Spinodal Phase Separation in Semi-Interpenetrating Polymer Networks—Polystyrene-Cross-Polymethacrylate

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SYNOPSIS

Morphology control in semi-interpenetrating polymer networks has been achieved by means of a two-step process, separating morphology formation and polymerization/crosslinking. Phase textures formed during spinodal liquid/liquid demixing of a solution of atactic polystyrene in methacrylate monomers were arrested by thermoreversible gelation of the polymer-rich phase as this phase passed its glass transition temperature. The phase separated structure was permanently stabilized by low-temperature crosslinking ultraviolet (UV) polymerization of the methacrylate monomer, and studied by transmission electron microscopy. Thus, it was directly observed how the initial demixing process depended on the initial viscosity of the polymer solution and the mode of quenching. Arrest of the earliest stage of spinodal demixing resulted in separated domains of 0.05-0.08 μm thickness, which were separated by a distance of the spinodal wavelength \( \lambda \). A cocontinuous network only developed in a relatively late stage of demixing. © 1995 John Wiley & Sons, Inc.

Keywords: (semi-)interpenetrating polymer networks • morphology • phase separation (spinodal) • gelation (thermoreversible) • polystyrene/methacrylates

INTRODUCTION

As a special case of polymer blends, interpenetrating polymer networks (IPNs) form a class of materials in which two (or more) polymers are combined, of which at least one is crosslinked.1 If only one polymer is crosslinked, a semi-IPN is formed. Usually, phase separation takes place during IPN synthesis due to the incompatibility of most polymers. IPN-type materials find application in the field of impact resistant resins (e.g., in HIPS or modified epoxy resins). However, the morphology resulting from polymerization and crosslinking is difficult to control and to predict, and can differ significantly within nearly identical experiments. The degree of crosslinking as well as the rate of polymerization and crosslinking networks have to be properly adjusted with respect to the rate of phase separation.1,2 As a result, IPN morphologies are usually rather coarse and the ultimate limitations in the structure and the corresponding structure-property relations are still subjects of ongoing research.

The present work has been aimed toward control of the formation of bicontinuous semi-IPN's at the initial stage of phase separation. Therefore, morphology formation and crosslinking/polymerization have been separated into two steps. The extent of phase separation is not determined by the rate of polymerization and crosslinking or by mechanical mixing, but by rapid thermoreversible gelation during (spinodal) demixing of a solution of a linear polymer in a monomer (solvent). Arrest of demixing occurs when the formed polymer-rich phase passes its glass transition, and it is expected that arrest can be obtained in a very early stage of demixing. An irreversibly fixed semi-interpenetrating polymer network with such an “early stage” morphology is obtained by polymerization and crosslinking the monomer-solvent after physical gelation. In contrast, gelation and chemical crosslinking cannot be separated in conventional (semi-)IPN formation where the viscosity of the polymer-poor phase, or
matrix phase, increases as a result of chemical conversion.\textsuperscript{14}

The preparation of semi-IPNs described here, makes it also possible to do transmission electron microscopy (TEM) studies on systems that are in the early stage of spinodal demixing. So far, few studies have been described in the literature in which attempts are made to visualize the early stage of spinodal demixing by microscopy. Most of them have been performed using light microscopy (in the case of polymer blends\textsuperscript{5,6}) or scanning electron microscopy (in the case of polymer solutions after solvent removal\textsuperscript{7-9}). With both methods only the interconnected network formed in the intermediate and late stages of demixing can be visualized. The polymer/monomer system (atactic polystyrene/methacrylate monomers) described here, does not require removal of the methacrylate solvent in order to do transmission electron microscopy investigations.

Various scattering methods have been used to study the development of the initial stages of spinodal demixing as a function of quench temperature in polymer blends.\textsuperscript{10-12} However, few scattering studies were performed on spinodal demixing in polymer solutions.\textsuperscript{13,14} These experiments were usually performed in order to investigate whether spinodal demixing proceeded according to the Cahn-Hilliard theory.\textsuperscript{15} It was generally found that demixed structures decreased in size when the quench depth was increased.

