Blends of poly(aryl ether ether ketone) with thermotropic liquid-crystalline copolyesters:
2. Crystallization kinetics

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The crystallization kinetics of blends of poly(aryl ether ether ketone) (PEEK) and thermotropic liquid-crystalline copolyesters have been studied by differential scanning calorimetry and optical microscopy. The overall crystallization rates of the blends were found to be dependent on the blend composition. With increasing mesomorphic content, the rate increased to pass through a maximum and then decreased to lower values. The linear spherulite growth rate of PEEK in the blends during isothermal crystallization was found to be smaller than that of pure PEEK. On the other hand, the nucleation density determined in the blends was about two orders of magnitude higher than that observed in a pure PEEK specimen, which is shown to be a more important factor in influencing the overall crystallization rate of these systems. On the basis of experimental results and theoretical treatments, it was believed that the crystallization process of the blends was initiated by heterogeneous nuclei, which were formed by the existing microdomains of the liquid-crystalline polymer, and that the number of heterogeneous nuclei was mainly determined by the size of the microdomains instead of the amount of liquid-crystal component present in the blends.

(Keywords: poly(aryl ether ether ketone); thermotropic polyesters; aromatic polymer; liquid-crystalline polymer; copolyester; blend; crystallization kinetics; heterogeneous nucleation; spherulite growth rate; microdomain)

INTRODUCTION

Investigation of polymeric blend systems containing a thermotropic liquid-crystal polymer (TLCP) has attracted increasing attention in recent years[1–6]. The liquid-crystalline component in the blends shows great promise to improve the processing and performance of these materials. For the blends with crystallizable polymers, the presence of a rigid TLCP component may influence to a significant extent the morphology, crystallinity, crystallization kinetics and melting behaviour of the crystallizable component. This, in turn, will affect the ultimate solid-state properties of the materials.

Poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene), commonly known as poly(aryl ether ether ketone) or PEEK, is a semicrystalline polymer with balanced properties as a high-performance engineering resin as well as a thermoplastic matrix for advanced structural composites. Consequently, it is of great interest to investigate the systems of PEEK blended with TLCP. Such studies were suggested based on the following considerations: (1) the melt viscosity of PEEK may be reduced by adding a TLCP component; (2) at the same time, PEEK will be reinforced with the rigid microdomains of TLCP as suggested by the concept of '*in situ* composite'[7] to form a new kind of composite material; and (3) the addition of a rigid-chain polymer component may reduce or influence the anisotropy of fibre-reinforced PEEK composite materials. In a previous report[8], we described the phase morphology and melting behaviours of PEEK blends, as obtained by solution precipitation, with a thermotropic wholly aromatic copolyester. Phase segregation upon heating was observed for the as-precipitated blends. The phase morphology and the melting behaviour of the blends were affected by the TLCP component. Both higher crystallinity and smaller crystal size were found with increasing TLCP content. It was believed that the presence of the TLCP component imposed contrary effects of nucleation and dilution on the crystallization of the PEEK component. Enhanced overall rates of crystallization have been found for the blends containing 5–20 wt% of TLCP.

In order to understand the effects of TLCP on the crystallization behaviour, it is the purpose of this paper to investigate the isothermal crystallization processes of these blends. Isothermal crystallization kinetics data were obtained by d.s.c. and were treated by related theoretical equations. The spherulite growth rates of the blends were determined by optical microscopy as a function of TLCP composition. Another aromatic copolyester TLCP with similar chemical structure as the one used in the previous work but with more rigid chain segments was also used in this work to examine the effect of the chain structure of TLCP on the crystallization behaviour of the blends. The origin of the change in the crystallization rate of PEEK in the blends was discussed.

