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Phase separation in free-radical crosslinking copolymerization: formation of heterogeneous polymer networks

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Abstract

A model combining both the thermodynamic and kinetic aspects of free-radical crosslinking copolymerization (FCC) is presented to predict the formation conditions and the properties of heterogeneous (porous) networks. The model involves thermodynamic equations describing the phase equilibria between the network and separated phases during FCC of vinyl/divinyl monomers and kinetic equations giving the concentration of reacting species and the polymer properties as a function of the monomer conversion. Calculation results are presented for styrene/*m*-divinylbenzene (S/*m*-DVB) copolymerization system in the presence of inert diluents. S/*m*-DVB copolymerization system at a high *m*-DVB concentration, or, at a low monomer concentration phase separates at the gel point and results in the formation of a microgel solution. The calculation results also show that the heterogeneity in S/*m*-DVB copolymer networks increases on increasing DVB or diluent concentration, or, on decreasing the solvating power of the diluent, in accord with the experimental data published previously. The model also predicts correctly the equilibrium volume swelling ratio of heterogeneous networks in solvents.

Keywords: Phase separation; Heterogeneous networks; Kinetic–thermodynamic modeling

1. Introduction

Heterogeneous (porous) polymer networks are widely used as starting materials for ion exchangers and as specific sorbents, and, therefore, have been the subject of a large number of studies [1–3]. These materials are prepared mainly by free-radical crosslinking copolymerization (henceforth referred to as FCC) of vinyl/divinyl monomers, e.g. styrene/divinylbenzene or acrylamide/N,N′-methylene (bisacrylamide), in the presence of an inert diluent. The diluent, which is a solvent, a nonsolvent, or a linear polymer, is included in the FCC system as a pore forming agent, and plays an important role in the design of the pore structure of crosslinked materials [2].

If the diluent remains in the gel throughout the copolymerization, an expanded network structure is obtained. The expanded networks thus formed collapse during the removal of the diluent after their synthesis and therefore, they are nonporous in the glassy state. Heterogeneities in the network structure appear if the diluent separates out of the gel phase during polymerization. The incipient phase separation during FCC may occur before the onset of macrogelation; this results in the formation of a polymer dispersion in the liquid phase. Otherwise, if the system phase separates beyond the gel point, the gel shrinks and results in a dispersion of the expelled liquid droplets in the network phase. In both cases, after complete conversion of the monomers a heterogeneous network consisting of network and diluent phases is obtained. Removing of the diluent from the network creates voids (pores) of sizes 10 Å up to 1 μm in the glassy state.

Relationships between the synthesis conditions and the structure of heterogeneous networks have been the subject of intensive studies during the last four decades [4–21]. Experiments showed that a phase separation during FCC is promoted, i.e. the pore volume of the final network increases as the concentration of the divinyl monomer or that of the diluent increases, or as the solvating power of the diluent decreases. It was also shown that good solvents as a diluent create small pores and therefore, a large specific surface area, whereas bad solvents or linear polymers produce materials with irregularly shaped large pores.

Although many experimental studies have dealt with the porosity formation in FCC in the presence of several diluents, only a few were concerned with the theory of formation of heterogeneities in such systems. Dusek was the first who treated the phase separation during the network formation process under the assumption of thermodynamic equilibrium between the network and separated phases [22–24]. By using Flory's theory of swelling equilibrium and the

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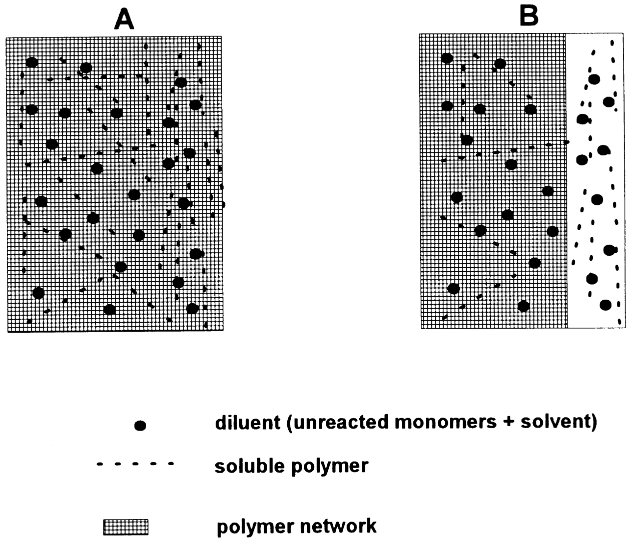

