PHASE SEPARATION IN LIQUID-CRYSTALLINE COPOLYMER/POLY(METHYL METHACRYLATE) BLENDS

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Dedicated to Dr Blahoslav Sedlacek on the occasion of his 70th birthday.

The phase separation in the blends of poly(methyl methacrylate) and liquid-crystalline polymer (copolymer of ethylene terephthalate and *p*-hydroxybenzoic acid) has been studied by the light scattering method and the cloud point curves have been obtained. Simultaneously some morphological features of the blends have been observed. It was found that the initial blends are in the state of forced compatibility and that thermally induced phase separation occurs by the mechanism of spinodal decomposition but presumably in the non-linear regime.

Considerable research activity can be seen at present in the field of so-called "molecular composites" (ref.[1]) i.e. systems with rigid rod-like macromolecules introduced into a matrix formed by flexible chains. The role of the rod-like macromolecules can be played, e.g., by liquid-crystalline polymers[2] (LCP) whose chains are distributed in the matrix at nearly molecular level. Such systems show a dramatic viscosity decrease during their processing, the matrix of the blend being effectively reinforced.

The reinforcing effect of LCP is due to specific morphology of the solid blend and to interfacial adhesion in phase-separated blends. That means that the thermodynamic compatibility or miscibility plays a very important role in the reinforcement[3–8]. These factors have attracted considerable attention to studies of phase behaviour of the blends of LCP and polymers with flexible chains[5–13] and of relations between phase state (compatibility) establishing the interrelation between phase state (or compatibility) and physical and mechanical properties of molecular composites[5–8]. Molecular composites are considered to be a new class of high performance polymer materials in which rigid rod-like macromolecules act as reinforcing elements in the polymer matrix[13]. Due to

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poor compatibility between the two components, a molecular composite may be obtained mainly by rapid coagulation of a ternary solution starting slightly below its critical concentration. Such blends may be considered to be in a state of "forced compatibility" and undergo thermally induced phase separation above the melting or glass transition temperatures of flexible component[8–11]. Depending on the blend composition, the phase separation may proceed either according to the mechanism of spinodal decomposition or by the mechanism of nucleation and growth[13], i.e. like blends of polymers with flexible chains[14].

In majority of cases the phase behaviour was studied for the blends of LCP with crystallizing polymers, where formation of the phase structure becomes complicated because of crystallization of flexible matrix[3,4,7,9,13]. Only few works were dedicated to the blends of LCP with amorphous polymers with flexible chains[4,11,15,16]. In particular, investigation of the behaviour of fibres drawn from isotropic melts of blends of poly(methyl methacrylate) (PMMA) with a side-group liquid-crystalline polymer revealed[15] that the liquid-crystalline phase was dispersed as droplets of ca 1 μm diameter in PMMA matrix up to content of 20 wt.% LCP. At higher concentration of LCP, the morphology of larger and partly interconnected structure was identified.

The bispheric structure (isolated beads) was also observed in mixtures of liquid-crystalline main chain polyesters with polystyrene[16]. However, for the mixtures of the same liquid-crystalline main chain polyesters having polystyrene side chains of various length with the same polystyrenes, the structure formed is best characterized as a three-dimensional network penetrating the polystyrene matrix due to improvement of compatibility of the components.

The aim of the present work is to study the phase behaviour of the blends of PMMA with a main-group liquid-crystalline polymer. The phase diagram has been found and the phase behaviour of the system at various stages of the process of mixing was studied.

EXPERIMENTAL

Materials. PMMA was a commercial product with $M_\eta = 2 \,.\, 10^5$ g mol^{-1}. A copolymer of ethylene terephthalate (60 mole %) and *p*-hydroxybenzoic acid (40 mole %) was used as the liquid-crystalline polymer (LCP); the intrinsic viscosity [η] was 0.051 m^3 kg^{-1} (trifluoroacetic acid), melting point, T_m = 460 K; the temperature of transition in the liquid-crystalline state[17] was 478 K.

Sample preparation. The blends of PMMA and LCP of various ratios of components were prepared by dissolving both the polymers in a mixture of trifluoroacetic acid and 1,1,1-trichloroethane (60 : 40 by vol.), at room temperature for 1 day. The concentration of solutions was taken 0.5–1.05 wt.%. The ternary solutions are single-phased and optically isotropic systems at this temperature. The blend films were produced by rapid coagulation on glass plates[5]: the glass plates wetted with the solution were immersed in cold ethanol or 1-propanol. Such a rod/coil mixture was "frozen" to overcome the unfavourable thermodynamic driving force for phase separation. The films were dried first at room temperature for 2 days and then at 338 K in vacuum for 4 h. The as-cast blends films were visually slightly opaque but did not show any macroscopic morphological pattern in the phase contrast microscope.