EXPERIMENTAL

Materials

The PEEK sample used in this work is an ICI product

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(450P). The as-received sample was purified by first dissolving in *p*-chlorophenol followed by precipitating in methanol to remove any impurity that may exist. The liquid-crystal polymers are thermotropic wholly aromatic copolyesters of Xydar type, a copolymer of *p*-hydroxybenzoic acid, terephthalic acid, *m*-phthalic acid and 4,4′-biphenol, which were kindly supplied by the Silicone Research Centre, Chengdu, China. The one used in the previous study[8] has been referred to as LCP-111 with $[\eta]=0.50\,\mathrm{dl\,g^{-1}}$ measured in *p*-chlorophenol at 35°C; the other with more rigid chain segments, as known based on knowledge of its chemical structure and phase transition behaviour, is referred to here as LCP-116 with $[\eta]=0.60\,\mathrm{dl\,g^{-1}}$. LCP-111 forms a nematic phase in the range 300–450°C, while LCP-116 forms such a phase at 300–500°C. The nematic texture can be readily preserved upon cooling. Both LCP samples were also purified by solution filtration followed by precipitation prior to use.

Sample preparation

Solution blending was the method used for preparing blends of PEEK/LCP, which is believed to be the better way to produce well mixed polymeric blends more suitable for detailed investigations. A known amount of PEEK/LCP purified powder was first dissolved in *p*-chlorophenol at about 150°C; the solution was then precipitated with methanol. The precipitate was dried in a vacuum oven at 70°C to remove solvent. The pure PEEK sample used was also precipitated via the same procedures as for preparing blends.

Crystallization kinetics measurements

Differential scanning calorimetry (d.s.c.) has frequently been used to investigate the rate of crystallization of polymers and blends[6,9–11]. The crystallization kinetics data were collected using a Perkin–Elmer DSC-2C calorimeter operating under nitrogen flow. Samples for isothermal crystallization measurements were first heated to 380°C at $20°\mathrm{C\,min^{-1}}$ and held at that temperature for 3 min; and then cooled at $-320°\mathrm{C\,min^{-1}}$ to the desired crystallization temperature T_c for a prolonged period (at least 5 min depending on the T_c used). During the crystallization process, the heat of crystallization was recorded as a function of time. The fractional weight crystallinity, X_t, developed at time t was evaluated by the ratio of the crystallization area at time t over the total area of the exothermal peak.

Spherulite growth rate measurement

A Leitz Orthoplan polarizing microscope with a heating stage was used to measure the spherulite growth rate. A small amount of blend powder sandwiched between two clean microscope coverglasses was heated to 410°C for a few minutes and then cooled quickly to the crystallization temperature. The linear growth rate of the PEEK spherulites was monitored by measuring the increment of the spherulite diameters (an average of at least 10 spherulites) from micrographs taken at successive time intervals.

RESULTS

Isothermal crystallization experiments were carried out at 298, 300, 302 and 305°C, respectively. The selection of these crystallization temperatures is based on the fact that, with the addition of the mesomorphic component, the crystallization processes of PEEK became too fast to ensure the isothermal condition at lower temperature. Since it was found that the liquid-crystalline components, namely LCP-111 and LCP-116, did not crystallize in the temperature range, the heat developed during isothermal crystallization can be attributed totally to the PEEK component. In *Figures 1* and *2*, plots of fractional weight crystallinity X_t *versus* time are shown for blends of PEEK/LCP-111 and PEEK/LCP-116, respectively, crystallized at 300°C. It is evident that, for blends with 10–50 wt% of liquid-crystal copolyester, the presence of mesomorphic polymer causes the crystallization isotherms to shift towards shorter crystallization time. This may be seen in a more quantitative and straightforward way by comparing their crystallization half-time $t_{0.5}$, as listed in *Table 1*. A remarkable decrease of $t_{0.5}$ by a factor of more than 2 is found for the blends with 10 wt% of TLCP over the range of T_c studied. Whereas for blends with TLCP content higher than 70 wt%, increases in the value of $t_{0.5}$ over that of pure PEEK are observed for both the TLCPs used. Because the variation of crystallization rate of the blends does not simply increase or decrease with increasing TLCP content, these data reflect the results of competition between several different effects as the mesomorphic phase is involved in the crystallization process of PEEK.

