Polymer Bulletin 45, 253–258 (2000)

Polymer Bulletin

Phase behavior of poly (pyromellitimide)s having flexible (*n*-alkyloxy)methyl side chains

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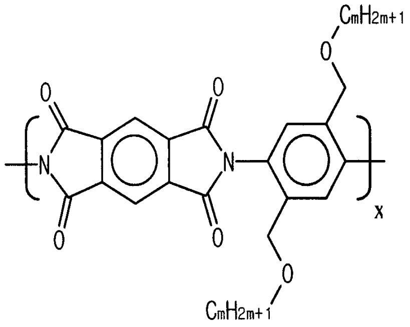
Received: 7 July 2000/Accepted: 22 September 2000

Summary

Phase behavior of poly(pyromellitimide)s having (*n*-alkyloxy)methyl side chains ($-CH_2OC_mH_{2m+1}$, m=4, 6, 8) has been studied by wide angle X-ray scattering, differential scanning calorimetry and ^{13}C solid-state NMR. While there are no observable transitions in the polymers bearing short side chain(m=4, 6), there is one transition in the polymer bearing the longest side chain(m=8), which is assigned to mesophase-mesophase transition. All the samples show layered mesophase at room temperature, in which the side chains are amorphous but the main chains form two-dimensional crystals in each layer. In the polymer bearing the longest side chain(m=8), it shows another layered mesophase at high temperature. In the high temperature mesophase, the main chains do not form two-dimensional crystals in each layer; only the lateral packing of the main chains remains undisrupted.

Introduction

There has been steadily growing interest in rigid-rod polymers having flexible side chains, since these polymers exhibit excellent solubility and fusibility combined with their high mechanical and thermal properties and unique layer-type packing structures[1-12]. The layered structures are characterized by a lateral packing of the rigid aromatic main chains into layers, with aliphatic side chains occupying the space between the layers. It has been postulated that the driving force for the adoption of such a structure is a type of microphase separation of the aliphatic and aromatic domains.



C_m-PY-PI (m = 4, 6, 8)

In a recent paper[13], Jung et al. have reported synthesis and properties of poly(pyromellitimide)s having (*n*-alkyloxy)methyl side chains with various lengths(C_m-PY-PIs). They were prepared by condensation of pyromellitic dianhydride with bis[(*n*-alkyloxy)methyl]-substituted, imidazole-blocked benzenediisocyanates. It was found that they form a layered structure at room temperature. While there are no observable transitions in the polymers bearing short side chain(m=4, 6), there is one transition in the polymer bearing the longest side chain(m=8). In the present work, we report the phase behavior of these polymers in detail, mainly based on X-ray and solid-state NMR studies.

Experimental

X-ray reflections(2° < 2θ < 35°) were measured by a Rigaku Denki X-ray generator in transmission mode using Cu-Kα radiation and a graphite monochromator installed in front of the counter. *In situ* X-ray measurements at various temperatures were achieved using an electric heating stage. Differential scanning calorimetry(DSC) measurements were performed on a Perkin Elmer DSC7 calorimeter at a constant heating rate 20°C/min under nitrogen atmosphere. Densities were determined from floating method using mixtures of THF and CCl_4.

For the study of the side chain conformation solid-state NMR was employed. ^{13}C MAS NMR spectra were recorded on a Bruker DPX-300 NMR spectrometer operating at 75.4 MHz with cross polarization-magic angle spinning(CP-MAS) accessory. Samples were contained in a cylindrical rotor made of zirconia and spun at speeds up to 4.1 kHz. The contact time was 3 ms, and the repetition time was 5 s. The ^{13}C chemical shifts were calibrated indirectly with adamantane as the external standard(29.5 ppm relative to tetramethylsilane).

Results and discussion

Phase behavior

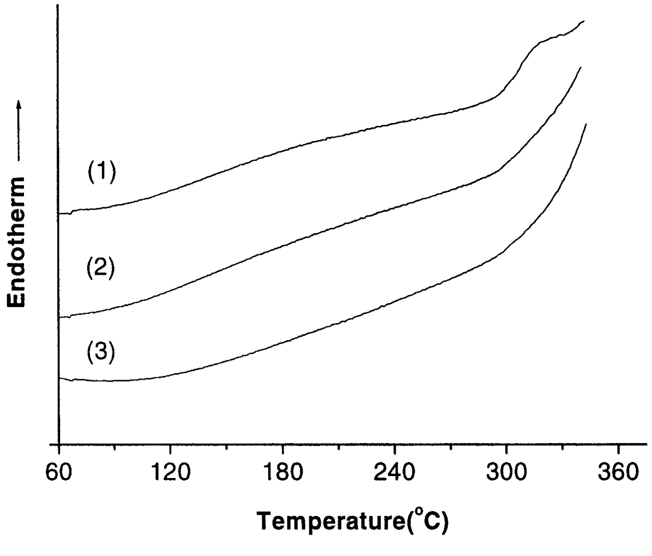


Figure 1. DSC thermograms of C_m-PY-PIs on heating. (1) C_8-PY-PI (2) C_6-PY-PI (3) C_4-PY-PI