The influence of cooling rate and efficiency on the ultimate morphology of demixed polymer solutions has to our knowledge been investigated only by Aubert and Clough,\textsuperscript{7} who prepared foams with cell sizes of 1 and 10 $\mu$m, by quenching a solution of atactic polystyrene, aPS, in cyclohexane until this solvent crystallized and phase separation was stopped. Significant variation of cell size with cooling rate was observed with higher density foams.

**EXPERIMENTAL.**

**Materials**

Atactic polystyrenes were prepared anionically with molecular weights as measured by GPC/LALLS (Waters, LALLS detector Chromatix KMX-6): PS2M, $M_n = 1,739,000$ g/mol, $M_w/M_n = 1.19$; and PS100K, $M_n = 100,000$ g/mol, $M_w/M_n = 1.23$. The radii of gyration were measured in cyclohexane at 35$^\circ$C, using a laser-modified Sophica 42000 apparatus. Measured radii: PS2M $R_g = 43.7$ nm, PS100K $R_g = 10.4$ nm.

A methacrylate mixture, RES, which was especially suited for microtoming and which had low shrinkage upon polymerization was obtained from Lowi (HM23, K11M), and mixed in a 1:3:1 ratio in order to obtain the correct solubility regime. The mixture contained the following monomers: ethylmethacrylate (30.4 wt%), butylmethacrylate (21.7 wt%), 2-hydroxypropylmethacrylate (15.8 wt%), 2-hydroxyethylacrylate (7.9 wt%), ethoxyethylmethacrylate (4.3 wt%) and methoxyethylmethacrylate (3.9 wt%). 1,3-butanedioldimethacrylate (14 wt%) was added as crosslinker.

**Phase Diagrams**

Cloud point curves were visually determined by turbidity measurements at a cooling rate of 0.2$^\circ$C/min. The temperature at which opalescence was observed was assumed to be the demixing temperature $T_D$ ($\pm 1^\circ$C). Gelation temperatures ($T_{GEL} \pm 2^\circ$C) of low concentrated solutions were determined by slowly cooling the solutions in test tubes, until elastic behavior was qualitatively observed, and the solution could be removed in one piece. Glass transition temperatures of highly concentrated solutions were measured by differential scanning calorimetry (DSC) (Perkin Elmer DSC7) and extrapolated to 1 K/min heating rate.

**Quenching**

Quenching was performed in an aluminum cooling block which was cooled to the desired temperature by liquid nitrogen, in a nitrogen atmosphere. Cylindrical samples (1) were cooled by injecting homogeneous polymer solutions into small polypropylene BEEM capsules (inner diameter 5 mm, height 8 mm) which were precooled to the quench temperature. Films (2) were prepared by filling molds at room temperature with the polymer solution and bringing them subsequently into contact with the cooling block, while a smaller precooled aluminum block was simultaneously pressed on top of the film. In the case of two-step quenches, the samples were kept in a liquid cooling mixture (chloroform/liquid nitrogen) above the gelation temperature for a certain period, before being transferred to the aluminum block at the lower quench temperature.

**Cooling Rates**

Cooling rates in the above mentioned sample geometries were measured using a K-type thermocou-
ple connected to a pen recorder. The temperature in the sample decreased exponentially with time. The gelation temperature in the films (−50°C) was reached within 0.3-1 s, in which range the decrease of temperature with time was still almost linear. Depending on the quench temperature, initial cooling rates in film samples ranged from 60°C/s ± 10 (quenched to −60°C) to 140°C/s ± 10 (quenched to −100°C).

Initial cooling rates in cylindrical samples ranged from 3°C/s ± 1 to 5°C/s ± 1 (quenched to −60 and −100°C, respectively). Gelation temperatures were reached in 10–25 s (quenched to −60 and −100°C, respectively).

