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Microphase separated semi-interpenetrating polymer networks from atactic polystyrene and methacrylates – a novel route

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Summary

A new route towards the formation of micro-phase separated semi- interpenetrating polymer networks (semi-IPN's) is described for the system atactic PS in methacrylates. It comprises the arrest of spinodal decomposition of an aPS solution by thermoreversible gelation (vitrification) of the polymer-rich phase. After low-temperature UV-polymerization and crosslinking of the methacrylate, the phase separated structure is preserved at room temperature. Thus the steps of morphology formation and polymerization are separated.

The demixing and gelation behaviour of solutions of atactic PS in several n-alkyl and branched methacrylates was studied. Gelation temperatures were found to be determined by the position of the demixing curves along the temperature axis and thereby the intersection points with the glass transition-concentration curve of plasticized PS. At polystyrene concentrations of 2 and 5 wt% a bicontinuous microphase separated morphology could be obtained with domain sizes of 0.2-0.5 μm.

Introduction

Crosslinked polymer systems are of great industrial interest for both rubbers and thermoharders. Interpenetrating polymer networks (IPN's) form a class of materials in which two (or more) polymers from which at least one forms a network, are synthesized in the presence of each other, though not covalently linked with each other (1). In case only one component is crosslinked, a semi-IPN is formed, e.g. high-impact polystyrene (HIPS, polystyrene phase crosslinked) (2). Due to the incompatibility of most polymers, phase separation usually takes place during IPN synthesis. In most cases this will finally result in a morphology consisting of a continuous matrix in which the second phase is dispersed as droplets.

Of special interest is the case in which both phases are continuous, e.g. for use as adhesives or noise damping materials (1). In order to get a bicontinuous morphology by simultaneous polymerization and crosslinking of both polymers, the reaction rates have to be adjusted and controlled strictly which often is not possible. Bicontinuity, however, often is observed in the case of sequential

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IPN's, which are synthesized by swelling (or in the case of a semi-IPN, dissolving) the first polymer in the second monomer and crosslinker, which are subsequently polymerized. The resulting morphology is determined by the crosslink density of the first component, its volume fraction, the polymerization rate of the second component, nucleation and growth of the phase domains and finally by shearing when the reaction mixture is stirred (1). In both types of IPN's, the morphology is in a non- equilibrium state in which further phase separation is suppressed by the interlocked three-dimensional structure, imposed by chemical crosslinks. In all cases, it is obvious that development of the phase texture depends on a large number of parameters and is thus difficult to control. Consequently, reports on phase separated IPN's are often not easily reproduced.

The present work is directed towards control of the formation of micro-phase separated semi-IPN's by separation of the morphology formation and the crosslinking polymerization steps. It is studied how a bicontinuous morphology can be formed by retardation of spinodal phase separation by thermoreversible gelation of the polymer- rich phase. A semi-IPN is obtained in a second step after polymerization and crosslinking of the solvent (monomer).

Arresting spinodal phase separation

When an ideal or regular homogeneous polymer solution is cooled, below a certain temperature phase separation will take place. A phase diagram exhibiting an upper critical solution temperature, UCST, is shown in figure 1a. Between the binodal and spinodal curve in the metastable region, phase separation takes place by nucleation and growth of the minor phase in a matrix of the second phase (figure 1b). In the spinodal region, decomposition starts due to small concentration fluctuations resulting in a bicontinuous structure of a polymer-rich phase and a polymer-poor phase (figure 1c). Bicontinuity can already be observed at very low volume fractions of polymer (3). By quenching rapidly through the metastable region into the spinodal region, nucleation of the secondary phase can be avoided and phase separation will be dominated by spinodal decomposition. If the quench temperature is low, a very fine network structure is initially formed.

Due to coarsening of the bicontinuous structure eventually a morphology will form in which only one phase is continuous (4). To prevent the demixed structure from coarsening it should be arrested as rapidly as possible. Chemically, rapid crosslinking of the monomer has been attempted in the special case of demixing homogeneous polymer blends of PPO/PS (5). Physical arrest of phase separation can be achieved by crystallization of the solvent (6), crystallization of the polymer (7), or, as it was recently recognized, by vitrification of the polymer-rich phase (8,9). The last two phenomena are also known as thermoreversible gelation.

