

Synthesis and Thermal Transitional Properties of Side-Chain Liquid Crystalline Polyacrylates Containing *para*-Nitroazobenzene as Mesogenic Groups

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SYNOPSIS

The synthesis and characterization of side-chain liquid crystalline (LC) polyacrylates containing *para*-nitroazobenzene (Pn) as mesogenic groups were described. Homopolymers with 3 and 4 carbon atoms in the spacers were non-LC polymers; for homopolymers with 6 carbon atoms in the spacer, nematic LC behavior was observed. Copolymers with acrylic acid as one component exhibited an S_{Ad} phase according to the WAXD results which showed the d/l of 1.4–1.54 for the copolymers with 3, 4, and 6 carbon atoms in the spacers. Considering the molecular structure as well as the WAXD results of the copolymers, the possible molecular arrangement in the smectic S_{Ad} phase was proposed, in which the smectic layers were composed of the antiparallel mesogens and the antiparallel arrangement was considered to be enhanced due to the H bond between —COOH and —NO₂. The stress-induced orientational phenomena of Pn in the LC states was also discussed. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Side-chain liquid crystalline (LC) polymers have been the subject of extensive investigation in recent years¹ because of their duality, e.g., the properties of macromolecules, such as the property of having a glass transition which allows the LC orientation frozen-in and the electrooptical property of the appropriately designed low molar mass mesogens.² Side-chain liquid crystalline polymers have attracted academic and technological interest due to their ease of processability and the novel self-orientational properties.

Most of the proposed applications for side-chain LC polymers is in the area of nonlinear optics² or information storage.³ The advantages of polymer liquid crystals (PLC) over the low molar mass liquid crystals as image storage material are their glass

transition phenomenon (T_g), good film-forming properties, and low fluidity, which are favorable for long-term stability of the stored image. Shibaev et al.⁴ and Coles and Simon⁵ reported laser-addressed PLC storage displays using heat-mode writing. Photon-mode image storage in PLC was first reported by Eich and Wendorff^{6,7} as “holographic” optical storage. In their system, photoisomerization of photochromic groups (azobenzene derivatives) incorporated into the PLCs induced “grating” in the PLC, which was a consequence of the change in the refractive index resulting from the isomerization.

Side-chain polyacrylates containing *para*-nitroazobenzene (Pn) were designed and synthesized in our laboratory.⁸ This kind of polymer may be used as information storage material because of the isomerization of its mesogens. Also, a nitro group (—NO₂) as an electron acceptor, the oxyalkyl group (—OR) as electron donor, together with phenyl rings and the azo group formed a delocalized π -electron system which possessed the property of charge transfer and a high dipole moment (4.2 D). It is easy for this kind of polymer to be oriented under a dc

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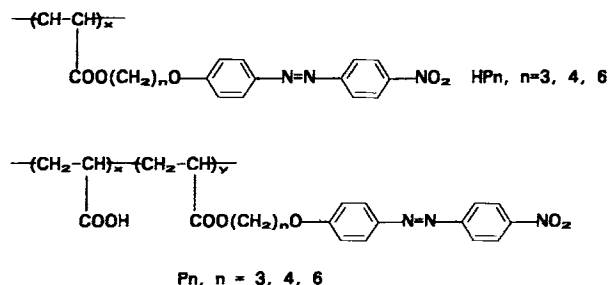


Figure 1 The molecular formula of the Pn copolymers and the HPn homopolymers.

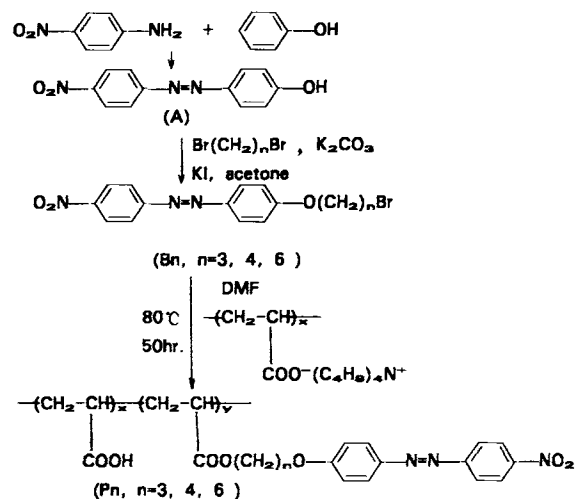
electric field to form noncentrosymmetric structures satisfying a basic requirement of second-order nonlinear optical materials. Our initial studies⁹ on films of this kind of polymer, oriented by the corona poling technique, indicated that they possessed second-harmonic generation (SHG) capability and the results showed that it is promising for this kind of polymer to be used as a waveguide material.