Phase transitions of C_m-PY-PIs are investigated by DSC and their DSC thermograms are reproduced in Figure 1. It shows that in all three thermograms scanned up to 350°C only one phase transition is noticed from C_8-PY-PI at 315°C. This is mesophase-mesophase transition($T_{meso-meso}$), which is supported by X-ray and NMR studies discussed below. In C_6-PY-PI and C_4-PY-PI no transition ascribable to $T_{meso-meso}$ was observed. In these two polymers the side chain content is too low to lower their $T_{meso-meso}$s down to the measurable range.

Figure 2 displays X-ray diffractograms taken from powder C_m-PY-PIs at room temperature, which indicates that these polymers display a layered structure. As described in the previous paper[13], the smallest-angle peak(designated as A) with its 2nd order

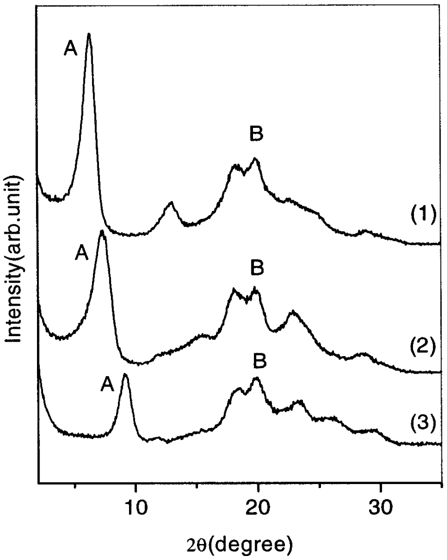


Figure 2. X-ray diffractograms of C_m-PY-PIs taken at room temperature.
(1) C_8-PY-PI (2) C_6-PY-PI (3) C_4-PY-PI

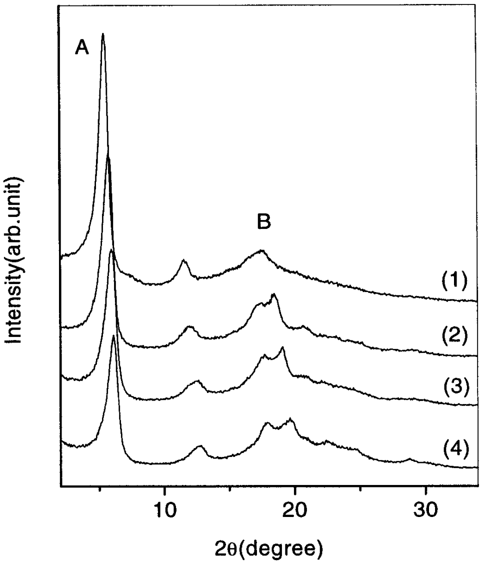


Figure 3. X-ray diffractograms of C_8-PY-PI taken at different temperatures.
(1) 330°C (2) 230°C (3) 130°C (4) 25°C

which shifts to smaller angles with increasing side chain length arise from the layer spacings between the main chain layers. On the other hand, the densities of C_8-, C_6- and C_4-PY-PIs at room temperature were measured to be 1.17, 1.20 and 1.29g/cm^3, respectively. From the measured densities, together with the length of the repeating unit(12.3 Å)[14] and the measured layer spacings(13.9, 12.1 and 9.7 Å for C_8-, C_6- and C_4-PY-PIs, respectively), the lateral spacing of the main chains is calculated to be 4.8 Å. This suggests that the reflections(designated as B) at about $2\theta = 20°$ corresponding to 4.5 Å spacing originate from a regular lateral packing of the main chains. The NMR studies discussed below indicates that the side chains are amorphous. Thus these polymers form layered mesophase, in which the side chains are amorphous but the main chains form two-dimensional crystals in each layer. The positional correlation between adjacent layers is not maintained because the side chains are amorphous. Up to now, a determination of the mesophase structure has not been successful due to insufficient number of reflections for structure analysis. Additional studies are planned to determine the mesophase structure.

