Influence of molecular structure on processing conditions and mechanical properties of graft rigid-rod copolymers*

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Dynamic and tensile mechanical properties of a series of graft rigid-rod copolymers were studied. The copolymers were single-component rigid-rod molecular composites consisting of a rigid-rod poly(*p*-phenylenebenzobisthiazole) backbone grafted with flexible-coil poly(oxy-1,3-phenylenecarbonyl-1,4-phenylene) side-chains. Dynamic storage moduli of the graft copolymers showed three characteristic regions: an initial plateau region, a transition zone and a second plateau region. The peak transition temperatures of the dynamic loss modulus curves were independent of the rigid-rod backbone length but decreased with increasing side-chain lengths, suggesting that the transition was a secondary transition associated with localized motions of the flexible side-chains. The graft rigid-rod copolymers were compression moulded into tensile test specimens at temperatures above their peak transition temperatures. Although the specimens appeared well consolidated as evidenced by the scanning electron micrographs of tensile-fractured surfaces, their tensile properties were relatively poor compared with those reported for rigid-rod molecular composite blends. The significance of poor tensile properties is discussed based on the structural characteristics of the graft copolymers, namely the length of rigid-rod backbone, the frequency of graft sites, and the average contour length of flexible-coil side-chains.

(Keywords: molecular composites; graft copolymers; rigid-rod backbone; poly(*p*-phenylene benzobisthiazole); flexible side-chains; poly(ether ketone); secondary transition)

INTRODUCTION

Rigid-rod molecular composites are, conceptually, materials containing a flexible-coil polymer matrix with rigid-rod polymer reinforcements uniformly dispersed on a molecular level. This concept was first outlined over 10 years ago with the objective of developing high-modulus and high-strength structural materials[1–3]. Implementation of this idea to a model system of rigid-rod poly(*p*-phenylenebenzobisthiazole) (PBT) with flexible-coil poly(2,5(6')-benzothiazole) (ABPBT) or poly(2,5(6')-benzimidazole (ABPBI) demonstrated that fibres spun from these materials exhibit tensile moduli satisfying the expression for the rule of mixtures[4]. These results suggested that nearly 100% reinforcement efficiency can be achieved from the dispersed PBT molecules. Furthermore, morphological studies[5] confirmed that the PBT molecules had minimal phase aggregation in the rigid-rod molecular composite blends of PBT and ABPBI.

Efforts were subsequently directed towards using thermoplastic polymers as host matrices to permit fabrication of bulk structural components. A number of rigid-rod/thermoplastic molecular composite systems, including PBT/poly(*p*-phenylenequinoxaline)[6], PBT/nylon[6,7] and PBT/poly(ether ether ketone)[8], were investigated. Although reinforcement efficiencies as high as 50–70% were achieved[7], wide-angle X-ray diffraction revealed significant aggregation of PBT molecules in these systems[8,9]. The kinetics of phase aggregation of PBT molecules was studied with PBT/nylon composite films using small-angle light scattering techniques[10,11]. Results showed that rigid-rod thermoplastic molecular composites underwent a thermally induced phase separation, and this phase transition was completed in time intervals significantly shorter than the duration of the consolidation process[7,11].

In an attempt to restrict the extent of phase separation during processing, a graft rigid-rod copolymer with thermoplastic poly(oxy-1,3-phenylenecarbonyl-1,4-phenylene) (poly (ether ketone), PEK) molecules grafted on the rigid-rod PBT molecules was prepared[12]. It was believed that the graft side-chains on the rigid-rod

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backbone would limit large-scale aggregations of the rigid rods, thereby yielding improved reinforcement efficiencies. In this paper, we discuss the influence of structural characteristics, such as the frequency and distribution of graft sites and the average contour length of graft side-chains, on the processing conditions and the dynamic and tensile mechanical properties of the graft rigid-rod copolymers.

