smectic phase as in  $(P2E)_{50}$  and  $(P2E)_{100}$ . Instead, a nematic organization is formed, in which the mesogens are oriented more or less parallel with the backbone. The nematic phase of (P2E)<sub>30</sub> was identified by univocal observations of schlieren features with typical disclinations of integer and half-integer order<sup>38</sup> (Figure 3b).

Substitution of an *N*-ethyl moiety in the PDR1M- $(P2E)_x$  series with an *N*-methyl group to obtain the



**Figure 4.** DSC heating curves (second scan) for the P2MAN- $(P2M)_x$  series.

 $P2MAN-(P2M)_r$  series affects significantly the transition temperatures and the mesophases stability and, in some cases, the type of mesophase formed. The DSC heating curves of the P2MAN-(P2M)<sub>r</sub> series are shown in Figure 4. All samples, but P2MAN, display a step in baseline due to glass transition and an endothermic transition that appears to be better defined than in the PDR1M- $(P2E)_x$  series. Comparison of the thermodynamic parameters of the two series (Table 3) reveals that the glass transitions of N-methyl polymers are 10-12 °C lower than those of *N*-ethyl counterparts, whereas the  $T_{\rm i}$  are higher. This brings about a rather extended mesophase  $(T_i - T_g)$  in *N*-methyl systems. For instance, the mesophase of  $(P2M)_{50}$  spans  $\sim 60$  °C while its structural cousin  $(P2E)_{50}$  displays the smectic phase only over 38 °C.

Such behavior can be rationalized as follows: on one hand, the smaller methyl group is expected to exert weaker steric constraints than the bulky ethyl group on intra- and intermolecular movements of chain segments as well as on the conformational changes of the backbones. This would decrease the energy required for cooperative segmental motion needed in going from the isotropic glassy to anisotropic LC state. As a result, a reduction in glass transition would occur, as in fact was observed. On the other hand, the effect of diminished steric hindrance caused by the methyl group strengthens the lateral interactions among the side mesogens, thereby promoting a more compact packing of the molecules to stabilize the LC phase. Accordingly, the methyl-substituted systems will tend to exhibit more ordered phases, at higher temperatures, than their ethyl analogoues. This is clearly indicated in our polymers by the larger enthalpy changes involved in the mesophasic transitions as well as by the higher  $T_i$  of methyl systems (Table 3). Furthermore, (P2M)<sub>30</sub> displays a higher order of mesomorphism (i.e., smectic order) than its closely related counterpart (P2E)<sub>30</sub>, which forms nematic structures. The first-order transition (not apparent in  $(P2E)_{30}$ ) can now be distinguished in the DSC scan of  $(P2M)_{30}$ . The more effective packing of mesogens also leads to LC order in P2MAN, with nematic and smectic phases,<sup>14</sup> in contrast to its related PDR1M.

The mesophases of *N*-methyl polymers, observed on POM, revealed significant differences as compared to *N*-ethyl systems, in both the LC texture and the time required for the texture to develop. Thus, whereas the smectic  $(P2E)_{50}$  and  $(P2E)_{100}$  reveal fine-grain textures (Figure 3a) after very long annealing times (up to 72 h),  $(P2M)_{30}$ ,  $(P2M)_{50}$ , and  $(P2M)_{100}$  display better developed mesomorphic textures such as fanlike areas after



Figure 5. Polarizing optical micrographs of  $(P2M)_{50}$  at 130  $^{\circ}C$  (magnification 200×).



**Figure 6.** DSC heating curves (second scan) for the P4MAN- $(P4M)_x$  series.

only 12 h of annealing. The fan-shaped texture, which is revealing of a smectic A phase, is shown in Figure 5 for  $(P2M)_{50}$ .

Analysis of the isotropization enthalpies reveals that  $\Delta H$  follows an increasing trend with increasing the fraction of BAz mesogens (Table 3). If we simply assume that  $T_i$  reflects largely the strength of the interaction between the mesogenic units, then it is immediately apparent that BAz core interactions are much stronger than MAz core interactions. Increasing the proportion of BAz groups intensifies these interactions and hence enhances  $\Delta H$ .