The Avrami equation has frequently been used to describe the overall crystallization for polymer spherulitic growth under isothermal conditions[12,13]. *Figure 3* gives a typical example of these plots for the blends of LCP-111/PEEK crystallized at 300°C. Values of the kinetic constant K and the Avrami exponent n obtained for all the samples crystallized at each T_c are also summarized in *Table 1*. It can be seen that adding TLCP as a minor component in the blend composition (i.e. <50 wt%)

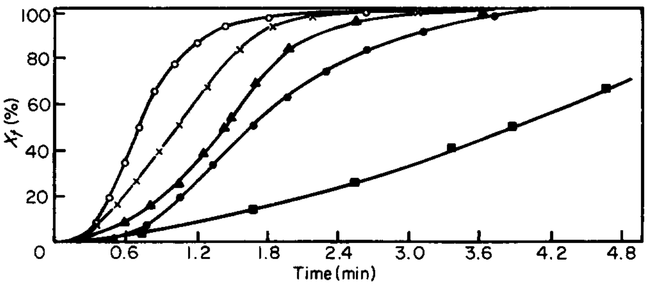

Figure 1 Plots of crystallization fraction X_t *versus* time t for LCP-111/PEEK blends crystallized at 300°C: PEEK (●); LCP-111/PEEK (○) 10/90, (△) 30/70, (×) 50/50, (□) 90/10

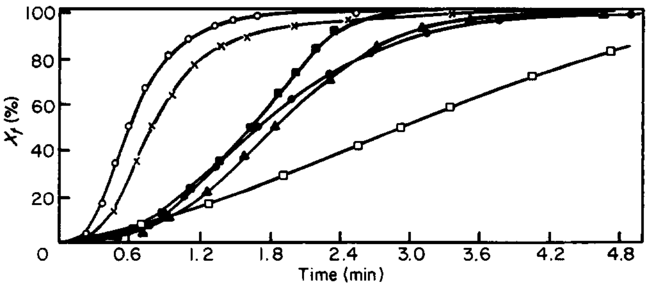

Figure 2 Plots of crystallization fraction X_t *versus* time t for LCP-116/PEEK blends crystallized at 300°C: PEEK (●); LCP-116/PEEK (○) 10/90, (△) 30/70, (×) 50/50, (■) 70/30, (□) 90/10

Table 1 Values of the kinetic parameters for the isothermal crystallization of LCP/PEEK blends at various T_c

	Parameters											
	298°C			300°C			302°C			305°C		
Sample	n	K	$t_{0.5}$	n	K	$t_{0.5}$	n	K	$t_{0.5}$	n	K	$t_{0.5}$
PEEK	2.5	0.13	1.71	2.5	0.17	1.69	2.6	0.05	2.51	2.4	0.02	3.79
LCP-111/PEEK												
10/90	1.9	0.96	0.79	2.1	1.22	0.72	2.2	0.49	1.00	2.6	0.13	1.68
30/70	2.0	0.16	1.94	2.3	0.32	1.46	2.2	0.10	2.54	2.0	0.05	3.95
50/50				2.3	0.68	1.07						
90/10				1.8	0.07	3.89						
LCP-116/PEEK												
10/90				2.2	1.64	0.60						
30/70				2.7	0.13	1.85						
50/50				2.2	0.80	0.80						
70/30				2.7	0.20	1.64						
90/10				1.8	0.12	2.95						