EXPERIMENTAL

Materials

The chemical structure of the graft rigid-rod copolymers is shown in *Figure 1*. In preparation of the copolymers, the rigid-rod backbone was first synthesized by copolycondensation of terephthaloyl chloride and 2-(2,6-dimethylphenoxy)terephthaloyl chloride with 2,5-diamino-1,4-benzenedithiol dihydrochloride in polyphosphoric acid. The rigid-rod backbone was then end-capped with 2,4,6-trimethylbenzoic acid to prevent an undesirable advancement of molecular weight or other side-reactions during the grafting reactions or the processing steps. The 2,6-dimethylphenoxy group on 2-(2,6-dimethylphenoxy)terephthaloyl chloride served as the graft site on the rigid-rod backbone for 3-phenoxybenzoic acid. The reactivity of 2,5-diamino-1,4-benzenedithiol dihydrochloride with 2-(2,6-dimethylphenoxy)terephthaloyl chloride was assumed to be the same as that with terephthaloyl chloride or, equivalently, the distribution of the graft sites was assumed to be random along the rigid-rod backbone. The percentage frequency of graft sites (*Y* in *Figure 1*) was determined by the ratio of 2-(2,6-dimethylphenoxy)terephthaloyl chloride to terephthaloyl chloride and 2-(2,6-dimethylphenoxy)terephthaloyl chloride. The grafting of 3-phenoxybenzoic acid to 2,6-dimethylphenoxy graft sites on the rigid-rod backbone was carried out by polycondensation in a mixture of methanesulphonic acid and phosphorus pentoxide.

A series of graft rigid-rod copolymers with different average lengths of the rigid-rod backbone, varying contour lengths of the flexible-coil side-chain, and different weight ratios of the rigid-rod backbone to the flexible-coil side-chain were synthesized. The detailed synthesis procedure is reported elsewhere[12]. A summary of the structural characteristics of the copolymers is listed in *Table 1*. The average repeat unit of the PEK side-chains was calculated from the weight ratio of the rigid-rod to the flexible-coil component and the frequency of graft sites along the PBT backbone. The weight-average molecular weights of the three PBT backbones corresponding to intrinsic viscosities of 4.6, 8.3 and 8.6 dl g^{-1} were calculated to be 13 700, 19 700 and 20 100 g mol^{-1}, respectively[13].

Dynamic and tensile mechanical characterizations

Rectangular specimens about 30 mm long, 9.5 mm wide and 1.0 mm thick were compression moulded from dry powdered materials in a microprocessor-controlled hot press. Suitable moulding conditions were adopted merely to consolidate the powdered materials into a useful form for dynamic mechanical characterization rather than for

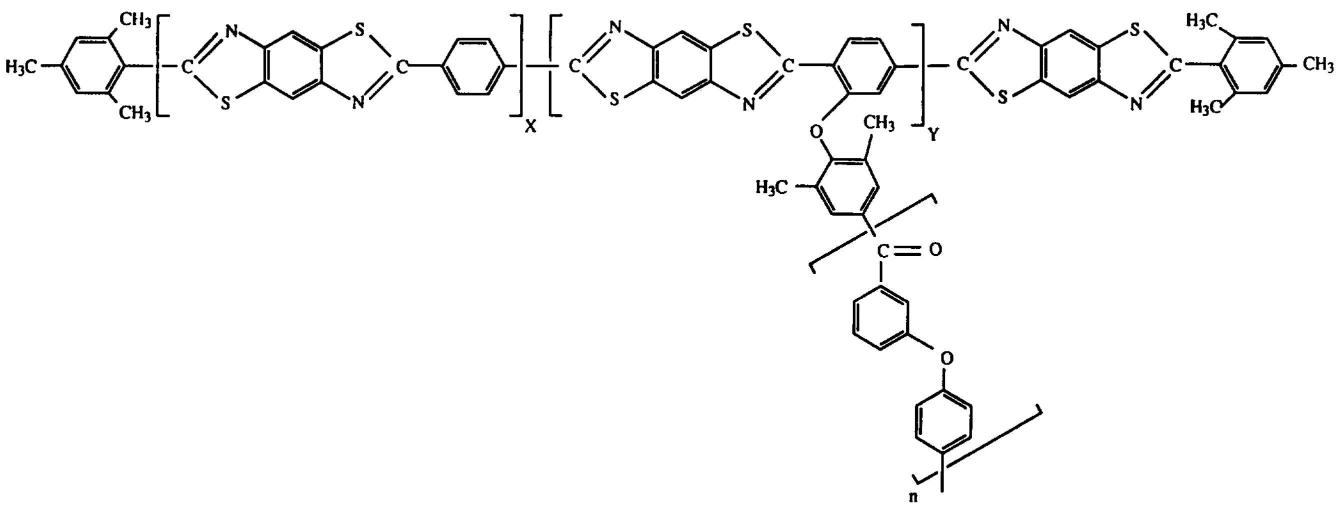

Figure 1 Structure of graft rigid-rod copolymers

Table 1 Structural characteristics and peak transition temperature of various graft rigid-rod copolymers

