

# Synthesis of Multi-Block Copolymer and Its Compatibilization to the Blends of Poly(ether ether ketone) with Thermotropic Liquid Crystalline Polymer

Yanhua Yang,<sup>1</sup> Wanchun Zhu,<sup>2</sup> Dong Jiang,<sup>1</sup> Rongtang Ma,<sup>1</sup> Zhenhua Jiang<sup>1</sup>

<sup>1</sup>Engineering Research Center of High Performance Plastics, Ministry of Education, Jilin University, Changchun, 130023, China

<sup>2</sup>Department of Physical Chemistry, College of Chemistry, Jilin University, Changchun, 130023, China

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**ABSTRACT:** A multiblock copolymer (BCP) containing amorphous poly(aryl ether ketone) (PAEK) and thermotropic liquid crystalline polymer (TLCP) segments was synthesized. The chemical structure and properties of BCP were characterized by fourier-transform infrared spectrometer (FTIR), differential scanning calorimeter (DSC), gel permeation chromatograms (GPC), thermogravimetry analysis, polar light microscope (PLM), and solubility test respectively. BCP can dissolve in chloroform because of soluble PAEK block bonded with TLCP block, which was insoluble. The peak of the original PAEK oligomer was no more present in the GPC traces of the block copolymer. These facts indicated that polymer synthesized should be copolymers of the two components rather than blends. A single  $T_g$  at 138.1°C and broad melting endotherm at 315.7°C can be observed. The liquid crystalline texture of BCP showed uniformity in the view after heat treated for 10 min above its  $T_m$

under PLM. Ternary blends of poly(ether ether ketone) (PEEK)/TLCP/BCP were prepared by extrusion and characterized by DSC. DSC results showed that the crystallization temperature of PEEK phase in the blends shifted higher with the addition of TLCP. Wide angle X-ray diffraction investigations indicated that the crystalline structure of PEEK was not disturbed by blending or compatibilizing. Scanning electron microscope and mechanical tests confirmed the compatibilizing effect of BCP. Reduction in dispersed phase TLCP size was observed when 2 phr by weight of compatibilizer was added to the blend. Measurement of the tensile properties showed increased elongation as well as improved modulus and strength to some extent. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 35–43, 2007

**Key words:** multiblock copolymer; poly(ether ether ketone); compatibility; interfacial adhesion

## INTRODUCTION

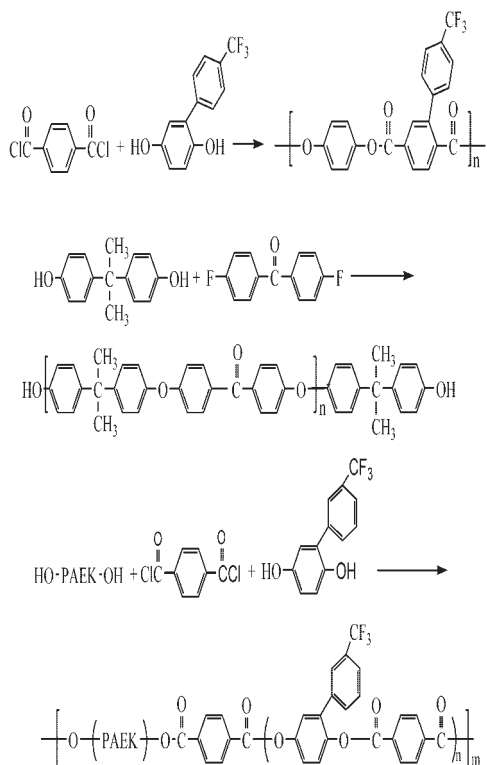
Blends of thermotropic liquid crystalline polymer with high-performance thermoplastics have attracted considerable attention in the past decades because of the academic and technical importance of the materials.<sup>1,2</sup> The addition of TLCP to a high-performance polymer can not only improve the processability for TLCP/thermoplastics blends, but also reinforce the mechanical properties due to the highly ordered fibrous structures of TLCP formed during melt flow. Both engineering thermoplastics and commodity resins have been reinforced using various TLCP. Most of the thermoplastics studied so far are incompatible and partially compatible with TLCP. This incompatibility between the matrix polymers and reinforcing TLCPs leads to poor interfacial adhesion. The reinforcing effect is less than that obtained from the miscible sys-

tem. Mechanical properties would be improved if the blends were miscible or compatible.

One of the ways to generate compatibility of the *in situ* composite is to add a third component as a compatibilizer.<sup>3–6</sup> Such ternary blends present an attractive approach to the development of reinforced systems. Compatibilizing agents are generally block or graft copolymers possessing segments with chemical structures or solubility parameters that are similar to those of the polymers being blended. In 1992, Noolandi<sup>7</sup> suggested that multiblock copolymers, which formed such a pancake structure at the interface between two incompatible homopolymers, would be more efficient as the compatibilizers than di- and triblock copolymers. Acting as polymeric surfactants, these multiblock copolymers reduce the interfacial tension, thus promoting interfacial adhesion, a finer dispersion, and more uniform distribution of the dispersed phase.

Thus, in this article, multiblock copolymer containing amorphous PAEK and TLCP segments was pre-

Correspondence to: Z. Jiang (yhyang@jlu.edu.cn).