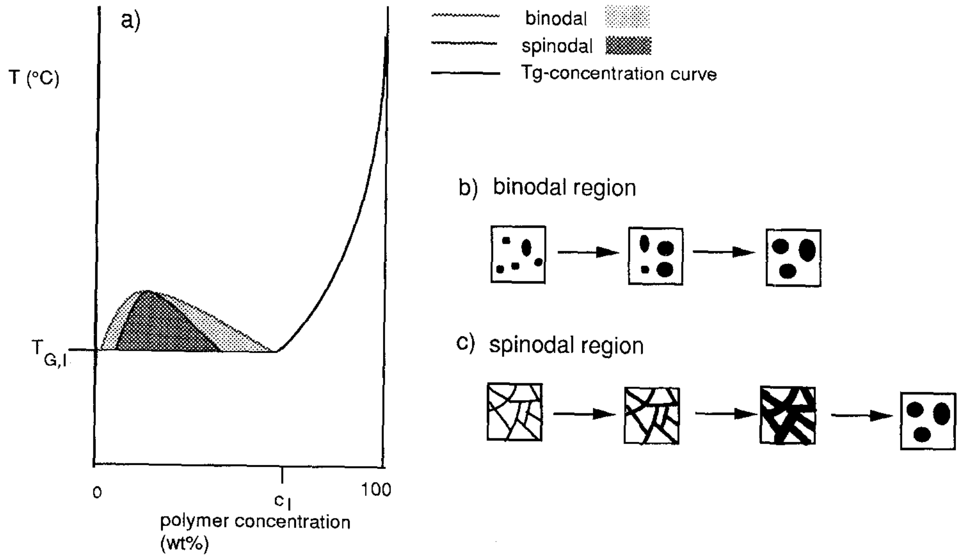


Figure 1: a) Schematic phase diagram showing both a liquid-liquid demixing curve and a glass transition-concentration curve. b) Morphology development in binodal region. c) Morphology development in spinodal region

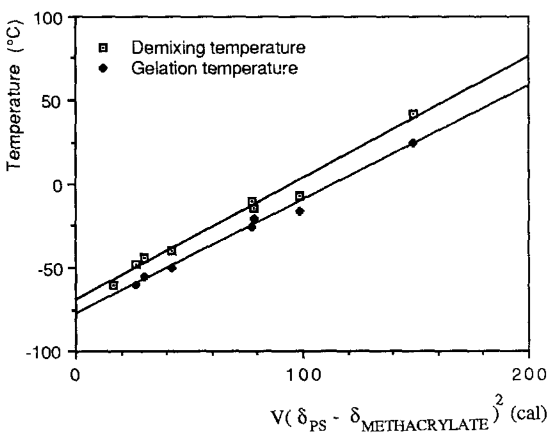


Figure 2: Demixing and gelation temperatures of 4wt% solutions of PS2M in several methacrylates as a function of $V(\delta_{PS} - \delta_{METHACRYLATE})^2$.

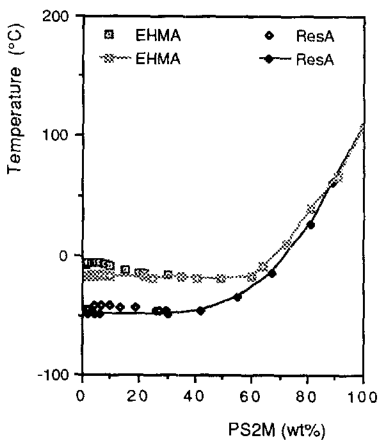


Figure 3: Phase diagrams of PS2M in EHMA and ResA. Full line: T_G-x curve.

Thermoreversible gelation

Gelation has been reported for several polymer solutions upon decreasing the temperature e.g. PE (10), PMMA (11,12), isotactic PS (13) and atactic PS (14). While gel formation upon crystallization of high molecular weight polymers from solution is well understood (12), different gelation mechanisms have been discussed for the gelation of polymer solutions where the polymer cannot crystallize or undergo specific non-dispersive interactions. A distinction has to be made between one-phase (clear) gels and two-phase (turbid) gels (7).