Copolymer No.	PBT $[\eta]^a$ (dl g^{-1})	PBT/PEK composition (w/w)	Graft sites (%)	PEK repeat units, *n*	*G*″ peak temperature (°C)
1	8.6	46/54	10	17	180
2	4.3	52/48	10	13	–
3	8.3	29/71	30	13	211
4	4.6	32/68	30	11	222
5	4.6	42/58	30	7	268
6	8.3	53/47	30	5	251

[a] In methanesulphonic acid at 30°C

the optimal mechanical properties. For instance, the moulding temperature was limited to below 250°C to ensure that the applied heat would not change the thermal characteristics of the materials, at least not those at temperatures above 250°C. The dynamic mechanical tests were conducted using a Rheometrics Dynamic Spectrometer (RDS 7700) at a frequency of $10\,\mathrm{rad\,s^{-1}}$ and a heating rate of $2°\mathrm{C\,min^{-1}}$ up to a temperature of 380°C.

Dogbone-shaped specimens were processed at various temperatures and pressures in a closed mould to obtain well consolidated samples for tensile mechanical tests. The specimens had a centre portion about 28 mm long, 4.5 mm wide and 1.0 mm thick. An Instron Universal Test Machine (model 1122) was used to measure the mechanical properties of the consolidated specimens. The strains were monitored by a half-inch (~13 mm) gauge length extensometer or using strain gauges bonded to the specimen. A crosshead speed of $0.05\,\mathrm{cm\,min^{-1}}$ was used for all measurements. Scanning electron microscopy was used to examine the tensile-fractured surface of the dogbone-shaped specimens.

RESULTS AND DISCUSSION

Figure 2 shows the dynamic mechanical spectrum of copolymer no. 1 as a representative case for the series of graft rigid-rod copolymers. The copolymer no. 1 had a rigid-rod backbone of about 76 PBT repeat units with 7–8 graft sites and an average of 17 PEK repeat units on the side-chains. The storage modulus (G'), which is a measure of the energy stored in the specimen in each dynamic oscillation, exhibited an initial plateau region up to 150°C, followed by a decrease of about an order of magnitude in G' over a temperature range from 150 to 275°C, and eventually a second plateau region above 275°C. The loss modulus (G''), which is a measure of the energy dissipated in the system in each dynamic oscillation, exhibited a maximum at a temperature of about 180°C. Other graft rigid-rod copolymers showed a similar behaviour in their dynamic mechanical properties; however, the transition temperature from the first plateau to the second plateau as indicated by the G'' peak temperature was found to be different for the various graft rigid-rod copolymers. The transition temperatures for the various graft rigid-rod copolymers are listed in *Table 1*.

