Synthesis and Characterization of a Series of Azobenzene-Containing Side-Chain Liquid Crystalline Polymers

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ABSTRACT: A series of poly{4'-{(X-methacryloyloxyalkylene)methylamino}-4-nitroazobenzene} (pXMAN, where X is the number of methylene units and varies from 2 to 12) polymers with liquid crystalline (LC) properties was synthesized. When annealed above their  $T_g$  values, the whole series of polymers exhibits a stable smectic A mesophase while only the material with the shorter spacer, p2MAN, presents a smectic phase followed by a nematic phase. The spacing of the smectic layers was determined by X-ray diffraction, revealing intermolecular reorganization by interdigitation of the side-chain mesogens since the smectic layer spacing was larger than a fully extended side chain but less than two extended chains. This behavior is confirmed by temperature dependent aggregation as observed by UV-visible spectroscopy during the transition from an amorphous state to a liquid crystalline phase. The stability of the mesophase is enhanced by intermolecular interactions as argued by enthalpic and thermochromic considerations. Systematic photoinduced birefringence measurements on the various states reveal that the maximum and remnant levels of birefringence decrease with increasing the spacer length and with decreasing the glass transition temperature of the considered liquid crystalline polymer.

## Introduction

Since first observations of Todorov and collaborators in 1984,<sup>1</sup> azobenzene containing polymers have been the subject of intensive research in particular for their interest in the field of photonics applications.<sup>2</sup> Such applications include reversible optical data storage,<sup>3</sup> fabrication of diffractive elements with specific polarization properties,<sup>4,5</sup> optical switching and/or slab waveguides<sup>6</sup> and many other purposes.

From guest—host to functionalized amorphous polymers with side-chain azobenzene chromophores, recent observations have demonstrated that the optical modulation of chiral properties is possible in azopolymers which display a liquid crystalline (LC) mesophase thus opening new and interesting possibilities.<sup>7,8</sup>

Thermal enhancement of the photoinduced anisotropy has also been reported in liquid crystalline polymers that contain azobenzene chromophores either in homopolymers or in copolymers, providing a new way to increase and stabilize molecular orientation.<sup>9,10</sup>

Many early studies describe optically induced reorganization of azobenzene LC polymers. Briefly, the photoinduced anisotropy in azobenzene containing materials results from a primary selective photoisomerization reaction from the "Trans" to the "Cis" azobenzene isomers. The isomerization is then followed by a reorientation of the rod-shape "Trans" moieties in a perpendicular direction with respect to the polarization of the actinic field. This scheme is general to amorphous and LC azobenzene materials. However, in liquid crystalline polymers, the mobility of the chromophore depends strongly on the considered mesophase and on mesogens properties.

Intermolecular interactions play a crucial role in azobenzene LC mesophase formation. Nikonorova et al.

Identical methacrylate polymers with spacers of six and eight methylene units have been synthesized by Andruzzi et al. and have clearing temperatures that also decrease with spacer length.<sup>12</sup> These results are in agreement with the clearing temperatures of the materials synthesized by Nikonorova et al., demonstrating an odd—even effect.

Han et al. report methacrylic azobenzene polymers comparable to those of Andruzzi and Nikonorova but containing a methoxy tail group that has no electron acceptor properties.<sup>13,14</sup> The polymer that has two methylene units in the spacer is amorphous whereas the polymer containing six methylene units exhibits a narrow smectic phase and a broad nematic phase. Similar observations are reported for an analogous material containing an ethoxy tail.<sup>15</sup> The polymer containing 12 methylene units in the spacer is smectic over a broad range. In their system, the formation of mesophase is promoted by the increased autonomy of the mesogens from the polymer backbone, not from intermolecular interactions.

Li et al., also report the synthesis of a methacrylate polymer identical to those of Andruzzi and Nikonorova with a nitro end group in the place of the cyano group.<sup>16</sup> Polymers with spacers containing three and four methylene units are amorphous while the spacer with six methylene units exhibits a nematic phase. The copolymerization with acrylic acid induced semicrystallinity

describe a series of acrylate and methacrylate pushpull side-chain azobenzene polymers with spacers as short as three methylene units that exhibit smectic mesophases.<sup>11</sup> In their system, a cyano group is used as an electron acceptor and is responsible for an interaction-stabilized mesophase. The clearing temperature of the analogous methacrylate polymers increases initially with a spacer length varying from three to five methylene units and is followed by a decrease for longer spacers.

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to all three copolymers, stressing the role of dipolar interactions in the formation of mesophases in azobenzene LC polymers.

Similar homo- and copolymers functionalized with azobenzene side chain moieties have been synthesized by Robello.<sup>17</sup> In his system, the six methylene units spacer is connected to the mesogen by a methyl amino group. This resulted in the formation of a smectic phase instead of a nematic phase even though the methyl amino group offers more steric hindrance than the oxygen atom. The nitro group appears to interact more favorably with amino groups than the oxygen atom in these instances. The dipolar interactions may be more favorable than steric interactions in developing mesophases.

In general, methacrylate azobenzene polymers containing push-pull substituents typically form smectic A phases.<sup>11,12,18</sup> Methacrylate amino-azobenzene polymers with short end tails are often nematic,<sup>11,19-21</sup> while they form smectic phase for longer tails.<sup>12,22</sup>

As reported in many previous studies by our group and collaborators, the characterization of optical and spectroscopic studies of homopolymers, like poly{4'-{-(2-(methacryloyloxy)ethyl)ethylamino}-4-nitroazobenzene} (pDR1M), and associated copolymers have led to a versatile material that presents only an amorphous phase. Unlike the polymer synthesized by Robello, the side chains of pDR1M are attached to the spacer by an ethyl amino group rather than a methyl amino, the former of which inhibits the mesophase formation, most likely due to steric hindrance.

In an effort to study the effect of spacer length on LC azobenzene polymers properties, we report here the synthesis and physical characterization of a series of side-chain liquid crystalline polymers. The poly{4'-{(X-methacryloyloxyalkylene)methylamino}-4-nitroazobenzene} liquid crystalline polymers (p(XMAN), where X is the number of methylene groups in the spacer and varies from 2 to 12) are prepared and stabilized in their glassy (amorphous) state or in their liquid crystalline mesophase. We emphasize in particular the structure property relationships as measured by differential scanning calorimetry and X-ray diffraction and the optically induced birefringence for the various observed phases.

