Notes

Segmented Polyimides with Poly(ethylene oxide) Blocks Exhibiting Liquid Crystallinity

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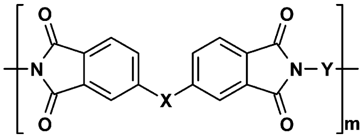
Received July 26, 2007
Revised Manuscript Received November 5, 2007

Introduction

Interest in polyimides has centered primarily on aromatic polyimides with high thermal-transition temperatures and good thermal stabilities. However, following early work by de Vissier et al. on polyimides derived from pyromellitic dianhydride and diamines with poly(ethylene oxide) sequences,[1] there has been continuing interest in polyimides with aliphatic moieties, e.g., in polyimides of structure **1** in which either or both **X** and **Y** incorporate aliphatic units and/or various linking groups. Although there have been a few studies of segmented polyimides containing other aliphatic sequences,[2−6] the main emphasis has been on those with sequences of methylene or ethylene oxide (EO) units. Thus, Harris and co-workers described polyimides in which **X** had various structures and **Y** included $-(O-CH_2-CH_2-)_n-O-$ sequences ($n = 1$ to 3 or 4) with phenylene linking units with different substitution patterns and, in some cases, methyl substituents.[7−13] Several of these polymers exhibited multiple endothermic (melting) transitions on heating. Within those studies, Cheng et al. reported that, of the polymers prepared from oxidiphthalic anhydride (**X** = **O** in **1**) but with diamines with $n = 1$ to 3 and with one meta- and one para-terminal phenylene, only that with $n = 3$ exhibited two melting transitions (50 °C apart) which were attributed to isomorphism.[12]



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In 1999, Kricheldorf published a review of polyimides, and related materials of various structures, and especially of polyimides with aliphatic spacers, concentrating on whether or not the polymers exhibited thermotropic liquid-crystalline behavior at elevated temperatures.[14] The bulk of the polymers that exhibited liquid crystallinity were poly(ester imide)s with polymethylene spacers, and it was concluded that inclusion of ester groups is important in enhancing formation of liquid-crystalline phases. Very few other polyimides exhibited liquid crystallinity, but they too had polymethylene sequences. No polymers with imide groups and oxyethylene units were found to exhibit liquid crystallinity. The evidence available in 1998, therefore, led to a perception that polyimides and poly(ester imide)s with oxyethylene spacers would not form liquid crystalline phases. Indeed, Kricheldorf's review states the following: "Hence, these results indicate that ether groups in the aliphatic spacers of PEIs [poly(ester imide)s] destabilise the LC-phase." "This result and the properties of the PEIs [poly(ester imide)s] ... clearly confirm that ether groups in general and oligo(ethylene oxide)s in particular are highly unfavorable for the existence of LC-phases in the case of polyimides." "Only the ether groups may totally prevent the existence of layered structures as illustrated by the PEIs [poly(ester imide)s]...". In an earlier paper on poly(ester imide)s, Kricheldorf et al. state: "Poly(ethylene oxide) spacers tend to suppress the crystallization and prevent the formation of layer structures."[15] Chiellini and Laus also remarked that poly(ethylene oxide) spacers have a lower mesogenic propensity and are less conducive to the formation of mesophases from weak mesogens than are polymethylene sequences.[16]

However, an earlier paper by Noel et al.[17] reported that aromatic polyesters with oxyethylene spacers (1, 3, or 9 ethylene oxide units) did exhibit liquid crystallinity at high temperatures. These polyesters were based on *p*-terphenyl with *p*-carboxyl units; both of these units have high mesogenic tendencies. Thus, formation of segmented aromatic polymers with oxyethylene spacers that exhibit liquid crystallinity is not totally precluded.

Kricheldorf and co-workers examined a series of polyimides, based on biphenyldianhydride (3,3′,4,4′-tetracarboxybiphenyl dianhydride, BPDA), containing alkane sequences in the diamine moiety.[18] They found that, in conjunction with BPDA, using α,ω-diaminoalkanes, α,ω-bis(3-aminophenoxy)alkanes, or α,ω-bis(4-amino-3-methylphenoxy)alkanes, the resulting polyimides did not form thermotropic liquid-crystalline phases. Only with α,ω-bis(4-aminophenoxy)alkanes were polymers formed that exhibited liquid-crystalline behavior. Eichstadt et al. also reported on poly(ether imide)s with methylene sequences but did not observe liquid-crystalline behavior.[19] Thus, liquid-crystalline behavior in polyimides is relatively unusual, and there is a considerable body of evidence indicating that spacers derived from ethylene oxide prevent formation of liquid crystalline mesophases in polyimides, and even poly(ester imide)s.