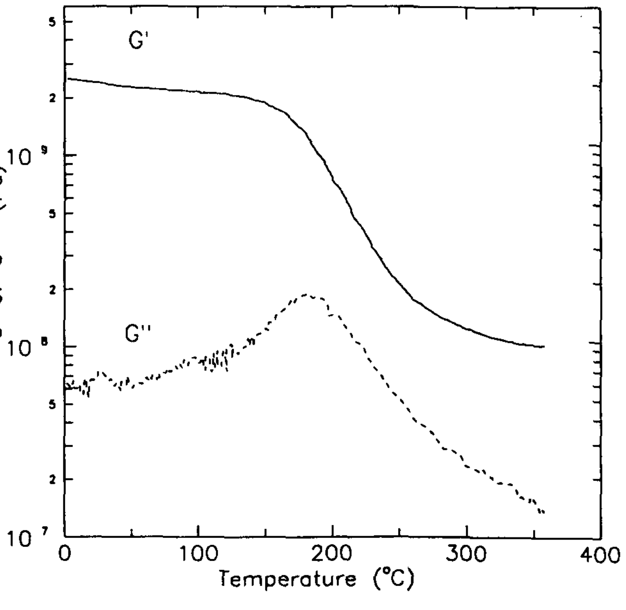

Figure 2 Dynamic mechanical characteristics of copolymer no. 1

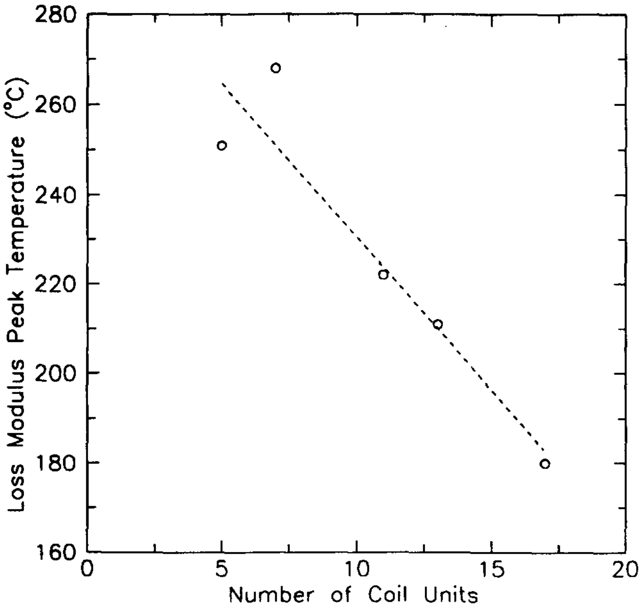

Figure 3 Correlation between loss modulus peak temperature and number of PEK units grafted to the PBT chain

The dynamic mechanical spectra observed for the graft rigid-rod copolymers are similar to those of high-molecular-weight polymers undergoing a glass transition from a glassy state to a rubbery plateau; however, the origins of the two mechanisms are different. The glass transition is a primary transition at which polymer chains acquire sufficient mobility to exhibit long-range segmental motions of the main chain. For the graft rigid-rod copolymers, the long-range main-chain movements are presumably dominated by the chain length of rigid-rod backbone. A comparison of the G'' peak temperatures of the graft copolymers reveals that the observed transitions cannot represent the glass transitions of the copolymers because they cannot be correlated to the chain lengths or, alternatively, the intrinsic viscosities of the rigid-rod backbones.

The G'' peak temperatures are plotted in *Figure 3* as a function of the number of repeat units of the PEK side-chains. A linear correlation is seen, with a decrease in G'' peak temperature with increasing PEK chain length at a rate of approximately 7°C per PEK repeat unit. This confirms that the transitions observed for the graft rigid-rod copolymers were not the glass transitions of the copolymers but secondary transitions reflecting only the localized segmental side-chain motions of PEK. The glass transition temperature of PEK homopolymer has been reported[14] to be 135°C. The decrease of peak transition temperature with increasing side-chain length implies that the localized motions are less hindered as the side-chain length is increased. Independent thermal analysis has shown that rigid-rod PBT polymer does not exhibit a glass transition or melting phenomenon prior to degradation.

The dynamic mechanical behaviour of the graft rigid-rod copolymers can then be described in terms of the characteristic behaviour of copolymer no. 1 shown in *Figure 2* as follows: (1) at temperatures up to 150°C, both the rigid-rod backbone and the graft side-chains exist in a glassy (frozen) state, leading to the exhibition of the initial plateau region; (2) at a temperature of about 150°C, the graft side-chains start to soften, resulting in a decrease of the storage modulus; and (3) at temperatures above 275°C, the side-chains are mobile, but the rigid-rod backbone still exists in a glassy state, yielding a second plateau in the storage modulus. The second plateau modulus displayed by the graft rigid-rod copolymers was found to be about two orders of magnitude greater than the typical rubbery plateau modulus of high-molecular-weight polymers[15,16]. The PBT backbone in a glassy state may account for the greater magnitude of the second plateau modulus.

Materials that do not exhibit a glass transition or a melting point are difficult to process because very limited flow can be achieved to consolidate the materials. A study of the dynamic mechanical spectra of the graft copolymers indicated that these materials might be processed at temperatures within the transition zone above the G'' peak temperature. Temperatures much greater than the peak transition temperature, such as those in the second plateau region, did not seem to provide enhanced flows or significant gains in processability. In accordance with the above arguments, dogbone-shaped specimens were compression moulded at various temperatures and pressures. The processing conditions and the preliminary tensile properties of these specimens are reported in *Table 2*. Also included in the table are the processing conditions and tensile properties of PEK homopolymer for comparison. The highest tensile modulus (E) and failure strength (σ) measured for the rigid-rod molecular composites as single-component graft copolymers were 8.3 GPa and 40 MPa, respectively, comparably lower than those reported for rigid-rod molecular composite blends[7]. The highest tensile strength measured for the graft copolymers was even lower than the tensile strength of the PEK homopolymer. As indicated by the small elongation at break (ε_b), the specimens were brittle in nature.

