Graft copolymers of rigid-rod polymers as single-component molecular composites*

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End-capped poly(*p*-phenylenebenzobisthiazole) structures containing randomly distributed 2,6-dimethylphenoxy pendants along the rigid-rod backbone were synthesized through the copolycondensation of 2,5-diamino-1,4-benzenedithiol dihydrochloride with terephthaloyl chloride and 2-(2,6-dimethylphenoxy)-terephthaloyl chloride in polyphosphoric acid. End-capping was accomplished through the addition of 2,4,6-trimethylbenzoic acid to the reaction mixture. Through control of reaction stoichiometry, copolymer intrinsic viscosities were limited to 8.6 dl g^{-1} (methanesulphonic acid, 30°C) or less. The 2,6-dimethylphenoxy moiety served as a graft site for grafting reactions with 3-phenoxybenzoic acid in a methanesulphonic acid/phosphorus pentoxide medium. Incorporation of the resultant thermoplastic poly(ether ketone) side-chains into the rigid-rod poly(*p*-phenylenebenzobisthiazole) structures was substantiated through infra-red spectroscopy and analysis of model reactions.

(Keywords: graft copolymers; rigid-rod polymers; poly(*p*-phenylenebenzobisthiazole); poly(ether ketone); molecular composites; thermal stability)

INTRODUCTION

The concept of reinforcement on the molecular level using truly rigid-rod polymers to form molecular composites was introduced by Helminiak[1–4] and has attracted much interest based on its potential application to structural materials with high modulus and strength. On a conceptual basis, a molecular composite consists of a rigid-rod polymer dispersed in a flexible-coil polymer matrix with the rigid-rod component serving as a reinforcing element. Maximum reinforcement is achieved if the dispersion occurs at the molecular level. However, a critical problem in the processing of such blends has been the incompatibility of the two components, attributable to the low entropy of mixing. While effective reinforcement can be readily realized in fibre and film forms, thermal consolidation of neat preforms has led to aggregation of the rigid-rod molecules, thus lowering their aspect ratio and reinforcement efficiency. Consequently, subsequent efforts in this laboratory have been directed towards the limitation of rigid-rod aggregation and phase separation through variation of processing conditions as well as modification of polymer structure.

We recently reported the synthesis of graft copolymers with articulated polybenzobisthiazole (PBT) backbones and poly(ether ketone) (PEK) side-chains that were generated from 3-phenoxybenzoic acid (PBA)[5,6]. These graft copolymers functioned as single-component molecular composites and could be thermally processed with limited phase separation into bulk forms with good mechanical properties. However, a shortcoming of this approach was the limited flexibility in graft copolymer structure modification since the length of the rigid-rod segments was controlled by the number of graft sites or points of articulation in the polymer backbone. An excessive number of graft sites would lead to unacceptably short rigid-rod segments for effective reinforcement. An alternative approach entailing the synthesis of PBT structures with pendant 2,6-dimethylphenoxy graft sites[7] was also discussed and preliminary grafting studies were carried out. A wide range of graft copolymer structures could be synthesized since incorporation of the 2,6-dimethylphenoxy graft sites did not lead to any breaks within the rigid-rod backbones nor to any adverse effects upon rigid-rod reinforcement efficiency. In this paper, the preparation of end-capped graft copolymers (PBT-*g*-PEK) **1** (*Figure 1*) with rigid-rod PBT backbones and flexible PEK side-chains is reported along with their preliminary characterization. Processing will be reported in a companion paper[8,9].

EXPERIMENTAL

General

All reagents were purified prior to use. Solvents were ACS grade and were used without further purification. 2,5-Diamino-1,4-benzenedithiol dihydrochloride was prepared according to Wolfe's procedure[10].