The aim of present work was to investigate the transitional properties of the polymers and to propose a model of the molecular arrangement in the LC state of the Pn copolymers. The molecular structure of the polymers studied is shown in Figure 1.

EXPERIMENTAL

Polymer Preparation

Polymers were synthesized through the reactions shown in Scheme I. The synthesis of the compound 4-hydroxy-4'-nitroazobenzene (A) by the coupling of a diazotized aniline with phenol was described elsewhere.¹⁰ The synthesis and spectroscopic data of monomers 1-bromo-*n*-(4-nitroazobenzene-4'-oxy)alkane (Bn) were given in a separate article.⁸ Pn copolymers were synthesized by the chemical modification of poly(acrylic acid) by the method described by Maa and Chen.¹¹ Poly(acrylic acid) (4.6×10^{-3} mol in carboxylic acid) with an average molecular weight $M_n = 3000$ was dissolved in methanol and to this solution 6 mL of methanol solution of tetrabutylammonium hydroxide (TBAH) was added. The mixture was stirred at 60°C for 24 h and was then isolated by precipitation from the methanol solution with an excess of diethyl ether. The precipitate poly(tetrabutylammonium acrylate) (PTBAA) was then dried under a vacuum for 24 h. Thus-prepared PTBAA was dissolved in DMF, to which a DMF solution of Bn was added and the mixture was reacted for 50 h at 80°C. The product



Scheme 1

was precipitated from the DMF solution with methanol. The molecular structure of the Pn copolymers was confirmed by IR spectroscopy. The coexistence of —COOH stretch and —NO₂ stretch vibration band demonstrated the proposed structure of Pn. The quantitative compositions of Pn was determined by elemental analysis performed by the analytical laboratory of Changchun Institute of Applied Chemistry, Chinese Academy of Sciences. The compositions of the Pn copolymers are listed in Table I.

CHARACTERIZATION

The proposed molecular structure of the monomers and the polymers were verified by IR spectroscopy, with a 5DX FTIR spectrometer and NMR spectroscopy with a Varian Unity 400 MHz NMR spectrometer and JEOL system FX-100 NMR spectrometer. The thermal properties of the samples were investigated by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-2C differential scanning calorimetry. The heating rate was 10 K/min. Texture observation was done on a Zeiss-Jena polarizing optical microscope equipped with a heating stage (produced by Hunjiang Optical Ma-

Table I Molar Ratios of the Two Components in the Pn Copolymers

	Sample		
	P3	P4	P6
<i>x/y</i>	30/70	41/59	62/38

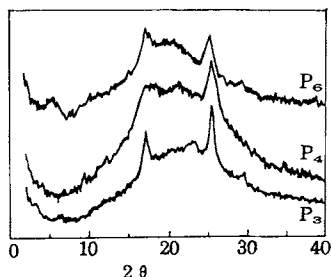


Figure 2 WAXD spectra of the Pn copolymers ($n = 3, 4, 6$) at room temperature.

chine Factory, China). The WAXD spectra were recorded on a Philips PW-1700 automatic powder diffractometer.

RESULTS AND DISCUSSION

The crystalline behavior of the Pn copolymer was studied by WAXD and DSC. The WAXD spectra of Pn at room temperature are given in Figure 2. It can be seen that Pn copolymers are all partially crystalline, and the three diffraction peaks are $d_1 = 0.52$ nm, $d_2 = 0.35$ nm, and $d_3 = 0.30$ nm, which are similar to that of the homopolymers HPn.⁸ The relative intensity of the diffraction peaks changed with the length of the spacers and the content of acrylic acid in the copolymers, but the d -spacings of the diffraction peaks did not change, which indicated that the crystalline region of Pn is formed due to the arrangement of the mesogenic groups, while spacers and the noncrystalline component only influence the crystallinity of Pn.

