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Note

ROLE OF DECOMPOSITION PRODUCTS IN THE THERMAL PHASE DIAGRAM BEHAVIOR OF DIBENZOYL PEROXIDE SINGLE CRYSTALS

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The decomposition of dibenzoyl peroxide single crystals and polycrystalline samples has been subjected to several investigations [1–5]. The decomposition products were found to be phenyl benzoate, biphenyl and benzoic acid. It was indicated that benzoic acid could affect the phase behavior during the decomposition of DBP and, thus, DBP melts at temperatures much below the melting point. This was thought to be the reason for the autocatalysis of the DBP decomposition reaction, since rates of reaction in the liquid state are much higher than their counterparts in the solid state.

In this study, the phase diagrams of mixed crystals of DBP with each of phenyl benzoate, biphenyl and benzoic acid are reported.

EXPERIMENTAL

DBP and phenyl benzoate were prepared and crystallized by conventional methods. Chemically pure grades of benzoic acid and biphenyl were carefully crystallized from ethanol.

Mixed single crystals of the systems DBP/phenyl benzoate, DBP/benzoic acid and DBP/biphenyl were prepared by the slow crystallization of chloroform solutions containing molar ratios ranging between 10 and 90% of each component of the three systems.

Analyses of mixed crystals were done iodometrically by the determination of DMP content [6]. The phase behavior was observed microscopically using a hot-stage microscope.

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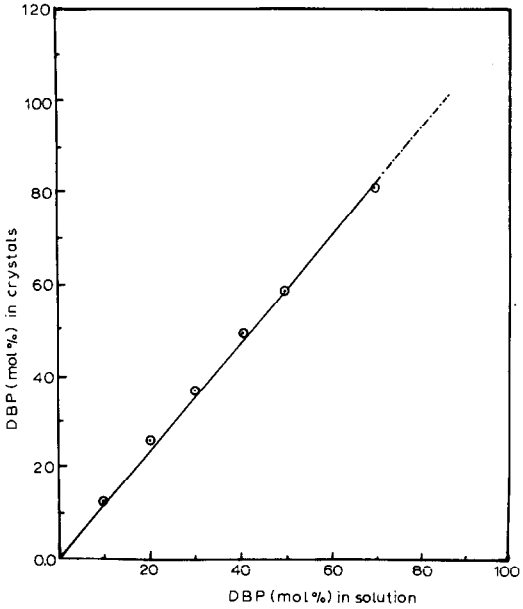

Fig. 1. A typical diagram showing the effect of DBP concentration in solution on its representation in mixed single crystals with PhCOOPh.

RESULTS AND DISCUSSION

Phenyl benzoate was found to form mixed crystals with DBP at all molar ratios. Chemical analyses have shown that the mixed crystals generated are

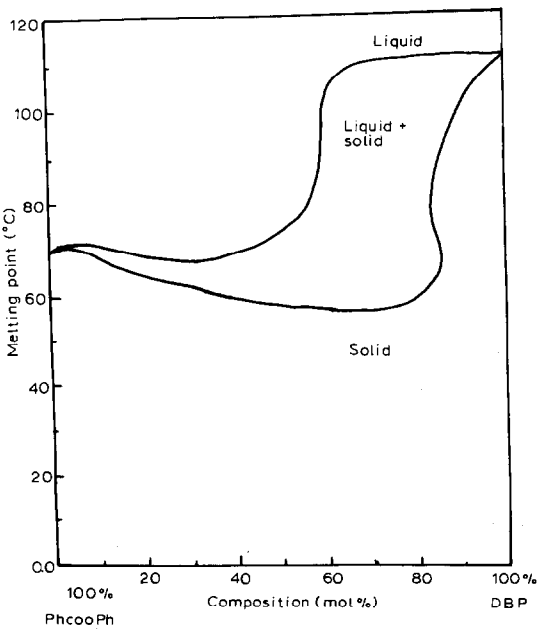

Fig. 2. Melting point–composition phase diagram of the DBP/phenyl benzoate system.