**UV-Polymerization**

Polymerization was performed in a nitrogen atmosphere in the aluminum cooling block described above. UV polymerization was initiated below \( T_{GEL} \) using benzoinmethylether as an UV initiator. After 4–5 days (capsules) or 10 hours (films) at low temperature the solid samples were postcured by UV irradiation at room temperature, to ensure a high conversion of the methacrylate monomer. Samples with a polystyrene concentration above 20 wt% were subjected to a heat treatment of 20 min at 100°C without noticeable changes in the morphology. Two 4W lamps were used for UV irradiation (366 nm) at low temperature, room temperature polymerization was performed with one 15W UV-lamp (366 nm).

**Morphology**

A JEOL 200 CX transmission electron microscope (200kV) was used to study the morphology. Samples for transmission electron microscopy were cut on a LKB 2188 Ultratome Nova. Specimen from the cylindrical samples were collected from the outer shell of the samples. Specimen from film samples were cut out of the middle of the films. Sections of 80–100 nm thickness were transferred to copper grids and the PS-rich phase was stained with RuO₄ vapor to enhance contrast.¹⁶

**CONCEPT**

In previous reports we described a two-step synthetic route for the formation of semi-IPNs, starting from a solution of a polymer in a monomer.¹⁷,¹⁸ Requirement for this process is the intersection of a liquid-liquid demixing curve and the glass transition-concentration \( (T_G-\phi_{PS}) \) curve for the plasticized polymer (see Fig. 1).

In the first step, liquid/liquid phase separation into a polymer-lean and a polymer-rich phase is induced by cooling the polymer solution into the binodal or spinodal region of the phase diagram. Binodal demixing proceeds by a mechanism of nucleation and growth of a dispersed phase, and typically results in the formation of a continuous phase in which the minor component is dispersed as droplets. Inside of the spinodal region, the mixture becomes unstable to infinitesimal concentration fluctuations and phase separation occurs spontaneously.¹⁹,²⁰ Arrest of such stages of demixing can lead to the formation of bicontinuous semi-IPNs, also in the case the volume fractions of the two components are rather unequal (see Fig. 2).

The process of phase separation is arrested by thermoreversible gelation of the polymer-rich phase as it passes its glass transition temperature and vitrifies.³,²¹ Glassy domains act as physical crosslinks and the system forms a gel. Demixing and coarsening processes are strongly determined by the diffusion coefficient \( (D) \) of the polymer.²² Thus phase formation will be increasingly retarded with increasing polymer molecular weight, increasing concentration \( (\phi) \), and decreasing temperature \( (T) \). Phase growth can be expected to be effectively stopped at a short

![Figure 1](image-url)
time scale. Because $D\eta/T$ is a constant, the solution viscosity ($\eta$) is an important parameter for the demixing process.

In the second step, the phase texture is fixed chemically by UV polymerization and crosslinking of the monomer at a temperature below the gelation temperature. As discussed below, no changes in the morphology were indicated due to the polymerization process, thus demonstrating that the texture of the semi-IPN is very much similar to the structure of the phase-separated polymer solution.

**RESULTS**

**Phase Behavior of the Polystyrene/Methacrylate Solutions**

For the present study, monodisperse polymers were used to ensure: (1) that the measured cloud point curve closely represented the binodal; (2) that the critical point was the intersection of the binodal and the spinodal curve, and spinodal demixing could be expected for quenching samples around the critical concentration; (3) that during quenching nucleation could not occur due to a high molecular weight polymer fraction; and (4) that the gelation temperature did not vary with the polymer concentration.

Phase diagrams of PS2M and PS100K in RES are displayed in Figure 3, showing the dependence of $T_{GEL}$ of PS2M and PS100K solutions on the position of the demixing curve along the temperature axis. At the gelation temperature (the intersection of the $T_C$-line with the cloud point curve), the polystyrene concentration was only 40–60 wt % for PS2M and PS100K, respectively. The highest demixing temperature (critical temperature) measured for PS2M solutions was $-42^\circ$C at 4 wt % polystyrene, whereas the gelation temperature was $-50^\circ$C. Because of the flat contours of the cloud point curve, $T_C$ and $T_{GEL}$ were very close. PS100K solutions showed a critical temperature of $-55^\circ$C at 15 wt % polymer and a gelation temperature of $-65^\circ$C.