Fig. 1. Schematic representation of FCC system (A) before and (B) after phase separation.

theory of rubber elasticity, he derived relations between the volume of the network phase and the monomer conversion. Similar thermodynamic relations were also reported by Boots et al. to predict the onset of phase separation in crosslinking copolymerization of divinyl monomers [25]. An important assumption involved in the derivation of Dusek's and Boots equations is that all polymer molecules beyond the gel point belong to the gel. Thus, in these models, the existence of sol molecules in the reaction system is simply ignored. However, the gel fraction W_g, i.e. the weight fraction of polymer chains that belong to the gel, is known to be zero at the gel point and it increases as the polymerization proceeds, but never attains unity at a monomer conversion less than 100%. Therefore, a realistic thermodynamic model that describes the phase equilibria in FCC system should take into account the distribution of soluble polymers between the gel and the separated diluent phases. Moreover, in Dusek's and Boots models, the kinetics of FCC was not taken into account. For example, different vinyl group reactivities in FCC system as well as the variation of the gel crosslink density depending on the reaction condition are neglected.

In this paper, we combine thermodynamic and kinetic aspects of FCC system to predict the condition of phase separation and the volume of the separated phase as a function of the system parameters. In the present model, we take into account the kinetic features of FCC of vinyl/divinyl monomers. The effect of soluble polymers on the phase equilibria between the network and separated phases is also considered. In the following sections, we first consider the thermodynamic condition for a phase separation in FCC system consisting of a network, unreacted monomers, a diluent and soluble polymers (sol). Equations describing the thermodynamic equilibria between the network and separated phases for a given monomer conversion will be derived here. The solution of thermodynamic equations requires conversion-dependent network and polymer properties, which will be obtained from the kinetic treatment of FCC system examined later. In the last section, the kinetic–thermodynamic model is applied to the FCC of styrene/*m*-divinylbenzene in the presence of diluents. Finally, the simulation results are compared with the experimental data available in the literature.

In the treatment that follows, the main assumptions made are as follows: (1) thermodynamic equilibrium in every step of the reactions, (2) limitations of the Flory–Huggins theory, the theory of rubber elasticity and the kinetic theories of gel formation, (3) polymerization and crosslinking reactions in the network and separated phases are identical. (4) from the thermodynamic point of view, the soluble polymers beyond the gel point are monodisperse at any monomer conversion and, the number of segments on each chain is equal to the number-average degree of polymerization. Further, in the interest of simplicity, we assumed that (5) the diluent has the same thermodynamic characteristics as the monomer, and (6) the onset of phase separation occurs beyond the gel point. Although the last assumption can easily be removed from the model, the composite network structure formed in such polymerization systems cannot be studied within the framework of the Flory's theory of swelling.

2. Thermodynamics

2.1. *Swelling of polymer network in free-radical crosslinking copolymerization*

In the FCC of vinyl/divinyl monomers, the reaction system beyond the gel point involves the unreacted monomers, solvent, soluble polymers and a polymer network. For the following analysis, we will call the mixture of the unreacted monomers and the solvent as the diluent. The FCC system at a given degree of monomer conversion can thus be considered as a ternary system consisting of the diluent, network, and the soluble polymer (Fig. 1(A)). For this ternary system where components 1, 2 and 3 are the diluent, network, and soluble polymer, respectively, all concentrations and properties of the components are functions of the monomer conversion. Consider now the reaction system at a volume conversion of the monomers α, which is above the critical conversion for the onset of a phase separation. At this conversion, the diluent and soluble polymers will distribute between the network and separated phases, whereas the network will only exist in the network phase (Fig. 1B). We can thus analyze the system as a network immersed in polymer solution. Swelling of a polymer network in such a system is governed by at least three free energy terms [26,27], i.e., the changes in the free-energy of mixing ΔG_m, in the free energy of elastic deformation ΔG_{el} and in the free energy of electrostatic interactions ΔG_i

$$\Delta G = \Delta G_\mathrm{m} + \Delta G_\mathrm{el} + \Delta G_\mathrm{i}. \tag{1}$$