Because of the partial crystalline property of Pn, no glass transition or LC transition could be detected in the first heating cycle. However, the texture observation of Pn under a polarizing optical microscopy indicated that there was distinct birefringence after the melting of Pn. To obtain the clearing points of Pn, the copolymers were quenched from their LC state and were then scanned by DSC. Figure 3 shows the DSC curves of Pn quenched from the LC state. Each curve shows a second-order phase transition corresponding to the glass transition and a first-order transition corresponding to the mesogenic-isotropic transition. Compared with the corresponding HPn homopolymers, in which only HP6 with six carbon atoms in the spacer showed the nematic phase,⁸ HP3 and HP4 with 3 and 4 carbon atoms in the spacers, respectively, were non-LC polymers; Pn copolymers with 3, 4, and 6 carbon atoms in the spacer all exhibited LC behavior due to the incorporation of the acrylic acid component.

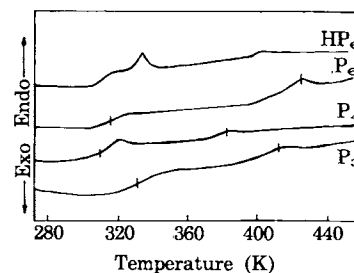


Figure 3 DSC curves of the Pn copolymers quenched at 360 K and HP6 quenched from the LC state (20 K/min).

Figure 4 shows the WAXD spectra of Pn quenched from its LC states. It can be seen that there are two sharp diffraction peaks corresponding to the first- and second-order diffraction and a diffuse diffraction peak corresponding to the third-order diffraction at low diffraction angles. A diffuse diffraction peak at about $2\theta = 20^\circ$ indicates that an intermolecular short-range order existed in the mesogenic states. WAXD results of Pn in the LC state shows that the Pn copolymers possess a typical molecular arrangement of smectic phases. Also, it can be seen that the d -spacings, d_1 , d_2 , and d_3 , increase with increasing length of the spacers, indicating that the flexible spacers participate in the molecular arrangement of the smectic layers. The relative intensity of the first- and second-order diffraction peaks increases with increasing length of the spacers. These results indicate that the hinderance of the polymer backbone with respect to the regular arrangement of the mesogens decreases and the regularity of the smectic layers increases with increasing length of the spacers.

The compositions, d -spacings, and calculated lengths of the side chains of Pn are listed in Table II, where d_1 , d_2 , and d_3 are the planar spacings of the first-, second-, and third-order diffraction peaks, and l is the calculated length of the side chains including mesogen, spacer, and the ester groups using

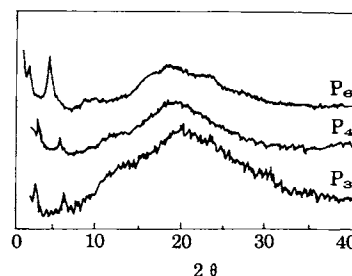


Figure 4 WAXD spectra of the Pn copolymers quenched from the LC state.

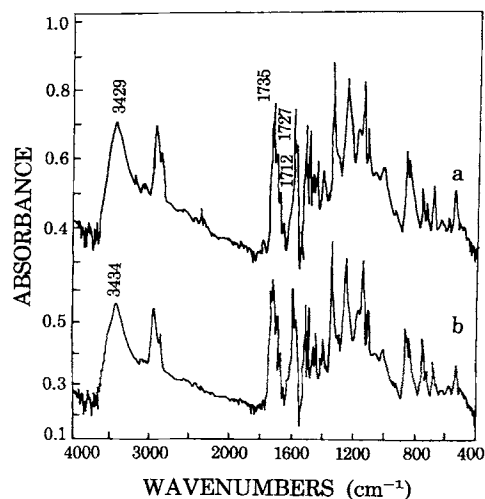
Table II *d*-Spacings and the Calculated length *l* of the Side Chains of Pn

	Sample		
	P3	P4	P6
d_1 (nm)	2.89	3.38	3.53
d_2 (nm)	1.35	1.48	1.74
d_3 (nm)	0.736	0.803	0.880
l (nm)	2.058	2.189	2.456
d_1/l	1.40	1.54	1.44

standard bond lengths and bond angles assuming that the $(\text{CH}_2)_n$ groups are in the all-*trans* conformation. It can be seen that the d/l ratios of Pn with different lengths of spacers are in the range of 1.4–1.54.