### **Experimental Section**

**General Procedures.** The general structure of p*X*MAN is shown in Chart 1. All the chemicals were purchased from commercial suppliers and used without further purification unless otherwise noted. Standard distillation procedures were

applied. The structures of all the precursors and final products were confirmed by solution <sup>1</sup>H NMR spectroscopy. All <sup>1</sup>H NMR spectra were taken in CDCl<sub>3</sub> at 200 MHz and chemical shifts are reported in ppm and calibrated against TMS. The synthesis of all polymers was similar, and only the steps toward making p2MAN are detailed.

*N*-(2-Hydroxyethyl-*N*-methylaniline). 2-Chloroethanol (11.5 g, 144 mmol) was mixed with freshly distilled *N*-methylaniline (15.4 g, 144 mmol), KI (0.7 g, 4.30 mmol) and K<sub>2</sub>CO<sub>3</sub> (20 g, 145 mmol) in a round-bottomed flask with 75 mL butanol. The mixture was heated at reflux for 4 days under nitrogen followed by cooling and filtration of salts suspended in the reaction mixture. The *N*-(2-hydroxyethyl-*N*-methylaniline) oil was purified by distillation under reduced pressure (*T* = 130°C). The *X*-hydroxyalkyl-*N*-methylaniline family of oils can also be purified by silica gel chromatography with 5% ethyl acetate in toluene by volume. Yield: 12.7%. <sup>1</sup>H NMR: *δ* = 1.78 (s, 1H), 2.93 (s, 3H), 3.43 (t, 2H), 3.78 (t, 2H), 6.77 (m, 3H), 7.21 (m, 2H).

**4'**-{**(2-Hydroxyethyl)methylamino**}-**4**-**nitroazobenzene**. *p*-Nitrobenzenediazonium tetrafluoroborate (5.01 g, 21.1 mmol) was suspended in 50 mL of 50% aqueous acetic acid with stirring at room temperature. *N*-(2-Hydroxyethyl)-*N*-methylaniline (3 g, 20.1 mmol) was dissolved in 10 mL of 50% aqueous acetic acid and added dropwise to the stirring suspension. After 4 h of stirring, the solution was neutralized with 30% NH<sub>4</sub>OH solution at room temperature. The dark red crystals were collected by vacuum filtration. The product was purified by chromatography column in a 50% EtOAc/hexane elution mixture followed by recrystallization in CHCl<sub>3</sub>. Yield: 63%. Mp: 175–177 °C. <sup>1</sup>H NMR:  $\delta$  = 1.58 (s, 1H), 3.14 (s, 3H), 3.66 (t, 2H), 3.89 (t, 2H), 6.84 (d, 2H), 7.91 (dd, 4H), 8.33 (d, 2H).

4'-{(2-Methacryloyloxyethyl)methylamino}-4-nitroazobenzene. In a three-necked flask, freshly distilled 4'-{(2hydroxyethyl)methylamino}-4-nitroazobenzene (1.75 g, 5.83 mmol) was dissolved in 50 mL of freshly distilled THF. Freshly distilled triethylamine (0.85 g, 8.35 mmol) was added to the three-necked flask by syringe through the rubber septum, and methacryloyl chloride (0.73 g, 7 mmol) was dissolved in 10 mL of freshly distilled THF. The reaction mixture was cooled to 0 °C, and the methacryloyl chloride solution was added to the reaction mixture dropwise while stirring over a period of 2 h. The reaction mixture was stirred overnight. The off-white solid was vacuum filtered and the THF was removed by rotary evaporation. The remaining red solid was then purified by chromatography column using dichloromethane as the eluting solvent followed by a recrystallization in acetone. Yield: 71%. Mp: 128–130 °C. <sup>1</sup>H NMR:  $\delta = 1.94$  (s, 3H), 3.18 (s, 3H), 3.83 (t, 2H), 4.43 (t, 2H), 5.60 (m, 1H), 6.08, (s, 1H), 6.85 (d, 2H), 7.99 (dd, 4H), 8.36 (d, 2H).

*N*-(*X*-Hydroxyalkyl)-*N*-methylaniline. *N*-(3-Hydroxypropyl)-*N*-methylaniline. Yield: 55%. <sup>1</sup>H NMR:  $\delta = 1.78$  (m, 2H), 2.87 (s, 3H), 3.67 (t, 2H), 3.89 (t, 2H), 6.70 (m, 3H), 7.18 (m, 2H).

**N-(4-Hydroxybutyl)**-**N-methylaniline.** Yield: 28%. <sup>1</sup>H NMR:  $\delta = 1.58$  (m, 4H), 2.86 (s, 3H), 3.27 (t, 2H), 3.60 (t, 2H), 6.67 (m, 3H), 7.17 (m, 2H).

**N-(5-Hydroxypentyl)-N-methylaniline**, Yield: 81%. <sup>1</sup>H NMR:  $\delta = 1.35$  (m, 2H), 1.59 (m, 4H), 2.85 (s, 3H), 3.30 (t, 2H), 3.62 (q, 2H), 6.63 (m, 3H), 7.20 (m, 2H).

**N-(6-Hydroxyhexyl)-N-methylaniline**, Yield: 65%. <sup>1</sup>H NMR:  $\delta = 1.27$  (m, 4H), 1.47 (m, 4H), 1.73 (s, 1H), 2.82 (s, 3H), 3.21 (t, 2H), 3.51 (t, 2H), 6.58 (m, 3H), 7.14 (m, 2H).

**N-(7-Hydroxyheptyl)-N-methylaniline**, Yield: 50%. <sup>1</sup>H NMR:  $\delta = 1.34$  (m, 6H), 1.55 (m, 4H), 2.90 (s, 3H), 3.58 (t, 2H), 3.62 (t, 2H), 6.63 (m, 3H), 7.17 (m, 2H).

