Time dependent crystal–smectic transformation in perylene-containing polyimides[☆]

Dianjun Yao, Zhi Yuan Wang, Pudupadi R. Sundararajan*

Department of Chemistry, Carleton University, 1125 Colonel By Drive, Ottawa, Ont., Canada K1S 5B6

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Abstract

The crystalline conformations of perylene polyimides (PPIs), with alkyl spacers varying in length from C_3 to C_{12} are discussed. Although modeling of single chains would suggest the possibility that those with odd number of CH_2 groups adopt a flat helical shape, X-ray diffraction suggests that the chains with odd and even spacers have the same conformation, due to the necessity to pack the perylene units. Upon annealing, the UV–vis absorption maximum red-shifts by about 10 nm, indicating enhanced π-stacking between the perylenes. Several changes in the spectra are seen with an increase in annealing time, at a given temperature. With an increase in annealing time, X-ray diffraction patterns show changes in the number of reflections, indicative of a crystal to mesogenic transition. The time required for this transition increases with a decrease in the spacer length, and annealing temperature, suggesting that the dynamics of this transition is very slow.
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1. Introduction

Perylene 3,4,9,10-tetracarboxylic dianhydride and its bisimides are some of the most thoroughly studied classes of organic semiconductors with possible applications in photovoltaic cells [1], light-emitting diodes [2], xerography [3], and field-effect transistors [4]. Perylene derivatives are remarkable in the diversity of colors that can be obtained by modifying the groups attached to the periphery of the chromophore. This essentially controls the extent of π overlap between the chromophores in the crystal structure. From the crystal structure data on a series of such substituted perylenes, Hädicke and Graser [5–9] related the color of the crystal to the molecular overlap. Liquid crystalline (LC) derivatives of perylene are also known [10, 11]. Cormier and Gregg [10] recently reported self organization in thin films of LC perylene diimides, with linear and branched poly(oxyethylene) derivatives. Struijk

[11] et al. discussed the LC behavior of N-alkyl-substituted perylene diimide derivatives, with 7, 12 and 18 carbon atoms. Thus, perylenes substituted with flexible side chains generally form LC phase.

For device fabrication, the pigment is usually either vapor deposited to form thin films or dispersed in a polymer binder. The latter is typical of a photogenerator layer of xerographic photoreceptors. There have also been efforts to covalently incorporate the pigment as a part of the polymer, with a view to increase the robustness and flexibility of the device as well as to address the issue of phase separation of the small molecule from the polymer matrix.

Polyimides are thermally stable polymers that exhibit good mechanical properties, low dielectric constant, low coefficient of thermal expansion and high radiation resistance. Since the first commercial polyimide-Kapton was produced by DuPont, polyimides have been extensively used in microelectronics, photonics, optics and aerospace industries [12,13]. In a previous study [14], the synthesis and xerographic characterization of polyimides containing perylenetetracarboxylic dianhydride and aliphatic diamines in the main chain (Fig. 1) were reported. These polymers are insoluble in common organic solvents, and inherent viscosities were measured in concentrated H_2SO_4. It was found that with the perylene-containing polyimides with a C_{12} spacer (PPI-12), the UV–vis absorption maximum
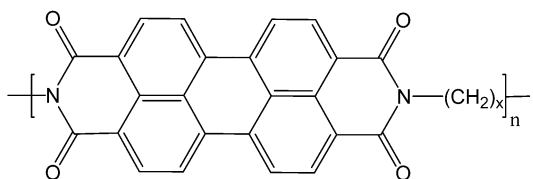

Fig. 1. Schematic of the perylene-containing polyimide polymers studied here ($x=3$–12, notations: PPI-3 to PPI-12).

red-shifted upon annealing at 320 °C, and the crystallinity improved as well. Based on the work of Hädicke and Graser [5–9], this was attributed to the enhanced packing of the perylene units upon annealing. A molecular dynamics simulation of a single chain of PPI-12 also showed that intramolecular chain folding could occur, which is facilitated by the alkyl segment [15]. The possibility of aggregation of perylene units in solution, via such intramolecular chain folding has been proposed by Neuteboom et al. [16], in the case of perylene bisimide polymers with polytetrahydrofuran segments. This polymer, of course, is soluble in solvents such as o-dichlorobenzene.