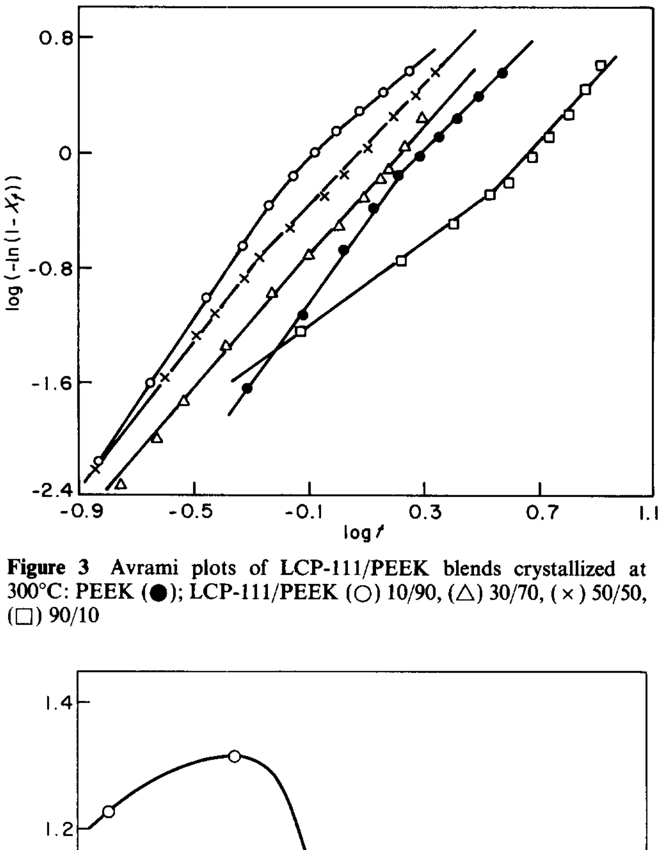

Figure 3 Avrami plots of LCP-111/PEEK blends crystallized at 300°C: PEEK (●); LCP-111/PEEK (○) 10/90, (△) 30/70, (×) 50/50, (□) 90/10

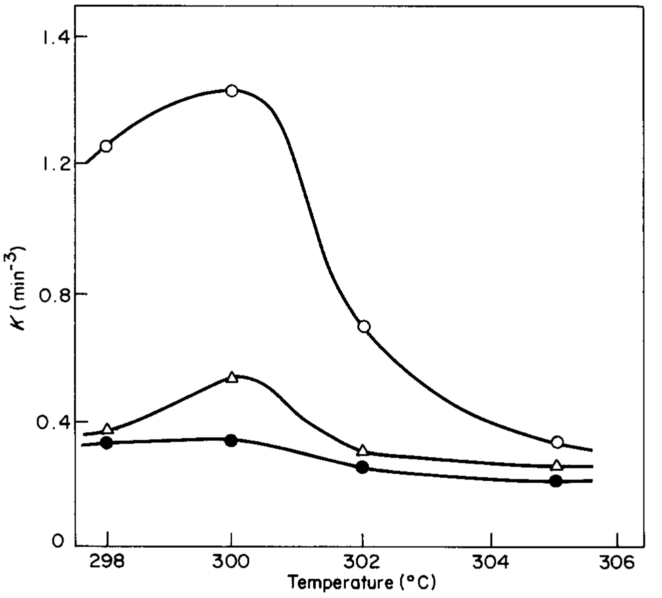

Figure 4 Comparison of crystallization rate of PEEK and LCP/PEEK blends with change of T_c: PEEK (●) (peak crystallization temperature 230°C[11]); LCP/PEEK (○) 10/90, (△) 30/70

results in an increase in the value of K. In addition, variation of K and $t_{0.5}$ of the blends seems more sensitive to the crystallization temperature than those of pure PEEK, i.e. for the blends a more significant difference in K values is found when changing T_c. As shown in *Figure 4*, a maximum is observed apparently for the 10/90(LCP-111/PEEK) blend at 300°C.

Except for the 90/10 blends, values of n obtained from the Avrami plots are between 2 and 3, and show little dependence on the blend composition and crystallization temperature, suggesting the heterogeneous nucleation nature of these systems. As shown in *Figure 3*, however, deviations from linearity are observed at higher crystallization conversions or times. The slope of the curves tends to smaller values of n and K, which is consistent with lower dimensional growth or secondary crystallization in the late stage of the crystallization process. From the plots in *Figure 3*, it can also be seen that the crystallization induction period for PEEK in the pure form is longer than that of blends. Approximately, all the curves for blend samples appear to meet in a common point very close to zero crystallization time, indicating again that the growth of PEEK crystals should be initiated by heterogeneous nucleation.