Since the publication of Kricheldorf's review little has changed, except that we reported the formation of a family of polyimides **1** with oxyethylene sequences **X** and α,ω-bis(4-aminophenoxy)oxyethylene sequences **Y** in which the oxyethylene sequences had 0 to 6 ethylene oxide units in each spacer.[20] In a study of the family of 49 such polymers only one, with

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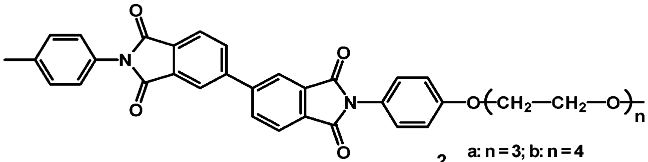
10.1021/ma071665p CCC: $40.75

one ethylene oxide unit in **X** and six units in **Y** did preliminary optical microscopy give evidence for thermotropic liquid crystallinity, indicating that ethylene oxide sequences do not totally bar the formation of liquid crystalline mesophases in polyimides.[20]

Here we report on polyimides based on BPDA and α,ω-bis-(4-aminophenoxy)oxyethylene units, i.e., polymers **2** (which have the same aromatic units as the polymers studied by Kricheldorf et al.[19]), which provide incontrovertible evidence for the formation of polyimides with oxyethylene spacers that exhibit liquid-crystalline behavior.


2 a: n = 3; b: n = 4
c: n = 5; d: n = 6

Experimental Section

Materials. BPDA was obtained from TCI, Japan The syntheses of the diamines **3** with up to four ethylene oxide units and terminal *p*-aminophenoxy units[7,10] and with five or six EO units[20] have been described previously.

Synthesis of Polyimides. The polyimides were prepared by a conventional, two-stage solution polymerization and imidization process, Scheme 1, as described in detail elsewhere.[20] Thus, 1 mmol of diamine **3** was dissolved in 5 cm^3 of *N*-methylpyrrolidinone (NMP) at room temperature and an exact stoichiometric equivalence of BPDA was added with stirring. After standing overnight, the mixtures formed highly viscous solutions of poly(amic acid)s **4** which were chemically imidized by the addition of 2 cm^3 of an equivolume mixture of acetic anhydride and pyridine at room temperature. After leaving for several hours the resulting polyimides **2** were isolated by precipitation into methanol. The high-molecular-weight polyimides were washed with boiling precipitant to remove residual solvent.

Techniques. Polymer molecular weights were determined by gel permeation chromatography (GPC) using DMF/LiCl(0.1 M) as the mobile phase with a flow rate of 1 cm^3 min^{-1}, columns packed with 5μ-PL gel polystyrene (Polymer Laboratories), a refractive index detector, and the instrument was calibrated with polystyrene standards (Polymer Laboratories).

Thermal-transition temperatures were determined by differential scanning calorimetry (DSC) using a Mettler 821^e calorimeter (scan rate 10 °C min^{-1}, under nitrogen) and by optical microscopy using a Leica Wild MPS 32 polarizing microscope equipped with a Linkam THMS 600 hot stage; textures were observed on cooling slowly (typically 2 °C min^{-1}) from about 30 °C above the clearing point. Samples were also examined by dynamic mechanical thermal analysis (DMTA) using a Polymer Labs MKIII analyzer with tensile geometry, operating at 1 Hz and a heating rate of 2 °C min^{-1}. Thermal stabilities were determined using a Perkin-Elmer TGA7 analyzer with a heating rate of 20 °C min^{-1} under nitrogen.

Small-angle and wide-angle X-ray scattering, SAXS and WAXS respectively, were carried out on Station 8.2 of the Synchrotron Radiation Source at the Daresbury Laboratory, U.K. Details of the beamline can be found elsewhere.[21] The samples were placed in a DSC pan equipped with mica windows to allow the transmission of X-rays, for further details see ref 22. The background scattering from an empty pan and windows was subtracted and the data were corrected for nonlinearity in the detector. The SAXS *q* axis was calibrated against wet rat-tail tendon, the WAXS against HDPE. The sample was heated at 20 °C min^{-1} from 100 to 350 °C, held for 1 min cooled back to 100 °C at the same rate and heated again at 20 °C min^{-1} to 350 °C.

