Phase Separation in Ternary Systems Induced by Crosslinking*

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Crosslinking of polymer molecules can lead to phase separation in sys-
tems composed of a polymer and diluents. The conditions for incipient phase
separation and postseparation equilibria are described in terms of statistical
theories of rubber elasticity and polymer solutions. Conditions are specified
under which demixing is controlled predominantly by polymer—diluent
interactions or by the presence of crosslinks and related to structural
parameters of the system and advancement of the crosslinking reaction.
Examples of phase separation in poly(2-hydroxyethyl methacrylate) and
polystyrene gels are given.

It is well known that liquid—liquid phase separation can take place when a non-
-solvent is added to the solution of a polymer, or a copolymer becomes only partly
miscible with the solvent when the composition of the copolymer changes. Intro-
duction of crosslinks can be another reason for partial miscibility of the polymer
with a given solvent. If a polymer is being crosslinked in the presence of a diluent,
the crosslinks limit the maximum degree of swelling of the network and the cross-
linking density can reach eventually such a value that the swollen network cannot
absorb the amount of diluent it contains and must demix into a liquid and a gel
phase.

Thermodynamics of phase separation

In terms of the statistical theory of elasticity of Gaussian networks with tetra-
functional crosslinks [1] the free enthalpy of swelling, ΔG_{sw}, is given by

$$\Delta G_{sw}/kT = \Delta G_{dil}/kT + (3\nu/2)(\overline{r_d^2}/\overline{r_0^2})(\varphi_p^{-2/3} - 1) + (\nu/2) \ln \varphi_p \qquad (1)$$

where $\overline{r_d^2}$ and $\overline{r_0^2}$ are the mean squares of the end-to-end distances of network chains
in the dry and reference states, respectively, ν is the number of crosslinked units
and φ_p is the volume fraction of the polymer. For $\Delta G_{dil}/kT$, usually the Flory—
—Huggins expression

$$\Delta G_{dil}/kT = \Sigma N_i \ln \varphi_i + \sum_{i>j} \chi_{ij} N_i \varphi_j \qquad (2)$$

is employed; N_i is the number of molecules i and χ_{ij} is the polymer—solvent inter-
action parameter.

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At incipient phase separation the chemical potentials of either component in both phases (l = liquid, g = gel) are equal. Using equation (1) one gets for the component i

$$(\Delta\mu)_i^l = (\Delta\mu_{\text{dil}})_i^g - RT\, \nu^*\, \overline{V}_i[\varphi_p^{1/3}\,(\overline{r_d^2}/\overline{r_o^2}) - \varphi_p/2]. \tag{3}$$

$\overline{V}_i$ is the partial molar volume of the component i and ν^* is the molar concentration of crosslinked units in the dry network. The equilibrium composition of both phases is obtained by solving the set of equation (3). The network elasticity term on the right-hand side of equation (3) is the same for all components except for the quantity $\overline{V}_i$; it is usually positive and proportional to the concentration of crosslinked units. Therefore, increasing crosslinking contributes positively to $(\Delta\mu_i)_{\text{sw}}$ and favours phase separation.

The ratio $\overline{r_d^2}/\overline{r_o^2}$ depends on the dilution of the network at the time of its formation. In many cases it is legitimate to assume that the network chains are not stretched when the network is formed, $i.e.$ that their dimensions approach the reference dimensions [2]. The dimensions of chains in the dry network are then connected with the volume fraction of the polymer in the system being crosslinked as

$$\overline{r_d^2} = (\varphi_p^0)^{2/3}\, \overline{r_o^2} \tag{4}$$

and at incipient phase separation

$$\varphi_p = \varphi_p^0. \tag{5}$$

After inserting relations (4) and (5) into equation (3), the condition for incipience of phase separation, equivalent to a point on the binodal or to the cloud point in solutions of linear polymers, reads

$$\Delta\mu_i^l = (\Delta\mu_{\text{dil}})_i^g + RT\, \nu^*\, \overline{V}_i\, \varphi_p^0/2. \tag{6}$$

The description of postseparation phase equilibria is more complicated because the volume of the network phase usually changes and the network is no more a simple but a composite one with a distribution of network chain extensions depending on the history of the crosslinking and phase separation process (for details see [2]).

Networks can be formed either by crosslinking of existing chains (vulcanization) or by crosslinking copolymerization, $e.g.$ of a vinyl and a divinyl monomer. The relations given above can be used straightforwardly for the former case. The crosslinking copolymerization has some special features: the monomers act as diluents, but their concentration decreases with increasing conversion; at the same time the crosslinking density of the network increases. The condition for incipient phase separation can still be used if one makes use of the dependence

$$\varphi_p^0 = \varphi_p^{00}\, \alpha \tag{7}$$

and takes into account that ν^* is a function of the polymerization conversion, monomer reactivity ratios and possibly dilution; for an ideal copolymerization [3]

$$\nu^* = \alpha_m\, f_2^0/\overline{V}_u. \tag{8}$$

In these expressions φ_p^{00} is the volume fraction of monomers in the system at the beginning of copolymerization, α is the volume conversion and α_m the molar con-

version of the vinyls, f_2^0 is the initial mole fraction of vinyls in the divinyl monomer and $\overline{V}_u$ is the molar volume of the monomer unit.