According to the definition of the smectic A ,¹² smectic A phases can be subdivided into three types based on the different ratios of d and l , which are S_{A1} , S_{Ad} , and S_{A2} . For the S_{A1} phase, the d/l ratio is approximately unity, for which case the side chains overlap fully; for the S_{A2} phase, the d -spacings are twice l , in which the side chains exhibit no interdigitation. Between the above extreme cases, the side chains are partially interdigitated, $l < d < 2l$, known as the S_{Ad} phase.

For low molar mass LC compounds with strongly polar end groups, such as NO_2 and CN , the interactions between neighboring dipoles can by no means be neglected. It is easy for these strongly polar compounds to form an antiparallel arrangement of the permanent dipoles. It is very interesting that the S_A phase of these strongly polar materials often consists of "bilayers," for which the molecules arrange themselves in an antiparallel, partially overlapping interdigitated structure with a layer spacing of about 1.4 times the extended molecular length. From inspection of the data listed in Table II, it can be concluded that the smectic S_{Ad} phase is formed for the Pn copolymers.

**Figure 5** FTIR spectra of P6 at (a) 298 K and (b) 360 K.

For comparison, the thermal transitional properties of the HPn homopolymers and Pn copolymers are listed in Table III. To our surprise, for the HPn homopolymers, which contain the same mesogenic groups as do the Pn copolymers, only the nematic phase is formed for HP6. However, S_{Ad} phases are observed for Pn with all lengths of spacers studied. On inspection of the structural difference between Pn and HPn, we considered that the antiparallel arrangement of the mesogens was enhanced due to the incorporation of an acrylic acid comonomer for the Pn copolymers. We believe that this is due to the hydrogen bond between the $-\text{COOH}$ and $-\text{NO}_2$ groups formed, which has been confirmed by an FTIR study on P6. Shown in Figure 5 are the FTIR spectra of P6 at different temperatures. The broad band at 3429 cm^{-1} was attributed to the $-\text{OH}$ stretch vibration, 1735 cm^{-1} was due to the stretch vibration of the $\text{C}=\text{O}$ of the ester groups, and 1727 and 1712 cm^{-1} were assigned to the vibration of the $\text{C}=\text{O}$ of the carboxylic groups. We know that the stretch vibration of $-\text{OH}$ centers at 3600 cm^{-1} for

Table III Thermal Properties of the HPn Homopolymers and the Pn Copolymers

	Polymer					
	HP3	HP4	HP6	P3	P4	P6
T_g	318.7	309.8	308.9	331	311	315.6
T_{KN}, T_{KS}	—	—	341.4	357	320.6	335.5
T_{KI}	324.3	340.6	—	—	—	—
T_{NI}, T_{SI}	—	—	401	412.8	383.8	426.7

K, crystalline; N, nematic; S, smectic; I, isotropic; g, glass transition; T in Kelvin.

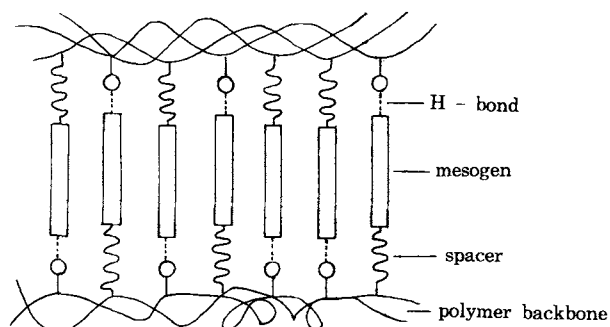


Figure 6 Schematic representation of the molecular arrangement of Pn in the S_{Ad} phase.

a free carboxylic acid. The shifting of the OH stretching vibration of P6, as well as the C=O stretch to lower frequency (for free carboxylic acid, the C=O stretch vibration is cited at 1770–1750 cm^{-1}), was due to the hydrogen bond. According to the standard IR spectrum of poly(acrylic acid),¹³ the stretching band of C=O is centered at 1700 cm^{-1} , and the OH, at 3100 cm^{-1} due to the strong hydrogen bonding between carboxylic groups in PAA. We knew that the NO_2 stretch frequency did not change much due to H bonding. According to the above analysis, we thought that some hydrogen bonding between $-\text{COOH}$ and $-\text{NO}_2$ existed in P6 either in its LC state or in its crystalline state. The regularity and the stability of the antiparallel arrangements of the mesogens in Pn are enhanced due to the hydrogen bonds, which made the LC behavior of Pn different from its corresponding HPn homopolymers. The effect of hydrogen bonding on the LC behavior has drawn attention since Jeffrey¹⁴ found that H-bonding plays an important role in LC phase formation in carbohydrates.