A mechanism for the formation of two-phase gels was given by Berghmans (8) and confirmed by Hikmet (9). Gelation results from liquid-liquid phase separation, followed by a vitrification process of the polymer-rich phase. Requirement for this type of gelation is the existence of both a liquid-liquid demixing curve and the glass transition-concentration (T_G-x) curve for the plasticized polymer which lies above the demixing curve (see figure 1a). Upon cooling a homogeneous solution, phase separation will occur after crossing the demixing curve. The (equilibrium) compositions of the coexisting phases at each temperature are determined by the binodal. When the solution is cooled below $T_{G,I}$ phase separation will proceed until the polymer-rich phase reaches concentration c_I, at which it will vitrify and the solution forms a gel. A network is formed in which the glassy domains act as physical crosslinks, giving the gel its elasticity. Frank and Keller (15) predicted that under equilibrium conditions the T_G-x curve in the binodal region should be curved. Actual measurements (8,9) show a straight T_G-x line, independent of the polymer concentration, indicating that phase separation is effectively arrested at reaching concentration c_I at $T_{G,I}$. The formation of clear gels from amorphous polymers, as they have been described for systems without liquid-liquid demixing is still under discussion. Analogous to the amorphous phase separated gels it is supposed that links are formed between a considerable number of chain segments (7), forming a vitreous cluster which however is too small to be detected or considered a second phase. The formation mechanism of these links is unclear, though a number of suggestions have been made (16, 17).

Experimental section

Materials: polymer: the polymer was an anionically prepared atactic polystyrene, with molecular weight M_N= 1,739,000 g/mol (M_W/N_N= 1.19, PS2M).

solvents: methacrylates with different side-groups (*n*-butyl, *t*-butyl, *n*-pentyl, *n*-hexyl, cyclohexyl, *n*-octyl, 2-ethylhexyl, *n*-decyl) were achieved from Röhm and Polysciences and used as received. Resin mixtures especially suited for microtoming and with low shrinkage upon polymerization were obtained from Lowi (HM23, K11M, for ResA mixed in a 1,3:1 ratio).

Phase diagrams: Demixing curves were determined by turbidity measurements at a cooling rate of 0.2°C/min. The temperature at which opalescence was observed was taken as T_D. Gelation temperatures (T_{GEL}) of low concentrated solutions were determined by slowly cooling the solutions in test tubes, until elastic behaviour was qualitatively observed. This was denoted as the condition that upon stirring the solution with a stick, the solution could be moved in one piece. Glass transition temperatures of highly concentrated solutions were measured by DSC (Perkin Elmer DSC7) at high heating rates and extrapolated to 1 K/min heating rate.

Polymerization: UV-polymerization was performed in a nitrogen atmosphere in an alumina cooling block which was cooled by liquid nitrogen. Homogeneous solutions were injected with a syringe in small polypropylene BEEM capsules which were precooled at the quench temperature. Polymerization was initiated at 15 degrees below T_{GEL} by benzoinmethylether as an UV-initiator. Two 4W 366 nm lamps were used for UV-irradiation and the system was kept at low temperature for 4-5 days to ensure complete conversion of the methacrylate monomer.

Morphology: Samples for transmission electron microscopy were cut on a LKB 2188 Ultrotome Nova. Sections were transferred to copper grids and stained with RuO_4 vapour. A JEOL 200 CX transmission electron microscope (200kV) was used to study the morphology.

Results and discussion

Phase behaviour of solutions of aPS in several methacrylates

By changing the substituents of the methacrylates, demixing temperatures of 4 wt% PS2M solutions could be varied from -48 to +42°C, from *n*-butylMA, *n*-pentylMA, cyclohexylMA, *n*-hexylMA, *n*-octylMA, *t*-butylMA, 2-ethylhexylMA to *n*-decylMA. Figure 2 shows how demixing temperatures can be correlated to the solubility parameters of polymer and solvent through $V(\delta_{POLYMER}-\delta_{SOLVENT})^2$, irrespective whether methacrylates were linear or branched. δ-Parameters were calculated using the boiling points of the methacrylates (18) ($\delta_{PS}=8.5$ cal/cm^3). V is the molar volume of the solvent (cm^3).

All 4 wt% solutions of PS2M in methacrylate (the critical concentration) showed a gelation temperature that was approximately 10 degrees lower than the demixing temperature. This indicates that the gelation temperature is determined by the position of the demixing curve along the temperature axis. Due to the similarity of the methacrylates, T_G-concentration curves of plasticized PS have the same position. The shape of the cloud point curves is more affected by the polydispersity of the polymer than by the methacrylate molecular structure. Consequently, a different methacrylate, with a different solubility parameter only causes a shift in the critical demixing temperature. As the intersection point of the demixing curve and T_G-x line changes its position, the gelation temperature alters (as does the polymer concentration at which gelation takes place).