**N-(8-Hydroxyoctyl)-N-methylaniline.** Yield: 65%. <sup>1</sup>H NMR:  $\delta = 1.26-1.55$  (m, 12H), 2.85 (s, 3H), 3.23 (t, 2H), 3.57 (t, 2H), 6.70 (m, 3H), 7.15 (m, 2H).

**N-(9-Hydroxynonyl)**-**N-methylaniline.** Yield: 73%. <sup>1</sup>H NMR:  $\delta = 1.33 - 1.58$  (m, 14H), 2.93 (s, 3H), 3.31 (t, 2H), 3.65 (t, 2H), 6.70 (m, 3H), 7.25 (m, 2H).

**N-(10-Hydroxydecyl)-N-methylaniline.** Yield: 82%. <sup>1</sup>H NMR:  $\delta = 1.25 - 1.50$  (m, 16H), 2.86 (s, 3H), 3.24 (t, 2H), 3.54 (t, 2H), 6.62 (m, 3H), 7.17 (m, 2H).

**N-(11-Hydroxyundecyl)**-**N-methylaniline.** Yield: 86%. <sup>1</sup>H NMR:  $\delta = 1.24-1.47$  (m, 18H), 1.86 (s, 3H), 3.24 (t, 2H), 3.57 (t, 2H), 6.62 (m, 3H), 7.17 (m, 2H).

**N-(12-Hydroxydodecyl)-N-methylaniline.** Yield: 70%. <sup>1</sup>H NMR:  $\delta = 1.22-150$  (m, 20H), 1.86 (s, 3H), 3.23 (t, 2H), 3.57 (t, 2H), 6.61 (m, 3H), 7.16 (m, 2H).

**4**'-{**(X-Hydroxyalkyl)methylamino**}-**4**-nitroazobenzene. **4**'-{**(3-Hydroxypropyl)methylamino**}-**4**-nitroazobenzene. Yield: 77%. Mp: 143–4 °C. <sup>1</sup>H NMR:  $\delta$  = 1.89 (m, 2H), 3.10 (s, 3H), 3.61 (t, 2H), 3.73 (t, 2H), 6.87 (d, 2H), 7.89 (dd, 4H), 8.29 (d, 2H).

**4'-{(4-Hydroxybutyl)methylamino}-4-nitroazobenzene.** Yield: 85%. Mp: 135–8 °C. <sup>1</sup>H NMR:  $\delta = 1.54$  (m, 4H), 3.09 (s, 3H), 3.49 (t, 2H), 3.70 (t, 2H), 6.74 (d, 2H), 7.89 (dd, 4H), 8.30 (d, 2H).

**4'**-{**(5-Hydroxypentyl)methylamino**}-**4**-nitroazobenzene. Yield: 85%. Mp: 136–9 °C. <sup>1</sup>H NMR:  $\delta = 1.23$  (m, 2H), 1.64 (m, 4H), 3.08 (s, 3H), 3.45 (t, 2H), 3.66 (t, 2H), 6.72 (d, 2H), 7.87 (q, 4H), 8.30 (d, 2H).

**4'**-{**(6-Hydroxyhexyl)methylamino**}-**4**-nitroazobenzene. Yield: 55%. Mp: 141–3 °C. <sup>1</sup>H NMR:  $\delta = 1.19-1.51$  (m, 8H), 1.64 (m, 4H), 3.04 (s, 3H), 3.40 (t, 2H), 3.60 (t, 2H), 6.68 (d, 2H), 7.85 (dd, 4H), 8.26 (d, 2H).

**4**'-{**(7-Hydroxyheptyl)methylamino**}-**4**-nitroazobenzene. Yield: 78%. Mp: 133–5. <sup>1</sup>H NMR:  $\delta$  = 1.37 (m, 6H), 1.67 (m, 4H), 3.07 (s, 3H), 3.42 (t, 2H), 4.12 (t, 2H), 6.73 (d, 2H), 7.91 (dd, 4H), 8.30 (d, 2H).

**4**'-{**(8-Hydroxyoctyl)methylamino**}-**4**-nitroazobenzene. Yield: 72%. Mp: 118–120 °C. <sup>1</sup>H NMR:  $\delta = 1.33-1.56$  (m, 12H), 3.08 (s, 3H), 3.42 (t, 2H), 3.62 (t, 2H), 6.72 (d, 2H), 7.88 (dd, 4H), 8.29 (d, 2H).

**4**'-{**(9-Hydroxynonyl)methylamino**}-**4**-nitroazobenzene. Yield: 60%. Mp: 99–102 °C. <sup>1</sup>H NMR:  $\delta$  = 1.32–1.57 (m, 14H), 3.08 (s, 3H), 3.43 (t, 2H), 3.62 (t, 2H), 6.72 (d, 2H), 7.88 (dd, 4H), 8.30 (d, 2H).

**4**'-{**(10-Hydroxydecyl)methylamino**}-**4**-nitroazobenzene. Yield: 63%. Mp 119–120 °C. <sup>1</sup>H NMR:  $\delta$  = 1.25–1.51 (m, 16H), 3.04 (s, 3H), 3.38 (t, 2H), 3.59 (t, 2H), 6.68 (d, 2H), 7.85 (dd, 4H), 8.26 (d, 2H).

**4**'-{**(11-Hydroxyundecyl)methylamino**}-**4**-nitroazobenzene. Yield: 53%. 96–8 °C. <sup>1</sup>H NMR:  $\delta = 1.24-1.54$  (m, 18H), 3.03 (s, 3H), 3.38 (t, 2H), 3.58 (t, 2H), 6.67 (d, 2H), 7.84 (dd, 4H), 8.30 (d, 2H).

**4'-{(12-Hydroxydodecyl)methylamino}-4-nitroazobenzene.** Yield: 83%. 119–122 °C. <sup>1</sup>H NMR:  $\delta$  = 1.26–1.55 (m, 20H), 3.08 (s, 3H), 3.42 (t, 2H), 3.62 (t, 2H), 6.72 (d, 2H), 7.89 (dd, 4H), 8.30 (d, 2H).