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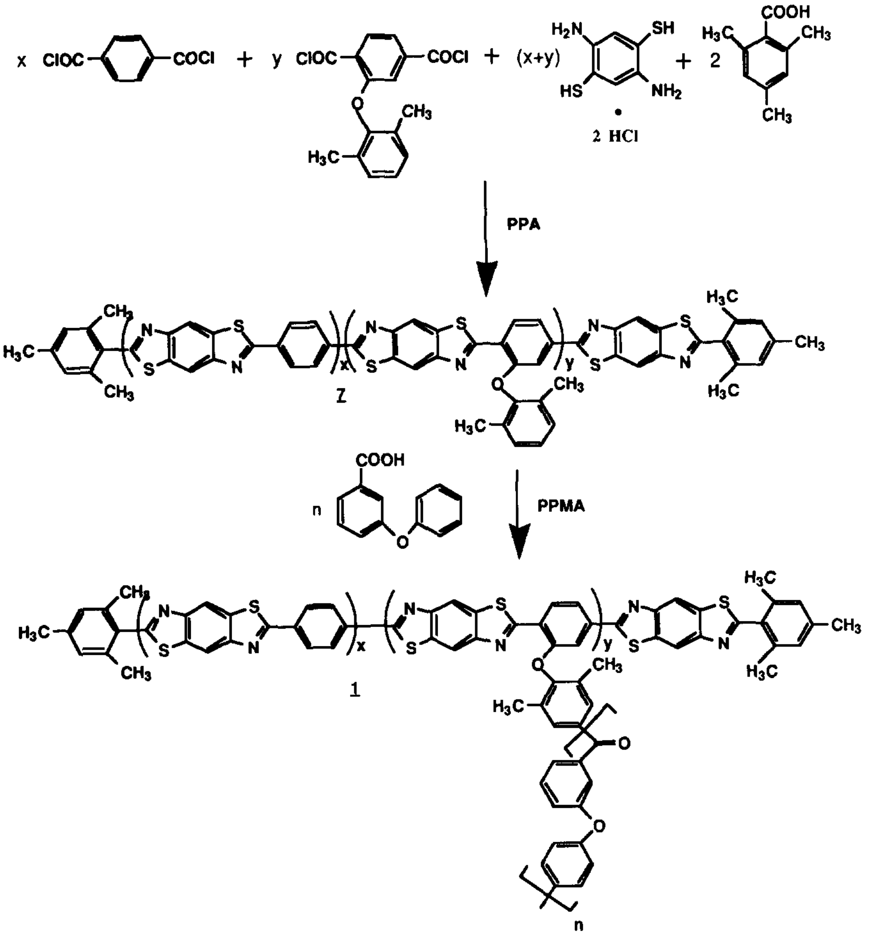

Figure 1 Monomer and model compound synthesis

Monomer synthesis

Dimethyl-2-(2,6-dimethylphenoxy)terephthalate. Potassium t-butoxide (90.6 g, 0.80 mol) was added to a stirred solution of 97.6 g of 2,6-dimethylphenol (0.80 mol) in 320 ml of dry toluene and 800 ml of dry *N,N*-dimethylformamide (DMF) under a nitrogen atmosphere. The reaction mixture was heated until a volume of 300 ml of toluene was removed by distillation, and was then cooled to room temperature. Dimethyl-2-nitroterephthalate (191.2 g, 0.80 mol) was added and the reaction was stirred at 100°C overnight. After the reaction mixture was allowed to cool to room temperature, approximately 600 ml of DMF was removed on a rotary evaporator at 80°C/50 mmHg. The remaining mixture was chilled and poured with stirring into ice–water. Following several extractions with ethyl acetate, the combined extracts were washed with saturated NaCl solution and were dried over anhydrous sodium sulphate. Removal of solvent from the dried solution yielded 88.4 g of dark brown liquid. Distillation of the brown material using a short-path apparatus at 150–153°C/0.1 mmHg yielded a yellowish solid. Recrystallization from ethanol followed by recrystallization from hexane gave 58 g (28% yield) of white solid (m.p. 82–84°C).

^{1}H n.m.r. ($CDCl_3$): 2.16 ppm (s, CH_3), 3.90 ppm (s, $COOCH_3$), 4.03 ppm (s, $COOCH_3$), 7.21–8.10 ppm (m, aromatic H). I.r. (KBr): 1734 cm^{-1}, 1727 cm^{-1} (C=O), 1228 cm^{-1} (ϕ–O–ϕ). M.s. (e.i.): 314 *m/e* (M^+). Elemental analysis: calculated for $C_{18}H_{18}O_5$, C 68.78, H 5.77; found, C 68.65, H 5.79.