Although the LC behavior of perylene derivatives (in monomeric form) has been reported, phenomena such as odd–even effect were not studied. In this paper, we describe the structural characteristics of a series of perylene based polyimides (Fig. 1) with different alkyl chain lengths ranging from C_3 to C_{12}, and changes induced by annealing of this series of polymers. The annealing induced changes are interpreted as a transition from the crystalline to smectic state. An interesting aspect of this transition is that it is very slow and it depends on the time of annealing at a particular temperature. We believe that this is the first reported case in which the time of annealing plays a role in crystal–smectic transition.

2. Experimental

The synthesis of perylene-containing polyimides, with $(CH_2)_x$ spacers ($x=3$–12) was reported previously [14]. These polymers are only partially soluble in m-cresol. No molecular weight information could be deduced, except to qualitatively describe their viscosity in concentrated H_2SO_4.

The X-ray diffraction patterns on films were recorded using a Statton-type flat film camera (William Warhus Co., Wilmington, DE). In addition, diffraction patterns were also obtained with a PW 1710 Philips automated powder diffractometer, and Nickel-filtered Cu K_α radiation ($\lambda = 1.542$ Å). The MDI scan 3.2 software (Materials Data Inc., Livermore, CA) was used for data collection. The results were analyzed using MDI Jade 5.0 XRD Pattern Processing software. The crystallinity (X_c) was calculated as the ratio of the intensity under the crystalline peaks above the background to the total intensity. All the samples were analyzed in powder form. Due to their poor solubility, films could not be prepared.

The UV–vis absorption spectra were recorded on a Perkin–Elmer 900 Spectrophotometer. Drops of the solution of the polymers in m-cresol were deposited on glass microscopic slides and left to dry. It can be best described as a dried dispersion rather than a film.

Thermal properties of the polymers were determined using a Seiko 220C differential scanning calorimeter (DSC) at a heating rate of 10°/min under 50 ml/min nitrogen flow. The DSC instrument was calibrated for temperature and energy with indium and tin reference samples. The degradation of the samples was determined using a Seiko 120 thermogravimetric analyzer (TGA) in the temperature range from 25 to 550 °C at a heating rate of 10 °C/min under 100 ml/min nitrogen or airflow.

FTIR spectroscopic measurements were carried out at ambient conditions using a Michelson M129 BOMEM Fourier Transform Infrared (FTIR) spectrometer. Data were collected using BOMEM GRAMS/386 software. The FTIR spectra of polyimides were obtained in the form of transparent KBr pellet. A background FTIR spectrum was taken for each experiment with the identical sample holder.

The molecular simulations were performed using the commercial software Cerius[2] version 4.3 (Molecular Simulations Inc., USA). Some energy minimization calculations were also performed using the HyperChem version 7.0.

3. Results and discussion

3.1. Thermal characteristics

The results of the thermogravimetric analysis are summarized in Table 1. These illustrate the good thermal stability of perylene-containing polyimides. The 5% weight loss in nitrogen was in most cases around 450–480 °C and the maximum peak temperatures of derivative thermogravimetry (DTG) are in the range of 470–530 °C. It is also seen that the thermal stability generally decreases with an increase in the length of the (CH_2) spacer, although we do not see a systematic trend. This is in accord with the theory

Table 1
Results of thermogravimetric analysis (TGA)

Aliphatic amine in PPIs	Polyimide ID	TGA (°C)	
		$T_{5\%}$ [a]	T_{max} [b]
Diaminopropane	PPI-3	456.1	526.6
Diaminopentane	PPI-5	485.4	523.0
Diaminoheptane	PPI-7	455.3	500.2
Diaminooctane	PPI-8	449.6	484.8
Diaminononane	PPI-9	477.8	501.8
Diaminodecane	PPI-10	461.2	518.2
Diaminododecane	PPI-12	424.4	474.9

[a] $T_{5\%}$: temperature at which 5% of the sample weight was lost.
[b] T_{max}: the temperature of maximum peak characterized by derivative thermogravimetry (DTG).

that the introduction of flexible swivel groups lowers the thermal stability [17]. The glass transitions (T_g) of these polyimides were not detectable. This is similar to the conclusion reported by other authors on similar polyimides [18,19]. In the case of rod-like polyimides, the transitions were very weak or not detectable. Such shallow transitions are also characteristic of LC polymers [20]. Because of these constraints, it was not possible to derive the effect of odd and even spacer lengths on the glass transition temperatures.