TABLE 1

Unit cell parameters of the materials investigated

Compound	Unit cell parameters	
Benzoic acid (PhCOOH)	$P2/C$ $Z = 4$	$a = 5.44$, $b = 5.18$, $c = 21.8$, $\beta = 97°5'$
Diphenyl (Ph–Ph)	$P2/C$ $Z = 2$	$a = 8.38$, $b = 5.82$, $c = 9.47$, $\beta = 94°46'$
Phenyl benzoate (PhCOOPh)	$P2/C$	$a = 5.74$, $b = 14.75$, $c = 12.45$, $\beta = 101°$
Benzoyl peroxide (PhC(=O)–OO–C(=O)Ph)	$P2_12_12_1$	$a = 8.95$, $b = 14.24$, $c = 9.4$

formed with the same composition as that present in solution (see Fig. 1). The phase diagram of the DBP/phenyl benzoate system is shown in Fig. 2 which indicates that the minimum temperature at which melting starts is 58°C.

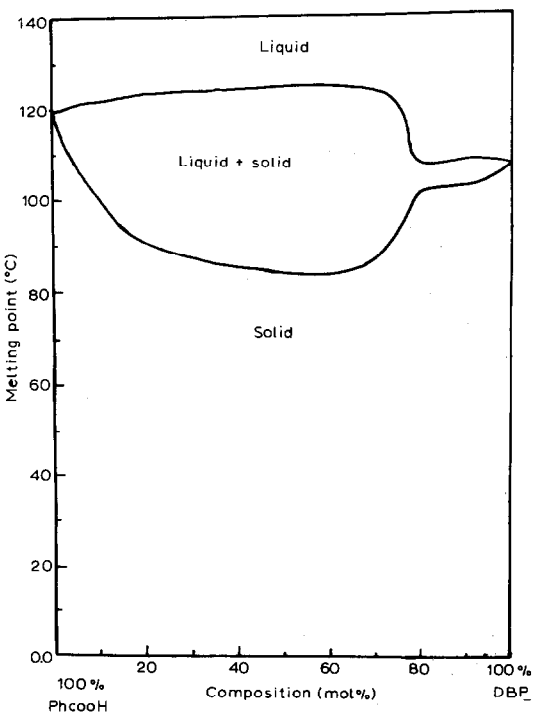

Fig. 3. Melting point–composition phase diagram of the benzoic acid/DBP system.

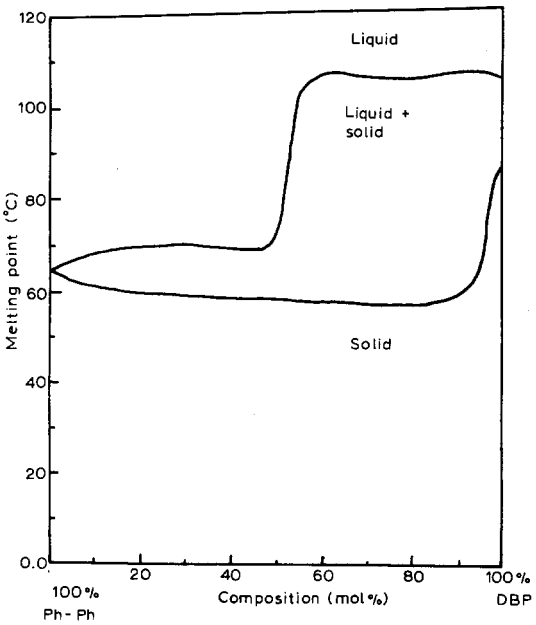

Fig. 4. Melting point–composition phase diagram of the diphenyl/DBP system.

The solid-state miscibility of phenyl benzoate in DBP is understandable both on the basis of unit cell parameters (see Table 1) and also on the basis of molecular structure [4].

The results of complete miscibility indicate that phenyl benzoate could be formed within the parent matrix of DBP without phase separation. This supports the earlier ideas of topochemical formation of phenyl benzoate along the [010] plane [3] of the parent crystals.

In case of DBP/benzoic acid and DBP/biphenyl systems, there was no 1 : 1 correspondence between the concentration of DBP in the crystals formed. The crystals were always richer in DBP than the solution from which it was grown. The phase behavior of these two systems is shown in Figs. 3 and 4.

In both these systems, it is shown that the minimum temperature at which melting occurs is 58°C. This is around 60 mol% of DBP in phenyl benzoate and 84 mol% of DBP in biphenyl while the minimum temperature at which softening occurs in the DBP/benzoic acid system is 89°C, at molar ratios of 65% DBP.

Finally, it was concluded that the decomposition of DBP single crystals cannot be guaranteed to occur completely in the solid state at all stages of the reaction unless the temperature is below 58°C.

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