**Scheme 1** Synthesis routes of TLCP, HO-PAEK-OH, and BCP.

pared to act as a compatibilizer to improve the interfacial characteristics between PEEK and TLCP phase. The morphology as well as mechanical properties of the blends after compatibilization was also investigated.

## EXPERIMENTAL

### Materials

Terephthaloyl dichloride (TPC) (CP) purchased from Shanghai Tingxin Chemical Factory was recrystallized from *n*-hexane, which was distilled after dehydrolysis by  $\text{CaH}_2$ . Benzophenone (CP) and bisphenol A (BPA) (CP) obtained from Beijing Chemical Factory and Tianjin Damao respectively were used as received. 2-(3'-Trifluoromethylphenyl) hydroquinone (TFHQ) (mp = 108°C) was prepared according to the procedure described by Wang et al.<sup>8</sup> 4,4'-Difluorobenzophenone (DF) and tetramethylene sulfone (TMS) were purified by distillation under reduced pressure. Other reagents and solvents were purified by common ways before use. Semicrystalline PEEK was supplied by JHPM Company (People's Republic of China).

### Synthesis of thermotropic liquid crystalline polyester

Poly(2-(3'-trifluoromethylphenyl) hydroquinone terephthalate)<sup>9</sup> was prepared by high temperature solution

polymerization. TFHQ (0.03 mol) and TPC (0.03 mol) were dissolved in 45 g of benzophenone. The solution was gradually heated to 180°C for 1 h, 220°C for 1 h and 250°C for 10 h under nitrogen atmosphere. The gel-like reaction mixture was diluted with benzophenone and precipitated into methanol. After extraction with methanol, the polyester was dried (99.5% yield). Hereafter, this polymer is referred to as simply TLCP. The inherent viscosity, measured in 50/50 (w/w) *p*-chlorophenol/tetrachloroethane solution ( $T = 25^\circ\text{C}$ ,  $c = 0.2 \text{ g/dL}$ ) with an Ubbelohde viscometer, was 1.2.

### Synthesis of hydroxy-terminated PAEK

0.3675 mol of BPA, 0.35 mol of DF, 0.39 mol of  $\text{K}_2\text{CO}_3$ , 300 mL of TMS, and 100 mL of toluene were added to 1000 mL flask and degassed repeatedly. The water was removed by azeotropic distillation through Dean-Stark trap. Toluene was distilled off not until the water was removed completely after 4 h. Then, the reaction mixture was heated to 220°C for 4 h. On cooling the mixture, it was precipitated into the slightly acidified (HCl) distilled water. Additional purification was performed by dissolution of the polymer in chloroform, filtration of the solution if necessary, and precipitation into methanol. The product was dried as a white solid in vacuum at 80°C (96.5% yield).  $\bar{M}_n$  (from GPC) = 7797,  $\bar{M}_w = 9358$ ,  $\bar{M}_w/\bar{M}_n = 1.2$ .

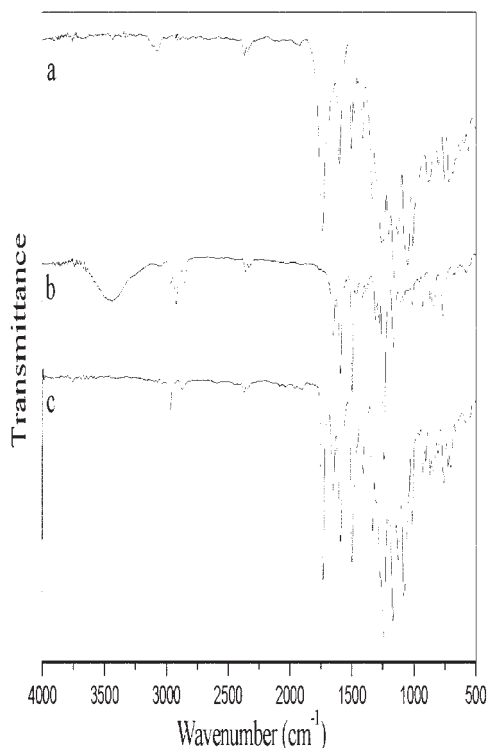
### Synthesis of block copolymer PAEK (7797)-*b*-TLCP (7499)

PAEK (7797)-*b*-TLCP (7499) is a block copolymer of PAEK, whose number-average molecular weight  $\bar{M}_n = 7797$  with TLCP, which should have  $\bar{M}_n = 7499$  according to the stoichiometry used.

TFHQ (9.5 mmol) and TPC (10 mmol) were added to a solution of 0.5 mmol PAEK (7797) in 22 g of benzophenone in 100 mL flask fitted with mechanical stirrer, thermometer, gas inlet, and dried tube under nitrogen atmosphere. The mixture was heated to 180°C for 2 h, 200°C for 36 h, and 250°C for 8 h with a constant flow of nitrogen to remove HCl completely. The reaction mixture was precipitated into methanol, extracted in a Soxhlet with methanol, and dried (86.6% yield).  $\bar{M}_n$  (from GPC) = 12,220,  $\bar{M}_w = 21,996$ ,  $\bar{M}_w/\bar{M}_n = 1.8$ . The synthesis routes of TLCP, hydroxy-terminated PAEK and BCP were listed in Scheme 1.