3.2. Effect of annealing on the UV–vis absorption behavior

As is well known, the extent of π overlap between the chromophores packed face to face in the crystal structure determines the color. With an increasing overlap, the absorption maximum shifts to longer wavelengths. It was noted before [14] that in the case of PPI-12, a red shift of the absorption maximum occurred when the polymer was annealed at 320 °C for 2 h.

Fig. 2 shows the effect of annealing at 320 °C, for different times, on the UV–vis absorption of PPI-7 and PPI-12. In all cases there is a red shift of 6–10 nm upon annealing. We could not detect any correlation between the alkyl chain length and the extent of the shift. It was noted that there was no change in the absorption characteristics with annealing for PPI-3 and PPI-5. It is perhaps due to the short alkyl segments not having enough mobility to cause any structural changes. With PPI-7 (Fig. 2(a)), initially a broad absorption is seen ranging from 450 to 600 nm, with a 'maximum' at 492, and 527 nm. Upon annealing at 320 °C for 1 h, three maxima are seen, at 475, 508 and 545 nm, with the absorption at 508 nm being more intense. The red and blue shifted bands are usually assigned to J-type and H-type aggregates [21]. The relative intensities of these maxima remain the same with 2 h of annealing. After annealing for 4 h, the blue maximum (475 nm) vanishes. A similar trend is seen with PPI-12 as well (Fig. 2(b)). Thus, annealing at 320 °C for 1–2 h causes a structural change, and increasing the annealing time to 4 h results in yet another structural transition. The differences in the intensities between the spectra from the original samples and those after annealing could be due to the variation in the thickness of the samples and the roughness of the sample surface. It was mentioned above that these were dried dispersions rather than films. Partial oxidation of the chromophore cannot be ruled out.

Struijk et al. [11] compared the solution and thin film spectra of the perylene diimide with a $(CH_2)_{18}$ side chain and concluded that the blue and red shifted absorption bands could be due to a rotation of the transition dipole moments of adjacent molecules and/or more than one type of aggregate being present. Note that the spectra shown in Fig. 2 were obtained by placing a drop of solution in m-cresol on a glass slide and letting it dry. Annealing was also performed on these samples, which can be considered similar to thin films.
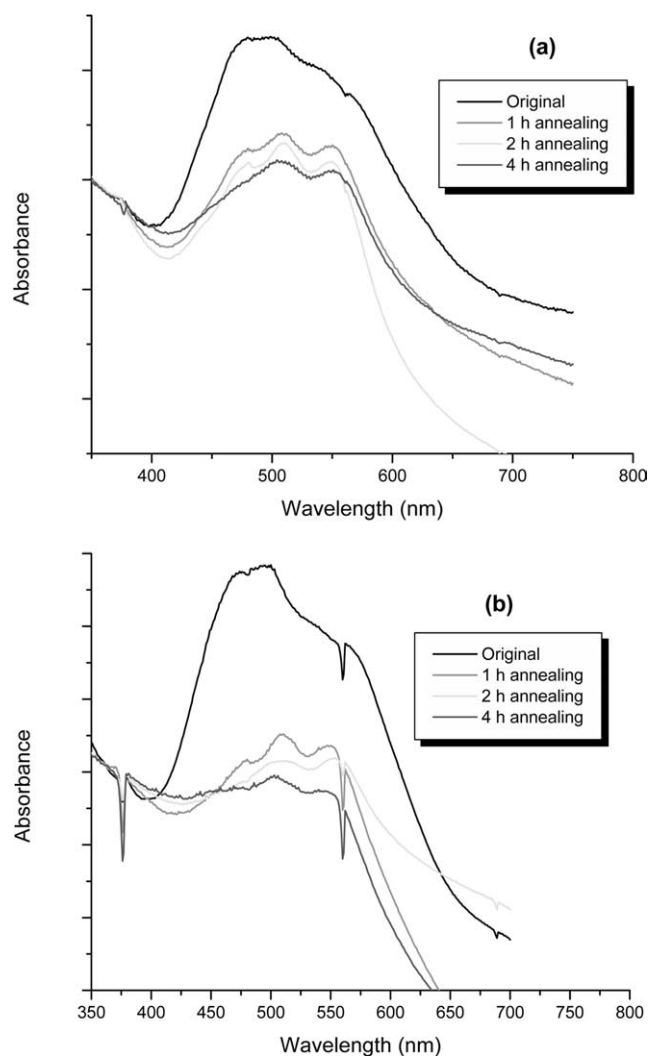

