

# Azopyridine Side Chain Polymers: An Efficient Way To Prepare Photoactive Liquid Crystalline Materials through Self-Assembly

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A new strategy for the preparation of azo-containing liquid crystalline polymers is presented. A polymethacrylate bearing an azopyridine group in the side chain was synthesized for the first time. The amorphous azopyridine polymer can easily be converted into liquid crystalline polymers through self-assembly with a series of commercially available, aliphatic and aromatic carboxylic acids including the acetic acid. The measurement of photoinduced birefringence reveals that these complexes may have very different behaviors. The study thus shows that azopyridine side chain polymers combine the photoactivity of azobenzene polymers with the capability of self-assembly promoted by the pyridyl group, which offers a new and robust approach toward the preparation and exploitation of photoactive liquid crystalline materials.

## Introduction

There is a growing interest in azobenzene-containing polymers because of their potential utilities in holographic storage and other optical and photonic applications.<sup>1</sup> Liquid crystalline polymers (LCPs) with an azobenzene group in the side chain are among the most interesting materials due to the large photoinduced anisotropy and the photochemical phase transition.<sup>1,2</sup> In an effort to explore novel azo-polymers, we have designed and synthesized, to the best of our knowledge, the first polymethacrylate bearing the azopyridine chromophore in the side chain. As compared to azobenzene polymers, azopyridine polymers have the advantage of possessing both the photoactivity related to the azo unit and the capability of self-assembly through the pyridyl group. As will be shown in this paper, azopyridine side chain polymers display surprisingly strong tendency toward self-assembly, which offers a new and efficient way to make photoactive liquid crystal (LC) materials.

Using intermolecular hydrogen bonding to make self-assembled LCs and LCPs is a well-established strategy.<sup>3,4</sup> Among the H-bond donors and acceptors, the pair of a carboxylic acid with a pyridyl group is the favorite choice in many studies. In the case of LCPs, Kato and

co-workers, in their pioneering work,<sup>4</sup> prepared polymers with a benzoic acid group in the side chain to interact with compounds containing a pyridyl group. Other works<sup>3e</sup> employed the reversed approach, using poly(vinylpyridine) (not azopyridine) to interact with compounds functionalized with a carboxylic acid. A photoactive LCP was also prepared by complexing a poly(4-vinyl-*co*-styrene) with an acid-functionalized azobenzene compound.<sup>5</sup> In most studies, the guest compound used to interact with the host polymer needs to be synthesized, and probably in all cases, the two parts (the polymer and the low molar mass compound) contain at least one aromatic unit. However, the use of azopyridine was only reported in a few works for self-assembling low molar mass LCs,<sup>6</sup> while no azopyridine polymers have been used for self-assembling LCPs. An epoxy-based polymer containing an azopyridine group was among a series of azobenzene polymers investigated for the recording of surface relief gratings.<sup>7</sup>

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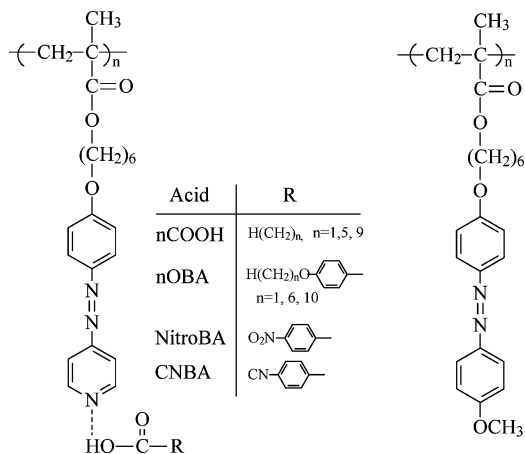
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**Figure 1.** Chemical structures of the amorphous azopyridine polymer and a liquid crystalline azobenzene polymer counterpart. The carboxylic acids used to complex with the azopyridine polymer are also shown.

The azopyridine side chain polymer we synthesized, denoted as PAzPy hereafter, has the chemical structure shown in Figure 1. The idea behind the choice of the structure is as follows. The structure should be close to that of a liquid crystalline azobenzene polymer counterpart, such as the one also shown in Figure 1. Since PAzPy has no terminal group, which is generally required for the formation of liquid crystalline phases,<sup>8</sup> it was expected to be amorphous yet very close to displaying the liquid crystallinity because what was lacked may only be a terminal group on the azopyridine chromophore. Adding such a terminal group could be accomplished through H-bonding with a carboxylic acid. As shown in the paper, this was found to be indeed the case. The azopyridine polymethacrylate is amorphous but can easily be converted into a LCP by complexing it with a large amount of commercially available aromatic and aliphatic carboxylic acids, including the acetic acid. The various acids, as well as their acronyms, used to self-assemble with PAzPy are also shown in Figure 1.