*N*-{(*X*-methacryloyloxyalkyl)methylamino}-4-nitroazobenzene. 4'-{(3-methacryloyloxypropyl)methylamino}-4-nitroazobenzene. Yield: 76%. Mp: 127−8 °C. <sup>1</sup>H NMR:  $\delta$  = 1.97 (s, 3H), 2.04 (m, 2H), 3.10 (s, 3H), 3.59 (t, 2H), 4.21 (t, 2H), 5.62 (m, 1H), 6.13, (s, 1H), 6.75 (d, 2H), 7.90 (dd, 4H), 8.30 (d, 2H).

**4'-{(4-methacryloyloxybutyl)methylamino}-4-nitroazobenzene**. Yield: 86%. Mp: 122–4 °C. <sup>1</sup>H NMR:  $\delta$  = 1.20 (m, 4H), 1.94 (s, 3H), 3.08 (s, 3H), 3.48 (t, 2H), 4.19 (t, 2H), 5.55 (m, 1H), 6.09 (s, 1H), 6.72 (d, 2H), 7.88 (dd, 4H), 8.30 (d, 2H).

**4'**-{**(5-methacryloyloxypentyl)methylamino**}-**4**-nitroazobenzene. Yield: 81%. Mp: 102–4 °C. <sup>1</sup>H NMR:  $\delta$  = 1.55 (m, 2H), 1.71 (m, 4H), 1.92 (s, 3H), 3.08 (s, 3H), 3.45 (t, 2H), 4.15 (t, 2H), 5.54 (s, 1H), 6.06 (s, 1H), 6.70 (d, 2H), 7.88 (q 4H), 8.30 (d, 2H).

**4**'-{**(6-methacryloyloxyhexyl)methylamino**}-**4**-nitroazobenzene. Yield: 79%. Mp: 106–7 °C. <sup>1</sup>H NMR:  $\delta$  = 1.40– 165 (m, 8H), 1.92 (s, 3H), 3.08 (s, 3H), 3.44 (t, 2H), 4.13 (t, 2H), 5.53 (m, 1H), 6.07 (s, 1H), 7.89 (dd, 4H), 8.29 (d, 2H).

**4'-{(7-methacryloyloxyheptyl)methylamino}-4-nitroazobenzene**. Yield: 70%. Mp: 81–2 °C. <sup>1</sup>H NMR:  $\delta$  = 1.37 (m, 6H), 1.67 (m, 4H), 1.92 (s, 3H), 3.07 (s, 3H), 3.42 (t, 2H), 4.12 (t, 2H), 5.53 (m, 1H), 6.07 (s, 1H), 6.73 (d, 2H), 7.91 (m, 4H), 8.30 (d, 2H). **4**'-{**(8-methacryloyloxyoctyl)methylamino**}-**4**-nitro**azobenzene.** Yield: 66%. Mp: 87–90 °C. <sup>1</sup>H NMR:  $\delta = 1.34-$ 1.56 (m, 12H), 1.92 (s, 3H), 3.07 (s, 3H), 3.42 (t, 2H), 4.12 (t, 2H), 5.52 (m, 1H), 6.07 (s, 1H), 6.72 (d, 2H), 7.89 (dd, 4H), 8.91 (d, 2H).

**4**'-{**(9-methacryloyloxynonyl)methylamino**}-**4**-nitro**azobenzene.** Yield: 82%. Mp: 60–3 °C. <sup>1</sup>H NMR:  $\delta = 1.31-$ 1.50 (m, 14H), 1.92 (s, 3H), 3.07 (s, 3H), 3.42 (t, 2H), 4.16 (t, 2H), 5.52 (m, 1H), 6.07 (d, 1H), 6.72 (d, 2H), 7.89 (dd, 4H), 8.29 (d, 2H).

**4**'-{**(10-methacryloyloxydecyl)methylamino**}-**4**-nitroazobenzene. Yield: 58%. Mp: 67–70 °C. <sup>1</sup>H NMR:  $\delta = 1.30$ – 1.65 (m, 16H), 1.92 (s, 3H), 3.08 (s, 3H), 3.42 (t, 2H), 4.12 (t, 2H), 5.52 (m, 1H), 6.07 (s, 1H), 6.72 (d, 2H), 7.88 (dd, 4H), 8.32 (d, 2H).

**4**'-{**(11-methacryloyloxyundecyl)methylamino**}-**4**-ni**troazobenzene.** Yield: 76%. Mp: 57–60 °C. <sup>1</sup>H NMR:  $\delta$  = 1.28–1.65 (m, 18H), 1.92 (s, 3H), 3.08 (s, 3H), 3.42 (t, 2H), 4.11 (t, 2H), 5.52 (m, 1H), 6.07 (s, 1H), 6.72 (d, 2H), 7.88 (dd, H), 8.32 (d, 2H).

**4**'-{**(12-methacryloyloxydodecyl)methylamino**}-**4**-ni**troazobenzene.** Yield: 78%. 72–74 °C. <sup>1</sup>H NMR:  $\delta = 1.26$ – 1.65 (m, 20H), 1.92 (s, 3H), 3.07 (s, 3H), 3.42 (t, 2H), 4.11 (t, 2H), 5.52 (m, 1H), 6.07 (s, 1H), 6.71 (d, 2H), 7.88 (dd, 4H), 8.32 (d, 2H).

**Polymers** were obtained by polymerization in 1,2-dichlorobenzene at 60 °C for 48 h with AIBN (5wt %). p2MAN and p3MAN were the only polymers to precipitate during the polymerization reaction. After reprecipitation from methanol only a 60% yield of p2MAN was found to be soluble in THF, dichloromethane (DCM) and dichloroethane (DCE). Most of the p3MAN monomer polymerized in 1,2-dichlorobenzene is insoluble in most solvents. The p3MAN monomer was polymerized in THF with AIBN (5 wt %); a 30% yield of soluble polymer and a 40% yield of insoluble polymer were obtained after precipitation from methanol. The other polymers were precipitated in methanol; they dissolve well in THF, DCM and DCE. All of the polymers were reprecipitated twice from THF/ methanol.

**Differential Scanning Calorimetry.** A Perkin-Elmer DSC 6 was used to determine the glass and phase transition temperatures of all polymers. The heating and cooling rates used for all polymers was 10 °C/min, and the polymers did not experience any thermal history before examination by differential scanning calorimetry (DSC).