According to the Flory–Huggins theory [28], ΔG_m is given by

$$\Delta G_\mathrm{m} = \mathrm{R}T\left(\sum_i n_i \ln v_i + \sum_{i<j} n_i v_j \chi_{ij}\right) \tag{1a}$$

where n_i is the moles of the species i ($\mathrm{i} = 1, 2$, and 3), v_i its volume fraction, χ_{ij} the interaction parameter between the species i and j, R the gas constant and T the temperature. For the free energy of elastic deformation ΔG_el, although several theories are available in the literature, the simplest affine network model will be used here to describe qualitatively the behavior of polymer gels [28],

$$\Delta G_\mathrm{el} = (3/2)(\mathrm{R}T/NV_\mathrm{s})\left(\left(v_2^0/v_2\right)^{2/3} - 1 - \ln\left(v_2^0/v_2\right)^{1/3}\right) \tag{1b}$$

where N is the average number of segments in the network chains v_2^0 is the volume fraction of polymer network in the network phase at a given degree of conversion, and V_s is the molar volume of solvent. Note that the validity of Eq. (1b) or any similar equation for gels containing dissolved polymer is unknown. Interchain entanglements between the network and polymers should be mentioned as the possible source of error with the use of Eq. (1b) for the present system. However, previous experimental works showed that the Flory–Rehner theory represented by Eq. (1) works satisfactorily if the equilibrium swelling degrees of the gels are calculated instead of energies [29,30]. This is, as pointed out by De Gennes and Brochard, owing to the favorable cancellation of two opposite approximations of the theory [31,32]. Another important point with the use of Eq. (1b) for the present system is that, after phase separation, the volume of the gel phase changes continuously, so that the gel growth occurs at different degrees of dilution, represented by v_2^0. This means that the configuration of the network chains is determined by the history of the network formation process. In order to account for this effect, Dusek used the two network hypothesis proposed by Andrews and Flory [23]. However, if one prepares a homogeneous network by FCC in the absence of any added diluent, the gel growth also occurs at different dilution degrees. (Here, the unreacted monomers whose concentration changes continuously act as a diluent.) Since the Flory–Rehner theory is well applicable to the swelling behavior of gels prepared by FCC, it is plausible to neglect this effect at this stage of the model development and include it into the second assumption mentioned in the introduction.

For weakly charged ionic gels, the free energy of electrostatic interactions ΔG_i may be written as follows [28]:

$$\Delta G_\mathrm{i} = \mathrm{R}T\frac{N_\mathrm{i}}{N}\frac{v_2}{v_1} n_1 \ln(N_\mathrm{i} v_2/N) \tag{1c}$$

where N_i is the average number of ionic units in a network chain.

Substitution of Eqs. (1a)–(1c) into Eq. (1) and differentiating with respect to the number of moles of the diluent n_1 and the soluble polymer n_3 yield the following equations for the excess chemical potentials μ of the components 1 and 3 in both network and separated phases:

$$\frac{\Delta\mu_1}{\mathrm{R}T} = N^{-1}\left(v_2^{1/3} v_2^{02/3} - v_2/2\right) + \ln v_1 + (1 - v_1) - v_3/y + (\chi_{12} v_2 + \chi_{13} v_3)(1 - v_1) - \chi_{23} v_2 v_3 - v_2 N_\mathrm{i}/N, \tag{2a}$$

$$\frac{\Delta\mu_1'}{\mathrm{R}T} = \ln v_1' + v_3'(1 - 1/y) + \chi_{13} {v_3'}^2, \tag{2b}$$

$$\frac{\Delta\mu_3}{y\mathrm{R}T} = N^{-1}\left(v_2^{1/3} v_2^{02/3} - v_2/2\right) + (1/y)\ln v_3 + (1/y)(1 - v_3) - v_1 + (\chi_{13} v_1 + \chi_{23} v_2)(1 - v_3) - \chi_{12} v_1 v_2 - v_2 N_\mathrm{i}/N, \tag{3a}$$

$$\frac{\Delta\mu_3'}{y\mathrm{R}T} = (1/y)\ln v_3' - v_1'\left(1 - y^{-1}\right) + \chi_{13} {v_1'}^2 \tag{3b}$$

where y is the number of segments in the soluble polymer. Note that the symbols with a superscript prime ($'$) relate to the separated phase, whereas those without this superscript relate to the network phase.

