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A. Blumstein [a] , J. Billard [a] & R. Blumstein [b]

[a] Department of Chemistry, Polymer Science Program, Lowell Technological Institute, Lowell, Massachusetts, USA

[b] Laboratoire de Physique de La Matiere Condensee, 11 Place Marcelin Berthelot, Paris V, FRANCE

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Polymerization of p-Methacryloyloxybenzoic Acid in Liquid Crystalline Solvents; Phase Diagrams of Some Model Systems

A. BLUMSTEIN, J. BILLARD and R. BLUMSTEIN

Department of Chemistry Polymer Science Program
Lowell Technological Institute
Lowell, Massachusetts USA

Laboratoire de Physique de La Matiere Condensee
11 Place Marcelin Berthelot
Paris V, FRANCE

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During the past few years, interest in reactions of molecules organized within a mesophase has developed considerably. In particular, an increasing number of publications describes the synthesis and polymerization of mesomorphic vinyl monomers. Vinyl oleate, for example, has been polymerized in its smectic state by Amerik and Krentzel.[1] Hardy and coworkers[2] have studied the kinetics of polymerization of cholesteryl acrylate in the smectic state and Paleos and Labes[3] have reported the kinetics of polymerization of N-(*p*-methoxy-O-hydroxybenzylidene) *p*-aminostyrene in its nematic state. Other reports of polymerization of cholesteryl acrylate and methacrylate[4,5,6,7] have also been published and recently Strzelecki and Liebert[8] have reported the synthesis and polymerization of various monomeric Schiff bases in their liquid crystalline state.

The polymerization of a non-mesomorphic monomer within a liquid crystalline solvent has been reported by Amerik and coworkers[9,10] and Blumstein and coworkers.[11] The monomer in both cases was *p*-methacryloyloxybenzoic acid (MBA) admixed into a smectogenic compound *p*-cetyloxybenzoic acid (CBA)[9,11] or a nematogenic compound such as *p*-heptyloxybenzoic acid (HBA).[10,11] The polymerizations were carried out with free radical initiators and isotropic solutions of MBA in dimethylformamide (DMF) or dioxan were used as reference systems.

Organization of the monomer within a mesomorphic solvent was found to have a considerable influence on the kinetics of polymerization, the molecular weight and also an influence on the microtacticity of the polymer. For example, the overall rate for the polymerization in HBA or CBA was found to be much higher than in DMF,[11,12] the overall activation energy of polymerization appears to be lower.[12]

Adequate interpretation of the results, however, must be based on a clear understanding of the structure of the two-component systems monomer-liquid crystalline solvent and the three-component systems monomer-liquid crystalline solvent-polymer (the latter as it appears "in situ"). Factors such as degree of orientation of the monomer molecules and solubility of the polymer in the mesophase must be considered and, in the case of monomer-solvent system, the compatibility of the monomer and the solvent must be established.

Phase diagrams for the systems MBA-mesomorphic solvents have not been previously established and two such phase diagrams are reported here for the systems *p*-propionoxybenzoic acid (PBA)-HBA and PBA-CBA. PBA was used as a model saturated compound because MBA itself polymerizes rapidly upon melting.

Results from differential scanning calorimetry (DSC) and thermal polarizing microscopy are given.

The preparation of all materials has been previously described.[11] Binary mixtures of PBA-CBA and PBA-HBA were prepared by melting a mixture of accurately weighed out quantities of both components until complete miscibility has been achieved (150–180°C), cooling the melt and reducing the crystals to a fine powder.

The phase diagrams were established by thermal microscopy (Leitz Panphot Microscope and Mettler Heating Stage) and Differential Scanning Calorimetry (Perkin Elmer Thermal Analyzer). The approximate shape of the phase diagrams was established using the well known contact method.[13] The accurate assessment of the diagrams was performed using spotchecks on mixtures of known composition by means of thermal microscopy and differential scanning calorimetry.

In the crystalline state MBA does not polymerize.[11] We have, for instance, irradiated the monomer crystals with γ-rays without detecting any polymerization after application of a dose of 44 Megarad (0.66 Mgrd/hour). Rapid polymerization is observed upon melting or dissolution in a mesophase. Consequently, the saturated model compound PBA was used to establish the phase diagrams.