**Gel Permeation Chromatography.** The molecular weights of all polymers were taken on a Waters Associates liquid chromatograph equipped with  $\mu$ -Styragel columns, a model 440 absorbance detector, and a R401 differential refractometer. Retention times were recorded at a flow rate of 1.0 mL/min in distilled THF and molecular weights were obtained by fitting polymer retention times to a curve obtained from five polystyrene standards.

**Polarized Optical Microscopy.** Texture analysis was carried out by polarized optical microscopy (POM) on a Nikon Eclipse E500-Pol microscope equipped with a Nikon Coolpix E995 digital camera. Samples for POM analysis where prepared by dissolving about 1-5 mg quantities of polymer solution in volumes of 0.5 mL of DCM followed by casting 2-3 droplets of solution on a microscope slide cover. The films were not homogeneous in thickness; polymer films with thickness between 1 and 5  $\mu$ m exhibited the most recognizable textures.

Polymers from p7MAN to p12MAN were heated to isotropization and then cooled to an annealing temperature right below the isotropization transition at 0.2 °C/min, which was maintained for about 24 h on an Instec HS-400 hot stage equipped with a series STC200 temperature controller. Polymers from p2MAN to p6MAN were simply annealed at  $T_{\rm g}$  + 35 °C for 24 h.

**X-ray Diffraction.** X-ray diffraction was used to confirm the nature of the LC phases and to determine the spacing of the smectic layers. A Scintag, X1 advanced diffraction system equipped with a  $\theta - \theta$  wide angle goniometer and a 80 mm<sup>2</sup> liquid nitrogen-cooled germanium detector was used for all X-ray diffraction (XRD) measurements. XRD samples were

Table 1. Physical Data of the pXMAN Series

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polymer	yield (%)	M <sub>n</sub>	dp	pd	<i>Т</i> <sub>g</sub> (°С)	T <sub>dec</sub> (°C)	$\Delta H_{\rm cryst}$ (J/mol)	$\Delta H_{\rm melt}$ (J/mol)
p2MAN	60	5000	14	1.4	110	225	NA	(1) 441, (2) 331
p3MAN	30	4400	12	1.5	80	217	684 <sup>a</sup>	NA
p4MAN	77	4400	11	1.6	85	210	1300 <sup>a</sup>	2350
p5MAN	85	3500	9	1.5	68	183	2300 <sup>a</sup>	3400
p6MAN	59	4000	10	1.4	70	185	2600 <sup>a</sup>	3000
p7MAN	89	8600	20	1.6	57		2300	3250
p8MAN	96	4600	10	1.9	45		3300	3900
p9MAN	79	3500	8	2.2	31		NA	NA
p10MAN	56	3200	7	1.3	25		NA	NA
p11MAN	54	4000	8	1.5	30		4000	8000
p12MAN	88	4800	9	1.7	25		4700	9800

 $^a$  The isotropization temperature was not reached during the first heating scans to prevent sample decomposition.

made by casting solutions (15 mg polymer in 1 mL of DCM) onto a 3  $\times$  2.5 cm<sup>2</sup> glass slide. Thick films (about 5  $\mu$ m) of p3MAN, p4MAN, p5MAN, and p6MAN were heated to 135, 140, 120, and 115 °C respectively for 2 h, cooled to room temperature, and measured by XRD. All other polymer films were heated to isotropization and cooled at about 0.5 °C/min to their texture forming temperature where they were annealed for at least 2 h followed by XRD analysis.

**Birefringence.** Birefringence was induced on thin films using a linearly polarized beam from an argon laser ( $\lambda = 488.0$  nm) with an irradiance of 70 mW/cm<sup>2</sup> and was probed in realtime at a wavelength of 674 nm during an orientation cycle (laser "on") followed by a relaxation cycle (laser "off"). For the birefringence measurements, thin films were made by dissolving 15 mg of polymer in 0.5 mL of dichloromethane followed by spin casting with a speed of 1500 rpm to obtain an absorbance of 1.0 at the maximum absorption wavelength in the visible range.<sup>9</sup> The thickness of the films was measured using profilometry and atomic force microscopy, and the values were estimated with an error of ±5%. Typical thicknesses of the films were observed to be varying from 150 to 250 nm.

## **Results and Discussion**

Thermal Characterization. Physical data of the pXMAN series are summarized in Table 1. Typical DSC scans of the second heating are shown in Figure 1a,b for the whole pXMAN series. p2MAN exhibits at least two first-order transitions as shown in Figure 1a; one small transition occurs right after the  $T_g$  (441 J/mol) followed closely by a melting transition (331 J/mol). Polymers between p3MAN and p6MAN exhibit broad clearing transitions, a trait typical of SCLCPs contain-ing short spacers.<sup>23,24</sup> All of these polymers decompose before reaching isotropization, which limits the temperature range at which they can be experimented with. As shown in Figure 1b, p7MAN and p8MAN exhibit broad clearing transitions and, surprisingly, p9MAN and p10MAN do not exhibit any first-order transitions during either heating or cooling procedures. An ordering transition is observed for p11MAN on heating, followed by a clearing transition, and p12MAN only exhibits a clearing transition.

The clearing enthalpy of p4MAN to p6MAN has been estimated by taking the area of the existing portion of the broad first ordered clearing transition in the their DSCs that occurs before these polymers decompose as shown in Figure 1a. The estimated clearing transition enthalpies allow for the comparison of all clearing and crystallization transitions as seen in Table 1. The clearing and crystallization transition enthalpies increase with the spacer length, which is representative of the increased mesogen autonomy from the polymer backbone with increasing spacer length.



**Figure 1.** Second heating differential scanning calorimetry curves for p2MAN to p6MAN (a) and for p7MAN to p12MAN (b).



**Figure 2.** Phase diagram for the p*X*MAN series.

The odd—even effect for clearing transitions is not observed for this series of polymers. The effect is typically strongest for polymers with the shortest spacers and cannot be observed here since these materials decompose before reaching their clearing temperature. The transitions observed for these polymers are summarized in the phase diagram shown in Figure 2.

