

## Phase behaviour of poly(benzophenoneimide)s having *n*-alkyloxymethyl side chains

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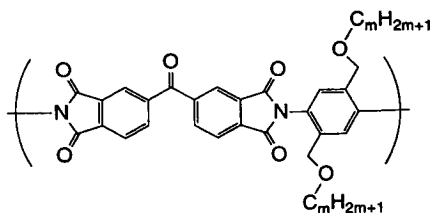
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### Summary

A series of poly(benzophenoneimide)s ( $C_m$ -BP-PIs) having *n*-alkyloxymethyl side chains ( $-\text{CH}_2\text{O}-n-\text{C}_m\text{H}_{2m+1}$ ,  $m=4, 6, 8$ ) have been examined by X-ray diffraction, differential scanning calorimetry (DSC) and polarizing optical microscopy. The samples showed basically two phase transitions and both transition temperatures decreased with increasing side chain length. The first transitions were ascribed to glass transitions and the second ones were assigned to liquid crystal-to-isotropic transitions. Eicosane ( $n-\text{C}_{20}\text{H}_{42}$ ) which is chemically very similar to the side chain was miscible with the side chains of  $C_8$ -BP-PI, which induced depression of the glass transition temperature.

### Introduction

In a number of recent publications it has been shown that appendance of flexible side chains greatly enhances solubility and fusibility of rigid-rod polymers and these rigid-rod polymers generally have layered structures to lower their energies by reducing the density of contacts between main chains and side chains (1-10). The layered structures are characterized by a segregated structure in which parallel stacks of polymer main chains are separated by regions filled by the flexible side chains. The flexible side chains act as a bound solvent or an internal plasticizer for the rigid main chain. The phase behaviour of these rigid-rod polymers is mainly governed by the strong segregation of main chain domain from side chain domain, being analogous to the microphase separation of block copolymers.



$C_m$ -BP-PI ( $m=4, 6, 8$ )

In a recent paper (11), Jung et al. have reported synthesis and properties of poly(benzophenoneimide)s having (*n*-alkyloxy)methyl side chains with various lengths ( $C_m$ -BP-PIs). They were prepared by condensation of imidazole-blocked 2,5-bis(*n*-alkyloxy-

methyl)-1,4-benzene diisocyanates with 3,3',4,4'-benzo-phenonetetracarboxylic dianhydride. In the present study, we report the phase behaviour of these polymers in detail.

### Experimental

X-ray reflections ( $2^\circ < 2\theta < 30^\circ$ ) were measured by a Rigaku Denki X-ray generator in transmission mode using Cu-K $\alpha$  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. Polarizing microscopic pictures were taken with Zeiss MC 100 microscope. As-polymerized powders of C<sub>m</sub>-BP-PIs were annealed at temperatures above glass transitions and then slowly cooled down to room temperature *in vacuo* before measurements.

### Results and discussion

Phase transitions of C<sub>m</sub>-BP-PIs are measured by DSC and their DSC thermograms are reproduced in Figure 1. C<sub>m</sub>-BP-PIs show basically two phase transitions and their transition temperatures are summarized in Table 1. The first transitions observed in all samples are glass transitions ( $T_g$ ) whose temperature decreases as side chain becomes longer like well-mixed polymer blends. The depression of  $T_g$  with increasing side chain length indicates that side chains act on main chains as a bound solvent or an internal plasticizer. Polarizing microscopy showed that C<sub>6</sub>- and C<sub>8</sub>-BP-PI were shearable and birefringent between the two transitions. This result, together with X-ray investigations discussed below, demonstrates that these polymers have a liquid crystal phase. The second transitions observed only in C<sub>6</sub>- and C<sub>8</sub>-BP-PI are liquid crystal-to-isotropic transitions ( $T_i$ ), as confirmed by polarizing microscopy.  $T_i$  also decreases with

