Phase separation by synthesis of semi-interpenetrating network on the basis of polystyrene and poly(butyl methacrylate) from homogeneous solution

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SUMMARY:
   Phase separation by semi-interpenetrating polymeric network formation based on the copolymer styrene-divinylbenzene (PS-DVB) and poly(butyl methacrylate) (PBMA) was investigated by light scattering. The time for phase separation was measured as a function of the rate of the copolymerization reaction and of the composition of the initial blend. The time until the outset of phase separation decreases with increasing content of PBMA in the blend. The change in concentration of DVB does not influence the process of phase separation.

Introduction

   Interpenetrating polymeric networks (IPN) presently attract great attention. Before some years ago it had been accepted that IPN might be considered as a mixture of two network chains on the molecular level. However, it has been shown by us[1–3] and others[4], that a microphase separation is typical in IPN, which is due to a thermodynamical incompatibility of two constituent networks. The degree of phase separation, the size and share of the microregions of phase separation and the thickness of the interphase layer are important characteristics of such systems. The peculiarity of IPN consists in the fact that the process of phase separation develops as a result of IPN formation from an initial one-phase system. Therefore the morphology of IPN and their properties should be dependent on the polymerization conditions of the components. It should be noted that in spite of thermodynamical incompatibility, the high degree of chain entanglements in IPN hinders phase separation. The degree of phase separation depends on concurrent factors, viz. the rate of three-dimensional network formation and the rate of interdiffusion of the components. As a result phase separation in fully formed IPN is not complete, leading to the appearance of non-equilibrium structures depending on the prehistory of the system. We have studied the formation of microphase structures in such systems, namely in semi-IPN based on a crosslinked copolymer of styrene with divinylbenzene (DVB)[a] and poly(butyl methacrylate) (PBMA). This semi-IPN can be considered as a mixture of linear and crosslinked polymers. In the present paper the results of a study of the time dependence of phase separation on temperature and on composition are given.

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[a]   A commercial divinylbenzene solution was used by us (nominally 55% by weight of divinylbenzene isomers, the remainder being ethylstyrene).

Experimental part

Solutions of poly(butyl methacrylate) (PBMA), divinylbenzene (DVB)[*] and benzoyl peroxide (BP) in distilled styrene were prepared at room temperature. Optically homogeneous solutions obtained after 30 min of mixing with a magnetic bar stirrer were put into glass tubes, which then were evacuated and sealed. The samples were inserted into the thermostated chamber of the optical diffractometer, normal to the incident beam of a He-Cd gas laser of wavelength λ = 441,6 nm. The intensity of the scattered light from the sample was measured at a scattering angle interval from 10° to 20° with a photomultiplier, connected to a preamplifier and pulse-height analyser. The beginning of phase separation was indicated as the moment of an abrupt increase of the scattered light intensity. It was assumed that the polymerization of styrene starts immediately after insertion of the sample into the thermostated apparatus.

Results and discussion

Fig. 1 shows the dependence of the time corresponding to the onset of phase separation on the PBMA concentration in the reaction mixture at different concentrations of DVB. It is seen that an increase of PBMA concentration leads to a lowering of the time until phase separation begins. The time of the appearance of a turbidity decreases significantly with increasing initiator content from 0,05 wt.-% to 0,1 wt.-% at constant concentrations of the other components. To obtain the necessary experimental accuracy for the following experiments we used mixtures with a low initiator content (0,05 wt.-%). A change in DVB content in the range from 0,5 to 1,5 wt.-% does not influence the moment of beginning phase separation and this concentration was chosen as 1% everywhere.

Fig. 2 shows the dependence of phase separation time on PBMA content for various temperatures (60 – 100 °C) at constant content of the cross-linking agent (0,5 wt.-%) and the initiator (0,05 wt.-%). It is seen that an increase of the temperature lowers the time for beginning phase separation. Fig. 3 represents the time dependence of the intensity of scattered light by phase separation in the systems with 5 and 40 wt.-% of PBMA. With increasing amount of PBMA the scattered light intensity increases as well.

According to published data polystyrene/poly(butyl methacrylate) (PS-PBMA) blends may be partially compatible or fully incompatible, depending on the molar masses of both polymers[5, 6].

The concentration dependence of the interaction parameter found experimentally for PS-PBMA blends shows that the systems should separate into two phases at PS contents above 25 wt.-%. No temperature dependence of the interaction parameter has been observed.