The DSC traces for the series with a longer spacer (n = 4) and methylamino functionality  $(P4MAN-(P4M)_x)$ are shown in Figure 6. Similar to previous polymers, a glass transition (at lower temperature) and a first-order transition (at higher temperature) are distinguished. Lengthening the spacer from two to four methylene units reduces the  $T_{\rm g}$  by about 20 °C, an effect often observed in SCLC polymers and which is ascribed to the internal plasticization action of longer alkyl spacer. By contrast to  $T_{\rm g}$ , the change in spacer length  $[(\dot{\rm P2M})_{50}]$ vs  $(P4M)_{50}$  and  $(P2M)_{100}$  vs  $(P4M)_{100}]$  has little influence on  $T_i$ . For instance,  $T_i$  of  $(P2M)_{50}$  is 159 °C, whereas that of  $(P4M)_{50}$  is 156 °C. The flexible spacer can affect  $T_i$  in two ways:<sup>34</sup> on one hand, extending the spacer length enhances the molecular anisometry of the side chains, resulting in better liquid crystalline properties and hence higher  $T_i$ . Such a dependence was reported for nitroazobenzene chromophores with a styrene backbone,<sup>34</sup> side-chain copolymers containing carbazolylmethylene-aniline and nitrobenzylidene-aniline groups,39 and 4-cyanoazobenzene-based polymethacrylates.<sup>40</sup> On



Figure 7. Polarizing optical micrographs of  $(P4M)_{100}$  at 135 °C (magnification 400×).

the other hand, increasing the spacer length also serves to dilute the mesogen-mesogen interactions, thereby depressing the  $T_i$ . Moreover, the mesogens with a longer spacer have a greater degree of freedom in their isotropic phase and hence a larger  $\Delta S_i$ . As  $T_i$  is determined by the ratio of  $\Delta H_i/\Delta S_i$ , the result would be also a decrease in  $T_i$ . The decrease of  $T_i$  with the spacer length was reported for 4-metoxybiphenyl-based polyacrylates,<sup>41</sup> polyacetylenes with side-chain biphenyl cores,<sup>35</sup> or polynorbornene systems with 4'-methoxy-4biphenyl mesogenic groups.<sup>42</sup> For the systems investigated here, it appears that the two opposite effects somehow balance so that no significant change in  $T_i$  is observed when the alkyl spacer is expanded.

When viewed on POM,  $(P4M)_{50}$  and  $(P4M)_{100}$ , annealed in their mesophase temperature for several hours, develop the elongated sharp-pointed particles (bâtonnets) (Figure 7). This indicates the smectic A phase.

X-ray Analysis. To complement DSC and POM observations and gain more information on the molecular arrangements, modes of packing, and types of order in mesophases, X-ray diffraction analysis was carried out on polymer films. The X-ray profiles under ambient conditions are shown in Figure 8, and the associated data derived from Bragg equation are listed in Table 4. In all samples, but  $(P2E)_{30}$ , the diffraction patterns display two sharp and intense reflections at low angles  $(2^{\circ} < 2\theta < 6^{\circ})$ , a result indicative of a periodic lamellar structure corresponding to smectic layers. The reciprocal spacings of the sharp diffractions are in 1:2 ratio (Table 4). In the wide-angle region, the diffractograms revealed only broad halos centered at about  $2\theta = 19-21^{\circ}$ , which correspond to an average intermolecular distance of approximately 4.6–4.2 Å. The broad halo (showed here only for (P4M)<sub>50</sub> in Figure 8b) suggests that the lateral packing of the molecules within the smectic layer is disordered, i.e., a liquidlike arrangement of the mesogenic groups in the layers. Such arrangement is consistent with a disorder mesophase of the smectic A or C type. Given the homeotropic regions, fan textures, or bâtonnets structures observed under POM, the smectic phases in our samples were assigned as being of A-type.