Fig. 2. The effect of annealing for different times, on the UV–vis absorption spectra of (a) PPI-7 and (b) PPI-12 at 320 °C.

3.3. Chain conformation

If the alkyl chain is in the all-*trans* conformation, and the torsion angle with the perylene unit C (pe)–N–C–C is close to 0°, odd number of (CH_2) groups would lead to a helical conformation of the chain and the even number would lead to a zig–zag structure. This is shown in Fig. 3, for the PPI-9 and PPI-12 polymers. For example, the Hyperchem software chooses this torsion to be 0° as default. Due to the length of the rigid perylene unit (11.2 Å), the helices would have a rather large cavity, ranging from 12 Å with PPI-5 to 30 Å, in the case of PPI-9. In addition, the perylene stacking distance in successive turns is more than 10 Å. Conceptually, this would create a rather large free volume, and due to the poor perylene stacking, the UV–vis spectra as seen in Fig. 2 would not arise. However, if the above torsion angle is shifted to about 90° with respect to the perylene plane, the chain with odd number of (CH_2) groups also would adopt an extended conformation (Fig. 3). Such a model, with the
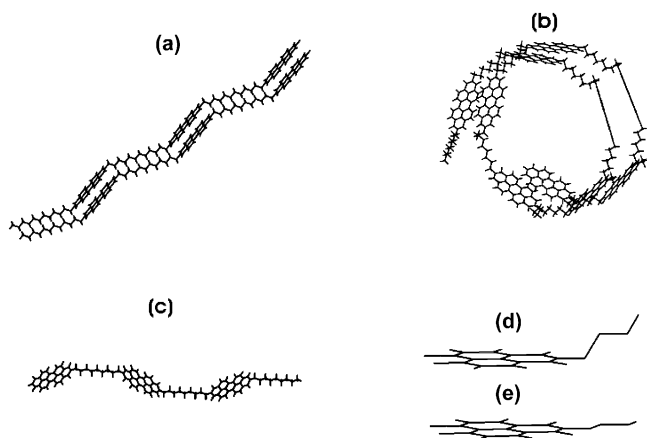
Fig. 3. (a) Extended zig–zag conformation of PPI-12 with 3 monomer units (b) helical conformation of PPI-9 with 10 monomer units; (c) extended conformation of PPI-9 when the aliphatic C–C bond is at about 90° with respect to the perylene plane; (d) and (e): schematics of the aliphatic C–C bond at 90 and 180° respectively, with respect to the perylene plane.

torsion angle of 90° between the aliphatic carbon and the perylene plane was proposed by Aroca et al., for the molecule 1,2-bis(propylimido perylene)ethane using AM1 for geometry optimization [22] (essentially, this molecule is a perylene dimer, bridged by $(CH_2)_2$). Interruption of the all-*trans* sequence with a few *t–g* conformations would also lead to a zig–zag shape for the chains with odd number of (CH_2) groups.

Since films could not be prepared with these polymers, and due to the low molecular weight, oriented X-ray diffraction patterns to derive the crystalline conformation could not be obtained. The discussion hence will be limited to some of the features of the powder diffraction patterns, and the effect of annealing.