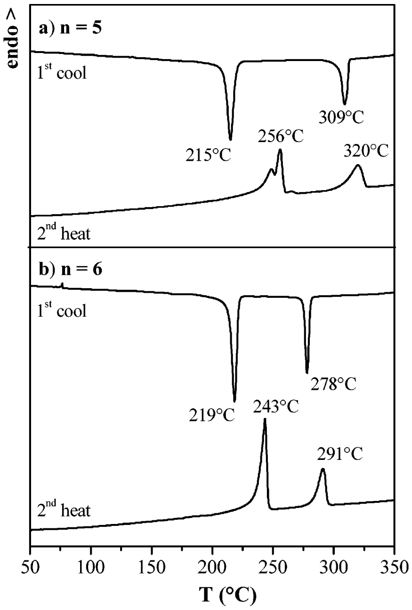


Figure 1. DSC traces for polymers: (a) **2c** and (b) **2d**.

Results and Discussion

The two-stage, solution−polymerization process between BPDA and the bis(4-aminophenoxy) diamines with poly-(ethylene oxide) sequences, **3**, in NMP solution, Scheme 1, led to viscous solutions of poly(amic acid)s which, on imidization with pyridine/acetic anhydride (50/50 v/v) mixture, yielded high-molecular-weight polyimides that were isolated by precipitation into methanol. Polymers were prepared from diamines **3** with $n = 3$, 4, 5, or 6. Of the resulting polymers only those from diamines where $n = 5$ or 6 were soluble in the eluant used for GPC. Molecular weights of the soluble polymers were determined by GPC and values at the peaks of the chromatograms for **2c** and **2d** were 73 and 66 kg mol^{-1}, respectively. Although these experimental values of molecular weight (which approximate to weight-average molecular weights), measured against polystyrene standards, are probably exaggerated by a factor of 2 or 3,[23] the values determined indicate degrees of polymerization of about 100 ($n = 6$) to 120 ($n = 5$). These values might translate to more realistic values of about 40 or 50, which are still very high for step polymerizations and indicate high conversions to high-molecular-weight polymers.

The several polymers prepared were examined by thermogravimetric analysis and their decomposition temperatures (T_D), identified as temperatures for 2% weight loss under nitrogen at a heating rate of 20 °C min^{-1}, are recorded in Table 1. On the basis of this conventional criterion, the results indicate that all samples were thermally stable to well over 400 °C. The observed values of T_D are much higher than those of other thermal decomposition temperatures of 324−364 °C and 280 °C that have been reported for poly(ethylene oxide),[24,25] but they are in accord with those for other segmented polyimides with poly-(ethylene oxide) sequences flanked by *N*-phenylphthalimide units.[7,10,20] Thus, poly(ethylene oxide) sequences with *N*-phenylphthalimide end groups clearly have enhanced thermal stability.

To identify their thermal-transition temperatures, all samples were examined by DSC and were repeatedly cycled at a scan rate of 10 °C min^{-1} for both heating and cooling. Each sample exhibited two endotherms on heating and two exotherms on cooling. After thermal treatment, all polymers were highly crystalline and, while it was not possible to determine their glass-

Scheme 1.

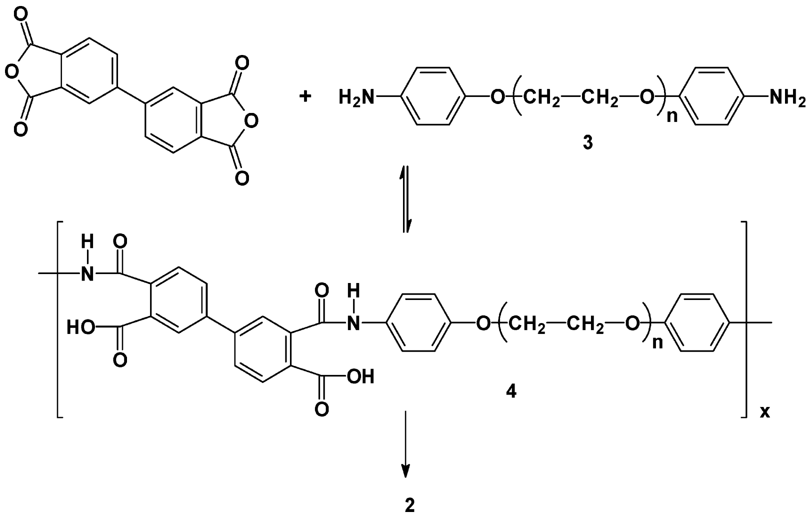


Table 1. Thermal Transitions Determined by DSC, TGA and DMTA

		sample			
	transition	**2a**	**2b**	**2c**	**2d**
DSC,[a] first cooling	$T_{\mathrm{i-lc}}$/°C	381	355	309	278
	$\Delta H_{\mathrm{i-lc}}$/J g^{-1}	n.d.	11.5	10.4	9.8
	$T_{\mathrm{lc-cr}}$/°C	306	245	215	219
	$\Delta H_{\mathrm{lc-cr}}$/J g^{-1}	33.5	22.7	20.9	20.9
DSC, second heating	$T_{\mathrm{cr-lc}}$/°C	352[b]	301[b]	256[b]	243
	$\Delta H_{\mathrm{cr-lc}}$/J g^{-1}	30.6	22.6	23.0	23.3
	$T_{\mathrm{lc-i}}$/°C	389	363	320	291
	$\Delta H_{\mathrm{lc-i}}$/J g^{-1}	~9	12.1	10.6	10.0
TGA	T_{D}/°C[c]	462	461	427	433
DMTA	tan δ_{max}	n.d.	n.d.	118	105