The lack of diffraction peaks in the low-angle region confirms the occurrence of nematic phase in  $(P2E)_{30}$ , in accordance with the schlieren texture observed under POM. For the remaining samples, several qualitative



**Figure 8.** Ambient temperature X-ray diffractograms: (a) in the low-angle region for BAz polymers; (b) in the  $1^{\circ} < 2\theta < 30^{\circ}$  region for (P4M)<sub>50</sub>.

<b>Fable 4. X-ray</b>	Diffraction	Data of	BAz	Polymers
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sample	$l_{\rm c}$ (Å)	$d_1(\text{\AA})$	$d_2({ m \AA})$	$2-d_1/l_{ m c}$
(P2E) <sub>50</sub>	24.4	36.4	17.2	0.50
(P2E) <sub>100</sub>	24.4	35.8	17.4	0.53
(P2M) <sub>30</sub>	24.2	32.8	16.1	0.64
(P2M) <sub>50</sub>	24.2	32.6	16.0	0.65
$(P2M)_{100}$	24.2	31.9	15.9	0.68
$(P4M)_{50}$	27.1	35.3	18.0	0.69
$(P4M)_{100}$	27.1	35.1	18.3	0.70

observations can be made. First, we noticed that the peaks sharpness and intensity relative to the broad halo vary with the size of amino functionality employed and the aliphatic spacer length, likely reflecting differences in mesogens packing. Thus, (P2E)<sub>50</sub> and (P2E)<sub>100</sub> yield the weakest and the widest reflection peaks presumably due to the bulkiness of an ethyl group that hinders an efficient packing of side mesogens. When the ethyl group is replaced by the methyl moiety and the spacer length is increased by two more methylene units, the reflection peaks become sharper and more intense (see (P4M)<sub>50</sub> and  $(P4M)_{100}$  peaks), further evidence that the more anisotropic mesogens favors improved organization. It is noteworthy that in all samples the first-order reflection is the most intense one, which may suggest that the polymethacrylate backbone is not strictly phase separated from the mesogens layers. For a phaseseparated system consisting of distinct polymer backbon layers and mesogen layers, the second-order reflection is strong and the first-order reflection vanishes.<sup>43</sup>

The thickness of smectic layer  $d_1$  determined from the first-order reflection was compared with the calculated molecular length  $l_c$  of the mesogens in their fully extended all-trans conformation. In all samples  $d_1$  is larger than  $l_c$  (representing orthogonal monolayer S<sub>A1</sub>



**Figure 9.** Schematic representation of  $S_{Ad}$  phase exhibited by BAz polymers; the filled and empty ellipsoids represent the BAz and MAz mesogens, respectively;  $d_1$  = layer spacing determined from X-ray data;  $l_c$  = extended molecular length calculated from molecular modeling.

phases) but smaller than  $2l_c$  (representing orthogonal bilayer  $S_{A2}$  phases). This implies an orthogonal partial bilayer structure ( $S_{Ad}$ ) in which the mesogenic cores are interdigitated in an antiparallel fashion, as shown in Figure 9. Such partial bilayer phases are commonly observed for low molar mass compounds and SCLC polymers possessing strong dipoles where the antiparallel pairs serve to minimize the dipolar energy.<sup>34,39,41</sup>

Although all samples exhibit similar  $S_{Ad}$ -type organization, the degree of overlapping of side chains, measured as the difference  $2 - d_1/l_c$ , is rather different. For a given copolymer composition and a given spacer length, the degree of interdigitation increases from 0.50 to 0.64 on going from  $(P2E)_{50}$  to  $(P2M)_{50}$  following the reduction in the bulkiness of amino functionality. In other words, the methyl systems overlap to a greater extent than does the ethyl systems, and consequently there is a higher packing density in the former polymers. It is this increased packing density that enhances  $T_i$  and  $\Delta H$  in the P2MAN-(P2M)<sub>x</sub> series when compared to their structural analogues (Table 3).