2-(2,6-Dimethylphenoxy)terephthalic acid. To a stirred solution of 17 g (0.425 mol) of NaOH in 25 ml of water were added 26.79 g (0.085 mol) of dimethyl-2-(2,6-dimethylphenoxy)terephthalate and 50 ml of ethanol. The reaction mixture was stirred at reflux overnight. After cooling to room temperature, the reaction mixture was acidified with conc. HCl to yield a precipitate, which was collected on a filter and suction dried to yield 24.45 g of white solid. Recrystallization from ethanol/water (3:1) yielded 22.6 g (93%) of white crystals, m.p. 315–317°C.

^{1}H n.m.r. (d_6-acetone): 2.16 ppm (s, CH_3), 7.20–8.20 ppm (m, aromatic H). I.r. (KBr): 3057 cm^{-1} (OH), 1697 cm^{-1} (C=O), 1289 cm^{-1}. M.s. (e.i.): 286 *m/e* (M^+). Elemental analysis: calculated for $C_{16}H_{14}O_5$, C 67.12, H 4.93; found, C 67.11, H 5.05.

2-(2,6-Dimethylphenoxy)terephthaloyl chloride, **2.** First, 2-(2,6-dimethylphenoxy)terephthalic acid (20.0 g, 0.069 mol), 100 ml of thionyl chloride and a few drops of DMF were stirred at reflux overnight. The excess thionyl chloride was removed by distillation, and 100 ml of toluene was added, and was then distilled to remove residual thionyl chloride. The remaining yellow material was distilled at 140–143°C/0.07 mmHg and the resultant solid was recrystallized twice from hexane to yield 14.7 g (65% yield) of white crystals, m.p. 65–67°C.

^{1}H n.m.r. ($CDCl_3$): 2.10 ppm (s, CH_3), 7.20–8.30 ppm (m, aromatic H). I.r. (KBr): 1776 cm^{-1}, 1758 cm^{-1} (COCl). M.s. (e.i.): 323 *m/e* (M^+). Elemental analysis:

calculated for $C_{16}H_{12}O_3Cl_2$, C 59.46, H 3.74, Cl 21.94; found, C 59.70, H 3.91, Cl 21.69.

Dimethyl-2-(2,4,6-trimethylphenoxy)terephthalate. In a similar procedure, 50 g of 2,4,6-trimethylphenol (0.367 mol), 87.86 g of dimethyl-2-nitroterephthalate (0.367 mol) and 41.25 g of potassium t-butoxide (0.367 mol) in a mixture of 165 ml of dry toluene and 409 ml of dry DMF provided 25 g (20% yield) of white product (m.p. 101–102°C) after three recrystallizations from methanol.

^1H n.m.r. ($CDCl_3$): 1.80 ppm (s, 6H, CH_3), 2.05 ppm (s, CH_3), 3.60 ppm (s, CH_3), 3.73 ppm (s, CH_3), 7.06 ppm (s, 1H, aromatic), 7.26 ppm (s, 1H, aromatic), 7.76–8.16 ppm (m, 3H, aromatic). M.s. (e.i.): 328 *m/e* (M^+). Elemental analysis: calculated for $C_{19}H_{20}O_5$, C 69.49, H 6.14; found, C 69.68, H 6.02.

2-(2,4,6-Trimethylphenoxy)terephthaloyl chloride, **3.** The purified diester was hydrolysed in ethanolic potassium hydroxide to the diacid, which was then converted to the diacid chloride by refluxing in thionyl chloride and a few drops of DMF. The crude diacid chloride was purified by distillation at 150°C/0.01 mmHg followed by recrystallization from hexane to give a 56% overall yield of purified diacid chloride, m.p. 60°C.

I.r. (KBr): 1776 cm^{-1}, 1758 cm^{-1} (COCl). M.s. (e.i.): 338 *m/e* (M^+). Elemental analysis: calculated for $C_{17}H_{14}Cl_2O_3$, C 60.55, H 4.18; found, C 60.87, H 4.15.

Model compound synthesis

1,4-Bis(2-benzothiazole)-2-(2,6-dimethylphenoxy)benzene, **4.** First, 2-(2,6-dimethylphenoxy)terephthaloyl chloride (1.00 g, 3.094 mmol) and *o*-aminothiophenol (0.923 g, 7.425 mmol) were stirred under nitrogen in 15 g of 77% polyphosphoric acid (PPA) at 165°C for 24 h. The homogeneous yellow solution was poured into ice–water and the precipitated yellow crude product was isolated by filtration. Air drying followed by recrystallization from toluene (charcoal) gave 1.35 g (95% yield) of white crystalline product, m.p. 252°C.

