Polyimines from Terephthalaldehyde and Aliphatic Diamines. 2. Studies of the Crystalline Structure by X-ray Diffraction

Haixin Yang and Almeria Natansohn*

Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6
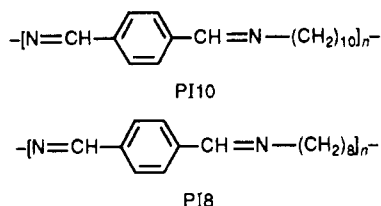
Received March 2, 1992; Revised Manuscript Received June 15, 1992

ABSTRACT: The X-ray diffraction characterization of polyimines from terephthalaldehyde and 1,10-diaminodecane (PI10) and terephthalaldehyde and 1,8-diaminooctane (PI8) is presented. PI10 is crystalline and also exhibits a liquid crystalline smectic G phase. PI8 exhibits two crystalline phases before changing to an isotropic melt. X-ray diffractometry and molecular modeling reveal that the mesogenic units in the crystalline phase have both "cis" and "trans" conformations. After the first transition on heating only the more extended trans conformation remains. The flexible spacers exist in an extended all-trans conformation in the crystalline phase; after the first transition there is also some gauche conformation. Structural units for both PI10 and PI8 above the first transition are longer than in the crystalline phase at room temperature.

Introduction

Recently, there has been a considerable amount of work investigating thermotropic liquid crystalline polymers by X-ray diffraction.[1] The crystalline structures of some small molecular imine liquid crystals have been previously investigated by X-ray diffraction.[2-4] In addition to X-ray diffraction, some spectroscopic methods were used to study the structure and conformation of liquid crystalline polymers. For example, Zerbi and his co-workers[5] used IR spectroscopy to investigate the structure of the flexible spacers in some liquid crystalline copolyesters as a function of temperature. Maravigna et al.[6] synthesized some polyimines and conducted direct mass spectroscopic studies on them. Kato et al.[7-9] and Spiess et al.[10] investigated some liquid crystalline polyesters by ^{13}C NMR. There is an extensive literature involving ^2H NMR studies.

In our previous paper,[11] the synthesis of a series of polyimines was reported. From thermodynamic data obtained by DSC, the polyimines

$$-[N\!=\!CH\!-\!\langle\bigcirc\rangle\!-\!CH\!=\!N\!-\!(CH_2)_{10}]_n-$$

PI10

$$-[N\!=\!CH\!-\!\langle\bigcirc\rangle\!-\!CH\!=\!N\!-\!(CH_2)_8]_n-$$

PI8

were tentatively assigned to be thermotropic liquid crystalline polymers and their liquid crystalline phases fairly ordered smectic phases. The conformation of the aromatic part of a series of polyimines having spacer lengths of 3-12 methylene units was investigated. PI10 and PI8 are two of the polyimines in this series. We proposed, on the basis of the analysis of the aromatic part of their solid-state ^{13}C NMR spectra, that the smectic liquid crystalline phase in PI10 forms from melting the "cis" conformation at the melting temperature (T_{k-s}) and that the smectic liquid crystalline phase changes into the isotropic phase by melting the "trans" conformation at the second transition (T_{s-i}). The cis and trans conformations are shown in Figure 1. Figure 2 presents the DSC thermograms of PI10 with the above-mentioned transitions. In this paper we present the analysis of the crystalline and liquid crystalline structures of PI10 and PI8 based on X-ray diffraction data. Molecular modeling is also used.
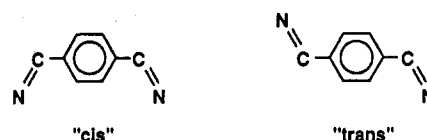

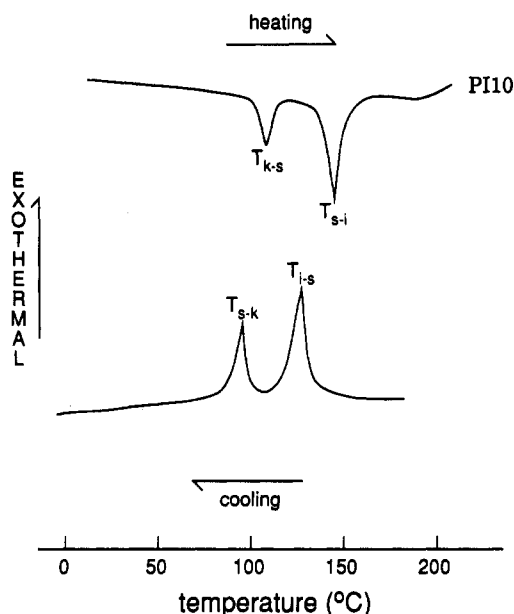**Figure 1.** Illustration of the cis and trans conformations of the aromatic part of the structural units.

Figure 2. DSC thermograms (the second heating and cooling scans) of PI10.