Fig. 4 shows the longest d-spacing (in the wide angle region) recorded for each of the polymers. It is seen that this spacing increases almost linearly with the number of CH_2 groups in the spacer, and parallels the monomer length, as calculated from energy minimized models, with an all-*trans* conformation for the alkyl segment. If the alkyl spacers are in the all *trans* conformation, successive pairs of CH_2 groups will add about 2.5 Å to the length of the perylene unit. Of course, defects in the alkyl spacer conformation would reduce this distance. Deviations from the all-*trans* conformation is indicated by Fig. 4, in which the longest d-spacing is 4–6 Å less than the monomer length in all cases. The systematic increase in the longest d-spacing with the number of CH_2 groups supports the proposal that polymers with odd numbered CH_2 groups also adopt an extended conformation, to facilitate stacking of the perylene units. Thus, in the case of these polymers, the chain is extended for both even and odd number of CH_2 groups in the spacer, being dictated by the π stacking.

We could not record the second or third order reflections corresponding to these spacings even in the powder sample. Hence, the repeat distance of the chain and the crystalline
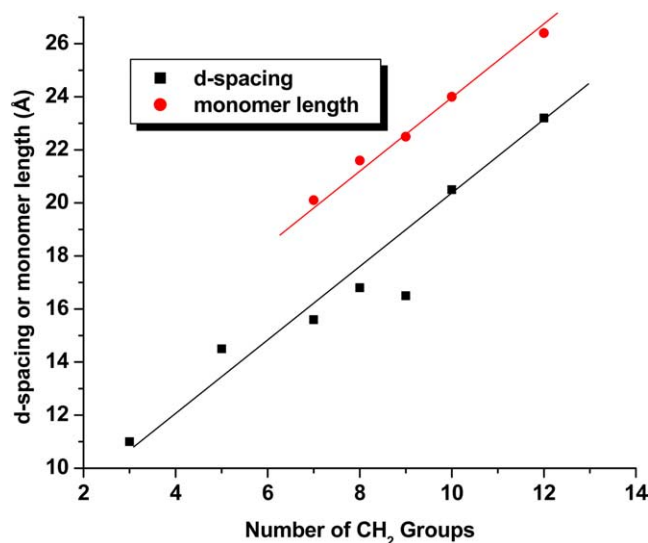

Fig. 4. Variation of the longest d-spacing with the number of CH_2 groups in the spacer (■); and the lengths of the monomers, with the spacers in the extended conformation (calculated using HyperChem) (●).

chain conformation could not be deduced, except to say that these are extended helices. Table 2 lists the d-spacings recorded for the polymers PPI-7, PPI-8, PPI-9, PPI-10 and PPI-12, by X-ray powder diffraction. It is seen that most of the reflections are common to both odd and even number alkyl groups. This also confirms that the chains are extended in both cases.

The length of the CH_2 spacer plays a role in the packing of the perylene units. Fig. 5 shows the X-ray crystallinity as a function of the number of CH_2 groups, for the as-prepared polymers. Although the crystallinity is small, an increase with the length of the spacer is seen. Neuteboom et al. [23] observed that in the case of perylene bisimide-polyTHF copolymers in *o*-dichlorobenzene solutions, enhanced
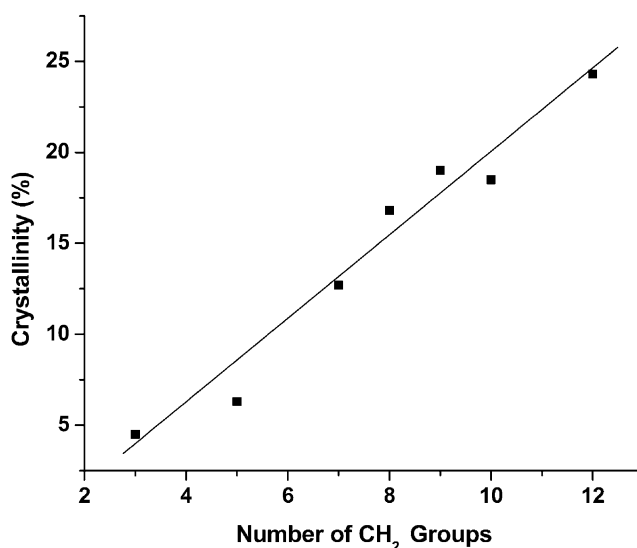

Fig. 5. The variation of crystallinity of perylene polyimides, with the number of CH_2 groups in the spacer.