^1H n.m.r. ($CDCl_3$): 2.24 ppm (s, CH_3), 7.23–8.82 ppm (m, aromatic H).^{13}C n.m.r. ($CDCl_3$): 166.5, 161.8, 155.6, 154.4, 150, 136.7, 136.5, 135.3, 131.3, 130.5, 129.5, 126.4, 126.2, 126.0, 125.5, 125.0, 123.9, 123.5, 123.1, 121.6, 121.3, 121.1, 111.7, 16.4 ppm. M.s. (e.i.): 464 *m/e* (M^+). Elemental analysis: calculated for $C_{28}H_{20}N_2S_2O$, C 72.38, H 4.33, N 6.00, S 12.80; found, C 72.41, H 4.54, N 5.98, S 13.28.

1,4-Bis(2-benzothiazole)-2-(2,4,6-trimethylphenoxy)-benzene, **5.** In a similar procedure, condensation of 2-(2,4,6-trimethylphenoxy)terephthaloyl chloride (1.00 g, 2.96 mmol) with *o*-aminothiophenol (1.48 g, 11.84 mmol) in 20 g of 77% PPA followed by recrystallization from toluene gave 1.47 g (99% yield) of yellow crystalline product, m.p. 215°C.

^1H n.m.r. ($CDCl_3$): 2.17 ppm (s, 6H, CH_3), 2.39 ppm (s, 3H, CH_3), 7.03–8.80 ppm (m, aromatic H). M.s. (e.i.): 478 *m/e* (M^+). Elemental analysis: calculated for $C_{29}H_{22}ON_2S_2$, C 72.77, H 4.63, N 5.85, S 13.39; found, C 73.09, H 4.64, N 5.86, S 12.92.

1,4-Bis(2-benzothiazole)-2-[4-(p-methylbenzoyl)-2,5-dimethylphenoxy]benzene, **6.** First, 1,4-bis(2-benzothiazole)-2-(2,6-dimethylphenoxy)benzene (3.02 g, 6.16 mmol) and *p*-toluic acid (0.855 g, 6.28 mmol) were stirred in a solution of 2.7 g of P_2O_5 and 27 g of methanesulphonic acid (MSA) under a nitrogen atmosphere at 120°C for 48 h. The resultant dark red solution was poured into ice–water and the precipitate was collected by filtration and air dried to give 3.6 g of crude product. After recrystallization from toluene/hexane, 3.1 g (86% yield) of white crystalline product was obtained, m.p. 204–205°C.

^1H n.m.r. (C_6D_6): 1.03 ppm (s, CH_3), 1.16 ppm (s, CH_3), 1.33 ppm (s, CH_3), 5.9–8.2 ppm (m, aromatic H). I.r. (KBr): 1658 cm^{-1}(C=O). M.s. (e.i.): 582 *m/e* (M^+). Elemental analysis: calculated for $C_{36}H_{26}N_2S_2O_2$, C 74.19, H 4.49, N 4.80, S 11.00; found, C 73.60, H 4.61, N 4.66, S 11.23.

Polymer synthesis

End-capped PBT copolymer, **7.** Initially, 2,5-diamino-1,4-benzenedithiol dihydrochloride (3.9878 g, 16.264 mmol), 2-(2,6-dimethylphenoxy)terephthaloyl chloride (1.5234 g, 4.714 mmol), terephthaloyl chloride (2.2332 g, 11.0 mmol) and 2,4,6-trimethylbenzoic acid (0.157 g, 0.9566 mmol) were stirred in 29.06 g of 77% PPA under a stream of nitrogen at room temperature for 1 h. The temperature was raised slowly to 40°C for 2 h, 60°C for 18 h and then 100°C for 2 h. After dehydrochlorination was complete, the yellow solution was cooled to room temperature and 13.12 g of P_2O_5 was added to the yellow reaction mixture to raise the final P_2O_5 content of the PPA to 83.0%. The mixture was heated to 100°C for 3 h, and the temperature was then raised rapidly to 165°C. The homogeneous mixture became dark red and stir opalescence appeared after 3 h. After being stirred at 165°C for 24 h, the extremely viscous mixture was then poured into water to precipitate the polymer. The precipitated polymer was stirred in a blender until it was broken up into a fine, fibrous form. It was washed with dilute NH_4OH and was extracted with water in a continuous extraction apparatus for 24 h. Drying *in vacuo* at 100°C for 24 h afforded 4.77 g (98% yield) of an orange-red fibrous polymer with an intrinsic viscosity of 12.0 dl g^{-1} (MSA, 30°C).

