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Miscibility and crystallization behaviour of poly(ether ether ketone)/polyimide blends

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The miscibility and crystallization behaviour of the blends of poly(ether ether ketone) (PEEK) with two thermoplastic polyimides (PI), PEI-E and YS-30, prepared by solution blending were studied by the use of small-angle X-ray scattering (SAXS), differential scanning calorimetry (d.s.c.) and polarizing microscopy techniques. The results obtained show that PEEK/YS-30 is miscible, while PEEK/PEI-E is partially miscible only in the composition range with PEI-E content up to 20 wt%. The crystallization behaviour of PEEK in PEEK/PI blends depends on the crystallization condition of the blend sample as well as the chemical structure and the content of the PI added. Our SAXS results indicate that the segregation of PI molecular chains during crystallization of PEEK chains in the blends is interfibrillar for PEEK/PEI-E blends, but interlamellar for PEEK/YS-30 blends. The compatibility and the crystallization behaviour are discussed in terms of charge transfer interaction between PI and PI molecules and between PI and PEEK molecules.

(Keywords: miscibility; crystallization; poly(ether ether ketone); thermoplastic polyimide; charge transfer interaction)

Introduction

Poly(ether ether ketone) (PEEK) is a high-performance engineering thermoplastic which is being increasingly used in technical and commercial applications requiring its high-temperature resistance and good mechanical properties[1]. It is especially suitable for use as a matrix material for thermoplastic composites because of its good adhesion to glass and carbon fibres, which is ascribed to the formation of a transcrystalline region at the fibre surface[2]. Polyimides (PIs) are also high-performance plastics with higher glass transition temperatures (T_gs), but they have lower chemical resistance than PEEK. Therefore, blending of PEEK with PI seems to be an interesting route to combine the complementary properties of both polymers[3–6]. In this work, the miscibility and crystallization behaviour of two pairs of PEEK/PI blends were investigated by using differential scanning calorimetry (d.s.c.) and small-angle X-ray scattering (SAXS) techniques.

Experimental

PEEK and thermoplastic PI YS-30 are commercial products from the Shanghai Institute of Synthetic Resins and Jilin University, respectively. Thermoplastic PI PEI-E was prepared in our laboratory. The chemical structures of PEI-E and YS-30 are shown in *Figure 1*.

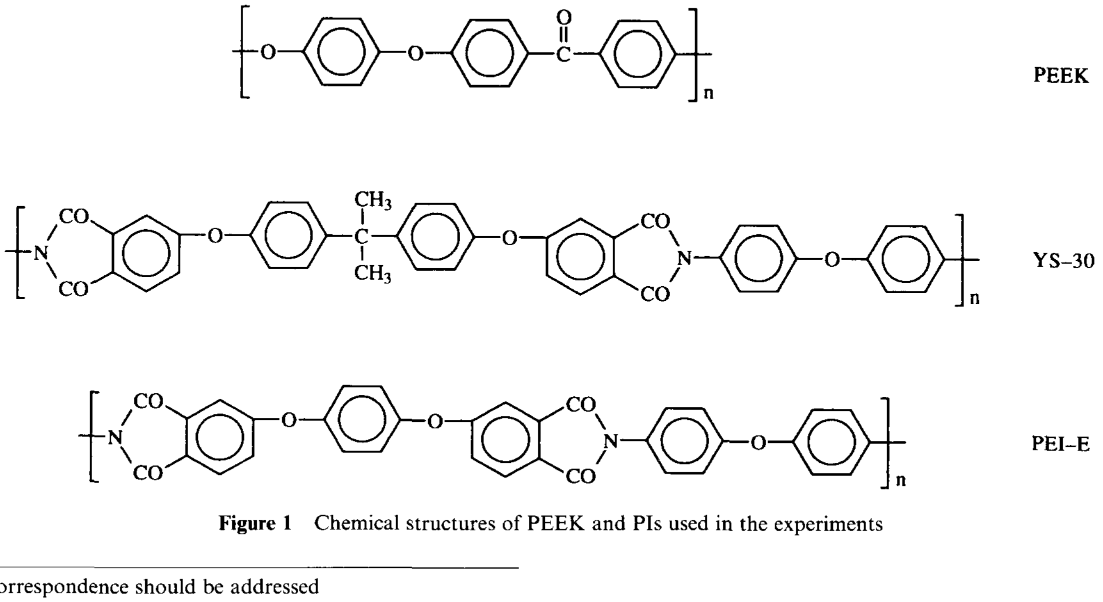

Figure 1 Chemical structures of PEEK and PIs used in the experiments

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Table 1 The glass transition temperatures of PEEK/PI blends (°C)