**Polarized Optical Microscopy.** Freshly cast films of the pXMAN series with no heat treatment are dark between crossed polarizers, revealing a glassy state, but exhibit birefringence domains when heated above the glass transition temperature. At small annealing times



Figure 3. Polarized optical micrographs of p5MAN (a), p7MAN (b), and p9MAN (c).

 $(t \approx 15 \text{ min})$ , the birefringence appears as tiny specks of light between crossed polarizers. After the sample was annealed for a longer time (t = 6-24 h), some of the polymers form textures reminiscent of low molecular weight liquid crystals; however, some never exhibit any recognizable textures.

p2MAN shows a nonclassical texture between crossed polarizers, probably due to the reduced mobility of the side chain due to steric hindrance. Polymers from p3MAN to p6MAN exhibit very small fan textures after annealing for 24 h as shown in Figure 3a for p5MAN. p7MAN shows large and recognizable fans as shown in Figure 3b, however, p8MAN-p12MAN exhibit unidentified textures (Figure 3c). It is peculiar that p7MAN exhibits a large, readily recognizable texture whereas the textures of the other polymers are nonclassical. Such difference may be due to the higher molecular weight of p7MAN ( $\dot{M_n} = 8600$ ), when compared to the  $M_w$  of other polymers in the series ( $M_n = 3200-4800$ ). The  $M_w$ dependence of LC properties in polymers is significant at low molecular weights,<sup>24-27</sup> which might explain the lack of recognizable textures for the other pXMAN polymers.

**X-ray Diffraction.** X-ray diffraction patterns for all of the polymers are shown in Figure 4 and confirm that all of the polymers except for p2MAN are smectic. As expected, the smectic layer spacings increase with the spacer length. The smectic layer spacings are calculated from the XRD peaks using Bragg's law and the results are reported in Table 2. Although, the diffraction



**Figure 4.** X-ray diffraction patterns of all polymers in their LC state.

 
 Table 2. Peak Angles (deg) and Smectic Layer Spacings for the pXMAN Series

			_				
polymer	2θ (1)	2θ (2)	2θ (3)	dist 1 (Å)	dist 2 (Å)	dist 3 (Å)	av spacing (Å)
p2MAN							
p3MAN	3.7		11	24		24	24
p4MAN	3.7	7.3	11	24	24	24	24
p5MAN	3.3	6.8	10	26	26	27	26
p6MAN	3.2	6.4	9.7	27	28	27	27
p7MAN	3.3	6.4	9.0	26	28	28	27
p8MAN	3.2	6.1	9.0	28	29	29	29
p9MAN	2.6	5.4	8.0	34	33	33	33
p10MAN	2.6	5.2		34	34		34
p11MAN	2.3	4.7		39	37		38
p12MAN	2.3	4.6		38	39		39

pattern for p2MAN does not show any reflections, DSC shows two transitions and p2MAN is expected to be smectic at temperatures between the  $T_{\rm g}$  and 160 °C and nematic between 160 and 180 °C.

**Discussion Concerning the Characterization.** As reported for the monomer of p6MAN by Robello, the monomers of the pXMAN series were not found to exhibit any liquid crystalline properties by POM; similar results have also been reported for comparable compounds by Li.<sup>16,17</sup>

The monomers are not liquid crystalline, probably because the rodlike character of these molecules is disrupted by the methylene unit attached to the first nitrogen and by the bulky carbonyl(methyl)vinyl group at the end of the side chain; these groups disrupt the linearity of the molecules, which is not favorable for LC formation.<sup>28–31</sup> Similar compounds without these bulky groups are liquid crystalline and as confirmed by Peterov, with some structure dependence, the nitro group in two- and three-ring derivatives does not create or promote mesophase formation.<sup>32</sup> The polymeric character of these SCLCPs probably makes liquid crystallinity possible since the main chains can stabilize the mesogens in LC phases.

Robello obtains different DSC results for p6MAN than those obtained in the present study. Rather than a broad clearing transition that ends before decomposition, his material clears sharply at between about 160-175 °C, but a reasonable focal conic texture is also observed, suggesting the presence of a smectic A phase.<sup>12,33,34</sup>

The pXMAN polymer that exhibits the largest and most recognizable focal conic texture is p7MAN. The

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fans obtained in the polymers from p3MAN-p6MAN are considerably smaller and the polymers from p8MAN-p12MAN do not form recognizable textures. Another discrepancy is that p9MAN and p10MAN do not show any first-order transitions by DSC although these polymers exhibit birefringence and small angle diffraction peaks above  $T_g$ . The lack of any first-order transition in the DSC is an evidence of a slow forming LC phase.

The discrepancies can be related to the degree of polymerization of the polymers. The literature confirms that the degree of polymerization of polymers affects the mesogenic properties of SCLCPs below a degree of polymerization of about 12–40, and the dependence in this range is strong at the outset but decreases rapidly.  $^{24-27,35}$  In this case, the onset of the LC phase of the low molecular weight p6MAN is less than that of the high molecular weight p6MAN synthesized by Robello ( $M_n = 10500$ ) but its transition range is increased.

Counterintuitively, p10MAN and p9MAN take a longer time to form LC phases than their shorter spacer counterparts, and p9MAN-p12MAN form particularly dark unrecognizable textures even though their mesogens are more decoupled from the polymer backbone than p2MAN-p7MAN, which should increase their LC character.<sup>36,37</sup> Interestingly, the enthalpy of melting obtained for these polymers (Table 1) is in accordance with increased decoupling for longer spacers since the isotropization enthalpy increases with spacer length. Polymers from p4MAN-p8MAN have smectic isotropization enthalpies, between 2 and 4 kJ/mol, comparable to those of similar polymers.<sup>12,25,38</sup> However, p11MAN and p12MAN have much higher isotropization enthalpies, between (between 7.9 and 9.8 kJ/mol), than structurally similar polymers reported by Craig (3.7 and 3.9 kJ/mol)<sup>25</sup> but not higher than that expected for an SCLCP smectic A phase.<sup>23,25</sup> The polymers synthesized by Craig et al. differ from the pXMAN series by the replacement of the nitro group with a cyano group and by the replacement of the methyl(amino) group with an oxygen atom.<sup>25</sup> The high enthalpy associated with the isotropization enthalpies of p11MAN and p12MAN is indicative of decoupling of the mesogens from the polymer backbone also present in Craig's series of polymers. However, the additional enthalpy obtained for p11MAN and p12MAN may come from intermolecular interactions due to the large charge transfer from the amino group to the nitro group along the azobenzene unit.