## Experimental Section

**1. Synthesis of the Azopyridine Polymer.** THF was refluxed over sodium and distilled; triethylamine was refluxed with potassium hydroxide and distilled.  $\alpha,\alpha'$ -Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol and stored at low temperature; 4-(decyloxy)benzoic acid was prepared according to a method in the literature.<sup>9</sup> The other chemicals were used without further purification. The route to the synthesis of PAzPy is depicted in Figure 2, with more synthetic details given below.

**4-(4-Hydroxyphenylazo)pyridine (1).** Phenol (5.0 g, 53 mmol) and sodium nitrate (4.0 g, 58 mmol) were dissolved in a 10% (w/w) NaOH aqueous solution (20 mL), which was added dropwise to a solution of 4-aminopyridine (6.0 g, 64 mmol) dissolved in a 7.3 N HCl solution (45 mL) at 0 °C. The reaction mixture was adjusted to pH = 6–7 by addition of a 10% (w/w) NaOH aqueous solution. An orange precipitate was collected by filtration, washed with water, and dried. Recrystallization from methanol and acetone gave 4 g of product. Yield: 40%. mp: 265 °C. <sup>1</sup>H NMR ( $\delta$ , THF-*d*<sub>8</sub>): 6.96 (d, 2H), 7.62 (d, 2H), 7.90 (d, H), 8.68 (d, 2H), 9.51 (s, 1H).

**4-(4-(6-Hydroxyhexyloxy)phenylazo)pyridine (2).** 4-(4-Hydroxyphenylazo)pyridine (4 g, 20 mmol), K<sub>2</sub>CO<sub>3</sub> (5.5 g, 40 mmol), and butanone (20 mL) were added in a flask and heated. A solution of 6-chloro-1-hexanol (3 g, 22 mmol) in butanol (2 mL) was then added dropwise and the reaction mixture was refluxed. The reaction was monitored by TLC. The product was purified by silica gel column chromatography with ethyl acetate as eluent; 2.8 g of the pure product was obtained as an orange powder. Yield: 44%. Mp: 125 °C. <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>): 1.4–1.55 (m, 4H), 1.55–1.7 (m, 2H), 1.85 (m, 2H), 3.68 (t, 2H), 4.06 (t, 2H), 7.02 (d, 2H), 7.68 (d, 2H), 7.96 (d, H), 8.8 (d, 2H).

**6-[4-(4-Pyridyazo)phenoxy]hexyl Methacrylates (3).** 4-(4-(6-Hydroxyhexyloxy)phenylazo)pyridine (3 g, 10 mmol) was dissolved in 50 mL of dry THF. Triethylamine (1.55 mL, 11 mmol) was added and a solution of methacryloyl chloride (1 mL, 11 mmol) in 10 mL of THF was then added dropwise at room temperature. The reaction mixture was stirred at room temperature overnight (about 14 h). Afterward, the mixture was poured into 400 mL of water and extracted with chloroform. The chloroform solution was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated. The residue was dissolved in ethyl acetate and separated by silica gel column chromatograph with ethyl acetate as eluent. The collected product was washed with hexane and dried, yielding 1.5 g of orange powder. Mp: 80 °C. <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>): 1.4–1.62 (m, 4H), 1.62–1.78 (m, 2H), 1.78–1.9 (m, 2H), 1.94 (s, 3H), 4.06 (t, 2H), 4.17 (t, 2H), 5.55 (s, 1H), 6.1 (s, 1H), 7.02 (d, 2H), 7.68 (d, 2H), 7.95 (d, H), 8.8 (d, 2H).

**Azopyridine Polymer (PAzPy).** In a 10 mL Schlenk flask, 6-[4-(4-pyridyazo)phenoxy]hexylmethacrylate (920 mg, 2.5 mmol),  $\alpha,\alpha'$ -azobis(isobutyronitrile) (40 mg, 0.025 mmol), and 2 mL of THF were charged. After three freeze–thaw cycles, the flask was sealed in a vacuum, placed in an oil bath preheated to 55 °C, and stirred overnight (14 h). The oil residue obtained after removing the solvent was dissolved in chloroform and precipitated in ether. The purification was repeated three times, and the collected polymer was dried in a vacuum oven. About 600 mg of the polymer (red solid) was obtained. <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>): 0.7–1.2 (m, 3H), 1.4 (m, 4H), 1.6 (b, 2H), 1.7 (b, 2H), 3.9 (t, 4H), 6.88 (d, 2H), 7.58 (d, 2H), 7.85 (d, H), 8.7 (d, 2H).

**2. Preparation of the Azopyridine Polymer/Acid Complexes.** To prepare a complex, PAzPy and a carboxylic acid with equimolar amounts of the pyridyl and acid groups were dissolved in THF to obtain a clear solution. Most of the solvent was first evaporated slowly at room temperature under atmospheric pressure. The remainder of the solution was then dried in a vacuum oven at 40 °C for about 10 h.