To investigate structural changes taking place at the transitions shown in the DSC thermograms, X-ray diffractograms for powders were measured at temperatures corresponding to the different phase regions. Figure 3 shows X-ray diffractograms of C_8-PY-PI taken at different temperatures. After passing the mesophase-mesophase transition, there are drastic changes in the X-ray diffractograms. Compared to the low temperature mesophase, the X-ray pattern for the high temperature mesophase is greatly simplified and exhibits only a few reflections. Many wide-angle reflections disappear and form a broad halo typical for a liquid. However, the reflection B superposed on the halo and the reflection A with its second order are still present. This demonstrates clearly that the layered structure and the lateral packing of the main chains in each layer still remain undisrupted.

Figure 4 shows X-ray diffractograms of C_6-PY-PI taken at different temperatures. Since C_4-PY-PI showed similar features to C_6-PY-PI, only the X-ray diffractogram of the latter

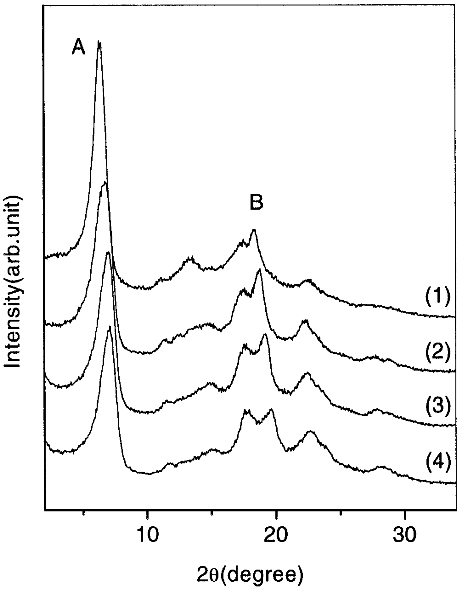


Figure 4. X-ray diffractograms of C_6-PY-PI taken at different temperatures. (1) 330°C (2) 230°C (3) 130°C (4) 25°C

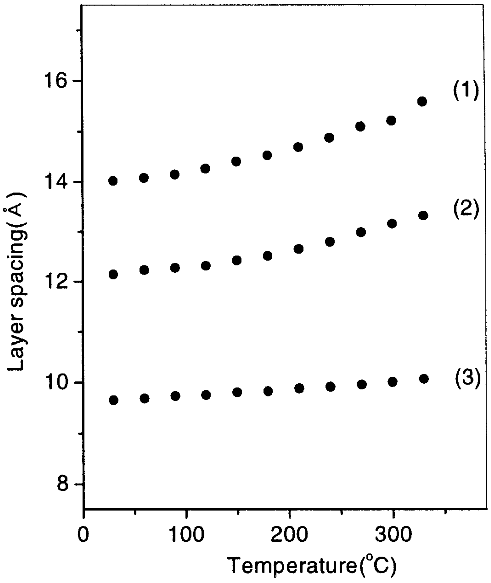


Figure 5. Temperature dependence of the layer spacing of C_m-PY-PIs. The layer spacings were measured by WAXS.

is reproduced as a representative example. Up to 330°C, there is little change in the X-ray diffractograms, which is consistent with DSC result which shows no transition up to 350°C.

In our previous study of related polyazomethine system[15], it was found that the layer spacing jumps suddenly at crystal-mesophase transition because of a sudden volume increase resulting from the melting of the side chain crystal. In this polyimide system, however, there will be no layer spacing jumps at the mesophase-mesophase transition since the side chains are amorphous both in low and high temperature mesophase. To observe the effect of the mesophse-mesophase transition on the layer spacing in C_m-PY-PIs, temperature dependence of layer spacing was measured, as shown in Figure 5. In the case of C_4-PY-PI and C_6-PY-PI, there is no substantial change in layer spacing except a small increase resulting from thermal expansion, which is consistent with DSC results. Despite of the mesophase-mesophase transition, however, C_8-PY-PI shows no substantial change in layer spacing. This result confirms that the side chains are disordered both in low and high temperature mesophase.