The low molecular weight of polymers p9MAN– p12MAN reduces the backbone stabilization effect associated with these SCLCPs, possibly increasing the time required for ordering and reducing the size of the LC domains as observed by POM but does not decrease the stability of the smectic phase as shown by the isotropization enthalpies of p11MAN and p12MAN.

The smectic phase is supported by intermolecular interactions between the methylamino group and the nitro group by an interdigitation of mesogens where the smectic layer spacing is greater than the calculated length of one side group<sup>39</sup> but smaller than the sum of two side chains as seen in Figure 5. Intermolecular interactions are also confirmed by analysis of thermochromism by UV spectroscopy as discussed in a previous study.<sup>9</sup> After spin casting, most p*X*MAN polymers exhibit an asymmetric absorption. As a representative example, the annealing to the  $T_g$  (Table 3) of a freshly



**Figure 5.** Smectic layer spacings determined by X-ray diffraction compared to calculated values of a fully interdigitated side-chain configuration and noninterdigitated configuration.

 Table 3. Annealing Temperatures for UV and

 Birefringence Experiments of Polymers in the pXMAN

 Series, Performed for 20 min unless Specified Otherwise

polymer	Т <sub>g</sub> (°С)	annealing 1 (°C)	<i>T</i> <sub>g</sub> + (°C)	annealing 2 (°C)	T <sub>g</sub> + (°C)
p2MAN	110	123	13	140 (1 h)	17
p3MAN	80	95	15	140	60
p4MAN	85	95	10	140	55
p5MAN	68	85	7	125	40
p6MAN	70	90	20	120	50
p7MAN	57	80	23	110	43
p8MAN	45	45	0	95	50
p9MAN	31	room temp (24 h)	NA	45	14
p10MAN	25	room temp (24 h)	NA	50 (2 h)	25
p11MAN	30	room temp (24 h)	NA	75	45
p12MAN	25	room temp (24 h)	NA	75	50

spin-coated film of p3MAN (State A), results in a significant hypsochromic shift ( $\Delta \lambda = -19$  nm) beneath the azobenzene absorption envelope suggesting H-aggregation due to the onset of smectic ordering (state B). Heating within the isotropization range results in a bathochromic shift ( $\Delta \lambda = +10$  nm) and the film scatters light showing a cloudy aspect (state C). This suggest the presence of large aggregated domains with sizes between 300 and 700 nm and the red shift also indicates the presence of free mesogens liberated from the H aggregates.

Recent thermochromism experiments suggest that the original state A contains largely unaggregated azobenzene chromophores and state B is the onset of a smectic phase with the aggregation of side chains azobenzenes in an antiparallel arrangement. The cloudy state C is obtained after heating inside the isotropization range suggesting that it consists of many free azobenzenes but the cloudiness obtained on cooling also proves the presence of larger stable smectic domains.<sup>9</sup>

**Birefringence.** To compare the mobility of the azobenzene chromophores in their various states, we have systematically measured the photoinduced birefringence during orientation-relaxation cycles for the whole polymer series. Thin films of each state A, B, and C of the p*X*MAN series were investigated, and the results of maximum and remnant birefringence are summarized in Table 4. Annealing conditions for states B and C are reported in Table 3.

The birefringence curves and levels for selected samples of the series are shown in Figure 6A–C. For

 Table 4. Maximum Birefringence Levels for the pXMAN

 Series in the Different States A, B, and C<sup>a</sup>

	state A	state B	state C
	(0)	(0)	- <u></u>
polymer	(% remnant $\Delta n$ )	(% remnant $\Delta n$ )	(% remnant $\Delta n$ )
pDR1M	0.100 (85)		
p2MAN	0.124 (84)	0.105 (89)	0.117 (86)
p3MAN	0.175 (94)	0.177 (94)	0.215 (96)
p4MAN	0.124 (90)	0.104 (91)	0.089 (97)
p5MAN	0.115 (81)	0.128 (84)	0.127 (90)
p6MAN	0.087 (82)	0.118 (92)	0.118 (92)
p7MAN	0.079 (72)	0.100 (85)	0.102 (86)
p8MAN	0.08 (63)	0.101 (68)	0.101 (68)
p9MAN	0.076 (40)	0.087 (59)	0.040 (65)
p10MAN	0.048 (24)	0.061 (30)	0.034 (41)
p11MAN	0.019 (26)	0.067 (63)	0.038 (47)
p12MAN		0.067 (63)	0.034 (76)

 $^a$  The degree of remnant birefringence after 500 s of relaxation is given as an indication.

sake of clarity, only the birefringence curves of p3MAN, p4MAN, p6MAN, p9MAN, and p11MAN are shown in Figure 6A–C in each state A, B, and C, respectively.

As a reference, it is noteworthy that p2MAN exhibits a maximum and remnant birefringence ( $\Delta n$ = -0.124, remnant birefringence = 85%) close to that of pDR1M, an amorphous polymer with a structure very similar to p2MAN.<sup>40</sup>

As described in a previous study by Lagugné-Labarthet et al., under an irradiance of 70 mW/cm<sup>2</sup>, the birefringence observed for the pXMAN series generally decreases with increasing spacer length (Figure 6A– C).<sup>9</sup> As the glass transition temperature decreases for longer spacers, the mobility of the azobenzene chromophores is higher and thermal back relaxation of photooriented chromophores is more favorable.

Isotropization temperatures are also important when considering photoorientation. Holme et al. conclude that optical anisotropy is randomized near the isotropization temperatures and similar observations have been made by Zebger et al. who notice that anisotropy is destroyed at laser intensities comparable to those employed in this study.<sup>41,42</sup> Therefore, the induced anisotropy decreases with the spacer length and the degree of remnant anisotropy is considerably lowered (85% for p2MAN and only 26% for p11MAN as shown in Table 4).