### Blend preparation

The polymers were dried in a vacuum oven at 120°C for 24 h before use. The blending was carried out using Haak PolyLab (length to diameter ratio of screw was 20) operating at a temperature region 280, 330, 330, 350, 355, and 350°C at 120 rpm. The compatibilized blends comprised an addition 2 phr of BCP.



**Figure 1** FTIR spectra of (a) TLCP, (b) HO-PAEK-OH, and (c) BCP.

PEEK was extruded under identical processing conditions to ensure the same heat history as those of blends, and was used as a reference. The blend samples were coded as PT1, PT2, PT3, PT4, PTc2, and PTc3 for the PEEK/TLCP compositions 98/2, 95/5, 90/10, 85/15, compatibilized 95/5, and 90/10 respectively.

### Measurement

The melting behavior and crystallization behaviors of the blends were investigated by means of a Mettler Toledo differential scanning calorimeter (DSC821<sup>o</sup>). Indium and zinc were used as the reference for the calibration of temperature and heat flow. The blend specimens for dynamic conditions were heated to 400°C and held for 5 min (and then quenched in air only for the synthesized sample measurement). The DSC heating and cooling traces were recorded at a scan rate of 10°C/min.

Wide angle X-ray diffraction (WAXD) investigations were carried out at room temperature with a compressed sheet, by SHIMADAZU XR-6000 type diffractometer, using Ni filtered Cu K $\alpha$  radiation. The diffraction scans were collected between 2 $\theta$  values of 5° and 40° using steps of 2°.

Polarizing optical microscopic examination was performed by using Leica DMLP microscope equipped with a Linkam TMS600 hotstage.

GPC investigations were performed by a Waters 410 instrument using for PAEK oligomer and BCP analysis tetrahydrofuran as an eluent at a flow rate of 1.00 mL/min. Molecular weights were calculated using polystyrene calibration standards.

To investigate the morphology of the blends, the specimens were fractured under cryogenic conditions using liquid nitrogen. The fracture surface was examined using scanning electron microscope (SEM). A SHIMADZU SSX-550 SEM was employed for this observation, before which the surfaces were coated with thin layers of gold to make them electrically conducting.

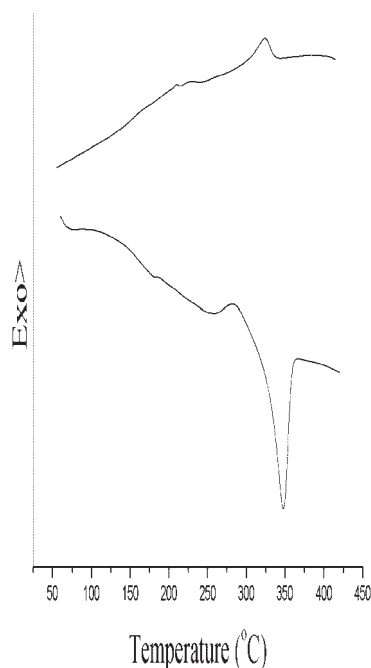
Tensile test specimens were dumbbell-shaped cut from the compressed sheet with effective dimensions 20 × 4 × 0.4 mm<sup>3</sup>. The tests were performed on a SHIMADZUAG-I20KN at room temperature, and a crosshead speed of 10 mm/min was used in all cases. Average values were obtained from at least five successive determinations. The data values of stress-strain curves were near to the average values.

A PE Pyris Diamond thermogravimetric analyzer was used to investigate the thermal stability of the blends. The samples (~3 mg) were heated under an air atmosphere from ambient temperature to 600°C and at a heating rate of 10°C/min in all cases.

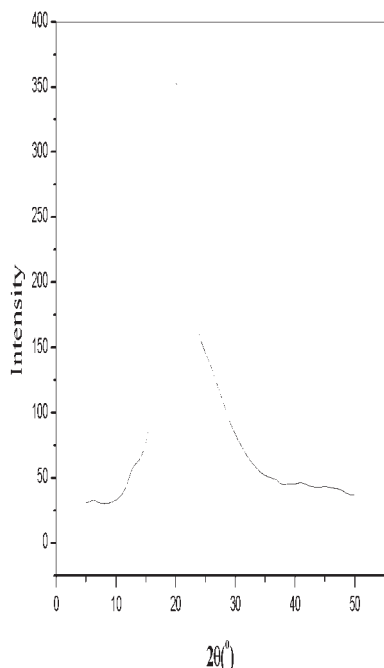
## RESULTS AND DISCUSSION

### Polymers synthesis and characterization

Poly(phenylene terephthalate) is an intractable material whose melting temperature reaches 600°C. By in-