Experimental Section

Synthesis and characterization by NMR, DSC, and polarized microscopy of the polyimines were reported in our previous publication.[11] X-ray diffraction spectra were recorded by a CSS/STOE 2P/L two-circle diffractometer with a high-temperature attachment. The samples were contained in thin-walled glass capillaries (wall thickness 0.01 mm) of 0.5-mm diameter. The capillaries were held in a copper block. Cu radiation was used ($\lambda_\alpha = 1.5418$ Å). The temperature of the irradiated region of the capillary did not vary by more than a few tenths of a degree during each experiment. The exposure time for each spectrum was 1.5 h. Crystallinity was calculated by integration of the area under all crystalline diffraction peaks against the total area including the amorphous curve. The amounts of the cis and trans conformations were obtained by deconvolution of the NMR spectra. The program used for the deconvolution and Glinfit (version 3.0) provided by Bruker.
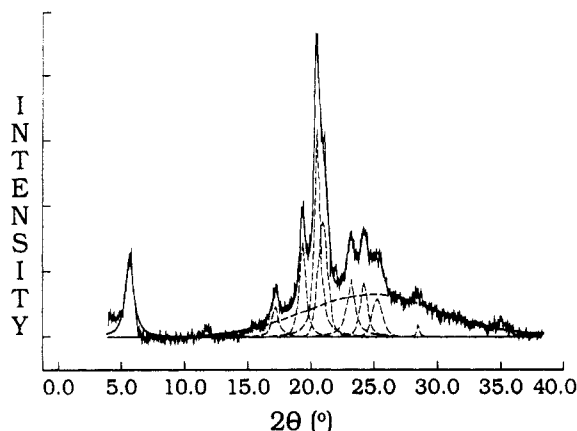
Figure 3. X-ray diffraction spectrum of PI10 at 23 °C.

Figure 4. X-ray diffraction spectrum of PI10 at 117 °C.

Molecular models of PI10 and PI8 were constructed using standard bond lengths and angles[12] except for two angles of the imine unit, C-N=C and N=C-C, which were adapted from Burgi and Dunitz,[13] as Morgan et al. did.[14] Conformations were defined by torsion angles of bonds. Modeling calculations were done using the ChemCad software (version 2.1e).

Results and Discussion

PI10. The transitions in the DSC thermograms (Figure 2) on the heating scan are crystalline to smectic liquid crystalline (T_{k-s}) and smectic liquid crystalline to isotropic (T_{s-i}). On the cooling scan, they are correspondingly indicated as T_{i-s} and T_{s-k}. In order to clarify the structure of PI10, X-ray diffraction was measured on the powder of PI10 in the crystalline phase (at room temperature) and in between the two transition temperatures. For each sample, four X-ray diffraction spectra were recorded: (1) at room temperature; (2) at a temperature which is above the first endotherm (T_{k-s}) but below the second endotherm (T_{s-i}); (3) at a temperature below the first exotherm (T_{i-s}) upon cooling from the isotropic liquid; and (4) after cooling back to room temperature. (1) and (4) gave the same X-ray diffraction spectra, and so did (2) and (3). The X-ray diffraction spectrum of PI-10 at 23 °C is shown in Figure 3. It is clearly seen from Figure 3 that PI10 is in the crystalline phase at room temperature and there is one sharp diffraction at a small diffraction angle ($2\theta = 5.71°$). This diffraction corresponds to a long distance ($D_{hkl} = 15.48$ Å) between a set of reflection planes (hkl). At larger angles, there is one very strong reflection at $2\theta = 20.47°$ and one weaker reflection at $2\theta = 20.90°$. These two reflections correspond to $D_{hkl} = 4.34$ Å and $D_{hkl} = 4.25$ Å. The X-ray diffraction spectrum obtained at 117 °C, between the T_{k-s} and T_{s-i} transitions, is shown in Figure 4. It can be seen that there are three relatively strong diffraction peaks and one weak diffraction peak.

These results are similar to those reported for some liquid crystalline polyesters[15] and small liquid crystalline imine molecules.[2] By indexing the X-ray diffraction data, a C-centered monoclinic unit cell is derived. The axis c is taken as the direction of the long molecular axis, and a and b are perpendicular to each other and parallel to the layers. Therefore, hexagonal packing in a plane perpendicular to the long molecular axis is believed to exist. Some other monoclinic and triclinic systems were considered, but the data fit was typically poorer than for the C-centered monoclinic unit cell. The C-centered monoclinic unit cell is the unit cell of the highest symmetry priority, which can be found from our data to represent the hexagonal packing. Figure 5 shows the unit cell orientation with respect to the layer. The cell parameters were computed by a least-squares fit to the experimental data. Tables I and II give
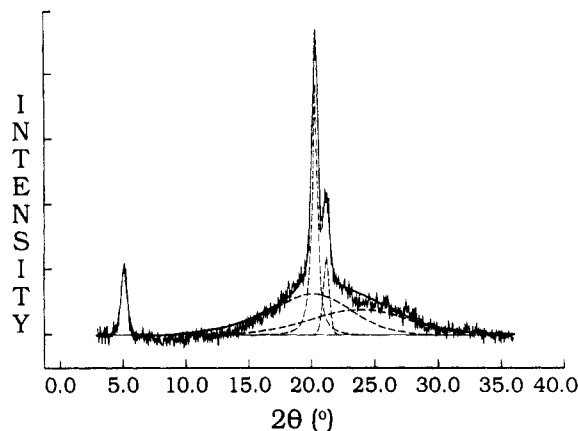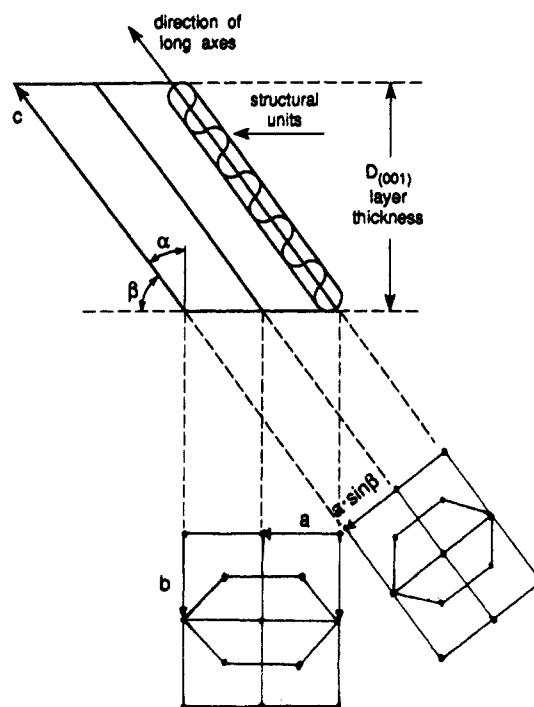

Figure 5. Arrangement of the PI10 structural units in the smectic unit cell. This figure is similar to Figure 12 of ref 15 and Figure 4 of ref 2 with slight modification.