Kato et al.'s¹⁵ study on a polymeric LC complex through a hydrogen bond showed that the stability of the LC arrangement can be highly enhanced due to H bonding. For a H bonded LC system, after the three-dimensional-ordered crystalline lattice melts, the ordered clusters due to H bonding still exist until the temperature is high enough to destroy the H bonding, at which temperature the system enters the isotropic state. Compared with HPn, Pn with spacers of a short length ($n = 3, 4$) exhibited a smectic A phase due to H bonding; the clearing point (426.7 K) of P6 was higher than that of HP6 (401 K). The different phase behavior between HPn and Pn was attributed to the H bonding which is stronger than van der Waals forces, which was attributed to the formation of the nematic phase in HP6.

Looking at the combined results of WAXD and FTIR, we know that the smectic layers of Pn consist

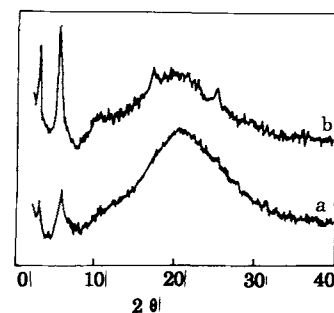


Figure 7 WAXD spectra of P6 quenched from the LC state: (a) under nonstress; (b) under stress.

of bilayers which were formed by a partially interdigitated antiparallel arrangement of the mesogens and the layers were stabilized by an H bond between $-\text{COOH}$ and $-\text{NO}_2$.

In the present study, we are not sure how the backbone is arranged; a model for the arrangement of the mesogenic groups of Pn in the smectic layers is given in Figure 6. To remove the ambiguity regarding the role of the backbone in smectic phase formation, Imrie et al.¹⁶ suggested that the relative intensities of the Bragg reflections can be used to construct the electron density profile of the layer.

Another interesting phenomenon of the Pn copolymers is that they exhibit a stress-induced orientational property in the LC state. Figure 7 is the WAXD spectra of P6 quenched from the LC state under stress and nonstress; it can be seen that the relative intensity of the diffraction peak of $d = 3.53$ nm is low without compressing on P6 in the LC state, while the relative intensity of this diffraction peak increases when a compressive force is applied on P6 in the LC state. These results indicated that the mesogenic groups of P6 can be oriented under a mechanical field. Figure 8 is the DSC curves of P6 quenched from the LC state under stress and nonstress. It can be seen that P6's prepared under different conditions show the same mesomorphic-isotropic transition temperature, but different transi-

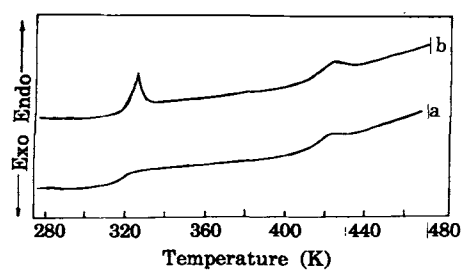


Figure 8 DSC curves of P6 quenched from the LC state: (a) under nonstress; (b) under stress.

tional enthalpic changes, indicating that the degree of orientation of the mesogenic groups changes, while the arrangement of the mesogenic groups does not. No stress-induced orientational phenomena were observed for HPn. As far as we know, there were no reports on the stress-induced orientational property of the side-chain LC polymers. Finkelmann¹⁷ reported the orientation of LC elastomers by mechanical forces. Considering the structural property of Pn, we think that the stress-induced orientational phenomena might be due to the existence of H bonding between —COOH and —NO₂ which allows the polymer chains to connect together by intermolecular forces and also makes the system act like a quasi-crosslinking network by physical forces. Some further investigations on this phenomenon of this system are undergoing.

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