Extending the spacer is known to reinforce the interactions between the alkyl parts, and this in turn drives the system toward a monolayer smectic structure.<sup>35,44</sup> Tang and co-workers<sup>35</sup> showed that an increase of the spacer from 2 to 4 methylene units in SCLC polyacetylene results in the growth of the monolayer structure at the expense of partially bilayer one. A further increment in the spacer length completely eliminated the S<sub>Ad</sub> phase. In our samples no transition toward a monolayer smectic phase occurred in  $(P4M)_{50}$ or (P4M)<sub>100</sub>, except a slight increase in the degree of interdigitation. This result implies that the dipolar interactions, mainly due to the nitro groups, are stronger than the energetically favored segregation forces, driving thus the system toward a partially bilayer structure. The  $d_1$  spacing of  $(P4M)_{50}$  and  $(P4M)_{100}$  is about 2.6 Å longer than the  $d_1$  spacing of (P2M)<sub>50</sub> and  $(P2M)_{100}$ . As this value is very close to 2.9 Å, which represents the theoretical increase from an ethyl to butyl spacer assuming an extended conformation, it indicates that the butyl spacer exist mainly in the alltrans conformation.

**Optical Studies of Polymer Films by Polarized UV-vis Spectroscopy.** Electronic spectra of the polymer films show two absorption bands: a peak in UV region, attributed to the benzene rings, and a more intense band in the visible range, which is assigned to the vibronic coupling between  $n-\pi^*$  and  $\pi-\pi^*$  electronic transitions of *trans*-azochromophores. The latter spectral absorption is due to the high charge-transfer interaction between the electron-donor group (amino)

as-cast film				annealed film			
sample	$\lambda_{\max}(nm)$	$A_{ m initial}$	$T_{\rm annealing}(^{\rm o}{\rm C})$	$\Delta \lambda_{\max}(nm)$	$A_{ m anealed}$	$S_{ m h}$	
(P2E) <sub>10</sub>	466	0.86	115	0	0.86	0	
(P2E) <sub>30</sub>	472	0.45	118	-3	0.38	0.18	
(P2E) <sub>50</sub>	482	0.91	138	-6	0.66	0.27	
(P2E) <sub>100</sub>	510	0.79	145	-8	0.43	0.38	
(P2M) <sub>30</sub>	474	0.73	112	-4	0.58	0.21	
(P2M) <sub>50</sub>	490	0.67	148	-7	0.45	0.30	
(P2M) <sub>100</sub>	512	0.81	166	-10	0.40	0.45	
$(P4M)_{50}$	466	0.90	145	-8	0.57	0.35	
$(P4M)_{100}$	483	0.76	168	-13	0.29	0.48	

Table 5. UV-vis Characteristics of Thin Films<sup>a</sup>

 $^{a} \lambda_{\text{max}}$  = maximum wavelength;  $A_{\text{initial}}$  = initial absorbance maximum;  $\Delta \lambda_{\text{max}}$  = the shift in maximum wavelength after annealing;  $A_{\text{annealed}}$  = absorbance maximum after annealing;  $S_{\text{h}}$  = out-of-plane order parameter.



**Figure 10.** UV–vis spectra of PDR1M-(P2E)<sub>x</sub> in polymer films.

and the electron-acceptor group (nitro). Figure 10 shows as an example the electronic spectra for selected members of the PDR1M-(P2E)<sub>x</sub> series. It can be seen that (P2E)<sub>100</sub> exhibits a maximum absorbance ( $\lambda_{max}$ ) at longer wavelength (510 nm) in comparison with MAz homopolymer (460 nm). This is due to the larger conjugated system of BAz chromophore that increases the  $\pi$ -electron delocalization and lowers thus the energy of the  $\pi-\pi^*$  transition. The  $\lambda_{max}$  of the copolymers is affected by composition, a bathochromic shift in their absorption maximum being observed as the fraction of BAz groups is increased. The  $\lambda_{max}$  of BAz samples is listed in Table 5.