In the system under investigation fragments of the network structure are formed at the initial stages of semi-IPN formation when radical-initiated copolymerization of styrene with divinylbenzene takes place. Thus, at the initial stages in the reaction sys-

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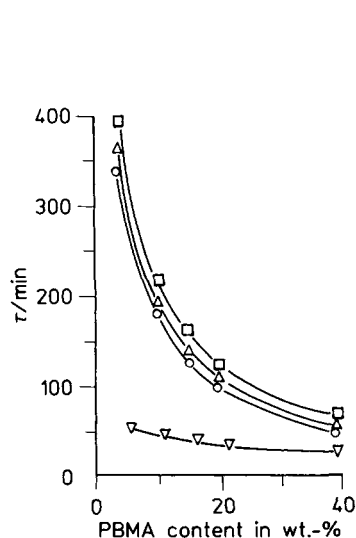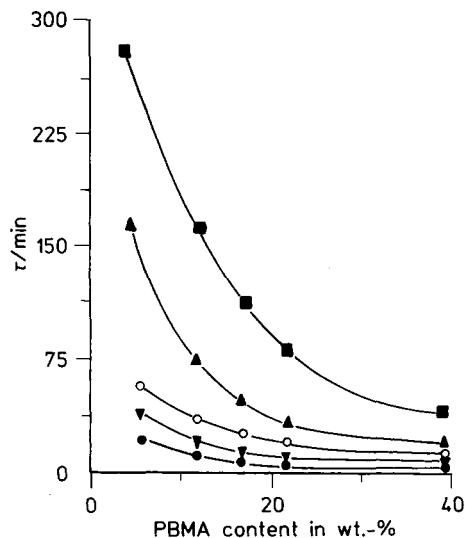
Fig. 1

Fig. 2

Fig. 1. Dependence of the time for the beginning of phase separation τ in the synthesis of semi-interpenetrating polymeric networks on the basis of the copolymer styrene-divinylbenzene (DVB) and poly(butyl methacrylate) (PBMA) upon PBMA contents at 60 °C: 1,5 wt.-% DVB, 0,05 wt.-% benzoyl peroxide (BP) ($\square$); 1,0 wt.-% DVB, 0,05 wt.-% BP ($\triangle$); 0,5 wt.-% DVB, 0,05 wt.-% BP ($\bigcirc$); 1,0 wt.-% DVB, 0,1 wt.-% BP ($\triangledown$)

Fig. 2. Dependence of the time of phase separation τ on poly(butyl methacrylate) (PBMA) contents at various temperatures. Contents of divinylbenzene (DVB) and initiator are equal to 0,5 wt.-% and 0,05 wt.-%, resp.: 100 °C ($\bullet$); 90 °C ($\blacktriangledown$); 80 °C ($\bigcirc$); 70 °C ($\blacktriangle$); 60 °C ($\blacksquare$)

tems there are present fragments of the network structure, linear polymer (PBMA), and residual monomers (styrene and divinylbenzene), their mixture being a solvent for both polymers.

Fig. 3. Time dependence of the intensity of the scattered light I in the synthesis of semi-interpenetrating polymeric networks on the basis of the copolymer styrene-divinylbenzene and poly(butyl methacrylate) (PBMA) of various compositions: 40 wt.-% PBMA (curve 1); 5 wt.-% PBMA (curve 2)
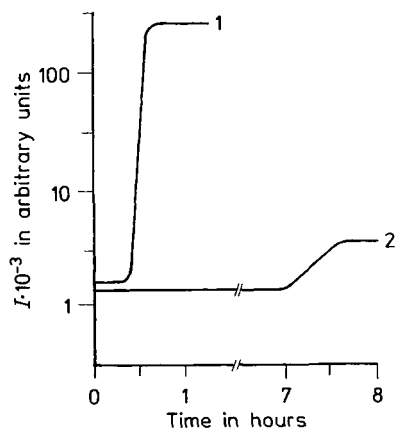
A hypothetical phase diagram of such a system is presented in Fig. 4. By copolymerizing the system passes from A to A_1 (see Fig. 4), corresponding to the mixture of the initial components and the semi-IPN formed, respectively. In the course of the copolymerization the concentration of the network structure fragments increases and
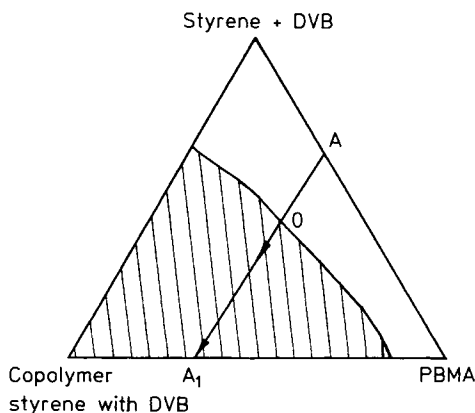
Styrene + DVB