Table I
Experimental and Calculated Crystallographic Parameters for PI10 at 23 °C[a]

intensity	exptl D_{hkl} (Å)	calcd D_{hkl} (Å)	hkl
24.91	15.48	15.48	001
9.79	5.16	5.16	003
28.62	4.59	4.59	202
63.40	4.34	4.34	201
35.32	4.25	4.25	111
17.72	3.85	3.86	200
16.72	3.69	3.69	11$\bar{1}$
11.19	3.54	3.53	205
3.56	3.15	3.10	005

[a] $a = 8.43$ Å; $b = 4.79$ Å; $c = 16.90$ Å; $\beta = 57.0°$.

the experimental and calculated values of D_{hkl} along with the experimentally obtained relative intensity of each diffraction (on an arbitrary scale) for PI10 at 23 and 117 °C. The experimental and calculated values are in good agreement.

From Table I, the reflection at the small angle is indexed as 001, and the interplane distance (D_{001}) is the distance between the layers. According to Table I, β (the angle of a and c) is 57.0°. Therefore, the long molecular axis is not

Table II
Experimental and Calculated Crystallographic Parameters for PI-10 at 117 °C[a]

intensity	exptl D_{hkl} (Å)	calcd D_{hkl} (Å)	hkl
21.41	17.07	17.07	001
77.71	4.36	4.36	201
24.01	4.11	4.11	$11\bar{1}$
2.16	3.42	3.40	205

[a] $a = 8.48$ Å; $b = 5.41$ Å; $c = 17.94$ Å; $\beta = 64.8°$.

perpendicular to the layers but tilted with an angle α ($\alpha = 90 - \beta$). Packing of the polymer repeat units of PI10 in the layers or in cut planes perpendicular to the long molecular axes (c) is not as perfect hexagonal close packing as reported for some polyesters[15] and for small imine liquid crystals.[2] If hexagonal packing were perfect on the layers, the ratio of the cell parameter a to b (a/b) would be 2 and on the cut planes $a \sin \beta/b$ would be $3^{1/2}$ (1.73). In the case of PI10 in the crystalline phase, these two ratios are 1.75 and 1.48, respectively.

At 117 °C, PI10 is in a liquid crystalline phase, and the X-ray diffraction pattern (seen in Figure 4) exhibits only four diffraction peaks. Three of them are relatively strong. On the basis of the unit cell of PI10 in the crystalline phase, these four retained reflections were indexed (see Table II). This indicates that the order between the layers is maintained in the liquid crystalline phase. The order within the layer is reduced. This phase is less ordered than the crystalline phase. D_{001} changes from 15.48 Å in the crystalline phase to 17.07 Å in the liquid crystalline phase. This shows that the distance between the layers has increased. From the cell parameters of PI10 at 23 and 117 °C in Tables I and II, it can be seen that c is longer at 117 °C (increased from 16.90 to 17.94 Å). Here c is assumed to be the length of the structural unit, on the basis of the results reported for some small imine liquid crystals[2] and liquid crystalline polyesters.[15] Therefore, the whole structural units of PI10 take on a more extended molecular conformation in the liquid crystalline phase than in the crystalline phase. Due to changes in molecular length and layer distance, the tilt angle becomes smaller. These changes are also comparable to values reported in the literature.[2,15] In spite of an increase in the cell parameters a and b, packing within the layers or the cut planes could still be assumed to be pseudohexagonal in the liquid crystalline phase. The increase in the cell parameters will be explained in terms of conformational change in the aliphatic chain later in this paper. The phase with this kind of packing in the layers plus a tilted arrangement of the molecular long axis can be assigned as a smectic G phase.[2,3,15]

The enthalpy changes obtained from DSC and microscopic observations also support the presence of a smectic G phase. The DSC thermograms of PI10 (in Figure 2) on heating show two strong transitions at 107 and 143 °C, and from the shape of the last peak, with an apparent shoulder, we assume that it also contains a weak clearing transition just above 143 °C. Corresponding enthalpy changes at 107 and 143 °C (including the clearing transition which is probably overlapped) are 8.7 and 13.1 KJ/mol. These two values are within the range of typical transition enthalpies from a crystalline phase to a S_G phase and from a S_G phase to an isotropic liquid phase.[15] A smectic G phase usually melts into an isotropic phase via a S_C, S_A, or nematic phase. The transition from any of these three phases into an isotropic one is usually weak. Therefore, the enthalpy change at the clearing transition does not contribute a lot to the 13.1 KJ/mol. $\Delta H = 13.1$ kJ/mol reflects the enthalpy change at the transition from a S_G
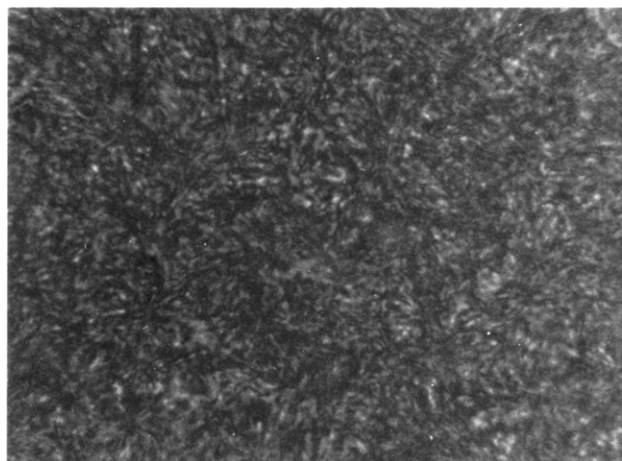