Side chain conformation

To investigate the side chain conformation of C_m-PY-PIs, solid-state NMR was employed. In order to ease the discussion on the side chain conformation, it was also employed on polyazomethine(C_m-PAMs)[15] and polybenzophenoneimide(C_m-BP-PIs) systems[16]. Since the side chains of C_m-PAMs are crystalline and those of C_m-BP-PIs amorphous, they are useful to determine whether the side chains of C_m-PY-PIs are crystalline or amorphous. Figure 6 shows the representative ^{13}C CP/MAS NMR spectra of C_8-PY-PI at room temperature, along with those of C_8-PAM and C_8-BP-PI for comparison. Since the NMR spectra of each series showed similar features independent of the side chain length, only those of m=8 are reproduced as representative examples The observed chemical shifts are summarized in Table 1. The assignment of *n*-alkyl peaks for the NMR spectra is performed by reference data on *n*-alkanes, cyclic alkanes, polyethylene[17-22], and analogue side chains in rigid-rod polymers[9, 23-27]. According to the reference data on analogue side chains in rigid-rod polymers(see Table 2), the CH_2 carbons in gauche containing conformations appear at higher field by 2-3 ppm than those in trans conformations.

Clearly, most of the side chains of C_8-PAM have all-trans conformations, which indicates that the side chains of C_8-PAM are crystalline. Most of the side chains of C_8-BP-PI have gauche containing conformations, which indicates that the side chains of C_8-BP-PI are amorphous. Most of the side chains of C_8-PY-PI have gauche containing conformations, which indicates that the side chains of C_8-PY-PI are amorphous.

In conclusion, phase behavior of poly(pyromellitimide)s having flexible side chains has been investigated. While there is only one type of layered mesophase in the polymers bearing short side chain(m=4, 6), there are two types of layered mesophases in the polymer bearing the longest side chain(m=8) depending on temperature. In the low temperature layered mesophase, the side chains are amorphous but the main chains form two-dimensional crystals in each layer. In the high temperature layered mesophase, only the lateral packing of the main chains is maintained undisrupted.

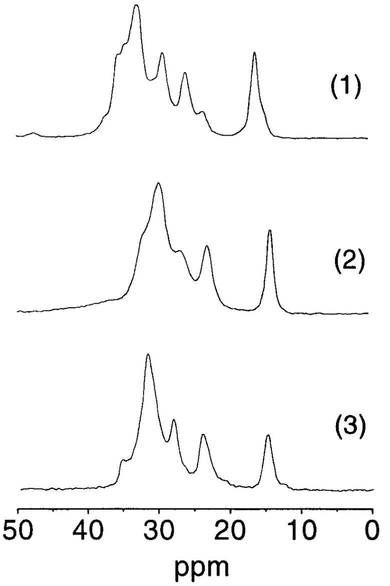


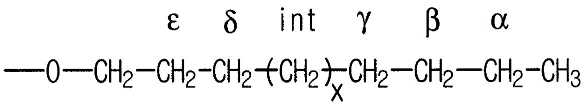
Figure 6. ^{13}C CP-MAS-NMR spectra at room temperature.
(1) C_8-PAM (2) C_8-BP-PI
(3) C_8-PY-PI

Table 1. Observed ^{13}C NMR chemical shifts for the aliphatic carbons of C_8-PAM, C_8-BP-PI and C_8-PY-PI. The side chain carbon atoms are labelled from 1 to 8 beginning with the methylene carbon atom connected to the oxygen atom. t and g denote trans and gauche containing conformations.

Code	2 (ε-CH_2)		3 (δ-CH_2)		4 (int-CH_2)		5 (γ-CH_2)		6 (β-CH_2)		7 (α-CH_2)		8 (CH_3)	
	t	g	t	g	t	g	t	g	t	g	t	g	t	g
C_8-PAM	33.1		29.4		33.1		33.1		?		26.1	23.7	16.4	
C_8-BP-PI		30.1		27.0		30.1		30.1	?			23.2		14.4
C_8-PY-PI		31.2		27.7		31.2		31.2	35.2			23.6		14.6

Table 2. ^{13}C NMR Chemical shifts for analogue side chains in rigid-rod polymers [9, 23-27]. t and g denote trans and gauche containing conformations.

Carbon	t	g
ε-CH_2	32-34	30-31
δ-CH_2	28-30	26-28
int-CH_2	32-34	30-31
γ-CH_2	32-34	30-31
β-CH_2	34-36	32-33
α-CH_2	25-26	23-24
CH_3	16-17	14-15



$$-O-CH_2-CH_2-CH_2-(CH_2)_x-CH_2-CH_2-CH_2-CH_3$$

Acknowledgements. This work was supported in part by the Center for Advanced Functional Polymers.

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