Table 2
Comparison of the d-spacings and the relative intensities observed in the X-ray diffraction patterns for the various perylene polyimides

PPI-7		PPI-8		PPI-9		PPI-10		PPI-12	
d (Å)	I (%)	d (Å)	I (%)	d (Å)	I (%)	d (Å)	I (%)	D (Å)	I (%)
				2.48	11.5				
				2.61	9.5				
				2.82	12.1				
						3.21	20.4	3.13	19.7
		3.32	53.1	3.37	39.3	3.37	27.1	3.29	56.4
3.41	42.9					3.49	25.6		
								3.65	41.1
		3.88	49.8					3.80	28.9
3.93	37.5	3.94	48.6	4.05	34.6	4.10	25.6	4.16	25.3
		4.34	41	4.39	32	4.37	24	4.42	30.5
4.62	29.2	4.65	34.7	4.67	31.8	4.7	20.7	4.71	24.3
								5.22	15.4
				6.28	33.8	6.17	18.1	6.10	16.2
6.48	46.8	6.41	40.5						
								7.29	63.9
8.33	71.0	8.16	69.3	8.08	62.8	7.92	35.8		
								8.56	26.2
								9.53	28.4
15.67	100								
				16.5	100				
		16.85	100						
								20.27	100
						20.50	100		
								23.23	94.4

aggregation occurs with the shortest polyTHF segments. The crystallinity in the solid state was not measured in this reference, and the presence of the solvent could play a role as well.

3.4. Mesomorphic transition

In the previous paper [14], we discussed the red shift of the absorption maximum of PPI-12, upon annealing at 320 °C for 2 h. To examine the changes if any upon prolonged annealing at this temperature, X-ray diffraction patterns were recorded after annealing for 4 and 6 h. The changes in the diffraction profile are shown in Fig. 6. It is seen that after annealing for 4 h, a number of reflections decrease in intensity, and only those corresponding to 3.29, 3.65, 7.29 and 9.58 Å remain. This is reminiscent of a partial transformation to a smectic state. The 3.65 Å reflection can be assigned to the π-stacking of the perylene units. Polymers with shorter alkyl spacer lengths (beyond PPI-7) also showed the same behavior, although the time required for the transformation was longer. It was also found that with lower annealing temperatures, the time required for the transformation was longer. Thus a mesomorphic transformation occurs, for all perylene polyimides, with alkyl spacers equal or longer than seven CH_2 groups. The time taken for the transformation increases with a decrease in the spacer length. This also parallels the changes in the absorption spectra with increasing annealing times. Normally, such mesogenic transitions of polymers can be easily detected

during the usual scan rate in DSC measurements. However, in the case of perylene based polyimides, this is a slow phenomenon.

This unusual behavior could not be followed with oriented films since these could not be prepared. Because of the inability to form films, the crystal–smectic transformation could not be studied by optical microscopy. In addition, due to lack of clarity of the thermal transitions (e.g., T_g) in the DSC, this technique was also unable to
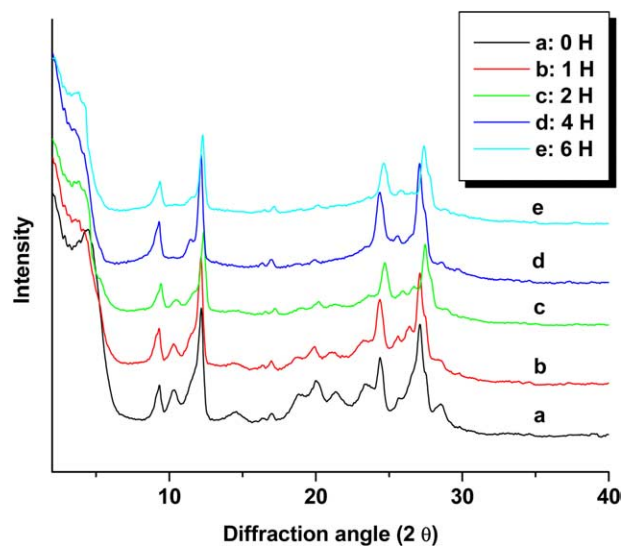