Figure 6. Texture of the S_G phase of PI10 photographed under cross-polarized light. The picture was taken on cooling, just after the liquid crystalline phase appeared.
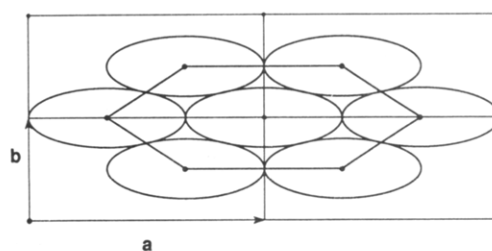

Figure 7. Illustration of the array of the structural units of PI10 in a cut plane perpendicular to the c axis.

phase to an isotropic liquid. Now the question is if on clearing there is an intermediate S_C, S_A, or nematic phase, i.e., whether the phase between 143 °C and the clearing temperature is a S_C, S_A, or nematic phase. The texture observed using polarized microscopy gives us indirect evidence that the phase is S_C. The birefringenece observed on cooling PI10 from the isotropic liquid shows a texture very similar to that of a S_C phase. It is well known[3] that a S_G phase exhibits different kinds of phase texture depending on the precursor phase from which it forms on cooling. When a S_G phase forms on cooling from a S_C phase, the S_G phase then takes the appearance of the S_C phase texture. The texture of the S_G phase of PI10 taken using a polarized microscope is shown in Figure 6.

When taking a closer look at the cell parameters of PI10, it can be seen that the cell parameters a and b become larger in the liquid crystalline phase compared with the crystalline phase. The cell parameter a increases slightly from 8.43 to 8.48 Å, and b increases from 4.79 to 5.41 Å. The dimension of the molecules in the b direction expands significantly. This can be explained as follows. The aliphatic chain is assumed to take an all-trans conformation at room temperature.[8-10] Our NMR data also support the all-trans conformation of the flexible spacer.[16] Hence, all atoms of a structural unit lie in a plane parallel to the ac plane. The cut plane of the repeat units perpendicular to the molecular long axis is elliptical in the crystalline phase. The array of these structural units with the cut plane of an elliptical cylinder shape within the layer is shown in Figure 7. In this case, it is understandable that the cell parameter a is much larger than the cell parameter b of a unit cell. In the liquid crystalline phase, which is less ordered, the aliphatic chain of a structural unit usually takes on some gauche conformation[7-10] so that the atoms of the aliphatic chain are no longer in the same plane. This has been observed in the NMR study of PI10 using variable-temperature CP-MAS NMR.[16] Therefore, the
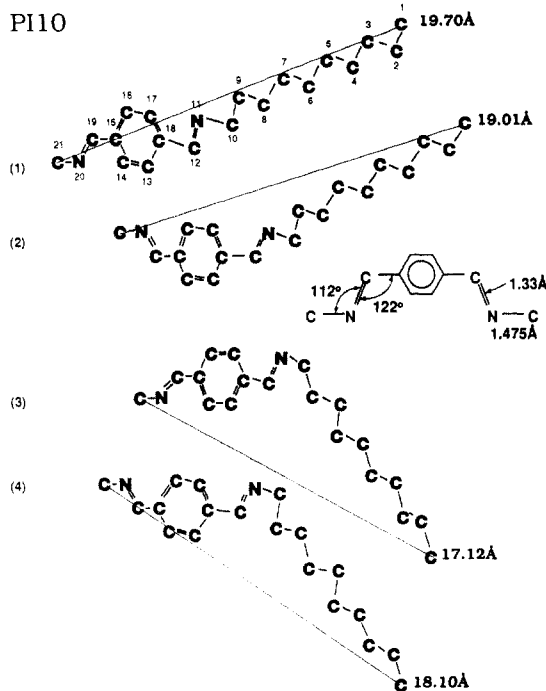
PI10

Figure 8. Model structures representing four different conformations of a structural unit of PI10.

Figure 9. Aromatic part of the deconvoluted NMR spectrum of PI10.

β-C – γ-C bond rotated by 60°

Figure 10. Model representing the gauche conformation of a structural unit of PI10 in the smectic liquid crystalline phase. The β-C–γ-C bond is rotated by 60°.

Table III
Amounts of the Cis and Trans Conformations and Crystallinities of PI10 and PI8 As Synthesized

	NMR spectra at room temp (%)			crystallinity by X-ray diffractn (%)	
	cis	trans	cis and trans	room temp	after 1st transition
PI10	23	34	57	52	36
PI8	24	40	64	60	42

cut plane of a structural unit becomes circular rather than elliptical. Thus, the cell parameter b should increase. In our case, the cell parameter b increases by 0.62 Å in the liquid crystalline phase while a increases only slightly.