**Figure 2** DSC thermograms of TLCP in the second heating and cooling cycle.



**Figure 3** WAXD diffractogram of TLCP.

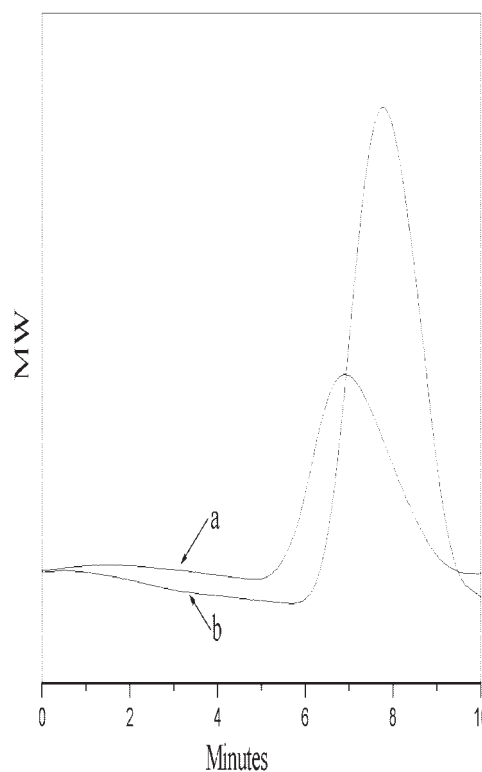
roducing trifluoromethylphenyl as substituent, the thermotropic materials were obtained and the melting point was lowered to satisfy the melt blend processing with PEEK. But, TLCP synthesized was not soluble in common organic solvents. The structure and properties of TLCP were characterized by means of FTIR, DSC, PLM, and DSC. FTIR results [Fig. 1(a)] showed the main characteristic absorptions at 1740, 1157, and 1259  $\text{cm}^{-1}$  attributed to ester group,  $\text{CF}_3$  group, and ether group respectively. From DSC curves shown in Figure 2, melting endotherm was observed at 348°C, which was corresponding to a crystalline to nematic phase transition, but  $T_i$  was not detected in both second heating and cooling cycles probably due to the detection limit in DSC. PLM was used to furthermore confirm the thermotropic liquid crystalline behavior. Upon heating to above the melting temperature, a texture typical for nematic liquid crystalline was observed by PLM [Fig. 6(a)] and can be readily preserved upon cooling.  $T_i$  was not observed until heating to 420°C. The WAXD diffraction of TLCP (Fig. 3) showed a dispersed peak at  $2\theta = 20^\circ$ . There existed a lateral order in chain direction because of uniaxial orientation of the mesogenic macromolecules in domains, which was typical for nematic liquid crystalline.

Block copolymers of PAEK-*block*-TLCP can be synthesized either from preformed blocks or by reacting PAEK block with a mixture of both TLCP ester monomers. The resulting structure should be practically the same. In this work, the latter was used. Therefore, hydroxy-terminated PAEK (HO-PAEK-OH) was synthesized at first by nucleophilic aromatic substitution

of DF with BPA. The molecular weight of HO-PAEK-OH was controlled by the ratio of BPA and DF. FTIR spectrum presented in Figure 1(b) shows the characteristic absorption peaks such as hydroxy, methyl, ketone, benzene ring, and ether groups. For comparison, acyl chloride terminated TLCP oligomer whose feed ratio of reacting monomers was the same as the BCP was prepared and used for the determination of  $T_g$ .  $T_g$  of PAEK and TLCP oligomer was determined at 121.3 and 155.8°C from DSC respectively. The blend of PAEK and TLCP oligomers was prepared in benzophenone for comparison.

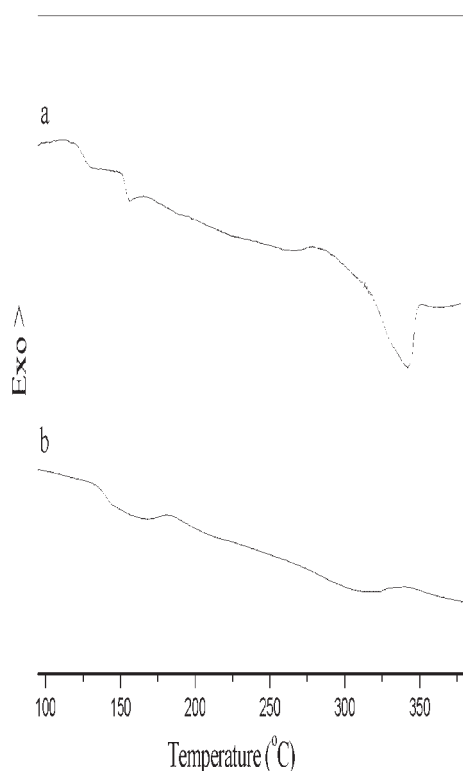
Owing to the insolubility of TLCP oligomer in common organic solvents, the method used for the chemical characterization was limited. The block copolymer can dissolve in chloroform because of soluble PAEK oligomer bonded with TLCP. So, it was confirmed that there did not exist unreacted TLCP oligomer in block copolymer.

The elution curve of block copolymer when compared with elution curve of the corresponding PAEK oligomers in Figure 4 confirmed a unimodal molecular weight distribution, i.e., homogeneous multiblock copolymer without residual oligomers. The increase in molecular weight was also shown by means of GPC curves. The peak of the original PAEK oligomer was no more present in the GPC traces of the block copolymer.



**Figure 4** GPC elution curves of (a) BCP when compared with the corresponding (b) PAEK oligomer.





**Figure 5** DSC curves of (a) blend of TLCP and PAEK oligomers and (b) BCP in the second heating cycle.

The thermal stability of the block copolymer was mainly determined by the PAEK block with a maximum weight loss at 514.5°C. A blend of PAEK and TLCP oligomer had a maximum weight loss at 465.7°C.

These facts indicated that samples prepared via the earlier method should be copolymers of the two components rather than blends.