**Morphology of Polystyrene-cross-Polymethacrylate Samples**

Homogeneous polymer solutions were quenched rapidly into the spinodal region, mostly through the critical point and either in a one-step or a two-step quench. UV polymerization/crosslinking of the methacrylate was performed subsequently below the gelation temperature. Although the mobility of the PS chains is limited in the vitrified state, the methacrylate monomer still is sufficiently mobile to be polymerized.

The final semi-IPN morphology was studied in dependence of polymer concentration, polymer molecular weight (material parameters influencing the solution viscosity), and the quench efficiency (process parameters, such as quench temperature, sample geometry, and the use of a two-step quench). In all cases, the samples were quenched to a preset temperature, and the cooling rate was determined by the temperature difference and sample geometry. In thin film samples, the initial cooling rate was found to be constant over the first 70 degree temperature decrease (i.e., until the gelation tem-
perature was reached) and to be 20-fold higher than in cylindrical samples (60–140°C/s versus 1–5°C/s).

**High Molecular Weight Polystyrene**

Samples which were rapidly quenched through the binodal region (at 0.5 wt % polystyrene) to −100°C and subsequently UV polymerized at that temperature, showed no phase texture in the TEM experiments. On the other hand, slow cooling of these solutions resulted in a liquid–liquid demixed system and UV polymerization of the solutions at room temperature led to an opaque sample with two-phase morphology. It can therefore be assumed that (1) binodal phase separation can be repressed by rapid cooling, and that (2) no detectable morphology was formed due to methacrylate polymerization.

Figure 4a–c depicts the morphologies obtained by quenching cylindrical samples of 2 wt % (a), 8 wt % (b), and 15 wt % (c) solutions of PS2M in RES to −80°C. A corresponding 4 wt % sample is shown in Figure 5d. All pictures showed a pattern of rather irregular black domains which are uniformly dispersed over the sample. As a consequence of preferential staining of the PS-rich phase by RuO₄, black domains could be assigned to PS, and grey domains to the methacrylate resin. In a first approach we assumed that the PS concentration necessary for effective staining of the PS-rich phase, corresponds approximately to the gelation concentration (φ_{gel}). In most cases, spherical inclusions were found inside of the black domains. The origin of this “fine” structure will be considered in the Discussion.

Proportional to the amount of initially added PS, an increase in the black phase was visible in Figure 4a to 4c. The dimensions of the PS domains (size of the inclusions and ‘width’ of the domains) remained approximately the same while the PS content increased. Above 4–5 wt % PS, the polystyrene clearly formed a second continuous phase. At 15 wt % PS, methacrylate inclusions gradually decreased in size, and samples with larger PS content had the same texture as the one shown in Figure 4c.

By quenching films of concentrated solutions (>20 wt %), it was possible to obtain transparent semi-IPNs. TEM pictures of these samples showed a very small extent of phase separation with a bicontinuous morphology of approximately 8–10 nm size.

The quench efficiency was varied, by (1) changing the quench temperature, (2) changing the sample geometry from film to cylindrical bulk samples, and (3) performing two-step quenches. Route (1) induces different quench depths, and thus different sizes of the demixed structure, but also determines the rate of cooling of the sample. Two-step quenches (3) were performed by allowing solutions of 4 wt % PS2M in RES to demix for a certain period of time at −50°C (above the gelation temperature) before they were cooled to −80°C. This process can also be denoted as isothermal aging.