The tensile-fractured surfaces of the dogbone-shaped specimens were examined by scanning electron microscopy (SEM) to investigate the consolidation condition of the graft rigid-rod copolymers. With copolymer no. 2 as a representative case in *Figure 4*, the fractured surface of the consolidated copolymers appeared to be smooth at the micrometre level and did not exhibit structures or domains at the submicrometre level. *Figure 5* shows the SEM micrograph of the tensile-fractured surface of consolidated PEK homopolymer. Fractographs of the copolymers exhibited structures very similar to those of the consolidated PEK homopolymer, suggesting that the dogbone-shaped specimens of the graft rigid-rod copolymers were well consolidated. The poor mechanical properties of the graft rigid-rod copolymers were then probably caused by the structural characteristics of the copolymers, such as the distribution, the frequency and the length of the flexible-coil side-chains.

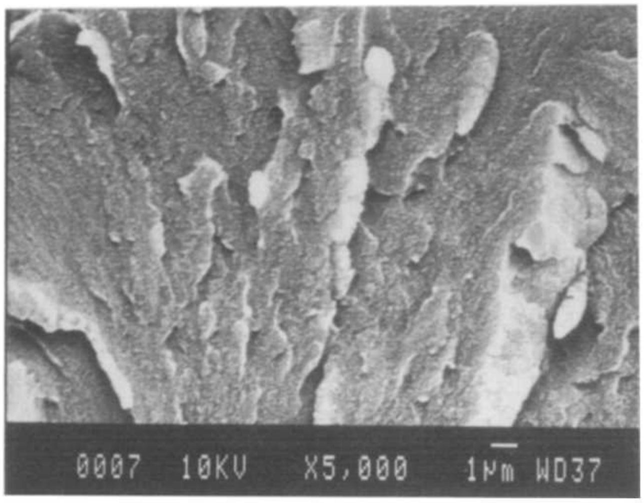

Figure 4 SEM micrograph of tensile-fractured surface of graft rigid-rod copolymer no. 2

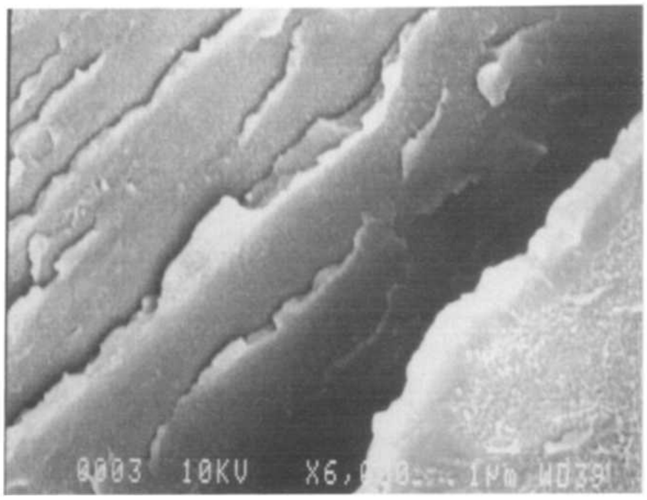

Figure 5 SEM micrograph of tensile-fractured surface of consolidated PEK

Table 2 Processing conditions and tensile properties of PEK and various graft rigid-rod copolymers

Copolymer No.	Processing conditions (temperature/pressure)	σ (MPa)	E (GPa)	ε_b (%)
PEK	149°C/5.2 MPa	61	3.9	1.9
	177°C/2.1 MPa	54	3.7	1.8
1	232°C/21 MPa	34	8.3	0.41
2	232°C/21 MPa	21	6.9	0.30
3	300°C/38 MPa	40	7.2	0.54
	300°C/44 MPa	24	7.9	0.36
6	290°C/31 MPa	24	8.1	0.35
	285°C/34 MPa	26	7.3	0.37

For a chopped-fibre composite in tension, a large part of the stress is carried by the reinforcing fibres while the matrix ensures uniform stress distribution within the composite. It was shown in a recent paper[17] that the tensile strength of a polymer increases rapidly with molecular weight and approaches an asymptotic value for large molecular weights. The asymptotic value is approached at a molecular weight greater than 10 times the chain entanglement molecular weight. In the graft rigid-rod copolymers, the longest side-chains were made up of only 17 repeat units of PEK, corresponding to a molecular weight of 3330 g mol^{-1}. Side-chains of graft rigid-rod copolymers of such low molecular weight may be insufficient to transfer stress effectively from one rigid-rod backbone to another. The effect of side-chain length on the mechanical properties of graft rigid-rod copolymers can be studied by incorporating longer side-chains onto the rigid-rod backbone or by blending a high-molecular-weight matrix resin with the graft rigid-rod copolymers.