FTIR spectrum of BCP presented in Figure 1(c) shows the characteristic absorptions at 2968 and 2870  $\text{cm}^{-1}$  assigned to methyl groups, at 1653  $\text{cm}^{-1}$  to the ketone group, 1734  $\text{cm}^{-1}$  to ester group, 1166  $\text{cm}^{-1}$  to  $\text{CF}_3$  group, and 1241  $\text{cm}^{-1}$  to ether group respectively.

From DSC curves shown in Figure 5(a), a single  $T_g$  at 138.1°C and broad melting endotherm at 315.7°C can be observed for PAEK (7797)-*b*-TLCP (7499). It

was found that the glass temperature of BCP lay between the ones of corresponding oligomers, which confirmed the good miscibility of two blocks in amorphous regions. The melting point of BCP decreased significantly because of the coupling of amorphous PAEK block with TLCP in comparison to TLCP oligomer's. A melting endotherm enthalpy also decreased, which was in agreement with the block copolymer of PSU with PET/HBA<sup>10</sup> and PEES with PEPPh.<sup>11</sup> Block formation resulted in an alternation of the glass transition and melting behavior. Alternations of the  $T_g$  of PAEK phase in the block copolymers referred to interaction between the different blocks, which were caused by their chemical coupling. In a simple blend of corresponding oligomers, melting endotherm enthalpy and melting point from DSC curves shown in Figure 5(b) decreased slightly in comparison with TLCP oligomer. Two  $T_g$ s were observed at 124.8°C and 153.4°C respectively, which were corresponding to the PAEK and TLCP oligomers because of the immiscibility of two oligomers. From above, it was concluded that the thermal behavior of blends was very different with the BCP's. The data is summarized in detail in Table I.

The liquid crystalline textures of blends and BCP are shown in Figures 6(b) and 6(c) respectively. BCP showed uniformity in the view under PLM. The distinct phase separation in BCP was not seen after heat treated above its  $T_m$  for 10 min. But the phase separation took place after heat treated above TLCP's  $T_m$  for 10 min for the blend of TLCP and PAEK oligomers. The phenomenon observed was in agreement with the results from DSC earlier. Compared to the BCP's liquid crystalline texture, the texture of the blend was very similar to the TLCP's.

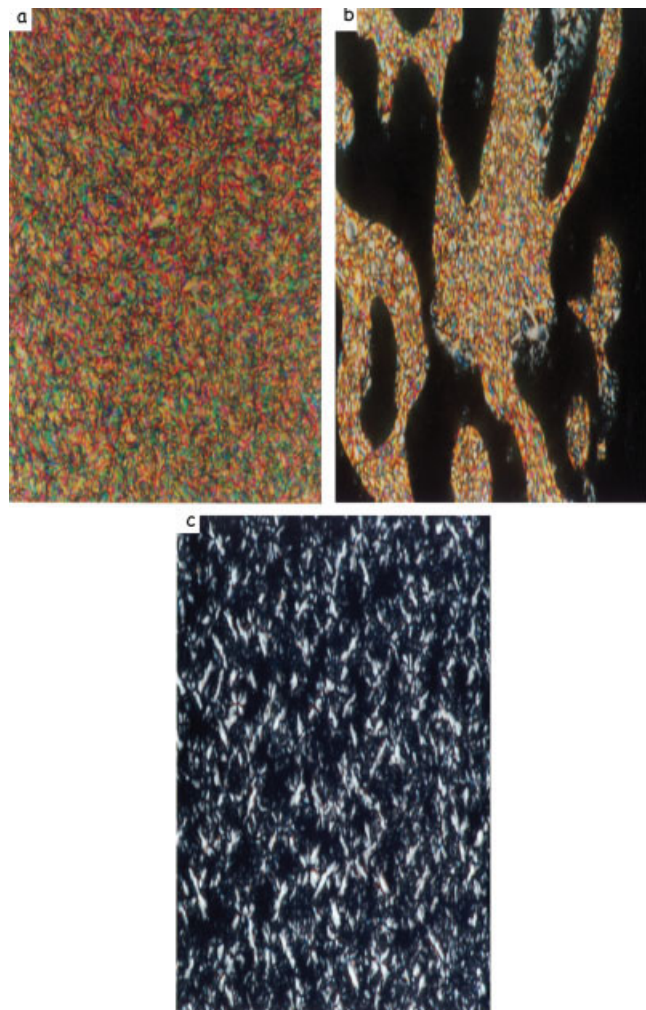
### Thermal properties

A detailed DSC analysis was performed to assess possible changes in the crystallite structure and overall degree of crystallinity of the matrix and blends. From the recorded first cooling and second heating, the thermal parameters such as crystallization temperature ( $T_c$ ), onset crystallization temperature ( $T_{c(\text{onset})}$ ),

**TABLE I**  
DSC Data of Polymer

Samples	Oligomers		$T_g$ (°C)	$T_m$ (°C)	Phase behavior
	PAEK (GPC)	TLCP (cal.)			
HO-PAEK-OH	7797	0	121.3	–	Isotropic
TLCP	0	7691	155.8 <sup>a</sup>	345.1	Liquid crystalline
Blend	7797	7691	124.8 (153.4)	341.5	Liquid crystalline
BCP	7797	7691	138.1	315.7	Liquid crystalline

<sup>a</sup> Obtained from the Cooling Cycle.