Two sets of factors determine the stability of systems containing a crosslinked polymer. The first one depends on segment-segment interactions described by a set of Flory—Huggins interaction parameters χ_{ij} which determine the thermo-
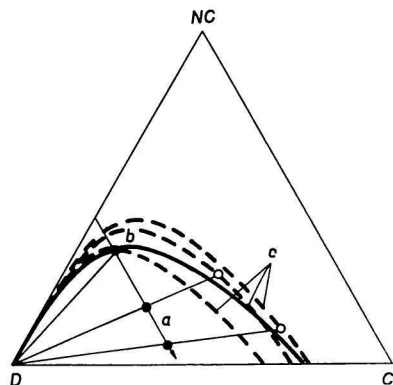

Fig. 1. Phase separation in the course of crosslinking of existing polymer chains in solution.

C, *NC*, and *D* are fractions of crosslinked and non-crosslinked units and of diluent in the system, respectively.

a) progressing crosslinking; *b)* locus of points of incipient phase separation; *c)* coexistence curves.

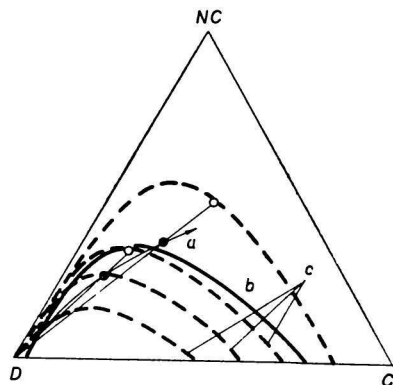Polymer—solvent interaction parameter $\chi = 0.45$, polymer of very high molecular weight.

Fig. 2. Phase separation in the course of ideal crosslinking copolymerization.

D includes unreacted monomers and the inert diluent.

a) progressing copolymerization; *b)* locus of points of incipient phase separation; *c)* coexistence curves; $\chi = 0.45$.

dynamic properties of the corresponding uncrosslinked system. The second set is directly related to the presence of crosslinks: as follows from equation (6) demixing is favoured by increasing degree of crosslinking, dilution and molar volume of the diluent. In crosslinking copolymerization, the critical polymerization conversion at incipient phase separation decreases with increasing concentration and reactivity of the divinyl monomer and increasing dilution with an inert diluent and its molar volume.

Examples of phase separation in a system composed of a crosslinked polymer and a single diluent are schematically shown in triangle diagrams where the diluent (D), the crosslinked (C) and uncrosslinked (NC) polymer segments are taken as components. Fig. 1 describes crosslinking of existing polymer chains in solution. Crosslinking takes place at constant concentration of the diluent which corresponds to moving along the straight line a parallel to the $NC-C$ triangle side. The system is homogeneous until a crosses the solid curve b which describes the incipience of phase separation (equation (6)) and is analogous to the cloud point curve. The point of intersection is at the same time the point of intersection of a with the corresponding coexistence curve c (dashed), which determines the equilibrium degree of swelling of gels with constant ratio $\overline{r_d^2}/\overline{r_0^2}$. When crosslinking proceeds, the volume of the network phase and dimensions of network chains are changed (decrease), what is reflected in a change of coexistence curves c. In Fig. 1 the curves c are projected on the triangle plane. The composition of coexisting phases is given by tie lines which go out from the triangle corner D and cross the corresponding coexisting curve. The situation formally reminds phase separation in quasibinary or quasiternary systems consisting of a polydisperse uncrosslinked polymer (see [4]), where the cloud point curve and coexistence curve do not coincide.

An example of phase separation in the course of crosslinking copolymerization is given in Fig. 2 and describes a system composed initially of monomers and a diluent both being thermodynamically equivalent except the polymerization ability so that a single parameter χ is able to characterize polymer—solvent interactions. We start moving from the corner D because the system contains in the beginning only the diluents (monomer(s) + inert diluent), and continue along the curve a, which describes the formation of the polymer and increase of the fraction of crosslinked units. Because of the shape of the curve a, phase separation either does not take place at all (low concentration of the crosslinking agent) or occurs at low conversions. The right-hand side of the "cloud point" curve is practically unaccessible, unless the divinyl monomer has much lower reactivity than the monovinyl monomer.