In figure 3 phase diagrams of aPS solutions in 2-ethylhexylmethacrylate (EHMA) and a 1,3:1 mixture of HM23 and K11M (ResA) are displayed, showing the dependence of T_{GEL} on the position of the demixing curve. It is visible that at gelation the polymer concentration in the polymer rich phase is only 50-60 wt%.

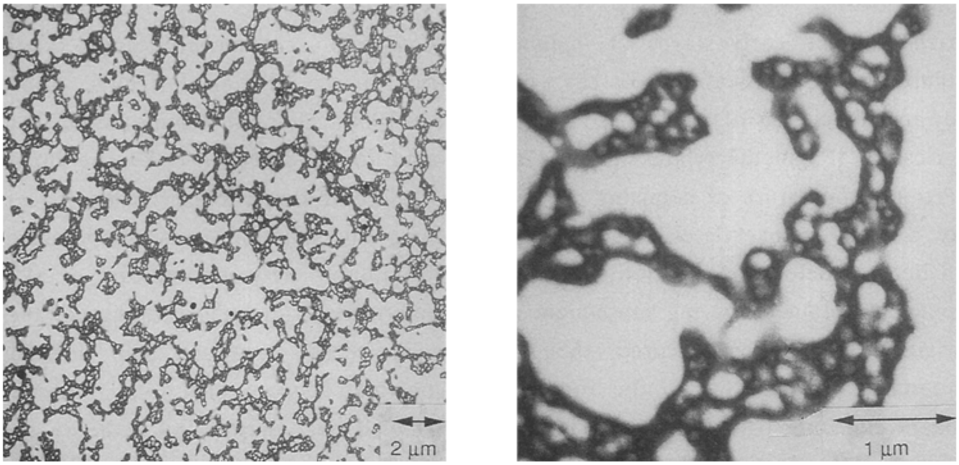
Morphology of the semi-IPN's

Micro-phase separated semi-IPN's were obtained by quenching a homogeneous solution to T_{QUENCH}, which in the case of ResA was -60 °C. The morphology obtained from 2 wt% and 5 wt% solutions of PS2M in ResA are shown in figures 4 and 5. The black phase is the stained PS-rich phase which has a structure that is three-dimensionally percolating in both phases, bicontinuous. Experiments showed that during UV-polymerization 15 degrees below T_{GEL} no further change of the domain texture occured, meaning that the observed pattern is formed due to initial phase separation of the polymer solution. However, inside of the PS-rich phase small spheres developed, indicating that a second phase separation step occurred during polymerization (see figures 4b and 5b). The methacrylates are polymerized radically, so at every moment during reaction there is both high polymer and unpolymerized monomer. It is very well probable that though movement of the PS- chains is restricted, methacrylate monomer is free to diffuse out of the PS-rich phase (which contains up to 50 wt% monomer) and to segregate into small domains. The resulting structure is reminiscent of high-impact polystyrene (2), and interesting mechanical properties, e.g. one very broad T_G are found.

The size of the demixed structure can be calculated using an adaptation of Cahn's theory for spinodally demixing polymer solutions (19). Molecular weight, critical demixing temperature (T_C) and quench temperature (T) are related to the most frequently found dimension D_M.

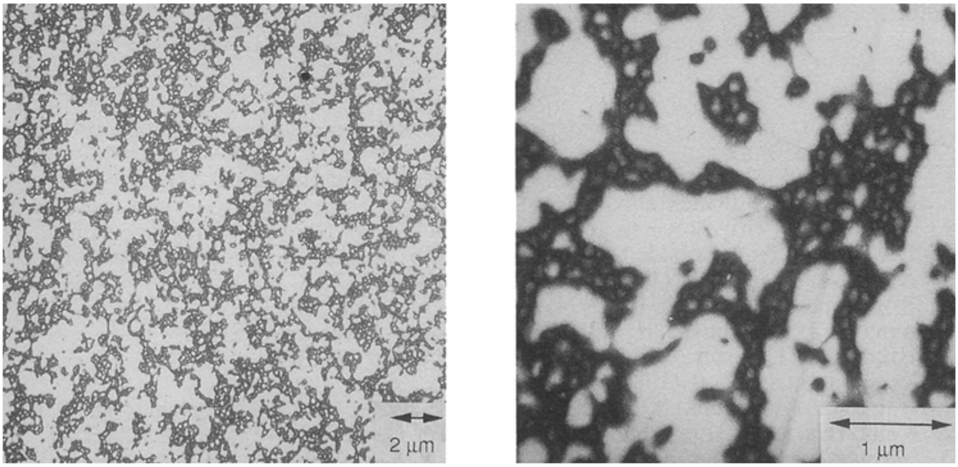
$$D_M = 2\pi l\left(3\left(l-\frac{T}{T_C}\right)\right)^{-1/2}$$