**Figure 6** Optical micrographs of (a) TLCP, (b) blend of TLCP and PAEK oligomers after heat treatment, and (c) BCP at their liquid crystalline state after heat treatment (magnification 400 $\times$ ). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

melting temperature ( $T_m$ ), and  $X_c$  are obtained and shown in Table I.  $X_c$  was calculated from the peak enthalpies normalized to the actual weight fraction of polymer according to

$$X_c = \frac{\Delta H_c}{\Delta H_c^o W_{\text{polymer}}} \times 100$$

Where  $\Delta H_c^o$  was 130 J/g, the theoretical value of enthalpy for 100% crystalline PEEK,  $\Delta H_c$  was crystallization enthalpy, and  $W_{\text{polymer}}$  was the weight fraction of polymer matrix. The calorimetric characteristic of the PEEK phase of the uncompatibilized blends showed that the presence of the TLCP dispersed phase led to a slight increase of the PEEK crystallization temperatures as well as onset crystallization temperature over the composition range investigated probably due to incompatibility of both components in the melt range. This effect can be more clearly observed in Table II. The increase of  $T_c$  for the blends was almost independent of TLCP composition.  $T_m$  of PEEK in the blends was not affected by the addition of TLCP. These results can be interpreted by a slightly increased nucleation rate of PEEK phase in the presence of TLCP dispersed particles during the crystallization of PEEK in the blends under dynamic conditions. However, it was clear that the presence of TLCP in these blends affected the crystallization of PEEK developed during the dynamic crystallization. Mehta and Isayev<sup>12</sup> observed an increase in the crystallinity of PEEK Victrex 380G when adding 2.5 wt % Vectra in samples transformed by injection. However,  $T_m$  and  $X_c$  in our work were almost independent of the presence of TLCP. The addition of the BCP to the blends in general decreased the PEEK crystallization temperature and retarded the beginning of the crystallization especially to PTc2 sample probably due to partial compatibility of both components.

### Wide angle X-ray diffraction

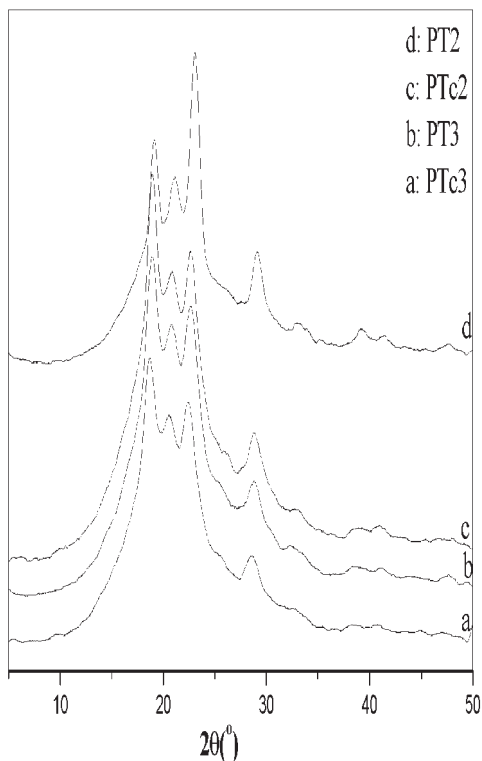
To investigate whether the crystalline structure of one component in the blend can be affected by the other component or the compatibilization agent, X-ray diffraction studies were made also on the corresponding pure components and blends. The X-ray diffraction patterns of PEEK showed four reflections at 19.2 $^\circ$ ,

**TABLE II**  
DSC Results of Uncompatibilized and Compatibilized PEEK/TLCP Blends

Samples	$T_c^a$ ( $^\circ\text{C}$ )	$T_c$ (onset) ( $^\circ\text{C}$ )	$\Delta H_c^a$ (J/g)	$T_m^b$ ( $^\circ\text{C}$ )	$X_c$ (%)
PEEK	297.4	302.4	49.41	339.1	38.0
PT1	299.5	305.0	40.21	340.2	31.6
PT2	299.6	305.1	46.92	339.1	38.0
PTc2	297.6	303.4	47.69	338.9	39.4
PT3	299.4	304.9	45.40	339.4	38.8
PTc3	299.0	304.4	45.53	338.9	39.7
PT4	299.4	304.9	40.0	340.2	36.2

<sup>a</sup> From the first cooling cycle

<sup>b</sup> From the second heating cycle.