Solubility of MBA in the mesophase was found to be very similar to that of PBA, but reproducible results were difficult to establish, even after addition of a

TABLE I

DCS phase transition temperatures of CBA and HBA

Compound	Temperatures (°C)		Transition
HBA	94		sol. sm.
	101		sm. nem.
	151		nem. isot.
	148		isot. nem.
	98	split into	nem. sm.
	89		
	80	four peaks	
	76.5		sm. sol.
CBA	63		sol. sol.
	93		sol. sm.
	135.5		sm. isot.
	133		isot. sm.
	88		sm. sol.

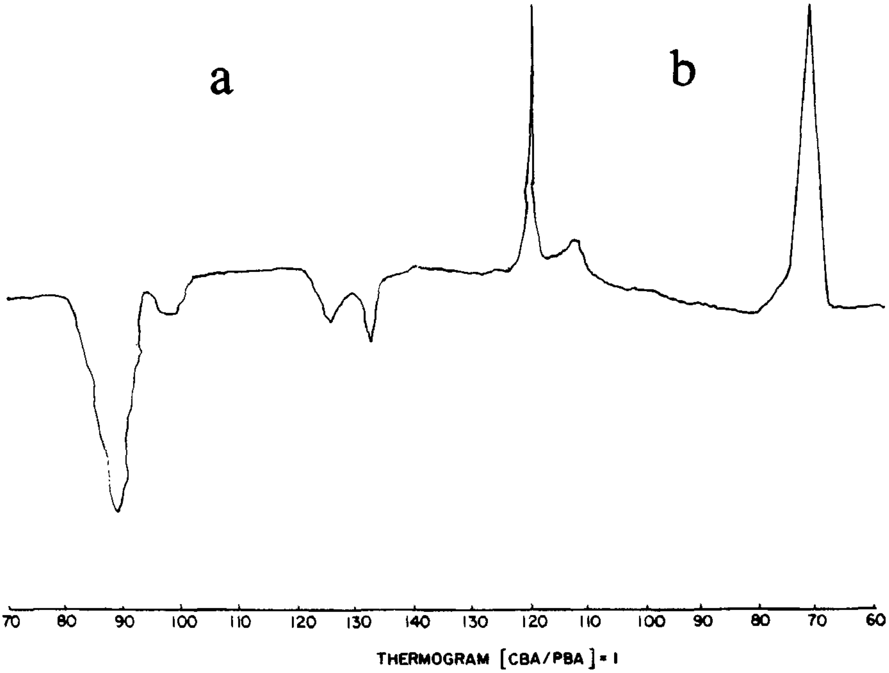


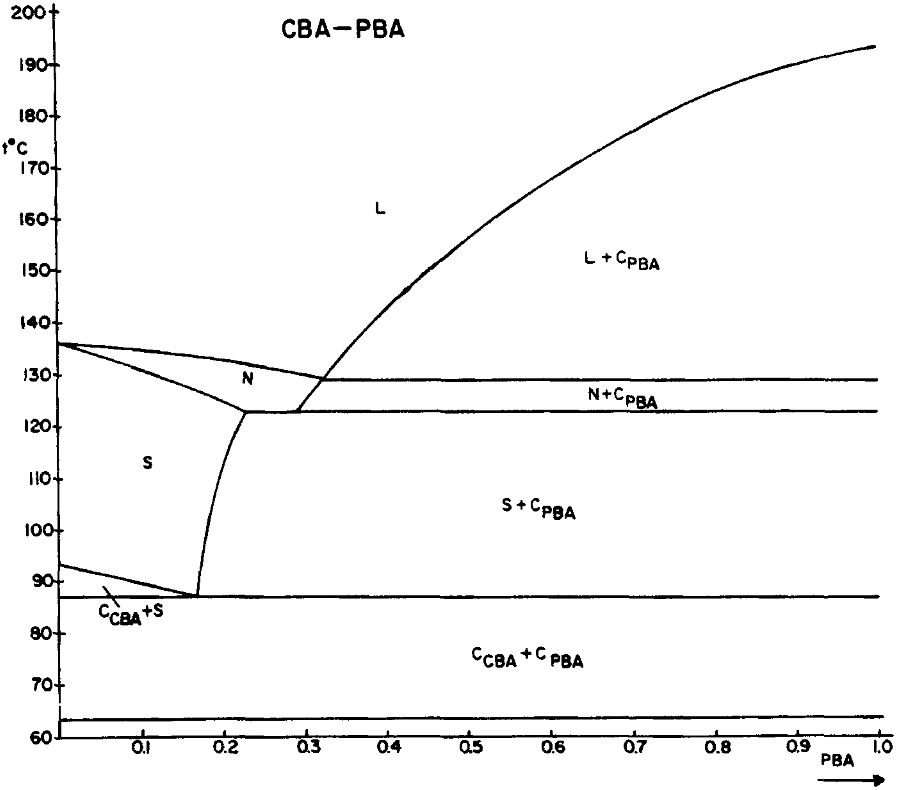
FIGURE 1 Thermogram for an equimolecular mixture PBA-CBA upon heating (1a) and cooling(1b).

polymerization inhibitor such as hydroquinone. Table I shows the phase transition temperatures observed by DSC for the two pure mesomorphic compounds. It is interesting to point out that we have observed for pure CBA a solid-solid transition at 63°C and a smectic-nematic transition close to the isotropic melting point.