The spherulitic growth rate of the blend and PEEK samples was monitored at a crystallization temperature of 300°C by optical microscopy in order to study the effects of liquid-crystalline component on the growth processes of PEEK crystals. The solution-cast films were first heated to 410°C in a hot stage, which has been considered to be a proper temperature at which any PEEK crystallites existed previously can be completely melted[14]. The melt was then cooled to the crystallization temperature in a few seconds. The linear growth rate was followed with time by measuring the spherulite diameters from optical micrographs taken at successive time intervals. *Figure 5* shows representative micrographs taken at different times during the crystallization processes of pure PEEK (*Figures 5a* and *5b*), LCP-111/PEEK (10/90, *Figures 5c* and *5d*) and LCP-116/PEEK (10/90, *Figures 5e* and *5f*). It can be noted that the number of spherulites in the pure PEEK film is much smaller than that observed for the blends if the same sample area is considered. When comparing samples blended with different TLCP component, those containing LCP-116 appear to have a smaller number of spherulites than that found for samples

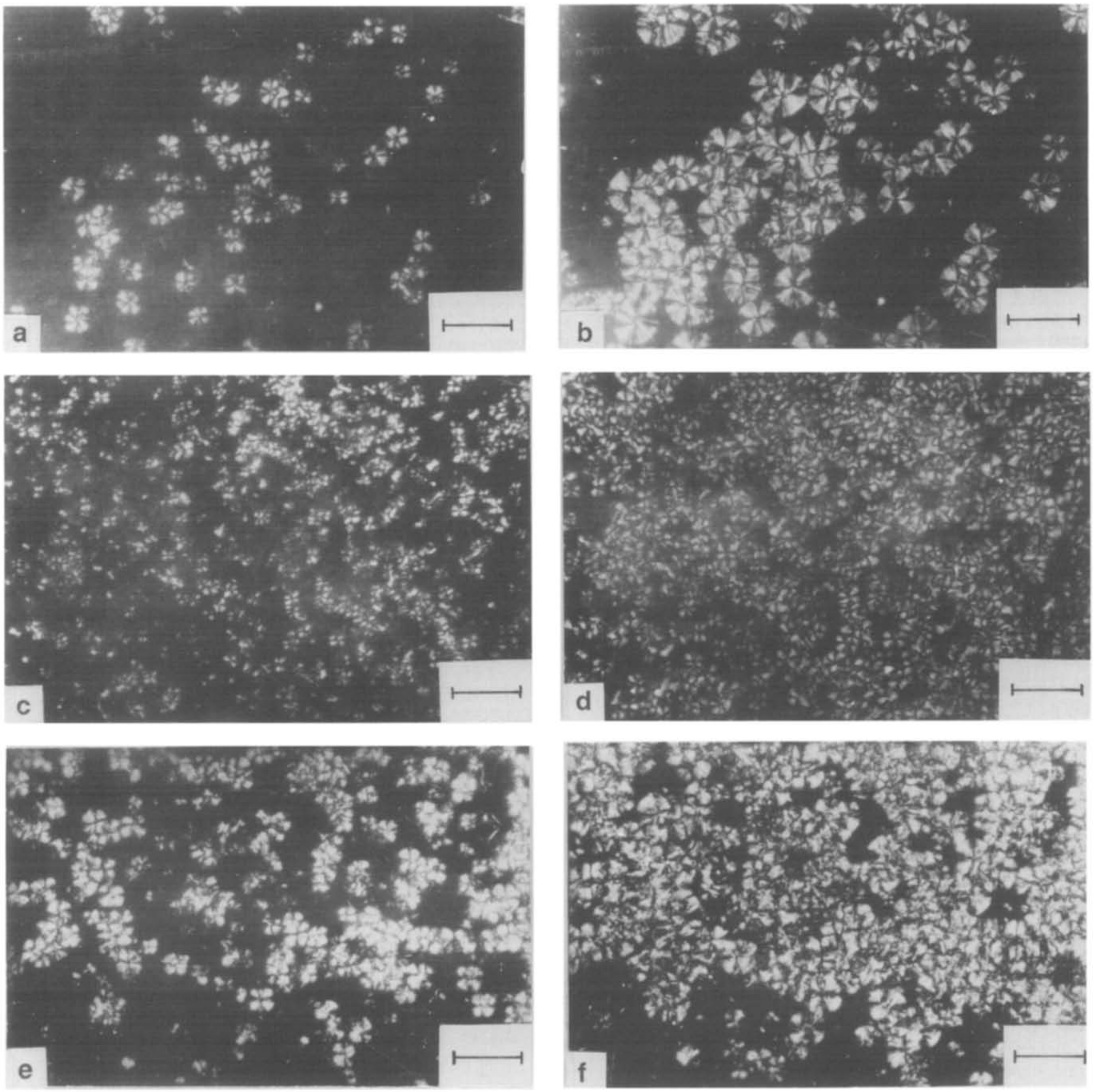

Figure 5 Micrographs of the crystallization process of the blends at 300°C for different times: (a) PEEK, 8 min; (b) PEEK, 13 min; (c) LCP-111/PEEK 10/90, 9 min; (d) LCP-111/PEEK 10/90, 14 min; (e) LCP-116/PEEK 10/90, 9 min; (f) LCP-116/PEEK 10/90, 13 min. The scale bar in each part is 40 μm