Fig. 6. X-ray diffraction patterns of PPI-12 annealed for different times at 320 °C.

provide confirmation to this transition. Thus, X-ray diffraction was the only technique that shows such a transformation, along with changes observed in the UV–vis spectra.

Based on the premise that the strong interactions between the perylene moieties cause such a slow transformation, we attempted to blend short chain alkanes or perylene in the hope of providing mobility to the chains and reduce the time or temperature required for the transition. However, because of the poor solubility, these attempts were not successful. Even physical blending did not prove useful.

The question naturally arises as to if these changes are due to the degradation of the polymer upon prolonged annealing at temperatures over 300 °C. From Table 1 it is seen that with PPI-12, a weight loss of 5% begins at 424 °C. A TGA analysis was performed without the nitrogen flow, holding the sample at 320 °C for 15 h. The weight loss was only 8%. Thus, if degradation occurs, it is not appreciable. The fact that the d-spacings of the prominent reflections do not change, also supports the conclusion that degradation is not the cause of the mesogenic transition. However, the flow of nitrogen does have an effect in slowing down the transformation. The PPI-12 was annealed in the DSC instrument, under nitrogen flow, for various times, and X-ray diffraction was recorded. It took nearly 15 h for the transition to occur. Fig. 7 shows the diffraction from PPI-12, and after annealing in air for 5 h and under nitrogen flow for 15 h. It is seen that there is no difference between the results from the two annealing procedures. The annealed sample was dissolved in *m*-cresol, and X-ray diffraction was recorded on the dried precipitate. Most of the original reflections (i.e., as from samples prior to annealing) were observed again, which also confirms that the structural transformations observed above are not due to degradation.

IR spectra also show changes in the absorption bands, corresponding to the carbonyl and CN bonds, upon
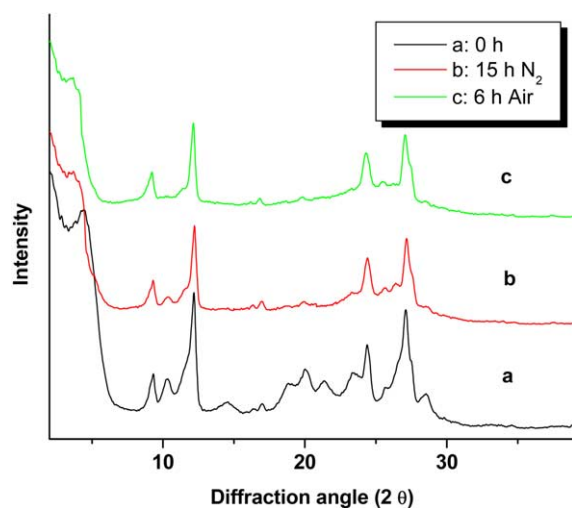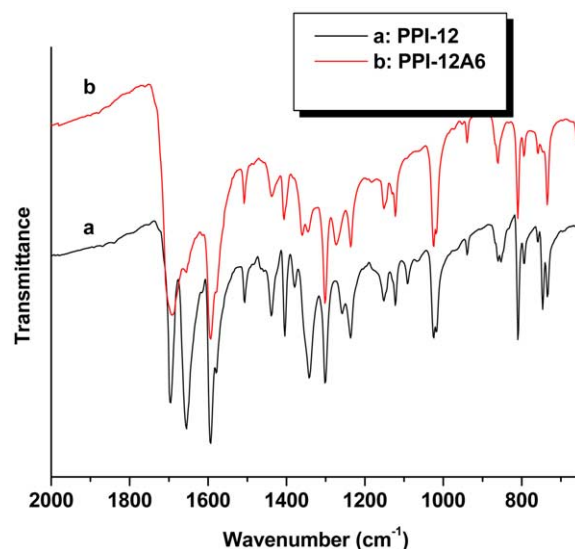