The objective of incorporating flexible-chain molecules onto a rigid-rod molecule as side-chains was to restrict neighbouring rigid-rod molecules from aggregating into bundles or domains. Aggregates reduce the reinforcement efficiency of the rigid-rod molecules by a reduction in the number and the aspect ratio (ratio of length to width) of the reinforcing elements in the system. According to Flory's theory[18], rigid rods with aspect ratio greater than approximately 6 will have a tendency to form aggregates.

The geometry of a graft rigid-rod copolymer may be approximated as a rigid rod if the side-chains are not greatly extended from the rigid-rod backbone. In a hypothetical case, to simulate a graft rigid-rod copolymer as a rigid-rod molecule with a larger diameter, the PEK molecule may be assumed to be a freely jointed chain with a repeat unit as rigid and as long as the repeat unit of the PBT molecule. With this assumption, a PEK molecule with 17 repeat units will have an end-to-end distance of about 4.1 repeat units, corresponding to a radius of gyration of 1.7 repeat units[19]. The PBT rigid-rod backbone with an intrinsic viscosity of $4.3\,\mathrm{dl\,g^{-1}}$ (or $13\,700\,\mathrm{g\,mol^{-1}}$ molecular weight) has an end-to-end distance of about 51 repeat units. As a first approximation, the hypothetical graft rigid-rod copolymer will have an aspect ratio of about 15, which is greater than the minimum (~ 6) required to induce phase separation[18]. If the graft rigid-rod copolymer is considered as a large rigid rod, then the shape of this rigid rod will not be as regular as that of the PBT backbone because of the presence of the graft side-chains. In this case, the aggregates of the graft rigid-rod copolymers may not be readily detectable by techniques such as wide-angle X-ray diffraction.

The graft sites for PEK in the copolymers were assumed to be randomly distributed along the rigid-rod backbone. In practice, this assumption may not be valid because the reactivity of 2,5-diamino-1,4-benzenedithiol dihydrochloride with 2-(2,6-dimethylphenoxy)-terephthaloyl chloride may not be the same as that with terephthaloyl chloride owing to the presence of the large 2,6-dimethylphenoxy group. It is conceivable that the structure of the graft rigid-rod copolymers will be further complicated if the graft side-chains are concentrated only at specific locations on the rigid-rod backbone. For instance, the degree of phase aggregation of rigid-rod backbones may be greatly enhanced if the graft sites are concentrated only at chain ends of the rigid-rod backbones.

2-(2,4,6-Trimethylphenoxy)terephthaloyl chloride may be used to replace terephthaloyl chloride in preparing the rigid-rod backbone to ensure a random distribution of the graft sites. Also, it may be argued, based on geometrical considerations, that the reactivities of 2-(2,4,6-trimethylphenoxy)terephthaloyl chloride and of 2-(2,6-dimethylphenoxy)terephthaloyl chloride with 2,5-diamino-1,4-benzenedithiol dihydrochloride are similar. Experimental studies are currently under way to address some of the issues described above. Results of these studies will be reported at a later date.

CONCLUSIONS

The influence of molecular structure on processing conditions and tensile mechanical properties was studied for a series of graft rigid-rod copolymers with different side-chain lengths, frequency of side-chains and rigid-rod backbone length. Dynamic mechanical spectra of these graft copolymers revealed three characteristic regions: an initial plateau region, a transition zone and a second plateau region. The transition, which led to the softening and processability of the graft copolymers, was a secondary transition associated with the localized mobility of the graft PEK side-chains. Preliminary results from the tensile tests indicated that the tensile properties of these graft rigid-rod copolymers were relatively poor compared with those of rigid-rod molecular composite blends. The significance of low tensile strength of the graft copolymers was believed to be due to low molecular weight of the PEK side-chains, insufficient to provide adequate chain entanglements within the matrix phase.

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