Annealing the as-cast polymer films above  $T_{\rm g}$  results in significant changes of the electronic spectra. As may be seen in Figure 11a for one of the copolymer samples (i.e.,  $(P2E)_{50}$ ) the maximum absorbance, recorded at normal incidence, fell by 27% of the initial value. Such drop of absorbance may arise from the partial homeotropic (out-of-plane) alignment of the chromophores, as has been observed for other azochromophores.<sup>15,16,45</sup> To gain insight into the spatial orientation of the chromophores, including the in-plane and out-of-plane modes, measurements of absorption spectra with s- and ppolarized probe light of the spectrometer were taken at various incident angles  $\theta_{i}$ . p-polarized light with the electric vector parallel to the plane of incidence is sensitive to the out-of-plane orientation, whereas spolarized light, with the electric vector perpendicular to the plane of incidence, is relatively inert to that. Three parameters, namely  $A_p/A_s$ , p- $\lambda_{max}$ , and s- $\lambda_{max}$  were employed, where  $A_p$  and  $A_s$  represent the absorbances at  $\lambda_{max}$  taken by p- and s-polarized light, and p- $\lambda_{max}$  and s- $\lambda_{max}$  are the maximum wavelengths observed with p-



**Figure 11.** Polarized UV–vis spectra of fresh and annealed films of  $(P2E)_{50}$  taken at  $\theta_i = 0^\circ$  (a) and  $\theta_i = 50^\circ$  (b) with s-polarized (solid line) and p-polarized (dotted line) probe light.

and s-polarized light. A dependence of the first parameter on the incident angle reveals the out-of-plane orientation of the chromophores, whereas a dependence of the last two parameters provides information on the orientation of the aggregated chromophores.

At normal incidence ( $\theta_i = 0^\circ$ ), the copolymer spectra recorded before and after annealing are superimposed as the polarization of the probe beam is changed from p to s (Figure 11a). That means the chromophores are optically isotropic in the film plane ( $A_p/A_s = 1$ ). However, when the annealed film is tilted toward the measuring beam at an angle of 50°, the s- and p-electronic spectra are no longer superimposed (Figure 11b). Instead, a significant anisotropy in aborbance is observed. As the incident angle is increased, p-polarized light, being



**Figure 12.** Changes in  $A_p/A_s$  as a function  $\theta_i$  for (P2E)<sub>50</sub>.

sensitive to the homeotropic alignment, "sees" more and more chromophores having such orientations. This brings about a rise in absorbance with respect to normal incidence absorbance. On the other hand, the absorbance recorded with s-light does not significantly with  $\theta_i$ . Accordingly, a plot of  $A_p/A_s$  vs  $\theta_i$ , with  $\theta_i$  varying from  $-50^{\circ}$  to  $50^{\circ}$ , displays in the case of annealed film a distinct minimum at  $\theta_i = 0^\circ$  (Figure 12). On the contrary, no clear  $\theta_i$  dependence of  $A_p/A_s$  ratio is observed for the as-cast film. These results reveal that the annealing process causes a spontaneous selforganization of the side chains to form a smectic phase in which the chromophores tend to align homeotropically to the film surface. The homeotropic order parameter  $S_h$  calculated using eq 2 (see Experimental Section) is 0.27.

Simultaneous with the absorbance drop, the annealing process leads also to a blue shift of  $\lambda_{\max}$  of about 6 nm. This blue shift can be related to the formation of H-aggregates ("card-pack" or "face-to face" aggregates), an assembly with linear chromphores arranged in such a way that their transition dipole moments are parallel to each other and ordered perpendicular to the stacking direction. The occurrence of such aggregates, caused by the  $\pi\pi$  stacking of the aromatic cores, is frequently encountered in ordered systems such as LC polymers<sup>16,45</sup> and Langmuir–Blodgett films.<sup>46</sup>

The molecular aggregation in (P2E)<sub>50</sub> appears to occur selectively for the chromophores oriented homeotropically to the film surface. p-polarized spectra of the annealed film display significant dependence on  $\theta_i$ : the larger  $\theta_i$ , the more p- $\lambda_{max}$  is blue-shifted, accompanied by the increment of absorbances (Figure 13a). Conversely, s-polarized spectra do not change considerably with  $\theta_i$ , which implies no marked occurrence of Haggregation in the film plane. Hence, the aggregates formed during annealing are homeotropically oriented to the film plane.