where *l* is a range of molecular interaction, taken to be equal to the radius of gyration. With T_C= -43 °C, T (=quench temperature)= -60 °C and the end-end distance of PS2M in methacrylate solution 200 Å, a dimension of approximately 0.27 μm is calculated. Indeed the dimensions found in the 2 and 5 wt% sample are in the order of 0.2- 0.5 μm, strongly indicating that phase separation proceeds by spinodal demixing. Due to the lower viscosity of the 2 wt% solution the domain sizes are somewhat larger than in the 5 wt% case because of faster demixing. The uniformity of the domain sizes is remarkable, indicating that coagulation of the



a) b)

Figure 4: TEM photograph of microphase separated semi-IPN from 2 wt% PS2M in ResA, quenched to -60°C. a) macrostructure, b) internal structure



a) b)

Figure 5: TEM photograph of microphase separated semi-IPN from 5 wt% PS2M in ResA, quenched to -60°C. a) macrostructure, b) internal structure

domains has not taken place to a large extent. Quenching to lower temperatures than -60°C will result in arresting spinodal decomposition at an earlier stage, as the time supplied for demixing is shorter. Preliminary observations indicate that bicontinuity is not reached at that stage for 2 wt% and 5 wt% solutions.

Conclusions

Arrest of the early stages of (spinodal) decomposition of an aPS/methacrylate solution by vitrification of the polymer-rich phase, is an effective route towards formation of microphase separated semi-IPN's. Gelation temperatures of a series of aPS/methacrylate solutions were found to be determined by the intersection temperature of demixing curves and T_G-concentration curve (which is equal for all the methacrylates studied). By quenching the solutions to a temperature 15 degrees below the gelation temperature, a continuous network structure of aPS could be obtained. During subsequent UV-polymerization, no further change of the original domain size occured, though a second phase separation step due to monomer diffusion led to the formation of polymethacrylate inclusions inside of the PS-domains. The size of the network could well be described by a theory for the spinodal demixing in polymer solutions, indicating that bicontinuity is the result of spinodal decomposition.

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References

1. Sperling L (1981), Interpenetrating networks and related materials, Plenum Press, New York
2. Donatelli A, Sperling L, Thomas D (1976) Macromolecules 9:671
3. Cahn J (1963) J.Chem.Phys 42(1):93
4. Utracki L (1990) Polymer alloys and blends, Carl Hanser Verlag, Münich
5. Hashimoto T, Takanaka M, Jinnai H (1989) Polymer Communications 30:177
6. Aubert J, Clough R, (1985) Polymer 26:2047
7. Rogovina L, Slominski G (1974) Russ.Chem.Rev.43:503
8. Arnauts J, Berghmans H (1987) Polymer Communications 28:66
9. Hikmet R, Callister S, Keller A (1988) Polymer 39:1378
10. Lemstra P, Smith P (1980) J.Mater.Sci 15:505
11. Berghmans H, Donkers A, Frenay L, Stoks W, et al. (1987) Polymer 28:97
12. Vanderweerdt P, Berghmans H, Tervoort Y (1991) Macromolecules 24:3547
13. Girolamo M, Keller A, Miyasaka K et al. (1976) J.Pol.Sci, Pol.Phys.Ed 14:39.
14. Wellinghoff S, Shaw J, Baer E (1979) Macromolecules 12:933
15. Frank F, Keller A (1988) Polymer Communications 29:186
16. François J, Gan J, Guenet J (1986) Macromolecules 19:2755
17. Hildebrand J, Scott R (1950) The solubility of non-elctrolytes, 3rd edn Rheinhold Publishing Corp., New York
18. Van Aartsen J (1970) Eur.Pol.Jour. 6:919

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