[a] Samples were heated to the following temperatures: **2a**, 400 °C; **2b**, 385 °C; **2c**, 360 °C; **2d**, 360 °C. [b] Complex peak; the temperature recorded corresponds to the highest peak. [c] Temperature corresponding to approximately 2% weight loss under nitrogen.

Table 2. Transition Temperatures Observed by Optical Microscopy

	transition			
sample	$T_{\mathrm{cr-lc}}$/°C	$T_{\mathrm{lc-i}}$/°C	$T_{\mathrm{i-lc}}$/°C	$T_{\mathrm{lc-cr}}$/°C
2c	230−275	324	312	220
2d	235	300	288	n.d.

transition temperatures by DSC, values of the temperatures for tan δ_{max}, an indicator for T_g obtained by DMTA, for samples **2c** and **2d** are recorded in Table 1.

For samples **2c** and **2d** cycling between 0 and 360 °C gave reproducible thermal-transition temperatures for both the endotherms and exotherms, as recorded in Table 1; for sample **2c**, the lower-temperature endotherm was a complex peak. However, for samples **2a**, **2b** it was necessary to scan to higher temperatures in order to observe the upper transitions on both heating and cooling; peaks for the lower endotherms were again complex. The transition temperatures recorded in Table 1 for sample **2b** were obtained by cycling to 385 °C and for sample **2a** to 400 °C. Even so, the upper endotherm for **2a** was not observed on first heating to 400 °C; the transition temperature recorded in Table 1 for **2a** was recorded on second heating. For both **2a** and **2b** repeated thermal cycling to 400 °C caused the transition temperatures for both endotherms and exotherms to decrease by about 15 and 20 °C per cycle, respectively. These results demonstrate that, although the decomposition temperatures for **2a** and **2b** determined by TGA for 2% weight loss (T_D in Table 1) are significantly higher than the maximum temperatures reached in DSC scans, there is sufficient slow degradation below 400 °C, on the time scales used, to affect the transition temperatures determined by DSC. The temperatures and enthalpies for the transitions in samples **2c** and **2d**, heated to a maximum of 360 °C, were reproducible and are considered reliable. DSC traces for these polymers **2c** and **2d** are shown in Figure 1 where it is seen that the transitions for **2d**, on both heating and cooling, are much sharper than those for **2c**.

The decrease in transition temperatures with increasing oxyethylene sequence length reflects the reduction in mesogen content which implies an increased flexibility of the macromolecular chain and parallels that observed for other segmented polyimides and polyesters with oxyethylene sequences.[12,17]

Optical microscopy was undertaken on equivalent samples to parallel the DSC studies. Although most solvent-cast films of the two polymers were initially amorphous, a minority of samples exhibited partial anisotropy. When examined by polarizing optical microscopy up to 400 °C, all polymers **2a**−**2d** were found to exhibit evidence for thermotropic liquid crystallinity between the upper and lower transition temperatures recorded in Table 1. In all cases, it was confirmed, from the appearance of the characteristic bâtonnets, that the liquid-crystalline phase was smectic A. Solvent-cast samples that were initially amorphous developed anisotropy on heating and liquid crystallinity above the temperatures of the lower endotherms. Thus, the transition temperatures and their associated transition enthalpies identified in Table 1 are indicated by the subscripts where cr refers to crystalline, lc to smectic A liquid-crystalline, and i to isotropic phases, respectively. However, slow thermal decomposition of samples **2a** and **2b,** at the high temperatures used to identify the clearing temperatures and formation of isotropic liquid states, caused instability in the field of view and compromised definitive characterization of their transition temperatures. No such problems were encountered with samples **2c** and **2d** when repeatedly cycled between room temperature and the isotropic liquid state, and the reproducible temperatures of the transitions between crystalline, liquid-crystalline, and isotropic liquid states are given in Table 2. It is with the further characterization of these two polymers that this communication is primarily concerned.