Light scattering measurements. Light scattering method was applied to determine the cloud point curve. The apparatus and experimental methods are described in detail in ref.[18]. The cloud points were determined at a constant heating rate (1.5 K min^{-1}), each point at the curve being the average of four readings.

Morphological examinations. The structure evolution of the blends was observed with the phase contrast optical microscope and by laser light scattering. A plane-polarized laser (atomic one-mode gas laser LGI-201, 8 mW, $\lambda = 630$ nm) served as the radiation source. The direction of the beam was varied by a polarization rotator containing a half-wave retardation plate as its essential part. The structure evolution of the blends was monitored with the use of the films which had been annealed at 466 K for various time intervals and then quenched by immersion in cold ethanol.

RESULTS AND DISCUSSION

Figure 1 shows the dependences of the intensity of light scattering on temperature for the films of various composition obtained from 0.5 wt.% solutions by coagulation in 1-propanol. These dependences are typical of the mixtures of polymer with flexible chains having lower critical solution temperature (LCST): the growth of intensity with increasing temperature is due to the onset of phase separation. Some films obtained by coagulation of either 0.5% solution in ethanol or 1.0% solution in 1-propanol exhibited some turbidity (e.g., Fig. 1, curve *1′* for ethanol) despite of the initial solutions being one-phase ones. With increasing temperature the turbidity diminished and then increased again. Hereby the temperatures of the onset of the intensity growth were distinguished only slightly from those ones for the films obtained by coagulation of 0.5% solutions in 1-propanol (compare Fig. 1, curve *1* with *1′*). The reason of such behaviour of films obtained from 1% solutions is not clear: the as-cast films do not reveal any structure when examined by optical microscopy. Note that the films obtained by coagulation of the solutions of pure LCP were afresh rather turbid (Fig. 1, curve *4*) and then become transparent at the temperature close to transition of LCP into the liquid-crystalline state.

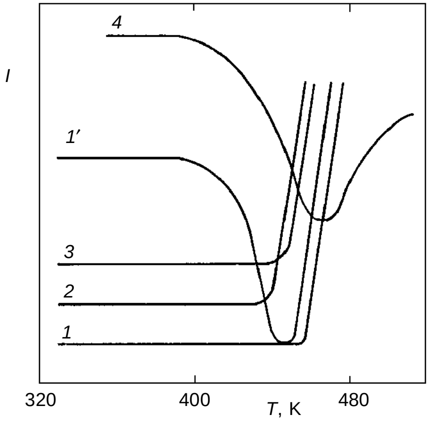

FIG. 1
Light scattering intensities, *I*, as a function of temperature for LCP/PMMA blends (*1*–*3*) and for LCP (*4*). Ratio of components (wt.%): *1*,*1′* 33/67, *2* 50/50, *3* 60/40. Curves *1*–*3* for the samples obtained by coagulation of 0.5 wt.% of ternary solution in 1-propanol (*1′*-coagulation in ethanol), curve *4* coagulation of 1.0 wt.% solution in 1-propanol

The appearance of the iridescent colouring of the film served as an evidence of the development of liquid-crystalline structure. In these cases the imperfect microcrystalline structure of LCP is possibly formed by coagulation. To prove this supposition it is necessary to perform X-ray investigations.

Figure 2 shows the cloud point curve found by averaging of light scattering data (see curves *1–3* in Fig. 1). The minimum of this curve corresponds to the 1 : 1 composition at the temperature 445 K that is lower than the melting point of LCP (463 K). It is possible that 445 K temperature is close to the temperature at which the onset of melting of LCP in the mixture occurs. Then, despite the peak melting point is not reached (463 K), the phase separation occurs because the LCP chains acquire some molecular mobility due to partial melting of microcrystals. However, this temperature is higher