containing LCP-111. Increasing the TLCP content in the blends did not appear to enhance the number of spherulites, not shown in *Figure 5*, but showed somewhat a decrease in the number. Corresponding to the number of spherulites in the films, average spherulite size reduced in the order of PEEK, LCP-116/PEEK and LCP-111/PEEK. The crystal morphology of the blends at lower TLCP content still appeared to be well defined spherulites with Maltese crosses. For blends with higher TLCP content, the crystals displayed less regular radial structure and less clear borders, so that accurate measurement of the diameters became impossible.

The linear isothermal radial growth of PEEK and blend spherulites at 300°C is shown in *Figure 6*, where the average spherulite diameter is plotted as a function of

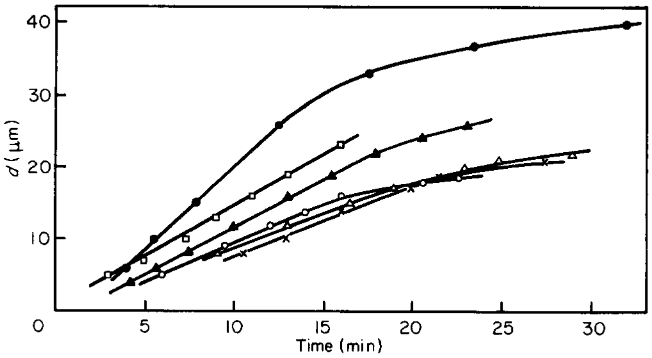

Figure 6 Plots of the spherulite diameter *versus* crystallization time at 300°C: PEEK (●); LCP-111/PEEK (○) 10/90, (△) 30/70, (×) 50/50; LCP-116/PEEK (□) 10/90, (▲) 30/70

Table 2 The radial growth rate, G (μm min^{-1}), of spherulites of the LCP/PEEK blends crystallized at 300°C

		LCP-111/PEEK			LCP-116/PEEK	
	PEEK	10/90	30/70	50/50	10/90	30/70
G	1.65	1.05	0.86	0.97	1.40	1.20

crystallization time. The growth was linear for an initial time period and then deviated from linearity with increasing crystallization time, due to the impinging of spherulites on each other. The values of radial growth rate G calculated from the slope of each curve are listed in *Table 2*. It should be noted that the growth rate is dependent on the blend composition and the highest rate value is found for the pure PEEK sample.