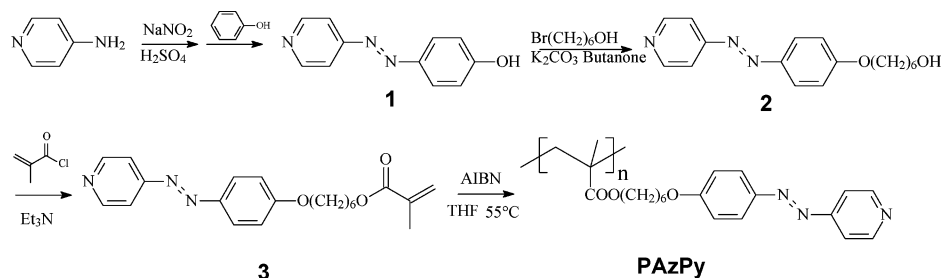
**3. Characterizations.** <sup>1</sup>H NMR spectra were recorded on a Bruker AC300 spectrometer (300 MHz). The molecular weight and polydispersity were measured on a Waters gel permeation chromatography (GPC) system equipped with a refractive index and a photodiode array detector, using THF as the eluent (elution rate: 0.5 mL/min) and polystyrene standards. The glass and phase transition temperatures as well as the phase transition enthalpies were measured on a Perkin-Elmer DSC-7 differential scanning calorimeter, using indium as the calibration standard and a heating or cooling rate of 10 °C/min. The glass transition temperature *T*<sub>g</sub> was determined as the midpoint of the step change in the heat capacity, while the phase transition temperatures were measured from the maximum of the endothermic peak. Textures of the samples were observed by using a Leitz DMR-P polarizing microscope equipped with a hot stage (Instec) and a digital camera (Leica DC-300). The X-ray diffraction measurements were conducted on a Bruker diffractometer with a two-dimensional position-sensitive wire-grid detector (Bruker AXS). UV–vis spectra were recorded with a HP 8452A spectrophotometer.

For the photoinduced birefringence measurements, an optical setup similar to that described elsewhere<sup>10</sup> was utilized. A

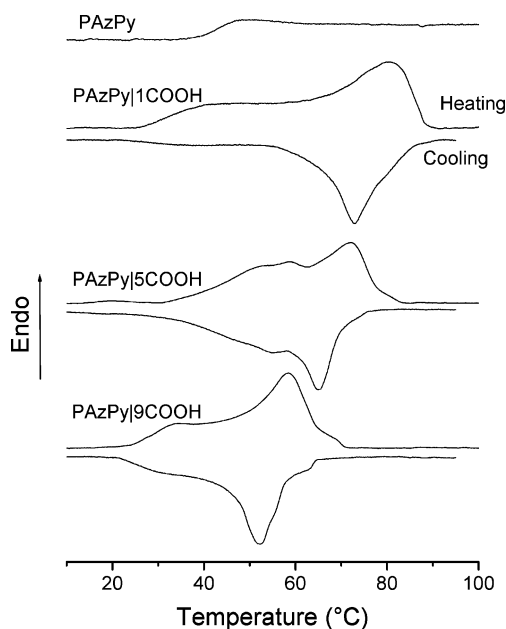
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**Figure 2.** Synthetic scheme for the azopyridine-containing monomer and polymer.



**Figure 3.** DSC heating and cooling curves (second scan) for PAzPy and its complexes with three aliphatic carboxylic acids.

Krypton UV laser ( $\lambda = 350$  nm,  $25$  mW/cm<sup>2</sup>) was used as the excitation beam, while a He–Ne laser ( $\lambda = 633$  nm,  $4$  mW) was used as the probe light. The thin film sample ( $\sim 5$   $\mu$ m thick) was placed between two crossed polarizers, to which the polarization of the excitation beam was set to  $45^\circ$ . A photodiode detector positioned behind the crossed polarizers was used to monitor the transmission of the probe light. Any anisotropy of the film arising from the photoisomerization of the azopyridine chromophore when illuminated with the excitation UV laser would result in changes in transmission of the probe light, which could be measured and used to calculate the photoinduced birefringence. For the observation of the photoisomerization, a Novacure curing system was used as the irradiation source. With an UV interference filter (10 nm bandwidth, Oriel), irradiation at  $\lambda = 360$  nm was produced with an intensity of about  $5$  mW/cm<sup>2</sup>.