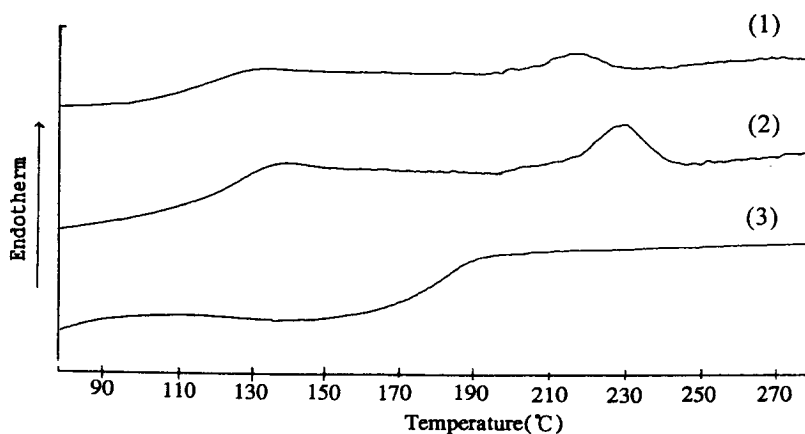


Figure 1. DSC thermograms of C<sub>m</sub>-BP-PIs (1) C<sub>8</sub>-BP-PI (2) C<sub>6</sub>-BP-PI (3) C<sub>4</sub>-BP-PI.

increasing side chain length for the same reason with  $T_g$ .  $C_4$ -BP-PI is believed to have such a low volume fraction of side chains that their action as internal plasticizer towards rigid backbones cannot lower the transition down to an observable range, whereas in other samples the volume fraction is sufficiently high.

Table 1. Phase transition temperatures of  $C_m$ -BP-PIs.

polymer code	$T_g(^{\circ}C)$	$T_i(^{\circ}C)$
$C_4$ -BP-PI	187	-
$C_6$ -BP-PI	131	231
$C_8$ -BP-PI	122	221

Figure 2 shows X-ray diffractograms of  $C_m$ -BP-PI at room temperature, which indicates that these polymers are not crystalline and do not display a well developed layered structure. Since unsubstituted BP-PI has a mesomorphic structure that consists of quasi-

helical chains exhibiting different individual conformations with different torsional angles(12), it will be difficult for  $C_m$ -BP-PIs to construct a well developed layered structure. Basically three diffuse peaks are observable, although it is difficult to resolve the peaks in the small-angle region in the case of  $C_4$ -BP-PI. Two diffuse peaks in the small-angle region shift to smaller angles as the side chain length increases. On the other hand, a diffuse peak in the wide-angle region practically remains at the same angle independent of the side chain length.

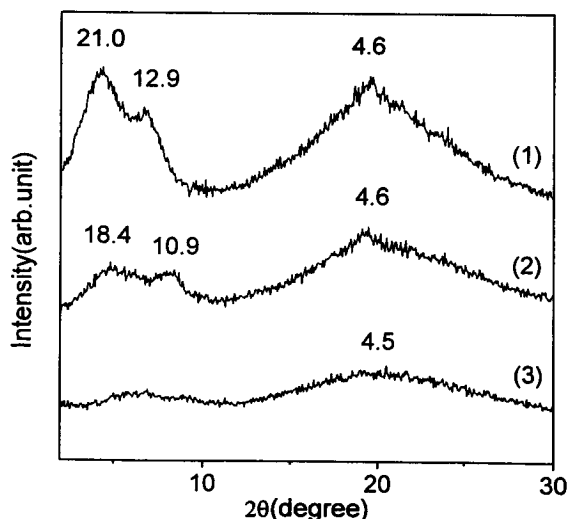


Figure 2. X-ray diffractograms of  $C_m$ -BP-PIs at room temperature. (1)  $C_8$ -BP-PI (2)  $C_6$ -BP-PI (3)  $C_4$ -BP-PI. The numerical values at the peaks denote the Bragg spacings in Angstrom unit.