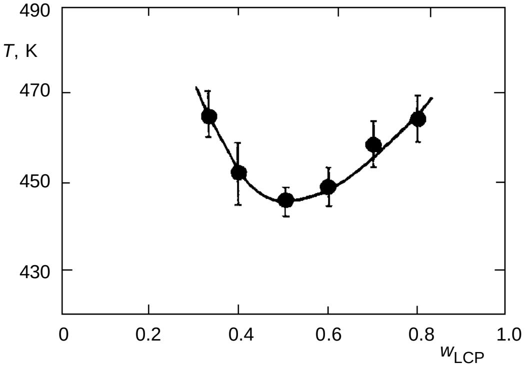

FIG. 2
Phase separation temperature as a function of composition for LCP/PMMA blends (w_{LCP}, weight fraction)

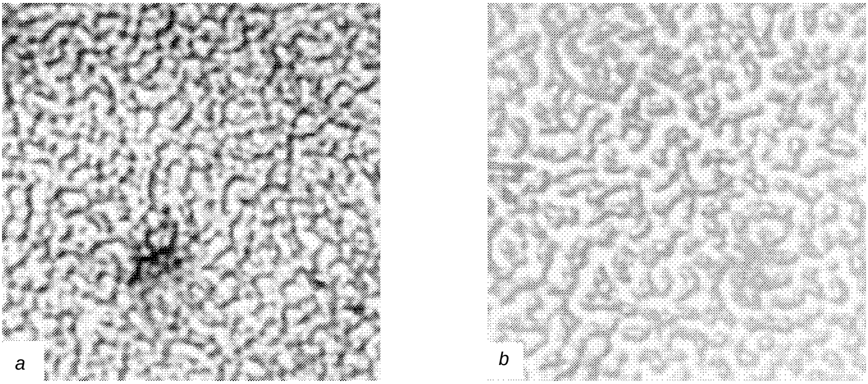

FIG. 3
Optical microphotographs of LCP/PMMA blend films (40/60) annealed at 466 K for 2 min (*a*) and 10 min (*b*)

than the glass transition temperature of pure PMMA where segmental motions are insufficient to initiate phase demixing.

Figure 3 shows the typical morphology of the blends obtained at 466 K for various annealing intervals. Practically for all the blends the interconnected morphology was observed that may be the result of the spinodal decomposition mechanism of phase separation. With increasing the annealing time, the size of periodic bicontinuous structures increases, the contrast between the coexisting phases showing a tendency to increase with increasing time, too. These findings are in agreement with the data on light scattering given in Fig. 4: the scattering pattern shows the "ring-scattering" with a scattering maximum at the angles Θ_{max} or at the scattering vectors q_m (refs[19,20]),

$$q_m = (4\pi/\lambda) \sin (\Theta_{max}/2) \quad ,$$

where λ is the wavelength of light in the medium. The maxima shift towards smaller angles or smaller scattering vectors when the annealing time is increased. This fact indicates that demixing and the appearance of thermodynamically unstable state involve the formation of the periodic concentration fluctuations with the wavelength λ_m that increases with time.

It has thus been shown that the thermally induced phase separation in the blends of PMMA and LCP with "forced compatibility" at the initial stages (in the time interval 2–10 min) in the whole range of compositions proceeds according to the mechanism of spinodal decomposition, but presumably in the non-linear regime.

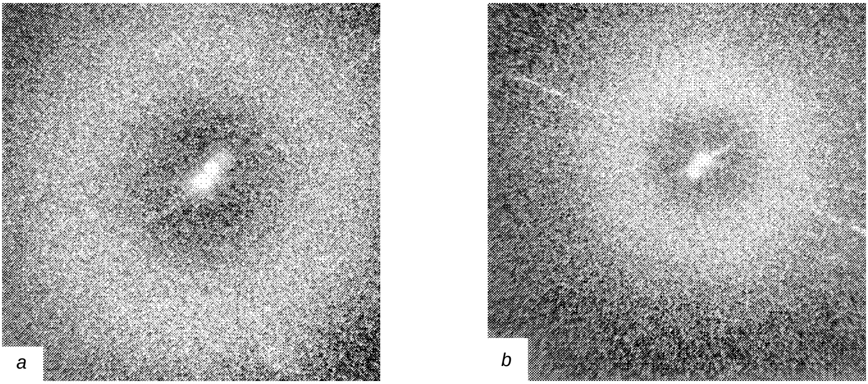

FIG. 4
Time evolution of scattering patterns (V_v) during demixing of 40/60 blend films at 466 K for 2 min (*a*) and 10 min (*b*)

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