On first heating, in the DSC instrument, neither amorphous sample showed cold crystallization at temperatures above their estimated T_gs, but did show endothermic transitions at the higher temperatures recorded in Table 2. Correlation with optical microscopy (see below) identified this transition as liquid crystal

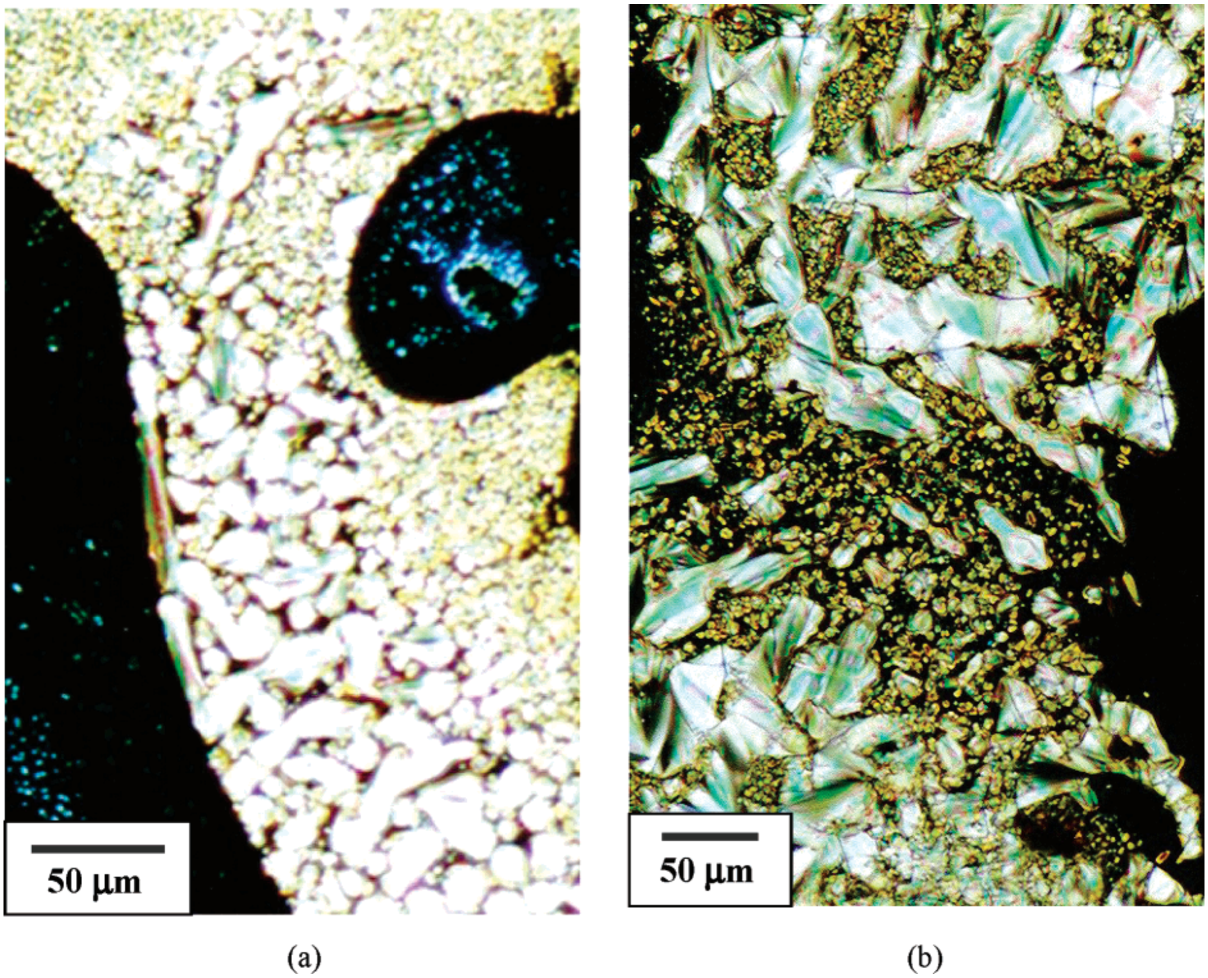


Figure 2. Optical micrographs of polymers (a) **2c** and (b) **2d**.

to isotropic liquid ($T_{\text{lc-i}}$). Since the initial samples were amorphous, the order responsible for these transitions developed too slowly to give identifiable signals by DSC. A sample of **2d** that exhibited some initial anisotropy gave a small transition corresponding to the lower transition recorded in Table 2 and subsequently attributed to the crystal to liquid crystal transition ($T_{\text{cr-lc}}$).