## Results and Discussion

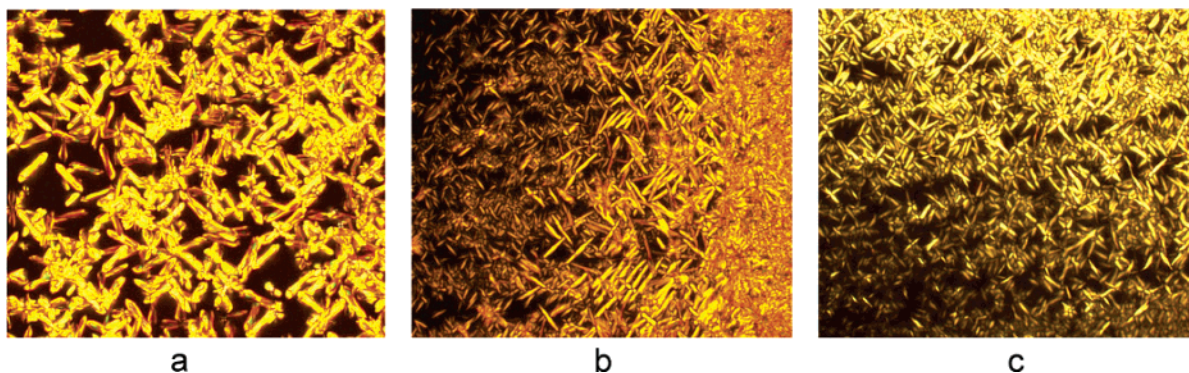
**1. Self-assembly Behaviors.** PAzPy is totally amorphous displaying only a glass transition temperature  $T_g$  at about  $40$   $^\circ$ C on DSC heating scan (Figure 3), in contrast with the azobenzene polymer counterpart (Figure 1) that has a nematic and a smectic phase above  $T_g$ .<sup>1c</sup> The GPC measurement of the average molecular weight and polydispersity yielded  $M_n = 3800$  g mol<sup>-1</sup> and  $M_w/M_n = 1.3$ . However, it should be noted that this value of  $M_n$  might be well below the actual molecular weight, which is caused by the interaction of pyridine side chain polymers with the PS gel in the GPC

column.<sup>11</sup> Mixing PAzPy with the three aliphatic carboxylic acids, acetic (1COOH), hexanoic (5COOH) and decanoic acid (9COOH), results in, in all cases, the formation of a LC phase for the polymer. Figure 3 shows the DSC heating and cooling curves (second scans) for the complexes. They all display a LC phase melting endotherm on heating and a LC phase formation exotherm on cooling from the isotropic phase. The thermal stability of the LC phase apparently decreases with increasing the length of the aliphatic chain on the acid. Of the three acids, acetic acid has the lowest boiling temperature,  $117$   $^\circ$ C, which nevertheless is sufficiently higher than that of THF,  $66$   $^\circ$ C, to allow the solvent to be removed by slow evaporation. However, no prolonged heating under reduced pressure could be applied for the complex with the acetic acid in order to prevent the evaporation of the small acid. For the two larger aliphatic acids with higher boiling points ( $204$   $^\circ$ C for 5COOH and  $270$   $^\circ$ C for 9COOH), their complexes with PAzPy could be repeatedly heated and cooled without inducing changes in the phase transition behavior.

As is seen from Figure 4, when viewed on polarizing optical microscope (POM), all the three complexes between PAzPy and the aliphatic acids annealed in the LC phase for several hours develop the batonnet texture that is revealing of a smectic-A phase. This may well be the first example of LCPs self-assembled from an amorphous polymer (the host) and aliphatic compounds (the guest) (two of the aliphatic acids are liquids at room temperature).

In addition to the aliphatic acids, five benzoic acids with different end groups in the para position (Figure 1) were also used to self-assemble with both PAzPy and its monomer (1:1 ratio). The phase transition temperatures of all complexes, together with the LC-to-isotropic phase transition enthalpy of the complexes with PAzPy, are summarized in Table 1. In essence, all complexed polymers are LCP. As an example, Figure 5 shows the DSC heating curves for pure 1OBA and 6OBA as well as their complexes with PAzPy. On one hand, the behavior of the complex with 1OBA is similar to that with NitroBA and CNBA. That is, the pure acid has only a crystal phase that melts at high temperatures, while after mixing with the azopyridine polymer, the complex shows two endothermic peaks with a new LC phase. This observation alone is strong evidence for the formation of H-bonded complex, because neither the pure acid nor PAzPy is liquid crystalline. On the other hand, the behavior of the complex with 6OBA is similar to that with 10OBA. In these two cases, the pure benzoic acids

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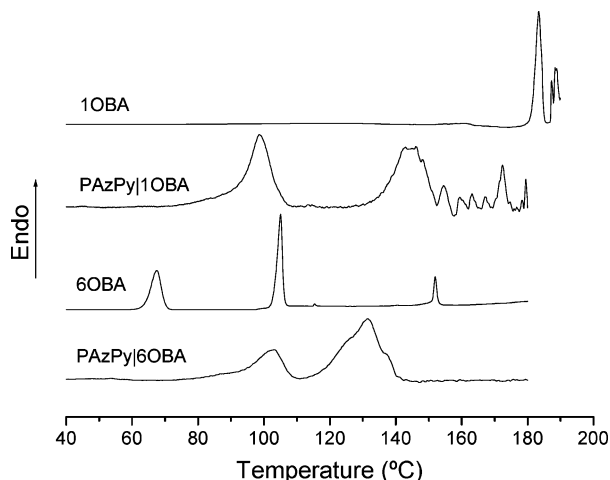


**Figure 4.** Polarizing optical micrographs for PAzPy complexed with (a) acetic acid (1COOH), annealed at 63 °C, (b) hexanoic acid (5COOH), annealed at 63 °C; and (c) decanoic acid (9COOH), annealed at 56 °C. Magnification 200 $\times$ .