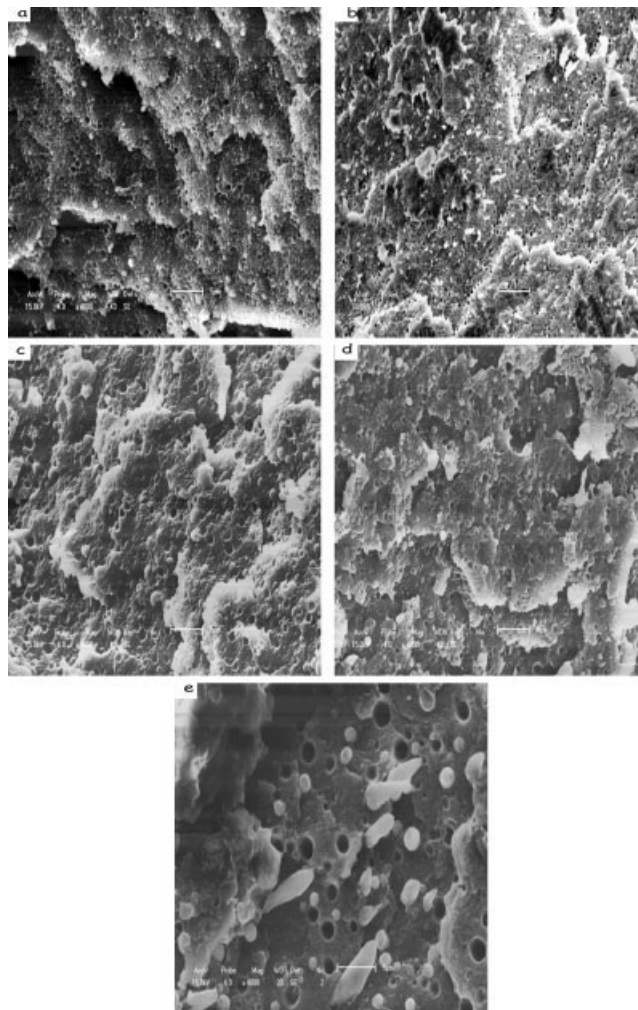


**Figure 7** X-ray diffractograms of uncompatibilized and compatibilized blends heat-treated at 180°C for 4 h.

21.1°, 22.9°, and 28.9° associated with the (110), (111), (200), and (211) planes, respectively, related to the orthorhombic structure. X-ray diffraction patterns were obtained for both PEEK/TLCP blends with and without 2 phr of BCP (Fig. 7). In both cases, several reflections were observed close to the pure PEEK's ones shown in Table III. These results confirmed that the blending or compatibilizing process did not disturb the crystalline structure of the PEEK component.

### Morphology

Figure 8 presents the SEM micrographs of the fracture surface of the blend specimens. The heterogeneous morphology was observed for all the blends. The micrographs demonstrated the poor adhesion between the two phases, an open ring was seen around the TLCP domain and a whole TLCP fibril was pulled out



**Figure 8** SEM micrographs of the fracture surfaces of (a) PT2, (b) PTc2, (c) PT3, (d) PTc3, and (e) PT4 extrudates.

during the fracturing of the samples. In contrast, there was no open ring around the TLCP domain in the compatibilized blends, reflecting better bonding between the phases. For the binary blends, the discrete TLCP particles with broadly distributed sizes ranging from 0.53 to 1.72  $\mu\text{m}$  in diameter shown in Table IV were dispersed in the PEEK matrix. After adding BCP to the blends, the morphology of the blends changed a little. The dispersed phase decreased to a half sized of

**TABLE III**  
Crystallographic Parameters for PEEK and Its Blends

Name	$2\theta(110)(^\circ)$	$2\theta(111)(^\circ)$	$2\theta(200)(^\circ)$	$2\theta(211)(^\circ)$
PEEK	19.2	21.1	22.9	28.9
PT2	19.1	21.1	23.0	29.1
PTc2	18.9	20.8	22.6	28.9
PT3	18.9	20.7	22.6	28.8
PTc3	18.6	20.3	22.3	28.4

**TABLE IV**  
The Relationship Between Components with Liquid Crystalline Fiber Diameter

Sample	$d_{\text{max}} (\mu\text{m})$	$\bar{d} (\mu\text{m})$
PT2	0.77	0.53
PTc2	0.38	0.23
PT3	1.67	1.14
PTc3	1.35	0.68
PT4	2.14	1.72



**TABLE V**  
**Tensile Properties of PEEK/TLCP Blends Compression Sheets**

Sample <sup>a</sup>	Tensile modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
PEEK	1786.5	91.1	40.04
PT1	2040.1	99.1	20.17
PT2	2010.6	98.9	12.16
PTc2	2080.7	102.9	20.93
PT3	2042.4	95.7	9.66
PTc3	2088.2	103.5	12.52

<sup>a</sup> Heat-treated at 190°C for 4 h.

the uncompatibilized ones. The interface between the TLCP particles and PEEK matrix became undiscerned. It might be a transesterification interchange reaction between the TLCP blocks of BCP and TLCP phase, while small part of amorphous PAEK blocks of BCP probably penetrated into PEEK amorphous phase region. It meant that the BCP had migrated to the TLCP particle surfaces, causing a strong reduction of the interfacial tension, which in turn led to the decrease of the dimensions of the dispersed phase, a finer dispersion, and more uniform distribution of the dispersed phase. These indicated that BCP acted as compatibilizer of the blends successfully.

Inclusion of 15 wt % TLCP gave rise to an obviously different morphology; there appeared some larger cavities on the fracture surfaces.

### Tensile properties

In general, the interfacial adhesion between phases and the morphology had direct influences on the mechanical properties of the blends.