To study the conformation of the structural units within the crystalline unit cell, molecular models of PI10 were constructed using ChemCad software. Model structures representing the four possible conformations of a structural unit of PI10 are illustrated in Figure 8. They are obtained from combinations of the aromatic cis and trans conformations and the two possible conformations of the =N—CH₂— bond. The distance between atom 1 (C) and atom 21 (C) for each conformation was calculated using standard bond lengths and angles[12] except for the angles N=C—C and C—N=C which were adapted from refs 13 and 14. The aliphatic chain is assumed to be in an all-trans form. That is, all methylene units are arranged in a zigzag and are in the same plane as the aromatic ring. The structural units of PI10 in the crystalline phase most probably take on the conformations represented by structures 3 and 4 in Figure 8; i.e., both the cis and trans conformations exist, as it was previously determined by NMR.[11] It was proposed[11] that a smectic liquid crystalline phase forms when the cis structures melt into the amorphous background and only the trans conformation remains pseudohexagonally packed in the smectic phase. This can be confirmed by comparing the amounts of cis and trans conformations with the crystallinity determined by X-ray diffraction. The percentages of the cis and trans conformations of PI10 as synthesized in the crystalline phase can be calculated from the NMR spectra. The aromatic part of the deconvoluted NMR spectrum of PI10 is shown in Figure 9. The amounts of cis and trans percentages are 23% and 34%, respectively. The crystallinity obtained by X-ray diffraction is 52%, comparable to the total percentage of the cis and trans which is 57%. In the liquid crystalline phase, since the part of the crystalline structure consisting of the cis conformation has melted and has been added to the amorphous part, the "crystallinity" obtained by X-ray diffraction decreases to 36%, comparable to the amount of the trans conformation, 34%. These data are summarized in Table III.
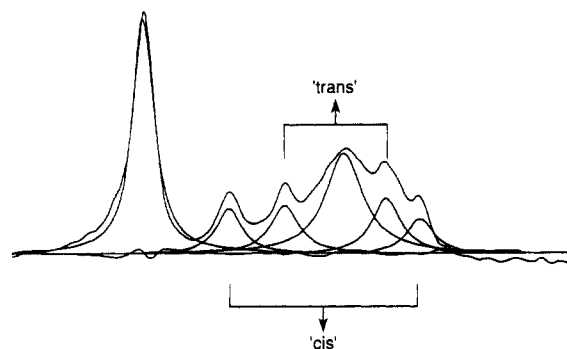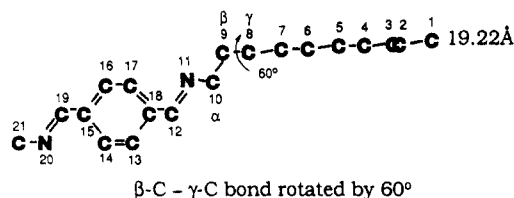
One can thus conclude that in the crystalline phase some unit cells contain structural units with the trans conformation shown in no. 3 and some other unit cells contain structural units with the cis conformation shown in no. 4 (Figure 8). Structures 3 and 4 appear more probable than structures 1 and 2 in the crystalline phase because their lengths compare well with the X-ray diffraction data. Since these two kinds of conformations are in the same phase or completely miscible, the length of a structural unit obtained by X-ray diffraction, 16.90 Å, should be comparable with the weight-averaged length of the structural units with the two different conformations. The weight-averaged length of structures 3 and 4 is 17.51 Å.

At T_{k-s} rotation of the alkyl chain starts to occur. It is possible that at T_{k-s} structure 1 is being formed and may predominate in the liquid crystalline phase. In the conformation shown in no. 1, the C(9) and C(12) are on the opposite sides of the N(11)–C(10) bond and the whole structural unit takes on the most extended conformation. The length of this most extended conformation is 19.70 Å which is greater than the length obtained by X-ray diffraction (17.94 Å). This difference can be explained as above by some trans–gauche transitions in the alkyl chain which occur at T_{k-s}. The NMR signals of the aliphatic carbons shift upfield by about 2–5 ppm above T_{k-s}.[16] These shifts are typical for gauche effects.[17] Due to the rotation of some C–C bonds, which becomes allowed above T_{k-s}, all methylene units will no longer be in a trans conformation. Some of them will take on the gauche conformation. A molecular model is shown in Figure 10 for PI10 in its smectic liquid crsytalline phase. A gauche conformation could appear anywhere along the aliphatic chain. As an example in Figure 10 only one bond is changed from trans to gauche. By changing the torsion angle, the β-C–γ-C

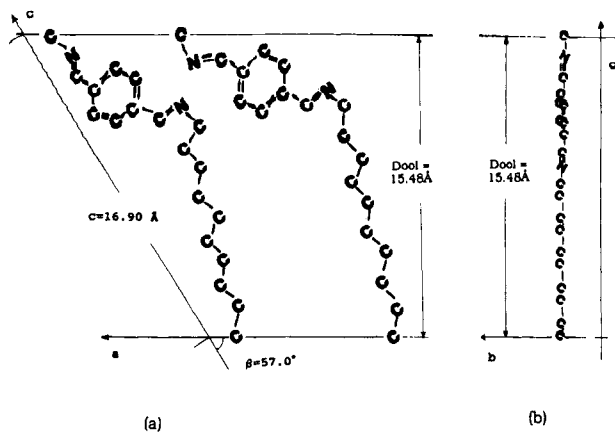(a)   (b)

Figure 11. Probable conformations of the structural units of PI10 in the crystalline phase at 23 °C: (a) the projection of the *ac* plane and (b) the projection on the *bc* plane.

bond is rotated, resulting in a 60° gauche conformation; i.e., atoms 1–8 are in one plane and atoms 9–21 are in another plane, at 60° to the former. The calculated length of the structural unit in this kind of arrangement is 19.22 Å. If all methylene groups were in the trans conformation throughout the whole aliphatic chain, the length of the structural unit would be 19.70 Å. The length obtained from X-ray diffraction is 17.94 Å. This clearly suggests that more than just one C–C bond rotates and takes the gauche conformation and thus makes the length of the structural unit even shorter, i.e., closer to the 17.94-Å value obtained by X-ray diffraction. Anyhow, the thermal motion above T_{k-s} is probably relatively high, so this model is only a static approximation. The appearance of the gauche conformation in the previously all-trans conformation of the spacer occurs at the crystalline to liquid crystalline transition.[16] The presence of the gauche conformation shortens the flexible spacer portion in the liquid crystalline phase. It also moves some methylene groups out of the plane of the aromatic ring, thus increasing the diameter of the structural unit in the *b* direction. This is reflected in an increased cell parameter *b* in the liquid crystalline phase. Shortening of the flexible spacers was also observed by Zerbi et al.[5] for some liquid crystalline polyesters at the crystalline to liquid crystalline transition using IR spectroscopy. Results[2] obtained by X-ray diffraction investigation of small liquid crystalline imine molecules also suggested some gauche conformation on the flexible chain.