Figure 1a and 1b show the thermograms of an equimolecular mixture PBA-CBA upon heating and cooling. The appearance of a nematic phase is clearly shown as well as a strong supercooling effect.

Figure 2 and 3 show phase diagrams for the systems PBA-CBA and PBA-HBA. The concentration of PBA is expressed in mole fraction, and the symbols N, S and C stand for nematic, smectic and crystal respectively. Solubility of PBA is rather limited, particularly in the smectic mesophase of CBA. At 110°C, for instance, the mole fraction of PBA in the saturated mesophase of CBA is 0.2.

In addition, one can see the existence of a nematic region, increasing in scope with increasing concentration of PBA, thereby confirming our previous observation of a nematic phase for pure CBA.[11] The solubility of PBA in HBA is not much higher at 100°C but increases at higher temperature to approximately 0.3



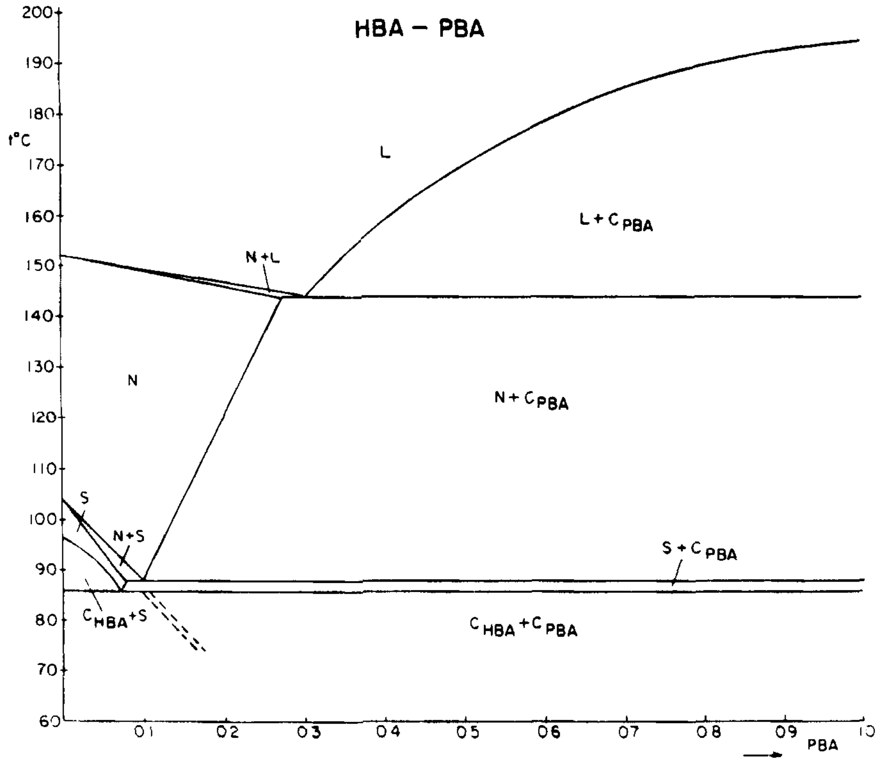


FIGURE 2 and 3: Phase diagrams for the systems PBA-CBA and PBA-HBA.

(mole fraction). A strong tendency toward supercooling is present in both cases. The dashed line on Figure 3 corresponds to the transition nematic – smectic for the supercooling nematic. One observes at this point a sudden formation of disclinations analogous to those observed by Scheffer and *al.*[14]. The nature of mesomorphic phases of HBA[15] as well as CBA has been identified as being isomorphic with the octyloxybenzoic acid.

As will be shown in a forthcoming publication, the excess monomer crystals merely serve as "reservoirs" from which the mesophase withdraws monomer during polymerization. The polymer appears to be insoluble in the mesophase and to precipitate out in the early stages of its formation.

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