For both **2c** and **2d**, the development of the liquid-crystalline state from the isotropic liquid on cooling was slow. For sample **2c**, the transition from isotropic liquid to liquid crystal started to occur at 286 °C. On continuous cooling from above 300 °C, **2c** exhibited very small features arising from a liquid-crystalline phase at 290 °C. To develop and identify the liquid-crystalline phases, samples of each polymer were cooled from above 300 °C in stages. Thus, polymer **2c**, on third cooling, exhibited some birefringence at 286 °C and after 10 min at that temperature bâtonnets were recognizable. Decreasing the temperature by intervals of 5 °C the same texture persisted and improved over a period of 2.5 h, Figure 2a. Similarly, bâtonnets were seen to develop at 290 °C in a sample of **2d** and developed further during stepwise cooling to 270 °C, Figure 2b. Further cooling of the partially liquid-crystalline samples to temperatures below the lower exotherm caused the samples to develop crystalline phases around the frozen liquid-crystalline phase. Thus, both samples exhibited enantiotropic smectic behavior over a wide temperature range, over 50 °C in each case.

Additional information on the natures of **2c** and **2d** was obtained by SAXS measurements made during repeated heating and cooling cycles. Thus, parts a and b of Figure 3 illustrate the scattering patterns from **2c** and **2d**, respectively, for similar sequences of heating and cooling. Figure 3a shows a double peak from partial crystallinity and frozen liquid crystallinity in an initial solvent-cast sample of **2c** that is transformed gradually into the liquid-crystalline phase. This is indicated by the transformation of the double peak into the single sharp peak on heating at 20 °C min^{-1}. Sample **2d** showed no initial order (Figure 3b) and very little development of order until just before crystal melting. The initially broad peak gradually grows and sharpens into a narrow peak indicative of the liquid-crystalline phase. The gradual development of the sharp peaks of the liquid-crystalline phases, on cooling from the isotropic liquid, is consistent with the gradual development of the liquid-crystalline morphology observed by optical microscopy. Figure 3 clearly shows the lack of order in the isotropic liquid phases above the clearing temperatures for both polymers. On cooling, also at 20 °C min^{-1}, it is seen that both samples gradually develop liquid crystallinity as the relevant peaks grow. In both cases there are sharp transitions, with a small degree of coexistence of both phases on cooling. Figure 3 further demonstrates the stability of the samples and reproducibility of the transition behavior on repeated heating and cooling cycles. Repeat distances d for both liquid-crystalline (d_{lc}/Å) and crystalline phases (d_{cr}/Å) were calculated and are presented in Table 3.

The sharp peaks of the liquid-crystalline phases indicate that all repeat units within each sample adopt identical lengths. The broad SAXS peaks at lower temperatures show that there is considerable strain within the lamellar stacks; this is corroborated by the small sizes of crystals observed by optical

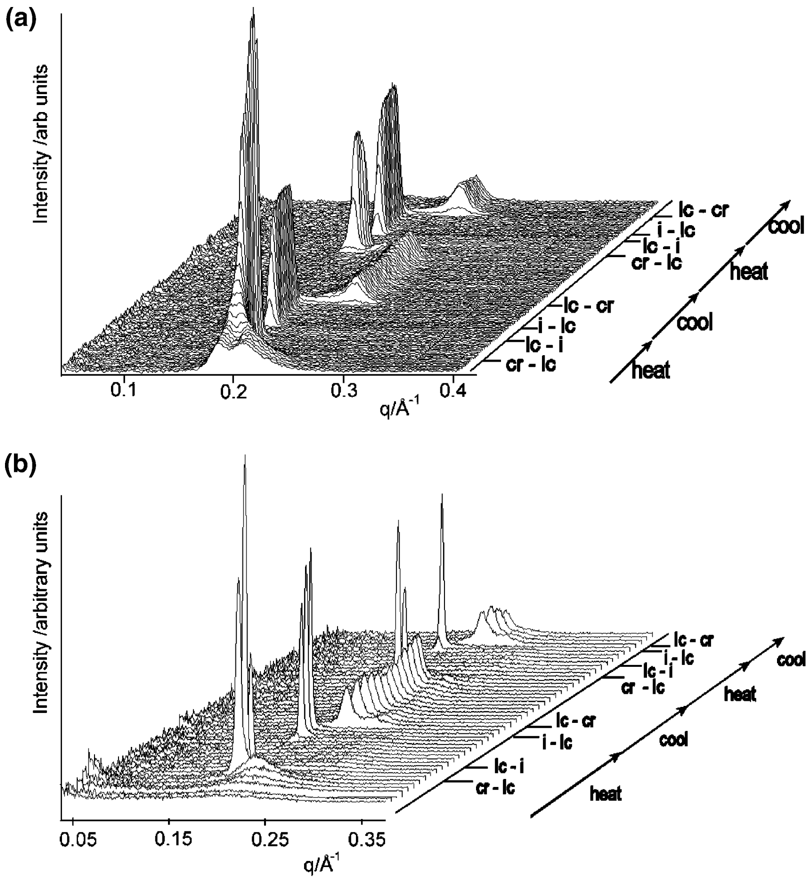


Figure 3. SAXS patterns for samples (a) **2c** and (b) **2d** during heating and cooling cycles.