χ- and v-induced phase separation

Both the increase of the diluent—network interaction parameter and increase of the crosslinking density can become operative in phase separation. If the crosslinking density is low, phase separation is controlled almost exclusively by the former factor. The copolymerization of 2-hydroxyethyl methacrylate with ethylene dimethacrylate can serve as an example. Water is a poor solvent for the polymer, the monomer is a better solvent and the monomer and water form a cosolvent mixture with maximum degree of swelling of a crosslinked gel and maximum of intrinsic viscosity [5]. Phase separation takes place when the concentration of water exceeds 40%. With increasing concentration of water the onset of phase separation

is shifted to lower conversions (Fig. 3). Although the whole coexistence curve changes considerably after introduction of crosslinks (from c to d), its left-hand-side lower part almost coincides with the part of the coexistence curve of an uncrosslinked polymer. Phase separation at low crosslinking levels is thus very little affected by crosslinks.
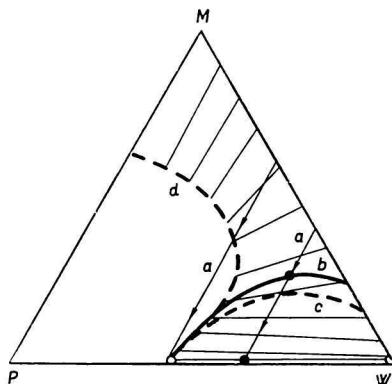

Fig. 3. Phase separation in the course of copolymerization of 2-hydroxyethyl methacrylate with ethylene dimethacrylate in the presence of water.

M, P, W are fractions of the monomer (2-hydroxyethyl methacrylate), polymer, and water, respectively.

a) progressing copolymerization; b) locus of points of incipient phase separation; c) coexistence curve for an uncrosslinked polymer; d) coexistence curve for a gel crosslinked with 0.2% ethylene dimethacrylate.

The ν^*-induced syneresis was studied in the course of crosslinking copolymerization of styrene with divinylbenzene in the presence of various diluents: good solvents for polystyrene such as toluene or ethylbenzene, precipitants such as iso-octane or heptane, and polymers such as polystyrene, poly(methyl methacrylate) or polydimethylsiloxanes [6]. The system monomers—toluene can be regarded as a quasibinary one because the interaction parameters polystyrene—toluene and polystyrene—styrene are almost the same ($\chi \approx 0.46$). The systems monomers——precipitant or monomers—polymer are typical quasiternary systems. Almost in all cases (with exceptions of systems with precipitants and a low concentration of the crosslinking agent) phase separation takes place at low conversions in the vicinity of the gel point. In Fig. 4 the calculated interdependence of the dilution and concentration of divinylbenzene necessary for phase separation to occur is plotted and compared with experimentally observed cloud point curves and appearance of porosity measured in the dry polymers. The agreement between the experimental data and values calculated using the procedure outlined in this paper is fairly good. The large difference between the porosity curve on the one hand and the cloud point and theoretical curves on the other at lower concentrations of the crosslinking agent is due to capillary contraction occurring on drying the gel in the rubbery state.

Fig. 4 shows that the phase separation is facilitated by dilution and increase of the crosslinking density. The dilution with toluene and polystyrene is a typical
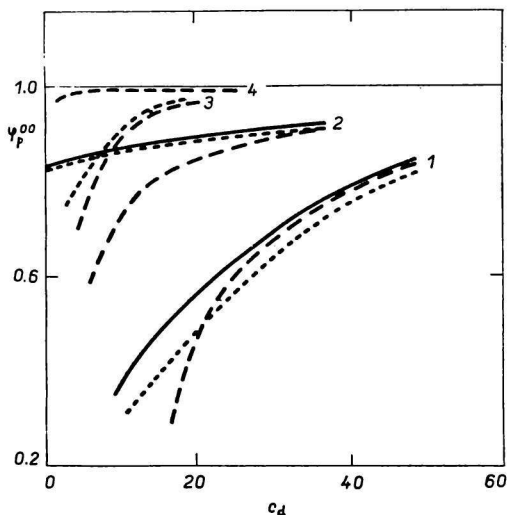
Fig. 4. Critical degree of dilution and concentration of divinylbenzene in the copoly-
merization with styrene for phase separation in the presence of various diluents.
Diluent: *1.* toluene; *2.* iso-octane; *3.* polystyrene of molecular weight 50,000;
4. polydimethylsiloxane 50 cP.
——————— development of turbidity;
- - - - - - - - - formation of networks porous in the dry state;
        theory.
         c_d concentration of divinylbenzene in the monomer.

example of ν-induced syneresis. Moreover, the dilution of the polymerizing system
with polystyrene illustrates the large effect of the molar volume of the diluent on
phase separation. This means that polystyrene of a not too low molecular weight
is almost completely excluded from a gel of medium degree of swelling although
the interaction between the diluent segments and identical network chains
segment is virtually zero. When the crosslinking density is low, phase separation
does not occur and this is also true for polystyrene of low molecular weight.
According to the expectation, the combination of high molar volume and low inter-
action between the diluent and network chain segments led to the most powerful
diluents with respect to phase separation. For example, polydimethylsiloxanes
yielded heterogeneous structures when they were used as diluents in concentration
as low as 0.5—1.0% (Fig. 4).

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