To investigate structural changes taking place at the transition shown in the DSC thermograms (Figure 1), X-ray diffractograms were measured at temperatures corresponding to the different phase regions. Figure 3 shows X-ray diffractograms of  $C_8$ -BP-PI taken at different temperatures. Since  $C_6$ -BP-PI showed similar features to  $C_8$ -BP-PI, only the X-ray diffractogram of the latter is reproduced as a representative example. There is no change in the X-ray pattern taken at  $180^\circ\text{C}$ . But, there is a change in the X-ray pattern taken at  $240^\circ\text{C}$ . The higher angle peak in the small-angle region disappears after passing the liquid crystal-to-isotropic transition. This indicates that the higher angle peak in the small-angle region is originated from the liquid crystal phase and thus the lower angle one from the isotropic phase. Therefore it can be concluded that the two phases coexist below  $T_i$ . On the other hand,  $C_4$ -BP-PI exhibited no change in X-ray patterns up to  $300^\circ\text{C}$ , which is consistent with DSC and polarizing microscopic investigations.

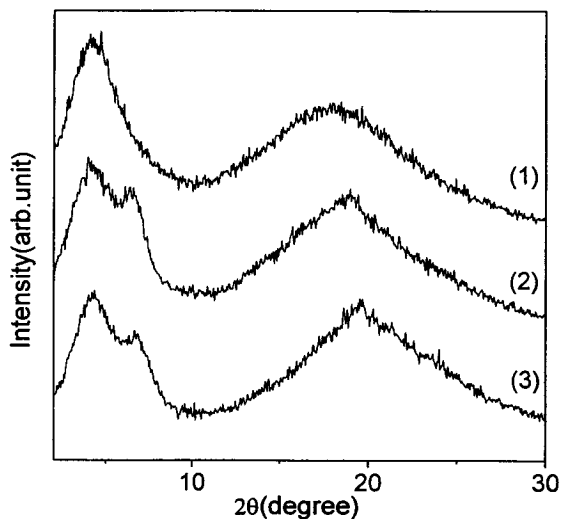


Figure 3. X-ray diffractograms of  $C_8$ -BP-PI taken at different temperatures. (1)  $240^\circ\text{C}$  (2)  $180^\circ\text{C}$  (3)  $25^\circ\text{C}$

With these X-ray data, a layered structure can be proposed for the liquid crystal phase in which the main chains form separate layers and the disordered side chains occupy the space between the main chain layers. The higher angle peak in the small-angle region can be attributed to the layer spacing between the main chain layers. The absence of its higher order peak indicates that the layered structure is not highly ordered. Each layer is formed by a disordered lateral packing of the main chains, as can be elucidated from the absence of a reflection characteristic of it. This may result from the quasi-helical conformations of the main chains. The peak in the wide-angle region can be attributed to the disordered side chains.

The density of  $C_8$ -BP-PI was measured to be  $1.18\text{g/cm}^3$  from the floating method using aqueous NaCl solutions at room temperature. Since  $C_8$ -BP-PI has both the liquid crystal and the isotropic phase at room temperature, the measured density must be less than the density of the liquid crystal phase. From the length of the repeating unit ( $17.25\text{\AA}$ ) (12) and the measured layer spacing ( $12.9\text{\AA}$ ), therefore, the average lateral spacing of the main chains is calculated to be less than  $4.3\text{\AA}$  for the layered structure.