Elemental analysis: calculated for $(C_{22}H_{12}S_2N_2O)_n$, C 68.72, H 3.74, N 7.28; found, C 67.25, H 3.75, N 7.24.

*Graft copolymer PBT-*g*-PEK*, **1.** End-capped PBT polymer (2.50 g) with 30 mol% graft sites ($[\eta] = 4.6$ dl g^{-1} in MSA at 30°C) was stirred under nitrogen at room temperature in a solution of P_2O_5 (11 g) and MSA (110 g) until a clear golden yellow solution was obtained. PBA (9.5 g) was then added to the solution, which was stirred until it became homogeneous. The reaction temperature was then slowly raised to 120°C. After 24 h, the resultant very dark red, viscous solution was poured into water to precipitate the graft copolymer. The precipitated copolymer was isolated by filtration, washed with dilute NH_4OH and then with water. It was then extracted with water in a continuous extraction apparatus for 24 h to remove any acid residue. After drying *in vacuo* at 100°C, the graft copolymer was extracted with methylene chloride in a continuous extraction apparatus for 24 h to remove any residual unattached PEK. The resulting dark brown product was dried at 100°C/1 mmHg to give 7.68 g of PBT-*g*-PEK ($[\eta] = 3.5$ dl g^{-1} in MSA at 30°C). From the methylene chloride extract, 3.52 g of unattached PEK were obtained ($[\eta] = 0.1$ dl g^{-1} in MSA at 30°C).

Elemental analysis: calculated for $(C_{14}H_6N_2S_2)_7(C_{22}H_{14}N_2S_2O)_3(C_{13}H_8O_2)_{32.7}$, C 74.98, H 3.69, N 2.92, S 6.79; found, C 67.80, H 3.54, N 2.79, S 9.36.

The PBT-*g*-PEK copolymer composition was determined from the mass balance of the PBT and the purified PBT-*g*-PEK according to the following equations:

$$\text{wt\% PBT} = \frac{\text{Initial wt PBT}}{\text{Yield wt PBT-}g\text{-PEK}} \times 100 = \frac{2.50}{7.68} \times 100 = 32$$

$$\text{wt\% PEK} = 100 - \text{wt\% PBT} = 100 - 32 = 68$$

RESULTS AND DISCUSSION

Synthesis

The diacid chloride monomer **2** containing the 2,6-dimethylphenoxy graft site was prepared through the nucleophilic displacement of a nitro group from dimethyl-2-nitroterephthalate by 2,6-dimethylphenol in DMF. The resultant dimethyl-2-(2,6-dimethylphenoxy)terephthalate was then saponified with sodium hydroxide to yield the free diacid, which was converted to 2-(2,6-dimethylphenoxy)terephthaloyl chloride **2** by treatment with thionyl chloride.

Reactivity of **2** under appropriate polycondensation conditions was established through reaction with 2-aminothiophenol in PPA (*Figure 2*). The presence of methyl substituents at the 2 and 6 positions of the pendant phenoxy group prevented side-reactions leading to xanthone formation[11]. A quantitative yield of the desired model compound **4** was recorded and the structure was verified by elemental analysis, nuclear magnetic resonance, infra-red and mass spectroscopy.

The feasibility of the grafting reaction and the reactivity of the *para* position of the 2,6-methylphenoxy group have been previously demonstrated by model reactions[6]. 1,4-Bis(2-benzothiazoyl)-2-(2,6-dimethylphenoxy)benzene **4** underwent reaction with *p*-toluic acid in a methanesulphonic acid/phosphorus pentoxide (PPMA) medium to give an 86% yield of model compound **6** (*Figure 2*). The structure was identified by elemental analysis, infra-red, mass and nuclear magnetic resonance spectroscopy. The regioselectivity of the grafting reaction on the *para* position of the 2,6-dimethylphenoxy graft site was demonstrated by another model grafting reaction. Model compound **5**, which was synthesized through a similar sequence as **4** but from 2,4,6-trimethylphenol (*para* position was blocked) did not react with toluic acid in PPMA (*Figure 2*).