A

O

Copolymer A_1 PBMA
styrene with DVB

Fig. 4. Schematic phase diagram for the system styrene-divinyl-benzene (solvent)-copolymer-poly(butyl methacrylate) (PBMA)

when reaching point O phase separation begins. This phase separation is resulting from two factors, leading to thermodynamical incompatibility. Increasing the fraction of polystyrene (PS) in the system leads to incompatibility with PBMA due to the concentration dependence of the interaction parameter. On the other side, the effective value of the interaction parameter for two polymers in a common solvent is determined by the expression $\chi_{1,2}(1 - \varphi_s)$, where φ_s is the volume fraction of the solvent and $\chi_{1,2}$ is the interaction parameter of the two polymers in the absence of solvent. As a result a decrease of φ_s leads to an apparent increase of the PS-PBMA interaction parameter, even if χ would not depend on the composition.

Therefore, in the initial stages of semi-IPN formation, when the concentration of styrene is high enough, the effective interaction parameter for the network fragment and the linear polymer is close to zero and the system remains homogeneous. With a decrease in styrene concentration (φ_s) the effective interaction parameter becomes higher. Together with the interaction parameter/concentration dependence, both these factors favour phase separation.

It is known[7] that phase separation can proceed either according to a nucleation and growth mechanism or to a spinodal decomposition mechanism. In both cases phase separation is accompanied by an increase in the intensity of the scattered light. For nucleating and growth the increase in the intensity of the scattered light is due to the growth of the size and number of microregions in the newly formed phase, whereas spinodal decomposition is the result of an increase of the concentration difference. As is seen from Figs. 1 and 2 an increase in linear polymer concentration in all cases leads to a lowering of the time for the beginning of appearing turbidity. This may be connected both with a decreasing compatibility of the components and with an increasing growth rate of microphase regions due to increasing PBMA concentration. The influence of the first factor is determined by the concentration dependence of the ratio of the interaction parameter for the pure components and the

effective interaction parameter in solution. In this case increasing PBMA concentration may lead both to a decrease and an increase of the time for the beginning of phase separation. A conclusion about the rate of microregion growth may be drawn from the increase in light scattering. For mixtures with a great amount of PBMA (40 wt.-%) the intensity of the scattered light increases during phase separation by some orders more than for mixtures containing only small (5 wt.-%) amounts of PBMA (see Fig. 4).

Thus, it is evident that increasing the concentration of linear polymer lowers the growth rate of the sizes of microregions or the concentration difference between various regions of phase separation. The latter possibility may be explained, if we take into account that the new phase regions, enriched in PBMA, are formed from smaller microregions separated from one another. This means, that the transport of PBMA macromolecules needed for the appearance of a visible heterogeneity takes more time. Thus the formation of microregions of the new phase does not proceed instantaneously. For some time the system is in a non-equilibrium state, viz. when the two-phase state is thermodynamically favoured, but the process of phase separation is not yet completed. In this respect the effect of the polymerization rate is of interest, because it determines the deviation of the system from the equilibrium state. The increase of the copolymerization rate of styrene with divinylbenzene with increasing temperature or initiator concentration (Fig. 1) leads to a marked diminution of the dependence of the time of beginning turbidity appearance upon the concentration of the linear polymer. It is probably connected with a more essential deviation of the system from equilibrium, when the reaction rate increases. The increasing thermodynamical force contributes to an acceleration of the microphase formation and the time of turbidity appearance depends on linear polymer concentration only to a lower degree, due to an increase of the diffusion rate. The weaker the dependence of the time of beginning turbidity upon linear polymer concentration, the stronger are the non-equilibrium conditions of the phase separation. It is possible that the finally formed heterogeneous structure of semi-IPN does depend on the polymerization rate. However, this statement needs additional investigation. The non-essential effect of the DVB content on the time of beginning turbidity appearance shows that the formation of networks of various cross-linking density does neither influence the thermodynamical interaction between PS and PBMA nor the phase separation in the polymerizing system.

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