Figure 4. TEM micrographs of cylindrical samples of PS2M in RES, quenched to −80°C (a) 2 wt % PS, (b) 8 wt % PS, (c) 15 wt % PS.
Figure 5. Development of the morphology in samples of 4 wt. % PS2M in RES: (a) film quenched to −100°C, (b) film quenched to −80°C, (c) film quenched to −60°C, (d) cylindrical sample cooled to −80°C, (e) cylindrical sample cooled to −80°C after 20 s demixing at −50°C, (f) cylindrical sample cooled to −80°C after 90 s demixing at −50°C, (g) non-quenched sample polymerized at room temperature.

Figure 5a–g shows a series of TEM pictures which have been ordered to demonstrate the 'chronological' development of the demixed phase texture as it could be deduced from our experiments. The pictures are ordered at decreasing cooling rate as obtained by different quench temperatures and sample geometries. Fastest cooling was achieved by quenching film samples with 140, 130, and 60°C/s (to −100, −80, and −60°C, respectively, Figs. 5a–c). Subsequent stages of demixing were obtained by cooling cylindrical samples at 4°C/s (to −80°C, Fig. 5d) and by performing two-step quenches. In this case, bulk samples were kept at −50°C for 20 s and 90 s before cooling to −80°C (Fig. 5e and f). For comparison,
The cellular structure resembles the foams prepared by Aubert and Clough in appearance and size.7

Low Molecular Weight Polystyrene

Because of the viscosity of the aPS/methacrylate solutions, the demixing process is expected to be as faster as the molecular weight of the polystyrene is lowered. In addition, the demixing curve will shift to lower temperatures, and both the critical concentration and the gel concentration will increase.

Figure 6a shows the morphology obtained by quenching a film of a 10 wt % solution of PS100K in RES to −80°C (high quenching rate). The obtained morphology is reminiscent to that of a PS2M sample which was quenched at lower rate, and thus was arrested after a longer demixing time (e.g., Figure 5e). As expected for a solution containing 10 wt % polystyrene, the fraction of visible PS in Figure 6a was higher than in the case of a 4 wt % solution (Fig. 5e). Thus, it was possible to preserve the ‘spinodal’ network, even in low molecular weight polymer solutions, although much faster quenching was necessary.

Quenching the same sample slowly (cylindrical sample to a temperature of −80°C at 4°C/s) resulted in a cellular structure with pore sizes of 2–6 μm and a well-developed fine structure in the cell walls (Fig. 6b). For comparison, a 30 wt % film which was quenched to −95°C, and which even became optically transparent, is shown in Figure 6c. A continuous PS phase with very small methacrylate inclusions was observed. This can be explained by the arrest of a very early stage of demixing due to the very high solution viscosity of 30 wt % solutions (1100 mPa.s).

DISCUSSION

First, the question to be addressed is to which extent the morphology is altered during the low temperature UV-curing. Different observations support the conclusion that the morphology which is initially formed upon demixing, is affected only slightly by the low temperature curing: (1) The observed TEM textures differed significantly depending on the quenching procedure. By quenching concentrated solutions (> 30 wt % PS), transparent or translucent samples could be prepared where TEM showed a very fine morphology (order nm), while after RT polymerization opaque samples with a cellular morphology were obtained (order μm), (2) TEM ex-
and that the morphology development of the semi-IPNs (Fig. 5) can be explained by the development of concentration fluctuations during spinodal demixing.

Regarding the observed variations in morphology as representative for different stages of the monomer-polymer demixing, we can attempt a correlation to the three stages of spinodal demixing:  

1. In the early stage of demixing, concentration fluctuations of different wavelengths and small amplitudes develop. According to the Cahn-Hilliard theory, the wavelength that will have the highest growth rate (the most dominant wavelength) results in the most frequently found domain size ($D_M$). $D_M$ can be calculated using an adaptation of Cahn's theory for spinodal demixing of polymer solutions. A relation between $D_M$ and molecular dimension, spinodal demixing temperature ($T_0$) and quench temperature ($T$) is obtained:

$$D_M = 2\pi l[3(1 - T/T_0)]^{-1/2} \quad (1)$$

where $l$ is a range of molecular interaction, usually taken to be equal to the radius of gyration.