DISCUSSION

The results of this work have shown that the crystallization rate of PEEK/LCP blends was dependent on the blend composition. With increasing TLCP content, the overall rate increased to pass through a maximum and then decreased, suggesting the existence of competition between opposing effects of the mesomorphic component on the crystallization processes of PEEK. The variation of kinetic constant K can be related to the linear growth rate G of PEEK crystals and the average nucleation density $\bar{N}$ in the blends. In the case of athermal nucleation and three-dimensional growth, the kinetic constant may be expressed as[15]:

$$K = \tfrac{4}{3}\pi G^3 \bar{N}$$

The average nucleation densities calculated using this equation are listed in *Table 3*. It is clearly seen that the addition of TLCP component significantly enhances the nucleation density in the blends. This is also consistent with the observations of microscopy shown in *Figure 5*, where the number of spherulites in the blend films is larger than that observed for pure PEEK. The effects of TLCP component on the crystallization processes should thus include at least two aspects, namely nucleation and dilution. For the nucleation effect, the introduction of the rigid-chain TLCP presents a large number of nuclei to the system, leading to an increase in crystallization rate; whereas the presence of a foreign component in the system will hinder the transport or diffusion of the crystallizable component to the crystal growth front. When, in the case of lower TLCP content, the nucleation effect dominates, the result is a higher crystallization rate; with the TLCP content increased, the diluent effect will become dominant, resulting in a lower rate. Consequently, the contrasting effects should compete with each other to reach an equilibrium at which a maximum in the overall crystallization rate at a certain blend composition may be found. In contrast, when PEEK was blended with an amorphous flexible polymer such as poly(aryl ether sulphone) with cardo side groups (PES-C)* or poly(aryl ether ether ketone) with cardo side groups (PEK-C)†, the crystallization rate of PEEK was found to decrease remarkably with increasing content of PES-C or PEK-C[16]. In these cases, the presence of an amorphous component results in diluting the concentration of PEEK in the unit volume and hindering the transport of PEEK chains, causing solely the rate to decrease.

Besides the facts discussed above, the significant increase in nucleation rate in the blends can also be evidenced by the decrease in the induction time for the crystallization processes shown in *Figure 3*. It is known that the growth of a polymer crystal occurs in at least two stages: nucleation and growth[13]. In a heterogeneous nucleation, the existence of crystal nuclei in the melt before the start of crystallization is required. For the blend systems studied in this work, the existence of rigid mesomorphic chains or segments of TLCP possibly provides the required nuclei, thus showing a shorter induction time. In addition, the occurrence of heterogeneous nucleation shifts the peak crystallization temperature of PEEK from ~230°C[11] for the pure form to ~300°C for the blends and narrows the temperature range within which satisfactory isothermal crystallization measurements can be carried out, as shown in *Figure 4*.

The presence of heterogeneous nuclei can also influence the lamellar thickness and perfection of PEEK crystallites formed during the crystallization process. The following equation can be used to evaluate this effect[17]:

$$T'_{\mathrm{m}} = T^{\circ}_{\mathrm{m}}\left(1 - \frac{1}{\gamma}\right) + \frac{T_{\mathrm{c}}}{\gamma}$$

where T'_{m} is the observed melting temperature, T°_{m} is the equilibrium melting temperature and γ is a factor relating the initial lamellar thickness to the mean final thickness at the end of the crystallization process. The results are included in *Table 3*, where values of γ are somewhat related to the nucleation density of blends. By definition, a value of γ that is close to unity would be indicative of less thickening of the initial lamella. The data, therefore, imply that in the blends the lamellar thickness experiences little thickening as long as they were initiated by the heterogeneous nuclei.

Since there exists a large number of heterogeneous nuclei, the crystal size of blends is governed mainly by the number of nuclei, as is evident in *Figure 5*. However, the nucleation density in the blend does not increase simply with increasing TLCP content as also seen in *Table 3*, where the nucleation densities of the blends were found to be of the same order of magnitude regardless of the increase in TLCP amount in several folds. These results indicate that the number of heterogeneous nuclei is not directly proportional to the amount of rigid chains and/or

Table 3 The average density of nuclei and the factor γ for the blends isothermally crystallized at 300°C

		$\bar{N}$ (cm^{-3})	γ
PEEK		8.83×10^9	1.10
LCP-111/PEEK	10/90	2.53×10^{11}	1.03
	30/70	1.22×10^{11}	1.04
	50/50	1.61×10^{11}	1.06
LCP-116/PEEK	10/90	1.43×10^{11}	
	30/70	1.82×10^{11}	

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* IUPAC nomenclature: poly(phthalidylidene-1,4-phenyleneoxy-1,4-phenylenesulphonyl-1,4-phenyleneoxy-1,4-phenylene)

† IUPAC nomenclature: poly(phthalidylidene-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenyleneoxy-1,4-phenylene)

segments (and the amount of TLCP therewith) in the blends.