**Table 1. Phase Transition Temperatures (°C)<sup>a</sup> and Enthalpy (J/g) of the Complexes**

acronym	pure acid	monomer <sup>b</sup> /acid	polymer/acid	$\Delta H_{LC-Iso}$ <sup>c</sup>
1COOH	C16I	C73I	g34S81I	8.3
5COOH	C-3I	C83I	g44S72I	7.01
9COOH	C32I	C52I	g30S58I	9.62
1OBA	C184I	C136(N101)I	C98S145I	9.53
6OBA	C <sub>1</sub> 67C <sub>2</sub> 105N153I	C100(S97)I	C103S131I	16.7
10OBA	C <sub>1</sub> 91C <sub>2</sub> 101S126N145I	C93S110I	C92S133I	17.7
NitroBA	C237I	C142I	C135S190I	16.3
CNBA	C221I	C133(N122)I	C113S185I	6.09

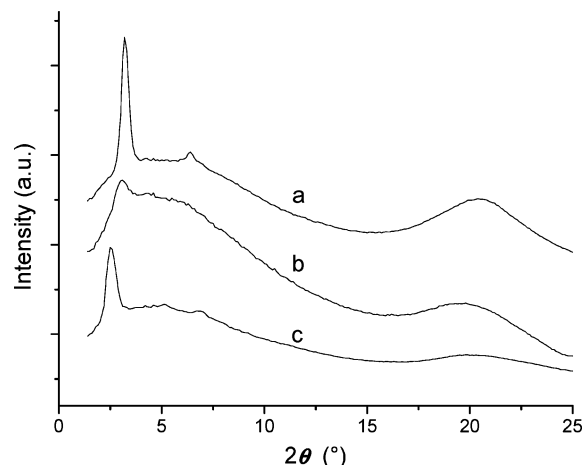
<sup>a</sup> g, glass transition; C, crystal; N, nematic; S, smectic, I, isotropic. <sup>b</sup> The azopyridine monomer has only a crystal melting temperature of 80 °C. <sup>c</sup> For the LC-to-isotropic phase transition in the complexes with PAzPy.



**Figure 5.** DSC heating curves (second scan) for pure 1OBA, pure 6OBA, and their complexes with PAzPy.

already have mesophases at some temperatures; but their complexation with PAzPy results in significant changes in phase transition temperatures and enthalpies.

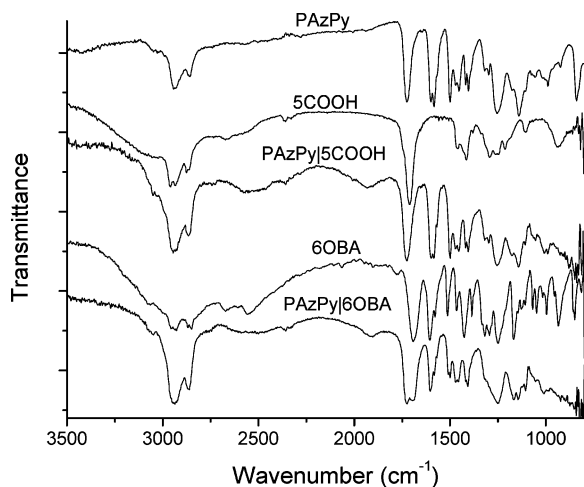
In contrast to PAzPy complexed with the aliphatic acids, for PAzPy complexed with the benzoic acids, no  $T_g$  was observed from DSC measurements and the texture in the LC phase was difficult to develop by annealing. However, the self-assembled LC phase is likely to be smectic according to the X-ray diffraction (XRD) measurements. Figure 6 shows the XRD patterns of three complexes in the LC phase, with 5COOH (60 °C), 1OBA (115 °C), and 6OBA (115 °C). In all cases, the low-angle diffraction at  $2\theta \sim 3^\circ\text{--}4^\circ$ , corresponding to the layer spacing, and the diffuse halo at  $2\theta \sim 20^\circ$ , associated with the liquidlike two-dimensional organization of the mesogenic groups within the layer, are indicative of a smectic phase. In conjunction with the



**Figure 6.** X-ray diffraction patterns of (a) PAzPy/5COOH (60 °C), (b) PAzPy/1OBA (115 °C), and (c) PAzPy/6OBA (115 °C).

batonnet texture observed on POM for PAzPy complexed with 5COOH (Figure 4), the results suggest a smectic-A phase formed in all self-assembled LCPs. The layer spacing calculated from the first-order diffraction peak is 27.8 Å for the complex with 5COOH, 29.2 Å with 1OBA, and 34.8 Å with 6OBA, which correspond approximately to the total length of the side chain (PAzPy side chain + the carboxylic acid) estimated from CS ChemOffice: 29.6 Å with 5COOH, 29.5 Å with 1OBA, and 35 Å with 6OBA. These data indicate a monolayer smectic-A phase.