2. In the intermediate stage, the polymer concentration in the polymer-lean and the polymer-rich phase, keep moving toward the equilibrium values determined by the binodal, and the wavelength increases with time. The demixing system is characterized by a high level of interconnectivity, both in the major and the minor phase, provided the volume fraction of the minor component is high enough.

3. The late stage of spinodal demixing is the period in which the domains grow in size and their boundaries are sharpened, while their concentration does not change significantly. Finally, the system will coarsen toward two macroscopically separated phases. The structure then becomes morphologically indistinguishable from binodally demixed solutions.

Huston et al. showed that in a first approach, two regimes of cooling rates can be discerned: (1) if the cooling rate is very high, and the applied cooling time is shorter than the time necessary for demixing, no detectable decomposition of the solution will be found during cooling; (2) when the cooling rate is

Figure 6. TEM micrographs of samples of PS100K in RES: (a) 10 wt % PS, film, quenched to $-80^\circ$C, (b) 10 wt % PS, cylindrical sample, quenched to $-80^\circ$C, (c) 30 wt % PS, film quenched to $-95^\circ$C.
slow enough for spinodal decomposition to be completed before the end of the quench process, there may still be enough time for a competing process, such as nucleation and growth to progress to an appreciable extent. In between these two regimes, the quenching rate can be fast enough to allow partial decomposition of the solution by the time the final temperature is reached. In the case of the present study, this means that the system will be only partially demixed before it vitrifies.

**Morphology Development**

The development of the morphology in Figure 5 can be discussed according to Figure 7. In the initial stage of spinodal demixing, concentration fluctuations occur with different wavelengths and amplitudes (Fig. 7a). Fluctuations with the most dominant wavelength grow in concentration difference between the polymer-rich and polymer-lean phase, while the wavelength remains constant. Arrest of (spinodal) phase separation can only occur if the viscosity of the polymer-rich phase increases jump-like, for instance due to passage of the glass transition temperature. It has been our hypothesis that the material starts to vitrify as it reaches the gelation temperature and the corresponding gelation concentration ($\phi_{GEL}$). This occurs first at the maximum of the concentration fluctuations (Fig. 7b). The earliest arrested phase will be a narrow strip of material, separated from other domains by a distance of the wavelength $\lambda$, or $n\lambda$ as not all fluctuations will have reached $\phi_{GEL}$.

An increase in amplitude of the concentration fluctuation, results in a larger area below the sinusoidal concentration line which is above the gelation concentration (Fig. 7c), and an increased volume of PS-rich phase can vitrify. The increase of the fraction of black material visible in Figure 5a to 5d, from 16% of the surface to 23% of the surface, confirms this explanation. In a rather late stage of demixing, coarsening results in separated domains of the bimodal concentration. The block-like concentration variations do not all have the same thickness and are separated by irregular distances (Fig. 7d). During subsequent UV polymerization of the methacrylate resin, the demixing curve will shift toward higher temperatures, resulting in an increase of the equilibrium concentration of the polymer-rich phase.

According to the considerations above, the most dominant wavelength $D_M$ can be determined from TEM pictures of the most rapidly quenched samples as the distance between dark domains. The distance between two polymer-rich domains was compared to the $D_M$ value calculated by equation (1) with $l = 43.7$ nm (radius of gyration), $T_{SPINODAL} = T_{CRITICAL} = -43^\circ$C, and $T = T_{QUENCH}$ (PS2M).