The parent PBT copolymer **7** (*Figure 1*) was prepared through the copolycondensation of terephthaloyl chloride and 2-(2,6-dimethylphenoxy)terephthaloyl chloride **2** with 2,5-diamino-1,4-benzenedithiol dihydrochloride in PPA. The synthesis of high-molecular-weight copolymers

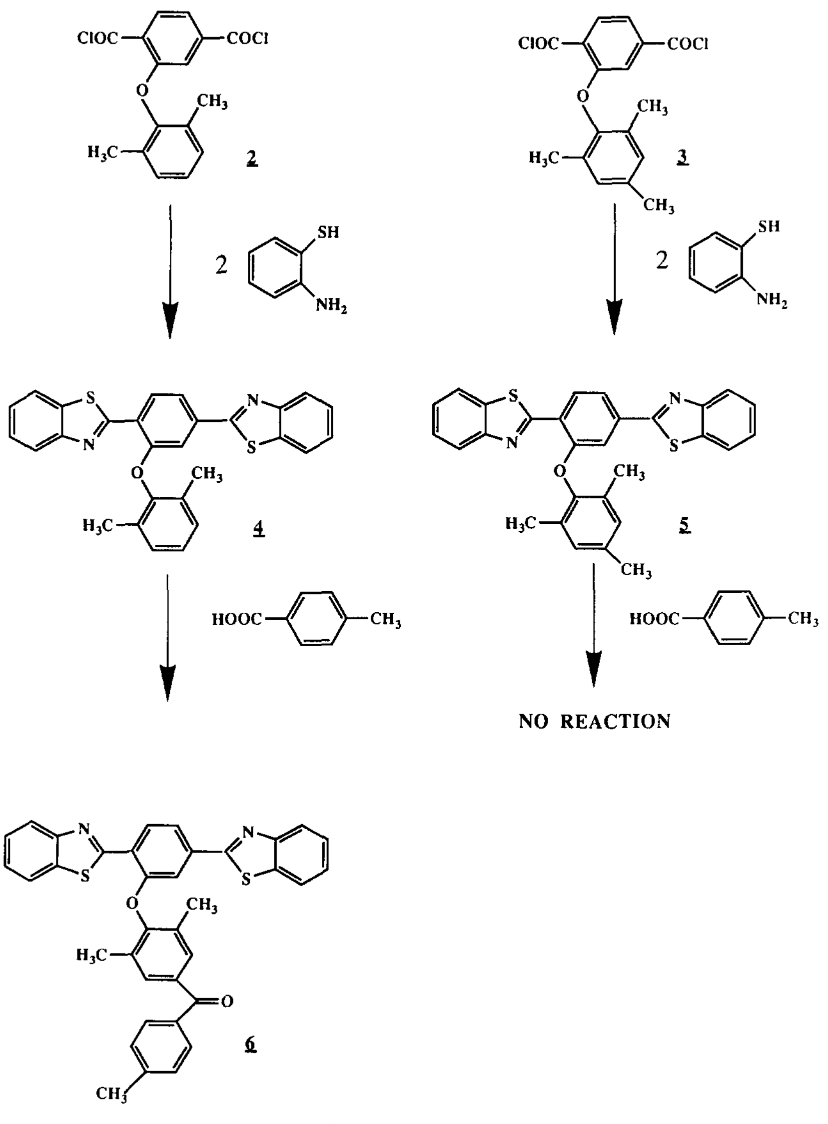

Figure 2 Synthesis of end-capped graft copolymer PBT-*g*-PEK

Table 1 Synthesis of PBT-*g*-PEK

Trial No.	Graft sites (mol%)	PBT $[\eta]^a$ (dl g^{-1})	PBT/PEK composition (w/w)	PBT-*g*-PEK $[\eta]^a$ (dl g^{-1})
1	10	8.6	46/54	3.7
2	10	4.6	52/48	3.2
3	15	8.2	54/46	5.3
4	30	4.6	42/58	3.8
5	30	4.6	32/68	3.5
6	30	8.3	29/71	2.2
7	30	5.3	53/47	6.1