In all complexes, the formation of the H-bonds between the pyridyl and acid groups is confirmed by FTIR. Some representative infrared spectra are given in Figure 7, showing the characteristic H-bonded O–H bands at about 1920 and 2500  $\text{cm}^{-1}$  for the azopyridine polymer complexed with 5COOH (aliphatic acid) and 6OBA (aromatic acid).<sup>4,12,13</sup> The disappearance of the out-of-plane OH wagging vibration band of the carbox-



**Figure 7.** Infrared spectra for PAzPy, pure 5COOH, pure 6OBA, and their complexes at room temperature.

ylic acid dimer at  $934\text{ cm}^{-1}$  also indicates the replacement of the dimers by the H-bonding between the acid and the pyridyl groups.<sup>14</sup> The infrared spectra were also recorded at various temperatures on cooling the complexes from the isotropic phase to room temperature. As can be noted from the results in Figure 8 for both PAzPy/5COOH and PAzPy/6OBA, the H-bonding between the pyridyl group and the carboxylic acid is well formed in the isotropic phase, and the extended side chains organize into the LC phase on cooling, with no noticeable changes of the  $1920$  and  $2500\text{ cm}^{-1}$  bands.

Finally, it is worth noting, from Table 1, that mixing the acids with the azopyridine monomer gave rise to very different results. LC phases were found only with four acids, including the two (6OBA and 10OBA) that already have LC phases before mixing. Furthermore, except the complex with 10OBA, the induced LC phases are monotropic and could only be observed on cooling (transition temperatures indicated in brackets). No LC phases were obtained by mixing the monomer with all the three aliphatic acids. The LC phases of the complexes with the monomer were characterized by POM, since the textures were easy to observe.

**2. Photoactivity.** In addition to the great ease of inducing self-assembled liquid crystallinity, azopyridine polymers are also photoactive due to the azopyridine unit. Figure 9 shows the UV-vis spectra of PAzPy and its complex with 6OBA in the solid state. For PAzPy, the absorption of *trans*-azopyridine around  $355\text{ nm}$  diminishes upon irradiation at  $360\text{ nm}$  ( $\sim 5\text{ mW/cm}^2$ ) as a result of the *trans*-*cis* photoisomerization. The photostationary state is attained quickly, after 5-s irradiation, but a significant portion of the *trans*-azopyridine remains in the equilibrated state (Figure 9a). Similar results were obtained for PAzPy complexed with the aliphatic acids. However, for PAzPy complexed with the benzoic acids, the photoisomerization behavior is different, as can be seen from Figure 9b for PAzPy/6OBA. In this case, the decrease in absorption of *trans*-

azopyridine is less important after 5 s of irradiation, while the photostationary state is achieved at a much longer irradiation time of about 300 s, at which only a small concentration of the *trans*-azopyridine remains. Note that the more intense absorption around  $260\text{ nm}$  for PAzPy/6OBA before irradiation comes from the contribution of the phenyl group of the benzoic acid.

The photoinduced birefringence was also measured for PAzPy and some of the complexes; the results corroborate the photoisomerization behavior as revealed by the UV-vis spectra. As shown in Figure 10, for the amorphous PAzPy, on illumination with a linearly polarized UV laser at  $\lambda = 350\text{ nm}$  ( $25\text{ mW/cm}^2$ ), the birefringence is induced quickly, peaks after about 20 s, and then stabilizes. When the excitation beam is turned off, about 60% of the photoinduced birefringence is lost due to the relaxation of the azopyridine groups. Similar to amorphous azobenzene polymers,<sup>1a</sup> the remaining photoinduced anisotropy can be erased by a circularly polarized excitation beam. The cycle of the birefringence induction, relaxation, and erasure can be repeated. However, the peak observed upon the first illumination is no longer present, which suggests the occurrence of some irreversible process during the initial irradiation. Again, similar photoinduced birefringence behavior was also observed for PAzPy complexed with the aliphatic acids (data not shown for the sake of clarity).