Fig. 8. IR spectra of PPI-12: (a) original sample, (b) annealing for 6 h at 320 °C.

annealing. The spectra are shown in Fig. 8 and the peak assignments are given in Table 3. The most relevant molecular vibrations of PPIs are the two strong carbonyl stretching vibrations at 1655 and 1695 cm^{-1} which correspond to the anti-symmetric and symmetric C=O stretches [22], respectively. Upon annealing at 320 °C for 6 h, the relative intensities of these bands change drastically, with the 1655 cm^{-1} band becoming weak, and broadening of the one at 1691 cm^{-1}. The absorption at 1342 cm^{-1} corresponding to C–N stretch, splits into a doublet, with much weaker intensity, at 1345 and 1359 cm^{-1}. There is no change in the positions of the absorption bands corresponding to the alkyl groups. Thus, annealing causes a change in the packing of the perylene moieties.

Fig. 7. X-ray diffraction patterns of PPI-12 annealed at 320 °C in nitrogen and air atmosphere.

Table 3
Observed IR wave numbers (cm^{-1}) and their assignments for PPI-12

PPI-12	PPI-12 Annealed at 320 °C for 6 h	Assignment
746	735	C–H perylene wag
810	810	C–H perylene wag
852	860	C–H perylene wag
939	939	C–H bending
1024	1024	C–H bending
1122	1122	C–H bending
1155	1151	C–H bending
1236	1236	Alkyl bending
1302	1302	Alkyl bending
1342	1345	C–N stretch
	1360	
1404	1406	Ring stretch
1441	1438	CH$_2$ scissors
1593	1593	C=C ring stretch
1655	1691	C=O, stretch
1695		

3.5. Chain folding

As noted in Section 1, a molecular dynamics simulation of an isolated PPI-12 chain suggested the possibility of intra-molecular chain folding of these polymers, and the nematic ordering of the perylene units [15]. However, the results presented here show that in the real system, the mesomorphic transition is very slow, due to the predominant intermolecular interactions between the chains. This rules out the possibility of intra-molecular chain folding in the solid state, as suggested by simulations on single chains. As seen from Fig. 4, the maximum d-spacing in the wide angle region increases with the length of the alkyl spacer, and parallels the calculated monomer length with the extended conformation of the spacer. This again confirms that intra-molecular chain folding, if any, is not predominant in this case. However, such intra-molecular chain folding has been suggested by Neuteboom et al. [16] in the case of alternating perylene bisimide-poly THF copolymers in solution. Wang et al. [24] reported folding of alternating conjugated chromophores and single stranded DNA in aqueous solution. The chromophore in this case was also the perylene tetracarboxylic diimide. Thus, while the intra-molecular chain folding as suggested by the molecular dynamics simulations has been observed [16,24] with perylene containing polymers in solution, such a possibility could not be examined for PPI-12 due to its poor solubility.

4. Conclusions

Perylene-containing polyimides with alkyl chain spacers of different lengths adopt an extended conformation, irrespective of whether the chain contains odd or even number of CH_2 groups. This is attributed to the tendency for stacking of the perylene units, which would not be possible if the chain with odd number of CH_2 groups were to take a helical shape. Insolubility of these polymers in common solvents and the inability to prepare films prevented us from obtaining oriented X-ray diffraction and deriving the detailed chain conformation in the crystalline state. The crystallinity of the as-prepared samples increases with the alkyl chain length. Annealing causes time dependent structural transformations, indicated by changes in UV–vis spectra, and X-ray diffraction. The former shows progressive changes with annealing time. The broad absorption maximum splits into three well-defined maxima with about 1 h of annealing, and further annealing results in the broadening of the blue shifted maximum. Prolonged annealing results in a smectic-like transition as indicated by X-ray diffraction and the time for such transition depends on the temperature of annealing and the length of the spacer.

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