[a] Measured in methanesulphonic acid at 30°C

has been previously reported[6]. Low-molecular-weight copolymers leading to more readily processible PBT-*g*-PEK graft copolymers could be obtained by adjusting the stoichiometry of the copolycondensation reaction in favour of the dihydrochloride salt. To prevent any undesirable side-reactions during subsequent grafting reactions, the relatively low-molecular-weight copolymers were then end-capped with 2,4,6-trimethylbenzoic acid. The concentration of graft sites varied from 5 mol% ($x=95$, $y=5$) to 30 mol% ($x=70$, $y=30$). Intrinsic viscosities of the resultant PBT copolymers were limited to 8.6 dl g^{-1} (methanesulphonic acid, 30°C) or less. Graft copolymers **1** of the parent PBT copolymers were prepared through reaction with PBA in a PPMA condensation medium. Reaction temperatures were limited to 120°C to minimize deleterious side-reactions resulting from the instability of PBA at higher temperature. As with the previously reported copolymers derived from articulated PBT polymers[6], the PBT-*g*-PEK composition (PBT/PEK) was dependent upon the initial stoichiometry of parent PBT copolymer and PBA in the grafting reaction as well as the reaction time and temperature. Unattached PEK was separated from PBT-*g*-PEK through extraction with methylene chloride. The results are summarized in *Table 1*.

Characterization

Graft copolymers PBT-*g*-PEK were obtained as fibrous, dark brown materials. The successful incorporation of PEK into the rigid-rod structure was indicated by infra-red spectroscopy. In all cases, a band at 1650 cm^{-1}, attributable to aromatic ketone, was observed as well as a substantially increased absorption at 1250 cm^{-1}, attributable to phenylene ether structure. The solubility of the PBT copolymer was changed by the grafting procedures. While the PBT copolymers were soluble only in methanesulphonic acid and PPA, PBT-*g*-PEK also exhibited solubility in trifluoroacetic acid. Dilute solution viscosity plots of PBT-*g*-PEK (MSA, 30°C) exhibited a pronounced negative slope ($\eta_{\mathrm{inh}} > [\eta]$) as had been observed for similar graft copolymers derived from articulated PBT[6]. This was in contrast to the plots of the parent PBT copolymers, PEK and identically constituted physical blends of PBT copolymer/PEK, which had positive slopes ($\eta_{\mathrm{inh}} < [\eta]$).

The thermo-oxidative stability of PBT-*g*-PEK was quite high although a slight penalty in stability was incurred through the incorporation of PEK side-chains into the very stable PBT copolymers. Under thermogravimetric analysis in air, substantial breakdown did not occur until the 430–450°C range. Thermogravimetric–mass spectral analysis *in vacuo* substantiated initial breakdown occurring in the PEK side-chains through the release of methane and many oxygen-containing species such as carbon monoxide, phenol, cresol, dimethylphenol, etc. Later breakdown at higher temperatures related to the release of characteristic products from the PBT copolymer backbone including hydrogen sulphide, hydrogen cyanide, carbon disulphide, benzonitrile, ammonia, etc. Further thermal characterization was indicative of successful grafting of PEK to the PBT copolymer. Dynamic mechanical analysis of PBT-*g*-PEK samples indicated softening temperatures in the range of 180 to 265°C but showed no transitions at 135°C (the T_g of PEK). In contrast, the parent PBT copolymers showed no transitions up to the point of decomposition. Previous studies have also shown that physical mixtures of the parent PBT copolymer and PEK exhibit a very sharp T_g at 135°C (the T_g of PEK) as opposed to the substantially higher T_g values exhibited by the graft copolymers[6].

Strong moulded samples could be obtained from PBT-*g*-PEK through the application of pressures of up to 6000 psi (41.37 MPa) and temperatures about 40 to 50°C above the softening temperature. Tensile moduli and strengths of approximately 1.2 Msi (8.27 GPa) and 4.9 ksi (33.79 MPa), respectively, were obtained for a representative PBT-*g*-PEK sample (Trial No. 1, *Table 1*).

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