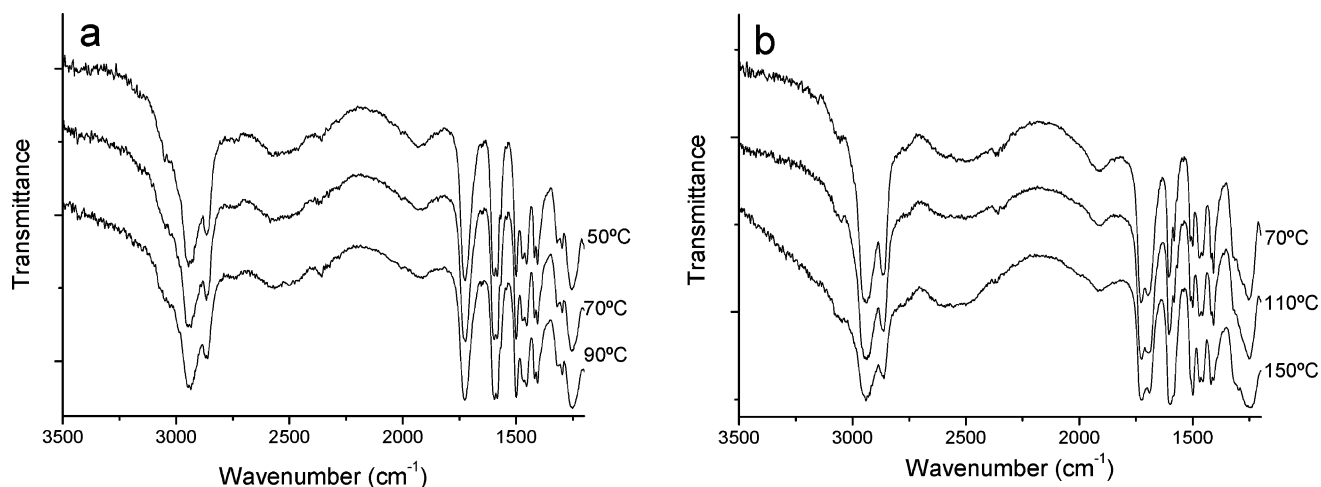
By contrast, PAzPy complexed with the benzoic acids behave differently, as is the case for PAzPy/6OBA. When the excitation beam is on, the birefringence increases slowly and continuously over the entire exposure time used (200 s). When the beam is turned off, the induced birefringence relaxes very slightly, and application of the circularly polarized beam can only partly erase the birefringence. Since the birefringence has not reached the maximum value during the first irradiation period, it continues to rise upon subsequent irradiations and is much greater than that of PAzPy. Considering the fact that the films used for the birefringence measurements were much thicker than those used for the photoisomerization observation described in Figure 9, the differences in the rate and magnitude of the photoinduced birefringence between PAzPy and the PAzPy/6OBA complex are consistent with the photoisomerization behaviors of the azopyridine group in the two samples.

The observation that PAzPy complexed with aliphatic acids displays little difference as compared to PAzPy seems to be quite surprising considering the smectic-A phase induced by the self-assembly. It is known that even for a smectic azobenzene polymer with covalently attached mesogenic side group, cooling thin films from the isotropic phase to below  $T_g$  may result in an amorphous glassy state so that it behaves like an amorphous polymer.<sup>1a</sup> We suspect the same for the complexes of PAzPy with the aliphatic acids, since no thermal annealing was carried out on the films. However, under the same conditions, PAzPy complexed with the benzoic acids shows great effects of the H-bonded compound on the photoactivity of azopyridine. Most significantly, the results in Figures 9 and 10 demonstrate that the effective self-assembly of side chain azopyridine polymers may produce new photoactive polymers with new properties to exploit.

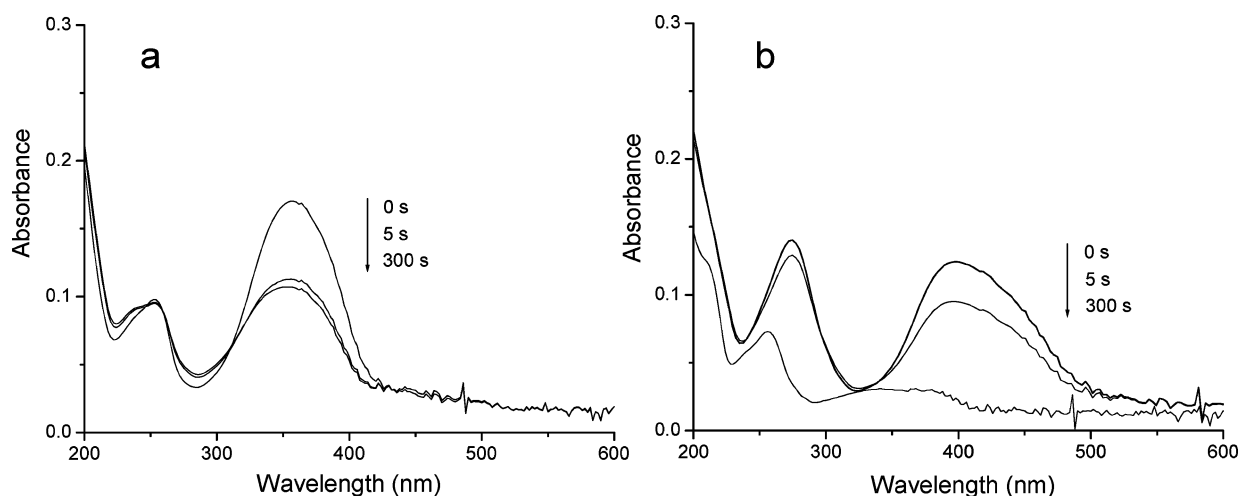
(12) Lee, J. Y.; Painter, P. C.; Coleman, M. M. *Macromolecules* **1988**, *21*, 954.