	100/0	80/20	60/40	40/60	20/80	0/100
PEEK/YS-30	161	160	180	189	193	221
PEEK/PEI-E	161	162	163	162	160	
			238	241	240	238

Solution blending of powders of PEEK and PI was used, i.e. they were dissolved in *p*-chlorophenol and then the solution was cast onto glass. The cast films of different blends were dried in a vacuum oven at 80°C for two weeks followed by 200°C for 5 h. The films thus obtained were heated at 300°C for 2 h (cold-crystallized) or heated to 400°C for 5 min and then cooled to 200°C at a rate of 10°C min^{-1} (melt-crystallized).

SAXS experiments were registered with a Kratky SAXS camera on a Philips PW 1700 automated powder diffractometer. The differential enthalpy of the samples was determined with a Perkin–Elmer DSC-2C differential scanning calorimeter with a heating rate of 20°C min^{-1}. A polarizing microscope was used for studying crystallization. The specimens used were prepared by casting the solution onto a piece of glass, then drying in a vacuum oven at 80°C for two weeks followed by 200°C for 20 h, then the specimens were melt-crystallized.

Results and discussion

Listed in *Table 1* are the glass transition temperatures of PEEK/YS-30 and PEEK/PEI-E blends, determined by the second d.s.c. traces. It is seen that PEEK/YS-30 blends exhibit only a single glass transition over the entire composition range, indicating that PEEK/YS-30 is totally miscible. However, the PEEK/PEI-E blend is partially miscible, since the blends with PEI-E content more than 20% all have two glass transitions.

The crystallinities (corresponding to PEEK) of PEEK/PI blends, determined by the d.s.c. method, are listed in *Table 2*. (A heat of fusion of 100% crystalline PEEK of 130 J g^{-1} was used.) From *Table 2* it can be seen that with the increase in PI content the crystallinity of PEEK changes within a rather narrow region in PEEK/PI blends for both the original and the 300°C cold-crystallized samples; however, the melting temperature T_m of cold-crystallized samples decreases with PI content (see *Figure 2*). On the other hand, the crystallinity of PEEK of the melt-crystallized samples, especially for PEEK/YS-30 blends, decreases rapidly with the increase in PI content, and the crystallinity is much lower than that of the original or that of the cold-crystallized samples. Moreover, the T_m of melt-crystallized samples remains nearly constant (see *Figure 3*). For the melt-crystallized samples, no crystallization of PEEK in PEEK/YS-30 blends takes place when the content of YS-30 is over 60 wt%. However, for PEEK/PEI-E blends, crystallization exists even when the PEI-E content reaches 80%. Shown in *Figure 4* are the polarizing micrographs of melt-crystallized PEEK/PI blends with different compositions. For PEEK/PEI-E blends, the crystalline structure of PEEK is obvious even when the PEI-E content reaches 80%; however, there is no crystallization in PEEK/YS-30 blends when the YS-30 content reaches 60%. These polarizing microscope observations are in good agreement with the d.s.c. results shown in *Table 2*.

There are two possible cases for the segregation of the PI molecular chains during the crystallization of PEEK in a PEEK/PI blend: interlamellar and interfibrillar segregation of the chains. A thorough study of the morphology and crystallization behaviour of PEEK/PEI blends has been reported by Crevecoeur and Groeninckx[3]. They found that the dominant morphology was interlamellar rejection of PEI during PEEK crystallization. For the PEEK/PI blends studied, since the T_m of melt-crystallized samples is constant for all compositions, i.e. the lamellar thickness is not expected to depend on the blend composition, so interlamellar segregation of PIs would result in an increase in periodicity (the sum of the lamellar thickness and of the amorphous layer between the lamellae) with increasing PI content. Listed in *Table 3* are the values of the long spacing L of crystalline PEEK domains, determined from melt-crystallized PEEK/PI blends by desmeared SAXS curves. From the data listed in *Table 3* it can be seen that the long spacing of PEEK domains remains nearly constant for the PEEK/PEI-E blends of different compositions studied, while the addition of YS-30 makes the long spacing L increase in PEEK/YS-30 blends. Hence, it is evident that the segregation of PI chains during crystallization of PEEK chains is interfibrillar for PEEK/PEI-E blends, and interlamellar for PEEK/YS-30 blends.