Thin Films with No Thermal History (State A). Interestingly, it is observed that p3MAN exhibits birefringence levels that are much higher and typically more stable than the birefringence observed for other polymers in this series. This result suggests that the delocalized side chain is beneficial to optically induced anisotropy, even at high laser intensities for polymers with short spacers. At similar laser intensities, p4MAN, with a  $T_{\rm g}$  close to that of p3MAN ( $T_{\rm g} = 85$  °C) exhibits a significantly lower value of maximum birefringence during writing but shows similar values of remnant birefringence. Since two parameters, the spacer length and the  $T_{\rm g}$ , may affect the mobility of the azobenzene side-chain chromophore, it is a difficult issue to understand clearly why photoinduced anisotropy in p3MAN is enhanced. However, we suggest that the torsional energy of the aliphatic skeleton is perhaps smaller for odd spacers than for even spacers. This would facilitate the angular reorientation of the azobenzene chromophore in p3MAN and would hinder it for p2MAN and p4MAN which have similar  $T_{gs}$ . In the case of p5MAN, as the  $T_g$  (70 °C) is lower than that in p3MAN (80 °C), thermal back-relaxation might inhibit the beneficial



**Figure 6.** Optically induced birefringence for p3MAN, p4MAN, p6MAN, p9MAN, and p11MAN films in three different states: freshly prepared (Å), after moderate annealing (B), and after annealing at higher temperatures (C). The linearly polarized laser light is turned on at t = 0 for 500 s. The laser is turned off at t = 500 s for a 500 s relaxation period. ( $\lambda_{pump} = 488.0$  nm and  $I_{pump} = 70$  mW/cm<sup>2</sup>).

lower torsional energy of the pentane spacer. By probing the symmetric and asymmetric streching vibrations of the methylene units, several studies using polarized infrared spectroscopy have reported that the aliphatic side chains were aligned preferentially in the perpendicular direction with respect to the laser polarization direction.<sup>42,43</sup> In an extensive study, Kulinna et al. have demonstrated that, for long spacers (more than six methylene units in the spacer), the anisotropy of the side chains is induced by mechanical tension due to the angular reorientation of the azobenzene chromophores.<sup>43</sup> Following the same thought, we can extrapolate that, for similar thermal properties of the polymer (same  $T_{\rm g}$ s), the side chains with the lower rigidity will allow a higher degree of anisotropy of the chromophores. At this stage, linear dichroism measurements in the infrared range are necessary to decouple the role of the spacer length on the orientational behavior of the azobenzene units and determine whether an odd–even effect of the aliphatic chain is present.

The lower writing and remnant birefringence levels exhibited by p2MAN also support the importance of spacer length, indicating that the increased rigidity supplied by a shorter spacer does not overcome the lack of decoupling from the polymer backbone. In general, the maximum and remnant birefringence levels of the pXMAN series decrease with longer spacer length and lower the  $T_{g}$ s after p4MAN

After spin casting, p12MAN is already in state B, probably because of its low  $T_g$ . p9MAN-p11MAN have comparable  $T_g$ s but they can be kept in the original red state by refrigeration. Since p12MAN is spectroscopically different from other spin cast polymers in the pXMAN series it is not included in this part of the study.

**Films Annealed at Moderate Temperature (State B).** Again, p2MAN has birefringence level similar to that of pDR1M and p3MAN has the highest level of birefringence. The polymers between p4MAN and p9MAN exhibit similar maximum obtainable values of birefringence, however, remnant birefringence tends to decrease with spacer length. p10MAN-p12MAN also have similar maximum levels of birefringence with low values of remnant birefringence.

A small fall in birefringence (noticeable on p11MAN, Figure 6A) during the writing process after a short time of irradiation is assigned to homeotropic arrangement of the chromophores in a perpendicular direction with respect to the film plane. Additional measurements (not shown here) as a function of irradiance show that such decrease is not observed when using lower irradiance.

**Films Annealed at Higher Temperatures (State C).** The birefringence levels obtained for the curves of these films exhibit a trend similar to that of state B (Table 4). In this state, only p2MAN and p11MAN exhibit the small decay observed in the writing portion of the birefringence curves, due to a homeotropic orientation.

The films of p3MAN-p8MAN in these experiments present a cloudy aspect, but for p2MAN and p9MAN-p12MAN, which were annealed at temperatures near or inside the isotropization range, their films were not cloudy. The lack of scattering indicates that the domain sizes formed in these polymers are smaller than the domains formed in p3MAN-p8MAN.

It is also observed that the rate at which birefringence is induced decreases significantly in these polymer films compared to those in states A or B. In these states, p3MAN reaches 97% of its maximum birefringence in the first 20 s of the experiment; conversely, even after 800 s of writing on the state C sample, the maximum birefringence level is still not reached. Comparatively, a film of p7MAN in its state B reaches 99% of its maximum obtainable birefringence in the first 50 s whereas in its smectic state p7MAN reaches only 90% of its maximum birefringence for the same irradiation time. These results suggest that the presence of domains hamper isomerization and angular reorientation of the mesogens, probably by limiting the mobility of the azobenzene groups as already shown.  $^{44-46}$ 

#### Conclusions

A series of azo-containing side-chain methacrylate polymers with variable spacer lengths was synthesized. p2MAN, the polymer with the shortest spacer exhibits both a nematic phase and smectic mesophase and all other polymers are smectic. As expected, the clearing transition temperature of the polymers generally decreases with spacer length, and the polymers with shorter spacers have broader first-order transitions temperatures.

The smectic phase is interdigitated as confirmed by X-ray diffraction and is observed through molecular interactions with temperature-dependent UV spectroscopy.

With a pump irradiation of 70 mW/cm<sup>2</sup>, the maximum induced birefringence of the polymers decreases with increasing spacer length due to the lower glass transition temperature. p3MAN exhibits the largest birefringence whatever the considered state, amorphous or smectic, due to an increased mobility of the mesogenic units. The origin of unexpected high level of birefringence is not clear but might be due to a lowered rigidity of the spacer and a high  $T_g$  that enhances and stabilizes the photoinduced anisotropy. Liquid crystalline polymers with longer spacers have lower  $T_g$ s that favor the thermal back relaxation at the employed irradiance. This results in a lower degree of photoinduced anisotropy and lower long-term stability.

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