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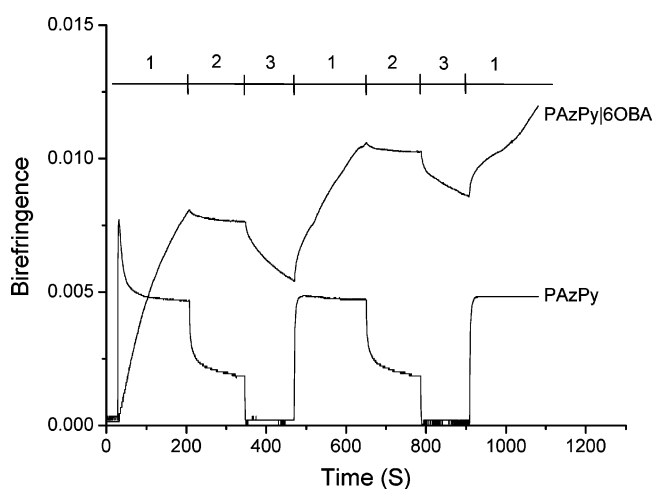
(14) Bhowmik, Pradip K.; Wang, Xiaobin; Han, Haesook. *J. Polym. Sci. Part A: Polym. Chem.* **2003**, *41*, 1282.



**Figure 8.** Infrared spectra at various temperatures for (a) PAzPy/5COOH and (b) PAzPy/6OBA.

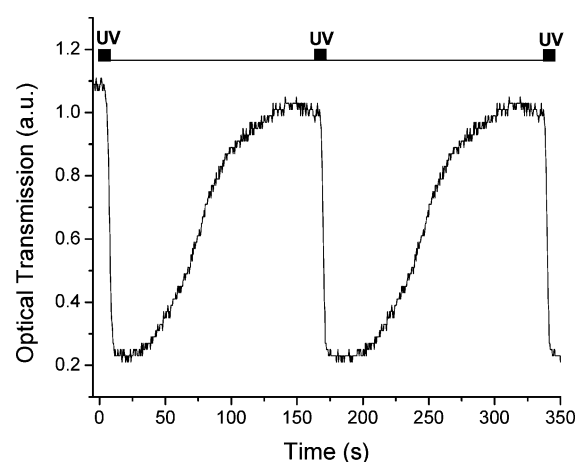


**Figure 9.** UV-vis spectra of thin films of (a) PAzPy and (b) PAzPy/6OBA before and after irradiation at  $\lambda = 360$  nm.



**Figure 10.** Photoinduced birefringence for PAzPy and PAzPy/6OBA: (1) the linearly polarized laser (350 nm, 25 mW/cm<sup>2</sup>) is on, (2) the excitation laser is turned off, and (3) the circularly polarized laser is on. See text for details.

Another feature of LCPs with azobenzene mesogens is the photoisomerization-induced LC-to-isotropic phase transition<sup>2</sup> due to the conformational change from the stretched trans isomer, which is compatible with the LC phase, to the bent cis isomer, which is incompatible with it. The photochemical phase transition was also observed for PAzPy complexed with the acids. An example



**Figure 11.** Photochemical LC-isotropic phase transition under UV irradiation for PAzPy complexed with 9COOH.

is given in Figure 11 showing changes in optical transmission of a film ( $\sim 5 \mu\text{m}$  thick) of the complex with 9COOH upon UV irradiation (centered at 365 nm,  $\sim 500$  mW/cm<sup>2</sup>). The film was placed under crossed polarizers and held at 55 °C, i.e., 3 °C below the smectic-isotropic phase transition. Upon irradiation, whose duration is indicated by the thick line, the trans-cis photoisomerization of azopyridine takes place and the smectic phase is quickly transformed into the isotropic phase, resulting in a decrease in optical transmission. When the irradiation

tion light is turned off, the thermally induced cis–trans back-isomerization occurs and the smectic phase is restored. The latter process is much slower, as revealed by the slow increase in optical transmission.

### Conclusion

A new strategy for the preparation of azo-containing liquid crystalline polymers is demonstrated, which is based on the use of side chain azopyridine polymers for the combined photoactivity and self-assembly. This unique feature distinguishes azopyridine polymers from both azobenzene polymers, which are photoactive but cannot self-assemble, and pyridine-based polymers, which can self-assemble but are not photoactive. The results reported in this paper show the effectiveness and robustness of using the self-assembly capability of azopyridine polymers to prepare photoactive liquid crystalline materials. The same amorphous methacrylate-based polymer can easily be complexed with a series of carboxylic acids through intermolecular H-bonding, regardless of whether they are aliphatic (as simple as the acetic acid) or aromatic and regardless of whether

they are crystals or liquid crystals. And the complexes may display very different photoinduced anisotropy. All the used acids, except one (10OBA), are commercially available. Considering the numerous compounds that could readily be complexed with this type of polymer, including chiral acids, phenols, and metals, the approach of using side chain azopyridine polymers offers the possibility to produce a large number of new photoactive liquid crystalline materials, with new properties to exploit, without the need for exhaustive synthetic efforts.

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