The crystallization behaviour of PEEK in PEEK/PI blends depends on both the preparation condition of the samples and the chemical structure of PIs. It is reported[7], and our previous work[8] has shown, that there is charge transfer interaction between imide group and the *p*-phenylene group of PI. The charge transfer interaction between the molecules in PEEK/PI blends includes two types: charge transfer interaction between PI and PI molecules, and that between PI and PEEK molecules (imide groups of PI and *p*-phenylene group of PEEK as electron acceptor and *p*-phenylene group of PI as electron donor). These two kinds of interactions are competitive with each other. As a general rule, if the

Table 2 The crystallinity of PEEK/PI blends (corresponding to the PEEK content) for different crystallization conditions (%)

	Crystallization conditions	100/0	80/20	60/40	40/60	20/80	0/100
PEEK/YS-30	Original	30.3	35.3	34.6	35.9	32.4	0
	Cold crystallization	58.2	55.4	56.1	59.4	54.3	0
	Melt crystallization	25.8	25.4	21.8	3.0	0	0
PEEK/PEI-E	Original	30.3	36.1	35.6	39.2	43.5	0
	Cold crystallization	58.2	51.4	51.8	55.4	49.8	0
	Melt crystallization	25.8	28.1	23.0	24.2	11.8	0

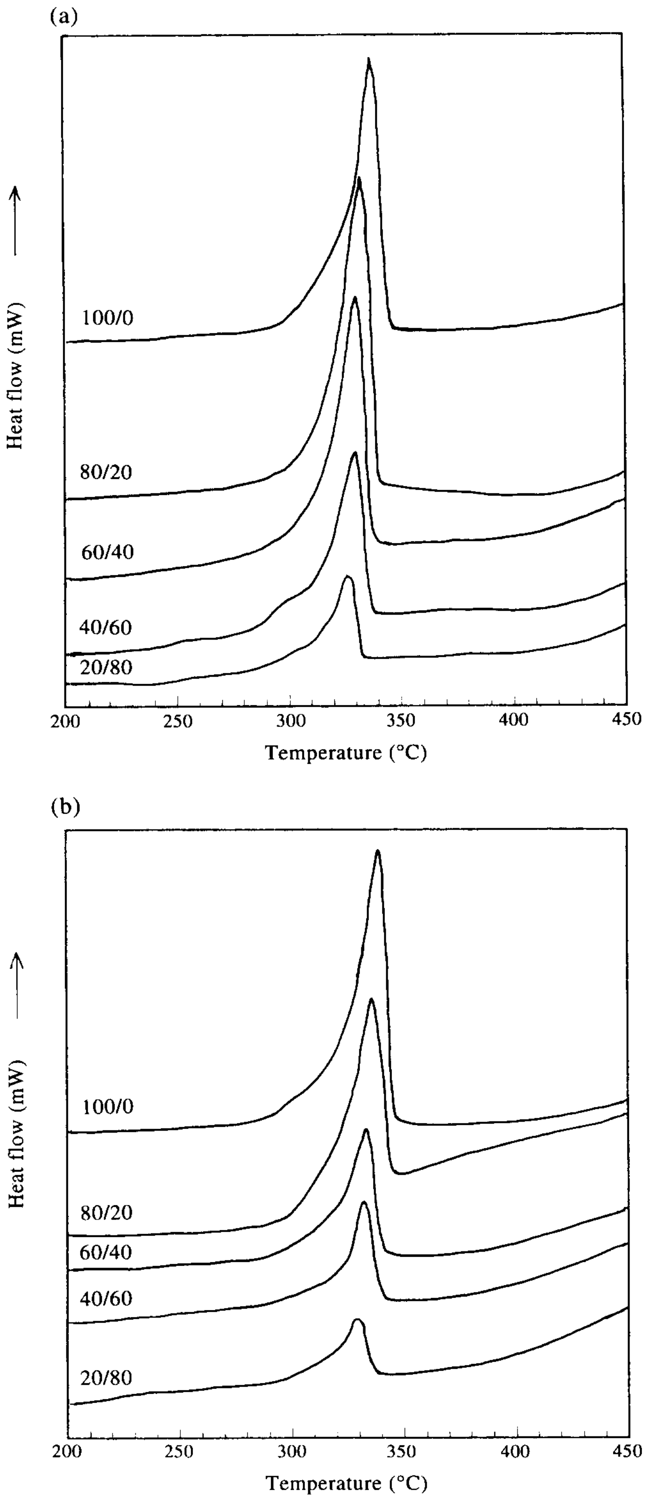

Figure 2 D.s.c. traces of cold-crystallized PEEK/PI blends. The samples were annealed at 300°C for 2 h: (a) PEEK/YS-30; (b) PEEK/PEI-E