As a brief summary for PI10, the positions and conformations of the structural units between the layers in the crystalline (at 23 °C) and the smectic G liquid crystalline phases (at 117 °C) are indicated in Figures 11 and 12. In the crystalline phase, the structural units are hexagonally packed in the layers and take on a tilted angle to the normal of the layers. The structural units take on the cis and trans conformations for their aromatic part and an all-trans conformation for their aliphatic chain. In the smectic liquid crystalline (S_G) phase, the orientation and position of the structural units within the layer is less ordered, but pseudohexagonal packing is still assumed. The structural units take on a less tilted angle with respect to the *c* direction. This is one explanation for the increase in the layer spacing. From a single chain conformation point of view, the aromatic part of a structural unit takes on only the more elongated trans conformation and the aliphatic chain takes on some gauche conformation. The combination of aromatic and aliphatic changes (C–N and trans–gauche rotation) produces an actually longer structural unit which is in the smectic liquid crystalline phase.
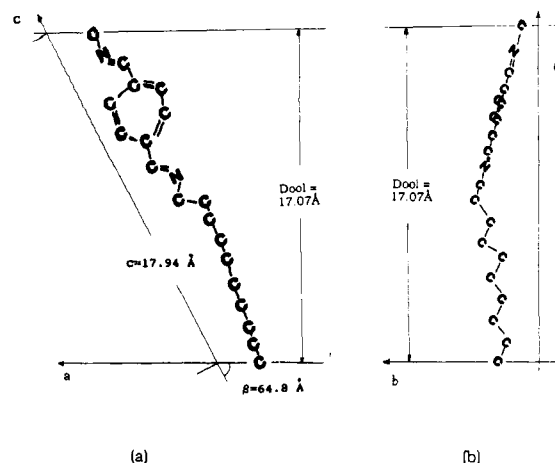

(a)   (b)

Figure 12. Probable conformation of the structural units of PI10 in the smectic G liquid crystalline phase at 117 °C: (a) the projection on the *ac* plane and (b) the projection on the *bc* plane.
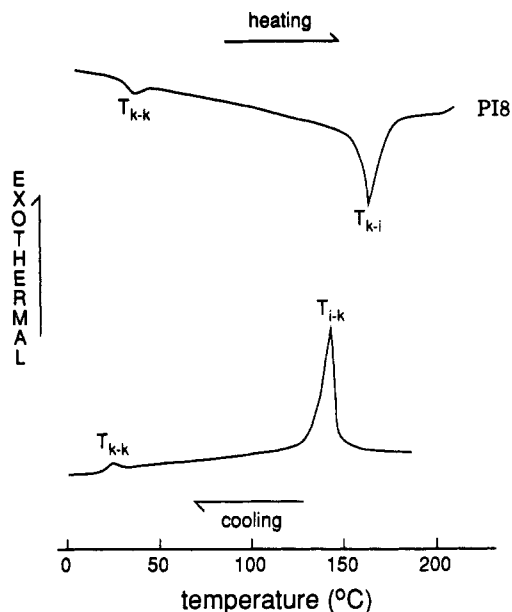

Figure 13. DSC thermograms (the second heating and cooling scans) of PI8.

PI-8. The DSC thermograms of PI8 are shown in Figure 13. It is seen from the second heating scan that there is a weak transition at 32 °C and a strong transition at 163 °C on heating. On cooling, there are also two corresponding transitions. According to the enthalpy changes associated with these two transitions,[11] the weak transition is assigned to be a crystalline–crystalline transition and the strong transition a crystalline–isotropic transition. To elucidate the crystalline structures of PI8, X-ray diffraction was measured on the powder of PI8 at 23 °C (below the first transition temperature) and 95 °C (between the two transition temperatures) in the same way as for PI10. The X-ray diffraction spectra at 23 and 95 °C are shown in Figures 14 and 15, respectively. Table IV gives experimental and calculated values of D_{hkl} for the diffraction peaks of PI8 at 23 °C. The results are fairly similar to those of PI10 obtained at 23 °C. The same unit cell, a C-centered monoclinic cell, was derived for PI8. The cell parameters are given in Table IV. D_{001} for PI8 is 13.90 Å, smaller than D_{001} of PI10. Hence, the layers in PI8 are more closely packed than in PI10. This is easily explained by the fact that PI8 has eight methylene units on the aliphatic chain of one structural unit, two methylene units less than PI10. This difference is reflected in the length of the long molecular axis of PI8. The *c* axis for PI8 is
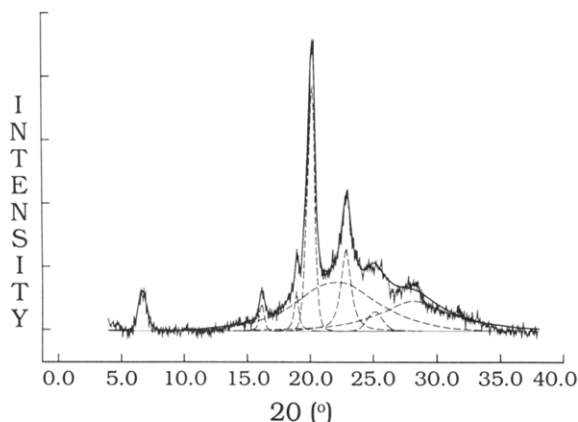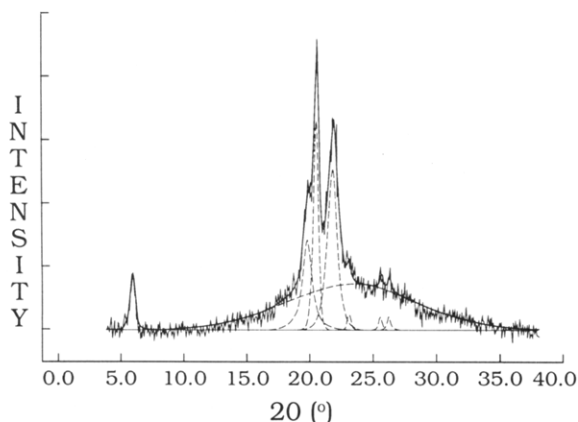
Figure 14. X-ray diffraction spectrum of PI8 at 23 °C.