To explain the experimental results, we propose that it is the size of the TLCP microdomains that determines the nucleation density in the blends. As also pointed out in the previous work[8], the blend of PEEK/LCP-111 (or 116) is a substantially immiscible blend system in which phase segregation occurs upon heating. The phase domain size of the liquid-crystalline polymer increases with increasing LCP content as observed by microscopy. It may then be expected that, once the size of the TLCP microdomains exceeds the critical nucleation size for PEEK crystallization, the nucleation function of the microdomains would be depressed or diminished. Another example of polymer crystallization nucleated by TLCP microdomains has been reported for the system of poly(ether sulphone) (PES), which is generally classified as an amorphous polymer, blended with a similar aromatic liquid-crystalline copolyester[18]. Spherulite-like globules can be formed in a PES/LCP solution-cast film in the case of LCP being a disperse phase in the blend. Moreover, attempts to grow the globular structure directly from the melt blend have failed, probably due to the difficulty of nucleation in the melt as phase segregation occurred on heating, which causes the size of the LCP microdomains to increase. Phase separation on heating is well known to be controlled by thermodynamic factors[19]. This can account for the greater temperature sensitivity of the variation of K and $t_{0.5}$ for the blends shown in *Figure 4*, because the phase morphology of the mesomorphic component is expected to be more temperature-dependent.

Additionally, chain flexibility of the TLCP component may be another factor to influence the crystallization behaviour of the blends. From *Tables 1* and *2* and *Figure 5*, higher values of K and G were observed for blends with LCP-116. Because LCP-116 is more rigid in its chain structure, the miscibility or interaction of its segments with PEEK chains or segments may be poorer than that of LCP-111. As evidenced by optical microscopy observation (photographs not shown), the phase segregation of LCP-116/PEEK sample is more significant and its microdomain size is larger. To account for the higher values of K and G, it is possible that although the number of nuclei in the LCP-116/PEEK blend is somewhat less (e.g. compare the 10/90 blends in *Table 3*) than that of LCP-111/PEEK blend, the poorer miscibility or interaction with PEEK can also reduce the diluent effect more significantly.

For the systems investigated in this work, it is believed that the growth of PEEK crystals should be initiated by athermal nucleation. The crystallization mechanism that theoretically fits the Avrami equation with an exponent $n \simeq 3$ is 'athermal nucleation and three-dimensional growth'; while for $n = 2$, the mechanisms of either 'athermal nucleation and three-dimensional circular lamellar growth' or 'athermal nucleation and two-dimensional circular growth'[13,15] may be involved. These mechanisms are qualitatively consistent with the crystallization processes observed in this study.

CONCLUSIONS

The crystallization kinetic studies on the blends of semicrystalline PEEK and aromatic liquid-crystalline copolyesters in this work have shown that the overall crystallization rate of blends depends on the blend composition. It was pointed out that the rate increased to pass through a maximum and then decreased with increasing mesomorphic content, due mainly to the existence of competition between the nucleation and diluent effects. The mean nucleation density in the blends was much higher than that observed for pure PEEK, whereas the linear spherulite growth rate for the blends was lower, suggesting the more important role of nucleation in affecting crystallization rate. The nucleation effect can also account for the lower induction time of crystallization and the higher peak crystallization temperature of the blends. Based on the experimental results, it was proposed that the size of microdomains of the liquid-crystalline polymer determined the nucleation density and thus the crystallization behaviour of these blend systems.

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