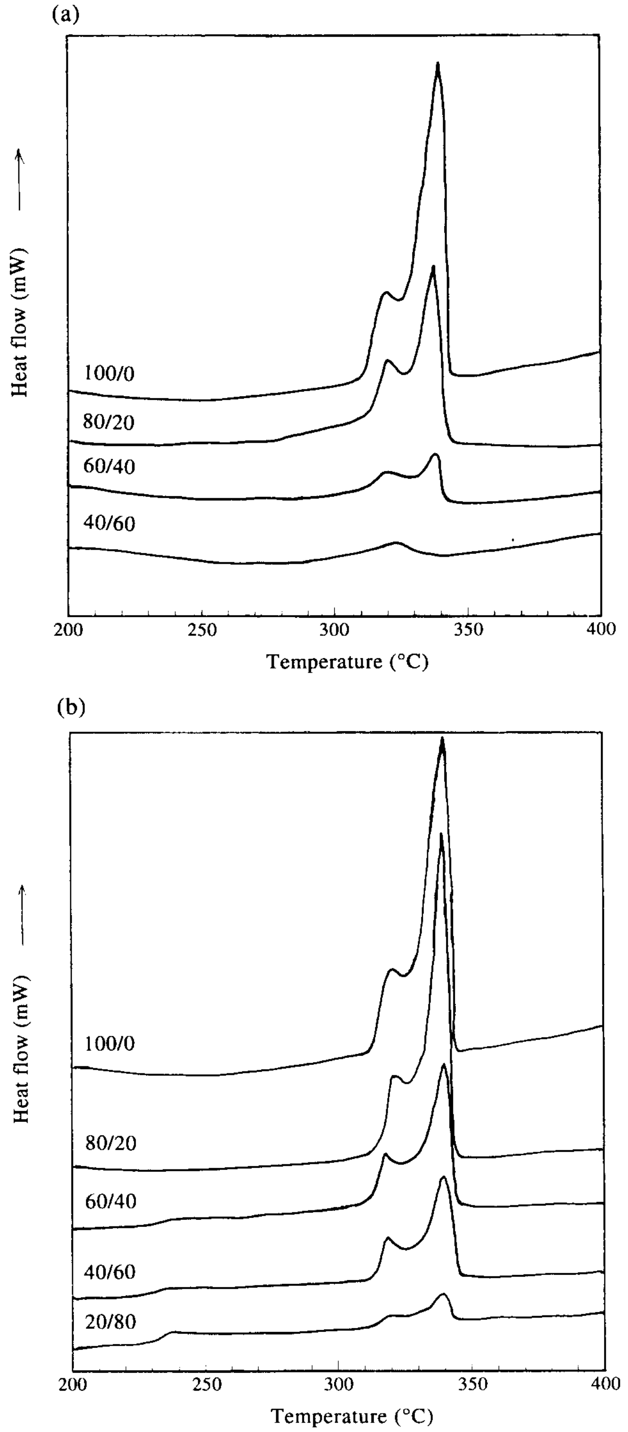

Figure 3 D.s.c. traces of melt-crystallized PEEK/PI blends: (a) PEEK/YS-30; (b) PEEK/PEI-E

latter interaction is stronger than the former one, then the blend will be compatible, the crystallization of PEEK will be hindered by the addition of PI, and the dominant morphology in such compatible PEEK/PI blends will be interlamellar. Otherwise, the blend will be incompatible, i.e. the effect of PI molecules on the crystallization behaviour of PEEK is weak, and the dominant morphology in such PEEK/PI blends is interfibrillar or interspherulitic. If the electron affinity of the anhydride moieties of PI is larger than that of the *p*-phenylene group of PEEK, the PI chains will aggregate and the interaction between PI and PI molecules is dominant, resulting in immiscibility of the blends. Otherwise, the interaction between the molecules of PI and PEEK will be dominant.

Segregation of two adjacent anhydride units along the chain by the introduction of some flexible linkages will always reduce the electron affinity of the anhydride moieties[9]. Since the anhydride of YS-30 is longer than