Since side chains are amorphous, chemically analogous n-alkanes may be miscible with the side chains and may solubilize into the side chain region. To study the miscibility, an equal weight of  $n\text{-C}_{20}\text{H}_{42}$  (m.p.  $36^\circ\text{-}38^\circ\text{C}$ ) was added to the  $C_8$ -BP-PI and the blend was investigated by X-ray diffraction and DSC. The X-ray diffractograms of pure  $C_8$ -BP-PI and  $n\text{-C}_{20}\text{H}_{42}/C_8$ -BP-PI blend taken at  $180^\circ\text{C}$  are reproduced in Figure 4. The higher angle peak in the small-angle region shifts to smaller angle, which implies that  $n\text{-C}_{20}\text{H}_{42}$  could be solubilized into the side chain region of  $C_8$ -BP-PI in the liquid crystal phase and the layer spacing was increased. This result is consistent with the recent work of Kim et al. (13), which reported the solubilization behavior of n-alkanes into polyazomethines having n-alkyloxymethyl side chains. From the increment in layer spacing, the solubilization of 19 vol % of  $n\text{-C}_{20}\text{H}_{42}$  into  $C_8$ -BP-PI in the liquid crystal phase was calculated. In addition, the lower angle peak in the small-angle region also shifts to smaller angle, which implies that  $n\text{-C}_{20}\text{H}_{42}$  could also be mixed with the side chain of  $C_8$ -BP-PI in the isotropic phase and increased the average distance of the main chains. The DSC thermograms of pure  $C_8$ -BP-PI and  $n\text{-C}_{20}\text{H}_{42}/C_8$ -BP-PI blend are reproduced in Figure 5. This shows that  $T_g$  of the blend is  $5^\circ\text{C}$  lower

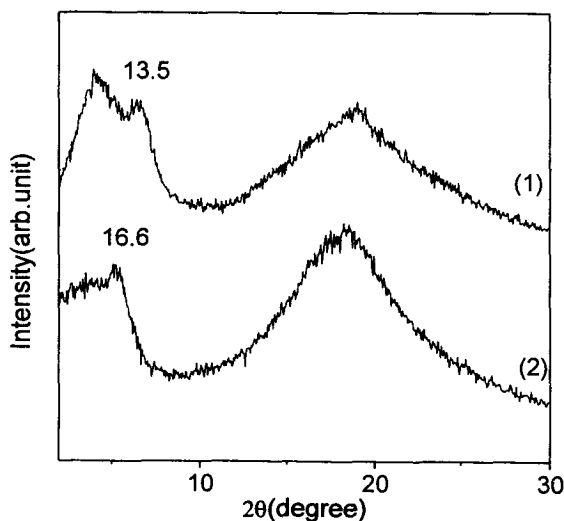


Figure 4. X-ray diffractograms of pure  $C_8$ -BP-PI(1) and  $n\text{-C}_{20}\text{H}_{42}/C_8$ -BP-PI blend(2) taken at  $180^\circ\text{C}$ . The numerical values at the peaks denote the Bragg spacings in Angstrom unit.

than that of the pure, which implies that  $n\text{-C}_{20}\text{H}_{42}$  mixed with the side chain acts as a plasticizer and hence depressed  $T_g$ . However, the change of  $T_i$  of the blend cannot be measured due to the vaporization of  $n\text{-C}_{20}\text{H}_{42}$ .

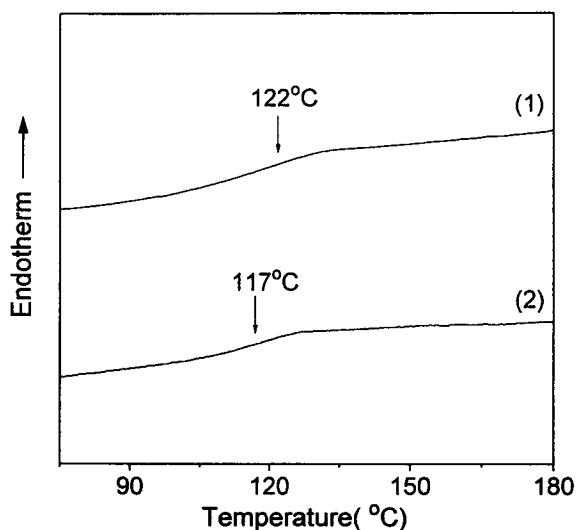


Figure 5. The DSC thermograms of pure  $\text{C}_8\text{-BP-PI}$ (1) and  $n\text{-C}_{20}\text{H}_{42}/\text{C}_8\text{-BP-PI}$  blend(2). The temperatures denote the glass transition temperatures.

#### **Acknowledgements**

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