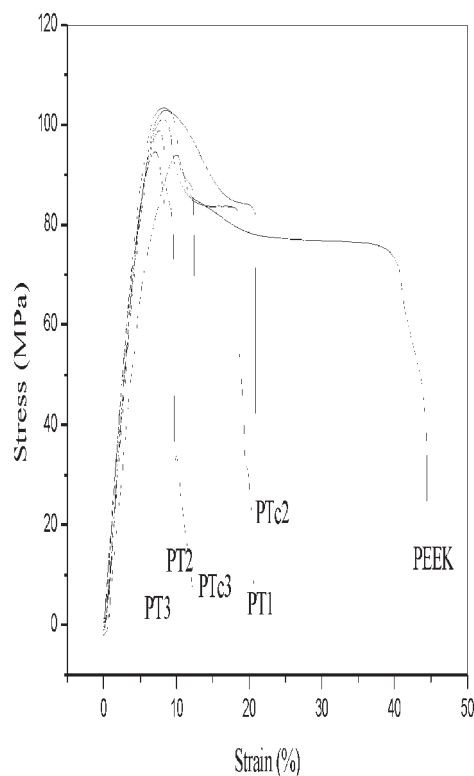
TLCP composition was fixed from 2 to 10 wt %. Tensile properties of the compatibilized and uncompatibilized blends were compared to see the compatibilizing effect shown in Table V. The stress–strain curves for PEEK/TLCP blends with and without compatibilizer are shown in Figure 9. From the figure and table, it can be seen that the tensile strength was altered for the compatibilized and uncompatibilized blends. It can be seen that both the tensile strength and the elongation at break decrease rapidly with increase of TLCP content, which was typical for an essentially incompatible blend system. The result was indicative of the poor adhesion between the PEEK and TLCP phases. For incompatible reinforced composites, the elongation at break generally decreased when the tensile modulus or tensile strength increased. Generally, the higher the modulus of the composites, the harder the composite was and the lower the elongation was.<sup>13–15</sup> After adding a small amount of BCP at 2 phr, the tensile strength and tensile modulus were improved to some extent. However, the mechanical

properties of compatibilized blends was not increased remarkably as expected possibly due to the relatively lower molecular weight of BCP synthesized and processing conditions. But from the earlier data, it was clearly seen that the mechanical properties of blends were increased after adding the compatibilizer BCP, although the extent was limited. Ductility was improved after adding 2 phr BCP. Simultaneous increase of tensile strength (or tensile modulus) and elongation can be explained by improved adhesion and better dispersion of the TLCP phase due to compatibilizer at the phase surface.

It was in accordance with SEM micrographs earlier. TLCP phase could not develop a fine fibrillar morphology with a high degree of orientation, leading to enhanced mechanical properties.

### Thermal stability

Thermogravimetry analysis (TGA) was applied to investigate the thermal stability of the blends. Figure 10 shows the TGA curves recorded in air, and the corresponding 5% weight-loss degradation temperature is listed in Table VI. It can be seen that the pure TLCP exhibited a two-step weight-loss mechanism. However, no apparently separate weight-loss step was observed for the blends, corresponding to the initial degradation of the pure components, possibly because



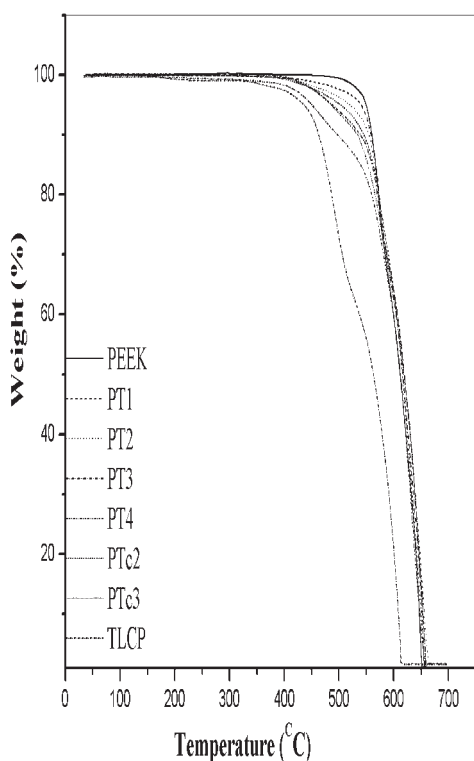
**Figure 9** Stress versus strain curves of PEEK and blends (standard deviation is less than 6% for all samples).



the TLCP content in the blends was small. If we compared the thermal stability of the two polymers, it was clear that PEEK was more thermal stable than TLCP and their blends. It was observed that the thermal stability of the blends greatly decreased with increases of TLCP content.

### CONCLUSIONS

Multiblock copolymer (BCP) containing PAEK and TLCP segments was synthesized by high temperature solution polymerization. Its structures and properties were confirmed by FTIR, DSC, GPC, and PLM. The results obtained indicated that polymer prepared should be copolymers of the two components rather than blends. Ternary blends of PEEK/TLCP/BCP



**Figure 10** TGA curves for the compatibilized and noncompatibilized PEEK/TLCP blends heated at 10°C/min in air.

**TABLE VI**  
5% Weight-Loss Degradation Temperature for the Polymer and Blends

Sample	$T_d$ (°C)
PEEK	549.9
TLCP	436.3
PT1	541.1
PT2	520.1
PT3	487.4
PT4	450.9
PTc2	503.4
PTc3	486.0

were prepared by extrusion. SEM and tensile properties results showed that the BCP acted as a compatibilizer effectively with the addition of BCP to the PEEK/TLCP blends. The decomposition temperature at 5% weight loss in air for blends was  $>450^\circ\text{C}$ , which indicated high thermal stability.

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