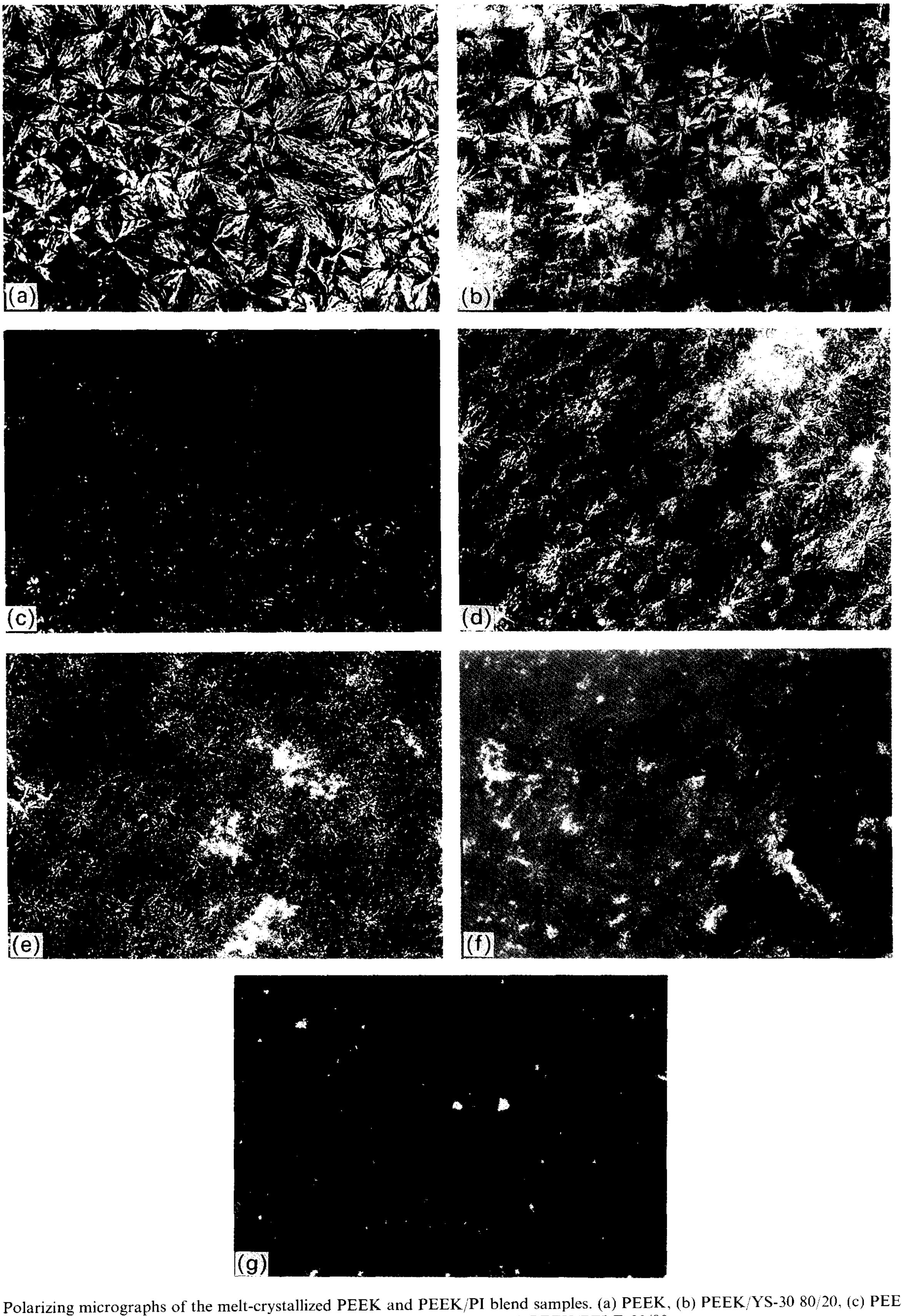

Figure 4 Polarizing micrographs of the melt-crystallized PEEK and PEEK/PI blend samples. (a) PEEK, (b) PEEK/YS-30 80/20, (c) PEEK/YS-30 60/40, (d) PEEK/PEI-E 80/20, (e) PEEK/PEI-E 60/40, (f) PEEK/PEI-E 40/60, (g) PEEK/PEI-E 20/80

Table 3 Long spacing L in PEEK/PI blends, determined by small-angle X-ray scattering (SAXS)

	PEEK	PEEK/PEI-E		PEEK/YS-30	
PEEK/PI (weight ratio)	100/0	80/20	60/40	80/20	60/40
Long spacing L (nm)	14.3	14.7	15.0	17.6	16.6

that of PEI-E, the affinity of YS-30 anhydride moieties is weaker than that of PEI-E, i.e. the interaction between PEEK and YS-30 chains will be dominant in PEEK/YS-30 blends. Therefore, the PEEK/YS-30 blends are miscible while PEEK/PEI-E blends are immiscible. Spectroscopic and n.m.r. studies of PEEK/PI blends are underway to clarify the effect of chemical structure of PI on the miscibility and crystallization behaviour of its blends with PEEK.

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