Figure 15. X-ray diffraction spectrum of PI8 at 95 °C.

Figure 16. Texture of the crystalline phase of PI8 photographed at 100 °C under cross-polarized light on cooling.

Table IV
Experimental and Calculated Crystallographic Parameters for PI8 at 23 °C[a]

intensity	exptl D_{hkl} (Å)	calcd D_{hkl} (Å)	hkl
12.77	13.09	13.09	001
8.25	5.45	5.47	202
12.23	4.67	4.67	111
77.33	4.42	4.42/4.45	200/110
26.36	3.88	3.88	11$\bar{1}$
6.20	3.53	3.59	20$\bar{1}$
9.72	3.14	3.12	114

[a] a = 9.86 Å; b = 5.16 Å; c = 14.60 Å; β = 53.5°.

Table V
Experimental and Calculated Crystallographic Parameters for PI8 at 95 °C[a]

intensity	exptl D_{hkl} (Å)	calcd D_{hkl} (Å)	hkl
17.43	14.80	14.80	001
28.78	4.47	4.47	111
66.66	4.33	4.33	200
51.53	4.07	4.07	11$\bar{1}$
4.87	3.84	3.83	20$\bar{1}$
4.20	3.48	3.55	11$\bar{2}$
4.18	3.39	3.43	204

[a] a = 8.91 Å; b = 5.18 Å; c = 15.20 Å; β = 70.7°.

14.60 Å, shorter than 16.90 Å for PI10. The angle β is 53.5°. Compared to β of PI10 at 23 °C, PI8 takes on a slightly more tilted angle. Results of X-ray diffraction of PI8 at 95 °C are tabulated in Table V. At 95 °C, most of the reflections at 23 °C remain, but the D_{hkl} spacing and the relative intensities change. Two-dimensional order within the layer plane is, therefore, believed still to exist. The order in the c direction is also kept. The tilt angle for PI8 at 95 °C is smaller than that for PI10 at 117 °C.
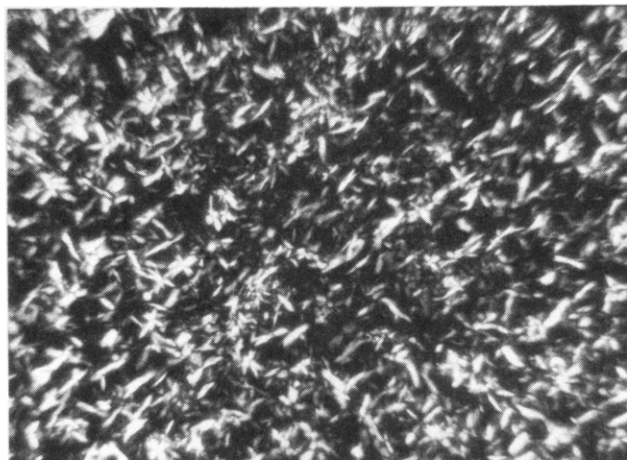
PI8 also possesses three-dimensional order at 95 °C. The interlayer distance, D_{001}, becomes larger above T_{k-k}, indicating an increase in distance between the layers in the second crystalline phase. The X-ray diffraction results also suggest that PI8 at 95 °C is in a crystalline phase.

The transition at T_{k-k} (T_{k-k} = 32 °C) is very weak: the enthalpy change is only 1.3 kJ/mol. However, the enthalpy change for the higher temperature, T_{k-i} (T_{k-i} = 163 °C) transitions, which are not resolved, is 14.6 KJ/mol.[11] This means that the structural change at 32 °C is relatively small while the structural change is greater at 163 °C. Observation on a polarized microscope at about 100 °C on cooling from an isotropic liquid shows some crystal-like pattern (seen in Figure 16). This is taken as another proof of the crystalline phase between the two transitions for PI8.