Except for  $(P2E)_{10}$ , which does not exhibit LC order, all other BAz samples show similar changes of electronic spectra, albeit of different extent, as  $(P2E)_{50}$  on annealing. Table 5 summaries the results. The spontaneous orientation of chromophores in BAz homopolymers leads to the largest decrease of absorbance, when measured at normal incidence, and consequently results in the highest order parameter  $S_{\rm h}$ . By copolymerization, the homeotropic order is reduced so that, ultimately, no homeotropic alignment is observed in the LC MAz homopolymers.<sup>13</sup>

Irradiation of isotropic azopolymer films with LPL induces a perpendicular orientation of chromophores with respect to the polarization direction of actinic light,



**Figure 13.** Polarized UV–vis spectra of (P2E)<sub>50</sub> annealed film at various incident angles ( $\theta_i$ ) of (a) p- and (b) s-polarized light.

giving rise to optical anisotropy. The propensity of thermally induced homeotropic orientation of chromophores in BAz polymers could play an important role in the photoinduced anisotropy process. For polymethacrylates containing 4-methoxyazobenzene chromophores and different alkyl spacers (CnMeO, n = 2, 6, 12 methylene units), Ichimura et al.<sup>16</sup> observed an exclusive in-plane photoorientation at both room and elevated temperatures for C2MeO and C6MeO. In contrast, in C12MeO, which is the only sample exhibiting homeotropic alignment upon heating, both in-plane and out-of-plane photoorientation occurred simultaneously at room temperature as well as elevated temperatures. Furthermore, the out-of-plane orientation was predominant when the film was annealed in the temperature region of the LC phase.

The photoinduced orientational behavior of chromophores in our samples will be the subject of a forthcoming paper.<sup>27</sup> In the synthesized polymers, to produce any motion of the chromophore with respect to its initial orientation, both N=N groups in bisazochromophores have to photoisomerize. If just one of the azo groups is photoisomerized to its cis configuration, the probability of returning to a trans configuration in the same position is overwhelmingly high. Thus, the process of orientation perpendicular to pump polarization was slower than in monoazo-based polymers as it requires many more cycles of trans-cis-trans photoisomerization. However, the photoinduced orientation was more stable than in monoazo polymers based on the fact that, again, two thermal cis-trans isomerizations should be taking place in the bisazochromophore to move from on orientated state to a random distribution.

#### Conclusions

In this study, a series of novel SCLC copolymers containing push-pull BAz and MAz side groups were synthesized and studied in regard to the effect of BAz content, the bulkiness of amino donor group, and the length of the spacer on the mesomorphic properties of the polymers. The copolymers with a very short spacer (two methylene units) and ethyl amino functionality show liquid crystallinity at a relatively low content (30%) of BAz units. Replacing the bulky ethyl group with methyl moiety increases the tendency toward smectic mesomorphism and expands the mesophases stability by lowering the  $T_{\rm g}$  and raising the  $T_{\rm i}$ . For the same methylamino functionality, extending the flexible spacer from two to four methylene units affects significantly the  $T_{\rm g}$  but has only a little effect on  $T_{\rm i}$ .

With few exceptions, most of BAz polymers exhibit smectic A mesophases as revealed by DSC, POM, and X-ray diffraction analysis. The S<sub>A</sub> phase involves a partial bilayer structure in which the side mesogens are interdigitated in an antiparallel fashion.

Annealing the polymer films above  $T_{\rm g}$  brings about a partial out-of-plane (homeotropic) orientation of the azochromophores, leading to the formation of H-aggregates. The findings reported here are anticipate helping the design of novel azopolymers for digital and holographic storage applications.

Acknowledgment. We thank Mrs. Lyn Kerns (RMC) for X-ray diffraction experiments. Funding from the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Department of Defense Canada is gratefully acknowledged. C.C. acknowledges the PGS B Scholarship granted by NSERC and Ontario Government. The authors dedicate this paper to the memory of Professor Almeria Natansohn.

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