As listed in Table I, separating distances calculated for film samples quenched to $-100$, $-80$, and $-60^\circ$C were in agreement with the domain structure of Figure 5a–c (quenched with 140, 130 and 60°C/s, respectively) if the actual quench temperature was considered. In contrast, the dominant wavelength calculated with $T_{GEL} = -50^\circ$C, was larger than the values experimentally found in the quenched cylindrical samples. Thus, it appears that demixing could not develop to the stage expected for the gel temperature. This indicated that during film quenching, the cooling rate of 130°C/s was faster than the demixing rate. The quench temperature was reached before demixing developed significantly. Phase development at the very low temperature was so much

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**Figure 7.** Schematic representation of the development of concentration fluctuations during spinodal demixing, and the arrested stages of demixing. (a) initial concentration fluctuations, (b) structure depicted in Figure 5a, (c) structure depicted in Figure 5d, (d) structure depicted in Figure 5g.
retarded that the early stages of demixing could be fixed (Fig. 5a–c). From the phase diagram it follows that over the whole polystyrene concentration range, the polymer-rich phase was below \( T_G \), so that the PS-rich phase was arrested as soon as it was formed.

Figure 5d and Table I also show that in case of cylindrical samples, cooling to \(-80^\circ\)C (at 3°C/s) resulted in almost continuous (percolating) domains, which were larger and less regularly spaced than predicted for the wavelength associated with \(-80^\circ\)C. It might be assumed that in this case, the rate of demixing approximately equaled the rate of cooling, and the morphology is developed during cooling, so concentration fluctuations associated with the gelation temperature were formed. In this case, demixing was arrested as the PS-rich phase vitrified at the binodal concentration of 40 wt % at \( T_{GEL} \). According to the scheme in Figure 7, samples cooled to \(-60^\circ\) and \(-50^\circ\)C (percolation stage) were expected to be completely phase-separated before arrest takes place. Equation (1) could no longer be used to calculate domain sizes in the late stage of demixing represented by Figures 5f and 7d.

In the case of rather dilute PS100K solutions (10 wt %) having a low viscosity, a stage of demixing before the network stage could not be arrested. Obviously, this would need a higher cooling rate than was possible in our experiments. For a PS100K solution quenched to \(-80^\circ\)C, the calculated dominant wavelength \( l = 10.4 \text{ nm, } T_e = -55^\circ\)C is 0.111 μm, which is a factor 4–5 smaller than the experimental value.

The change from dispersed nanometer domains (Fig. 5c) to a dispersed (coarsened) droplet state (Fig. 5f), via a bicontinuous network (Fig. 5d and e), indicates that spinodal demixing yielded separate domains when a very early stage of demixing was arrested. These separate domains later clustered to form a macroscopic network. The polymethacrylate inclusions observed in Figure 5c–f resulted from this merging of the separate domains. After formation of the macronetwork, phase separation had probably proceeded to the final stage, reaching the binodal concentrations (40 wt % or higher, depending on the temperature). In the late stage of demixing (Fig. 5f), coarsening into two separated macroscopic phases took place and the methacrylate inclusions were filled with the PS-rich phase. This resulted in a volume decrease of the PS-rich phase, and led to a morphology that was reminiscent of binodally demixed solutions.

From Figure 5a–e, it is also observed that an interconnected structure could be obtained already at a concentration of 4 wt % PS. According to Cahn, cocontinuous structures can only be expected for a volume fraction above 10–15%.15 However, the volume fraction of the PS-rich phase was approximately 10–15% even though the total concentration was only 4 wt %, because the PS concentration inside the PS-rich phase was only 40 wt %. When the volume ratio of both constituent components was closer to unity, bicontinuity was observed already in the initial stage of demixing. In general, higher PS concentrations resulted in a smaller and denser domain structure due to the lower polymer diffusion coefficient in solution and the corresponding decrease in demixing rate.

A morphology resulting from spinodal demixing could also be arrested when PS2M solutions were quenched by bringing the material inside the demixing gap above \( T_{GEL} \) (\(-50^\circ\), \(-35^\circ\)). In this case, the methacrylate polymerization was started not after gelation but after a large increase in the viscosity of the polymer-rich phase had been achieved. The rate of polymerization was controlled by monomer diffusion to the growing chains. Polymethacrylate chains also grew within the PS-rich domains which still contained 40–50% methacrylate. Thereby, the polystyrene-rich domains were subsequently trapped in a chemical network which was expected to retard chain movements and further demixing even more. Thus, both the viscosity increase in the PS-rich phase due to decreasing temperature and increasing concentration (physical fixation), and the interlocking methacrylate-network (subsequent chemical fixation) induced arrest of demixing and fixation of the morphology.