Table 3. *d*-Spacings Determined by Small-angle X-ray Scattering

sample	d_{lc}/Å	d_{cr}/Å
2c	34	26.3
2d	35	29.8

microscopy and located between the bâtonnets of the frozen liquid-crystalline phases. No discernible peaks were observed in the WAXS signals, but it must be stated that the detector then available was not ideal for this experiment.

The *d*-spacings measured (Table 3) are consistent with the formation of layered structures for both samples. However, it is necessary to consider how to accommodate the repeat units within these dimensions. The observed dimensions are too short for fully extended structures. The bis(*N*-phenylphthalimide) unit itself has a length of 22 Å and the EO sequences have very similar dimensions of approximately 22 Å. There is also a large disparity between the cross-sectional areas of the phthalimide units and EO chains in the all-trans conformations that would make packing of extended units inefficient. Therefore, EO sequences must be coiled to some extent. This conclusion is consistent with the difference in *d*-spacing between **2c** and **2d**, which is less than that of an EO unit in the all-trans conformation. Therefore, the EO sequences must have a high content of gauche conformations. Flory calculated that poly(ethylene oxide) chains will adopt a high proportion of gauche conformations,[26] and Chiellini and Laus attributed their reduced tendency to support the formation of liquid crystalline phases, compared with polymethylene sequences, to their higher tendency to adopt gauche conformations.[16] Even when highly coiled, space-filling molecular models show that the sums of the lengths of the aromatic and aliphatic units, in a linear arrangement, as depicted in Figure 4A, are greater than the repeat distances observed for each sample. To be consistent with the observation of smectic A structures for the liquid-crystalline phases, the directors of the aromatic units, parallel to the long-axis of the bis(*N*-phenylphthalimide) units, must be perpendicular to the planes of those units, i.e., parallel to the *c*-axis, Figure 4. Thus, to be accommodated within the observed repeat distances the EO sequences must be tilted out of the planes of the aromatic units. Therefore, it is concluded that the poly(ethylene oxide) blocks must be at an angle to the direction of the aromatic units and

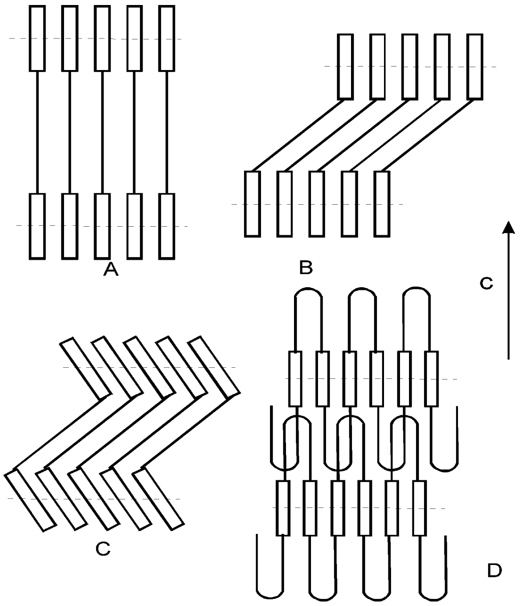


Figure 4. Schematic representation of morphologies of polyimide repeat units. Aromatic units are represented as rectangles and ethylene oxide sequences as continuous lines. *d*-Spacings are indicated by the vertical distances between broken lines.

the *c*-axis, as depicted in Figure 4B. Even in this arrangement, the EO sequences must be highly coiled to be accommodated within the observed *d*-spacings and to fill space. The temperatures corresponding to stable liquid-crystalline phases here (200−300 °C) are well above the crystal melting temperature of poly(ethylene oxide) (about 50 °C), below which the chains adopt a 7/2 helical conformation. Thus, the chains in the liquid-crystalline phases observed here must adopt some other irregular combination of trans and gauche conformations. Kricheldorf also concluded that aliphatic units in segmented polyimides with alkane sequences were primarily in gauche conformations in the liquid-crystalline phase.[18]