The crystallinity and amounts of the cis and trans conformations of PI8 are summarized in Table III. These data were obtained from the sample PI8 as synthesized. The crystallinity of PI8 obtained by X-ray diffraction is 60%, and the total amount of the cis and trans conformations is 64%. Above 32 °C, the crystallinity of PI8 obtained by X-ray diffraction is 42% which compares well with the amount of trans conformation (40%). Therefore, PI8 is also assumed to take on both cis and trans conformations in the crystalline phase below the first transition, and the cis conformation melts at the first transition, leaving only the trans conformation above T_{k-k}. The weight-averaged length of a repeat unit in the crystalline phase below the first transition is 15.23 Å calculated by ChemCad which compares fairly well with 14.60 Å obtained by X-ray diffraction. In the crystalline phase between the first and the second transition temperatures, the whole structural unit takes on a conformation similar to that for PI10 shown in Figure 10. The appearance of some gauche conformation in the aliphatic chain of PI8 in the crystalline phase at 95 °C (between the two transitions) is proven by the upfield shift of the aliphatic peaks in the solid-state NMR spectrum.[11] When the gauche conformation of one bond (torsion angle rotated by 60°) is assumed, the length of a structural unit becomes 16.83 Å. If an all-trans conformation were assumed, the length would be 17.21 Å. The length of one unit cell of PI8 in the c direction at 95 °C measured by X-ray diffraction is actually 15.20 Å. Therefore, the partial gauche conformation, similar to PI10, is also closer to the real conformation of the structural units of PI8 in the
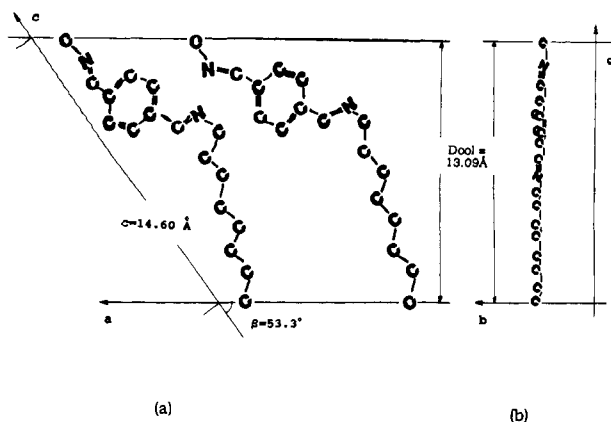
Figure 17. Probable conformations of the structural units of PI8 at 23 °C: (a) the projection on the *ac* plane and (b) the projection on the *bc* plane.
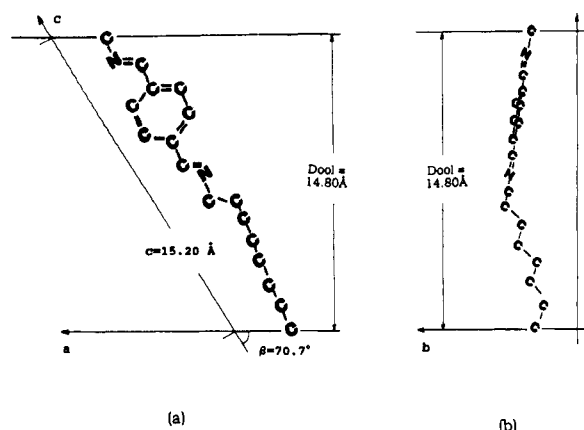

Figure 18. Probable conformation of the structural units of PI8 at 95 °C: (a) the projection on the *ac* plane and (b) the projection on the *bc* plane.

crystalline phase between the two transitions. The trans-gauche conformational transition, which shortens the flexible spacers, is compensated by the C–N rotation to produce an increase in the total length of the whole structural unit. Sketches showing the conformations and the arrangement of structural units of PI8 at 23 and 95 °C are presented in Figures 17 and 18.

Conclusions

The crystalline structure of PI10 and PI8 has been characterized by X-ray diffraction and molecular modeling. PI10 exhibits a crystalline phase and a liquid crytalline smectic G phase. PI8 shows two crystalline phases. The mesogenic units of both PI10 and PI8 take on the extended trans conformation while the flexible spacers take on some gauche conformation in the phases above the first transition. The total length of the structural units increases in the smectic phase for PI10 and in the second crystalline phase for PI8.

References and Notes

(1) A recent review: Noel, C. In *Side Chain Liquid Crystal Polymers*; Mcardl, C. B., Ed.; Blackie: Glasgow and London, 1989.
(2) Doucet, J.; Levelut, A.-M. *J. Phys.* **1977**, *38*, 1163.
(3) Gray, G. W.; Goodby, J. W. G. *Smectic Liquid Crystals-textures and structures*; Leonard Hill: Glasgow and London, 1984.
(4) Vries, A. *Mol. Cryst. Liq. Cryst.* **1970**, *10*, 219.
(5) Galbiati, E.; Zerbi, G.; Benedetti, E.; Chiellini, E. *Polymer* **1991**, *32*, 1555.
(6) Ballistreri, A.; Garozzo, D.; Giuffrida, M.; Maravigna, P.; Montaudo, G. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 331.
(7) Uryu, T.; Kato, T. *Macromolecules* **1988**, *21*, 378.
(8) Kato, T.; Fujishima, A.; Uryu, T.; Matsushita, N.; Yamaguchi, H. *New Polym. Mater.* **1990**, *2*, 255.
(9) Kato, T.; Uryu, T. *Mol. Cryst. Liq. Cryst.* **1991**, *195*, 1.
(10) Frech, C. B.; Adam, A.; Falk, U.; Boeffel, C.; Spiess, H. W. *New Polym. Mater.* **1990**, *2*, 267.
(11) Natansohn, A.; Yang, H.; Clark, C. *Macromolecules* **1991**, *24*, 5489.
(12) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.
(13) Burgi, H. P.; Dunitz, J. D. *Helv. Chim. Acta* **1970**, *53*, 1747.
(14) Morgan, P. W.; Kwolek, S. L.; Pletcher, T. C. *Macromolecules* **1987**, *20*, 729.
(15) Coassolo, A.; Foa, M.; Dainelli, D.; Scordamaglia, R.; Barino, L.; Chapoy, L. L.; Rustichelli, F.; Yang, B.; Torquati, G. *Macromolecules* **1991**, *24*, 1701.
(16) Natansohn, A.; Yang, H. *Macromolecules*, submitted for publication.
(17) Tonelli, A. E.; Schilling, F. C. *Acc. Chem. Res.* **1981**, *14*, 233.

Registry No. PI10 (copolymer), 135506-22-8; PI8 (copolymer), 135506-20-6; PI10 (SRU), 135506-17-1; PI8 (SRU), 135506-15-9.