Monomer diffusion out of the PS-rich domains and subsequent increase of the PS concentration in the domain during methacrylate polymerization, might account for the fact that domain boundaries

<table>
<thead>
<tr>
<th>( T_{QUENCH} ) (°C)</th>
<th>Calculated, PS2M*</th>
<th>Experimental, Films, PS2M</th>
<th>Experimental, Cylindrical, PS2M</th>
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<tr>
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<td>-100</td>
<td>0.32</td>
<td>0.25–0.35</td>
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<td>-80</td>
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<td>0.30–0.42</td>
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<td>0.55–0.70&lt;sup&gt;c&lt;/sup&gt;</td>
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<tr>
<td>-50</td>
<td>0.85</td>
<td>_b</td>
<td>0.60–0.80</td>
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*Calculated with \( l = 43.7 \text{ nm, } T_{SPINOAL} = T_{CRITICAL} = -43^\circ\).  
<sup>b</sup> Sample not prepared.  
<sup>c</sup> Sample not shown.
were rather sharp though the initial concentration fluctuations had gradual slopes. Another reason to be considered is that in order to effectively stain the PS-rich phase with RuO4, a minimum PS concentration should be present. In a first approach we can assume that this corresponded approximately to the gelation concentration. Therefore, it can not be expected to visualize the initial small concentration fluctuations of Figure 7a with TEM.

The experimentally observed development of liquid-liquid phase separation of a polymer solution from dispersed domains to a percolating phase, also closely resembles the (fractal) cluster formation of wax particles floating on water surface31 and computer simulations on clustering.32 Recently, the clustering of polystyrene spheres in salt water was investigated with low-angle static light scattering.33 After an initial period, the system was characterized by a unique length and the light-scattering intensity distributions could be scaled to a law similar to that holding for spinodal decomposition.

CONCLUSIONS

Semi-IPNs were prepared in a two-step procedure which separates phase separation and polymerization/crosslinking, in high molecular weight polymer solutions, the initial stages of spinodal demixing could be visualized as small domains. These domains were separated over a distance equal to one or several times the wavelength of spinodal demixing and it has been concluded that these domains represent the maxima of the concentration fluctuations. A cocontinuous morphology often associated with spinodally demixed systems, developed only in a relatively late stage of demixing. The observed semi-IPN morphology was determined by the cooling efficiency and quench temperature, and by the solution viscosity (polymer concentration and polymer molecular weight). By quenching films of concentrated solutions (> 20 wt. %), it was possible to obtain transparent semi-IPNs.

In principle, the concept of semi-IPN formation described here is universal, and any suitable polymer/monomer combination can be used, provided the polymer solution shows both a two-phase region and a glass transition temperature-concentration curve which intersect. UV-initiated polymerization is the most preferred type of polymerization, as this can even be performed at low temperature.

To our knowledge, this work represents the first attempt to visualize all stages of spinodal demixing in polymer solutions. The results are in agreement with computer simulations34,35 which were performed on the development of the phase texture in low-molecular weight (50/50) polymer blends during spinodal decomposition. The similar development of the spinodally demixed structure from separate small domains to a network stage with inclusions, can be taken as a support for the discussion above.

In the intermediate network stage of spinodal demixing (the network as shown in Fig. 5d and e), the systems are mechanically stable and this is therefore the most often observed arrested state of demixing in scanning electron microscopy experiments.7-9,21,22 However, remnants of the initially demixed structure are found in some SEM pictures of demixed polymer solutions reported in literature.7-9 These are the spherical inclusions, which can be shown to be in the order of the spinodal wavelength or multiples of this wavelength.

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REFERENCES AND NOTES


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