On cooling from the liquid-crystalline to crystalline phases, there are further reductions in *d*-spacings. From models, it seems impossible to accommodate this reduction by further coiling and shortening of the ethylene oxide sequences. We therefore suggest that this transition is associated with tilting of the aromatic units to some angle with respect to their plane, as depicted in Figure 4C; models suggest that actual repeat units can then be accommodated within the observed *d*-spacings. This transition thus removes the aromatic units from an arrangement consistent with a smectic A structure into one akin to smectic C, although the polymer here is in a rigid crystalline phase. There are no data available to us which precludes the transitional change from smectic A to smectic C liquid-crystalline phases during the rapid transition from mobile liquid crystalline to rigid crystalline phases, or vice versa. Demus and Richter reported an example of a transition from smectic A to smectic C on cooling di-*n*-dodecyl-4,4′ azoxycinnamate.[27] However, the enthlapies associated with the transition from smectic A to smectic C are normally lower than 1 kJ mol^{-1},[28] and the transient formation of a smectic C phase may have been undetectable. The "crystalline" state here refers to rigid anisotropic phases. It is unlikely that the short ethylene oxide sequences can crystallize into 7/2 helices and they probably retain a series of largely gauche conformations. Thus, the "crystalline" phase may be more like a frozen smectic C liquid-crystalline phase with some irregular stacking within the layers. Consistent with this view is the lack of any crystalline reflections observable by WAXS. The tilted arrangement of aromatic units, as depicted in Figure 4C, allows the terminal phenylene rings of the bis(*N*-phenylphthalimide) units to overlap with the phthalimide groups and hence develop the charge-transfer interactions considered responsible for the strong yellow color of many polyimides to develop;[29] these polymers have strong yellow colors in their crystalline states despite the low content of phthalimide units.

A further potential arrangement of aromatic and aliphatic units that should be considered is one in which the sequences of EO units, again in largely gauche conformations, are chain-folded, as in Figure 4D. Reasonable space-filling can be achieved if the poly(ethylene oxide) hair-pins interdigitate, as depicted. Molecular models indicate that this arrangement could be consistent with the *d*-spacings observed for the smectic A structures. The smaller spacings observed at lower temperatures could again be achieved by tilting the aromatic units with respect to the plane of their layers. In this arrangement the short EO sequences would not be able to adopt 7/2 helical conformations. We have no reason to suppose that this structure represents a dominant feature of these materials, but neither have we any evidence to preclude some proportion of the polymers adopting this form.

Initially, solvent-cast films of **2c** were amorphous but became anisotropic on heating to 125−130 °C and remained anisotropic on cooling, while solvent-cast samples of polymer **2d** were either amorphous initially or showed some initial anisotropy. In the former case anisotropy developed on heating to 245 °C and was retained on cooling. As mentioned previously, it was not possible to observe glass-transition temperatures for either polymer by DSC but these were estimated to be 118 and 105 °C, respectively, for **2c** and **2d** from DMTA measurements (tan $\delta_{\max}$); increasing the length of the aliphatic unit reduced the observed value of T_g, as would be expected.

Dielectric relaxation studies on the polymers, undertaken at low temperatures, showed the existence of two distinct relaxation processes that could be consistent with β-relaxations in the aromatic and aliphatic sequences, separately.[30] These, and other measurements of physical properties at ambient temperatures will be discussed in conjunction with data on a number of other polymers with related structures in a subsequent publication.

Conclusions

Polyimides with EO sequences in the diamine moiety are readily prepared from biphenyl dianhydride and diamines with terminal aminophenoxy units. Such polymers with three to six ethylene oxide units exhibit liquid crystallinity at elevated temperatures and rigid crystalline behavior at lower temperatures. However, the temperature regimes for liquid crystalline behavior for the polymers with sequences of three and four ethylene oxide units are close to the thermal decomposition temperatures. In contrast, the polymers with five or six ethylene oxide units exhibit liquid-crystalline phases stable over temperature ranges of 50 °C or more. The liquid crystalline morphology was smectic A in all cases. Enthalpies of transition between the crystalline and liquid-crystalline phases and liquid crystalline and isotropic liquid phases were determined. The former were on the order of 20 J g^{-1} and the latter were 10 J g^{-1}.

SAXS experiments established that the polymers with five or six EO units adopt layered morphologies and their *d*-spacings were determined. It was concluded that in order to accommodate the polymer repeat units within the observed *d*-spacings the EO sequences must be in a coiled conformation. It was further concluded that in order to achieve the decrease in *d*-spacing on cooling from the liquid crystalline to the crystalline phase the aromatic bis(*N*-phenylphthalimide) units must tilt from their orientation perpendicular to their layers, possibly and rapidly passing through an intermediate smectic C structure.

The several observations establish that it is possible to prepare segmented polyimides containing oxyethylene sequences that exhibit liquid crystalline phases at elevated temperatures of about 300 °C and which are stable over a temperature range of about 70 °C.

Acknowledgment. The authors wish to thank EPSRC for funds enabling this work to be carried out. We would also like to thank the Daresbury Synchrotron Source for their kind provision of beam time.

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MA071665P