2.2. Conversion-dependent phase equilibria in FCC system

The reaction mixture of FCC remains homogeneous as long as the growing polymer network is able to absorb all the available monomers and the diluent. As the copolymerization and crosslinking reactions proceed, that is as the crosslink density of the network increases, a critical point is passed, at which the equilibrium degree of swelling of the network in the diluent becomes equal to its degree of dilution. At this point, since the dilution of a homogeneous network cannot be greater than its equilibrium degree of swelling, the reaction system will separate into two phases: network and separated phases. Thus, the condition for incipient phase separation during FCC is given by:

$$v_2 = v_2^0 \tag{4}$$

After phase separation, both v_2 and v_2^0 will change with further copolymerization and crosslinking reactions, but the equality given by Eq. (4) still holds for the network phase. The state of equilibrium between the network and separated phases in FCC is obtained when the diluent and the soluble polymers inside the network phase are in thermodynamic equilibrium with those in the separated phase. This equilibrium state is described by the equality of the chemical

Table 1
Kinetic constants and parameters for S/*m*-DVB copolymerization at 60°C using AIBN as an initiator ($[I]_0 = 0.1$ M)

Constants	Ref.
$k_d = 0.85\times 10^{-5}$ (s^{-1})	[33]
$k_{pj1} = 145$ ($l\,mol^{-1}\,s^{-1}$)	[33][a]
$k_{pj2} = 165$ ($l\,mol^{-1}\,s^{-1}$)	[34]
$k_{pj3} = 19$ ($l\,mol^{-1}\,s^{-1}$)	[35]
$k_{tcij} = 2.9\times 10^{7}$ ($l\,mol^{-1}\,s^{-1}$)	[33]
$k_{tdij} = 0$	[33]
$f = 0.45$	[34]
$d_M = 0.91$ ($g\,ml^{-1}$)	
$d_P = 1.08$ ($g\,ml^{-1}$)	
$\alpha_i = 0$	
$\bar{V}_1 = 114.2$ $ml\,mol^{-1}$)	
$\bar{V}_2 = 142.9$ $ml\,mol^{-1}$)	

[a] Rate constant for the homopolymerization of styrene.

potential of these components in both phases. Thus, at swelling equilibrium, we have:

$$\Delta\mu_1 - \Delta\mu_1' = 0 \tag{5}$$

$$\Delta\mu_3 - \Delta\mu_3' = 0 \tag{6}$$

Substitution of Eqs. (2a), (2b) and (3a), (3b) into Eqs. (5) and (6) and using the phase separation condition given by Eq. (4), we obtain the following system of equations describing the equilibrium condition between the network and separated phases during FCC:

$$\begin{aligned} &N^{-1}v_2^0(0.5 - N_i) + \ln\left(\frac{v_1}{v_1'}\right) + (1 - v_1 - v_3') - (v_3 - v_3')/y \\ &\quad + \chi_{12}v_2^{02} + \chi_{13}(v_3^2 - v_3'^2) + (\chi_{12} + \chi_{13} - \chi_{23})v_2^0 v_3 \\ &\quad = 0, \end{aligned} \tag{7}$$

$$\begin{aligned} &-\ln\left(\frac{v_1}{v_1'}\right) + (1/y)\ln(v_3/v_3') + 2\chi_{13}(v_3' - v_3) \\ &\quad + (\chi_{23} - \chi_{12} - \chi_{13})v_2^0 = 0. \end{aligned} \tag{8}$$

Application of material balance to each phases gives the following two additional equations:

$$v_1 + v_2^0 + v_3 = 1, \tag{9}$$

$$v_1' + v_3' = 1. \tag{10}$$

At the start of the polymerization, the reaction mixture only contains the monomers and the solvent with volume fractions v_2^{00} and $1 - v_2^{00}$, respectively. Let W_g be the weight fraction of polymer chains that belong to the gel and v_g be the volume fraction of the network phase in the reaction system at volume conversion α, from the material balance, we have the following equalities:

$$v_2^0 = \bar{v}_p W_g / v_g, \tag{11}$$

$$\bar{v}_p(1 - W_g) = v_3 v_g + v_3'(1 - v_g) \tag{12}$$

where $\bar{v}_p$ is the volume fraction of sol + gel polymer in the whole reaction system (network + separated phases), i.e.

$$\bar{v}_p = \frac{\alpha v_2^{00}(1 - \varepsilon)}{(1 - \alpha v_2^{00}\varepsilon)} \tag{13}$$

ε is the contraction factor defined by $\varepsilon = 1 - d_M/d_P$, d_M and d_P being the densities of the monomers and the polymer respectively (we assume equal densities for the monomers used).

The system of the six equations, Eqs. (7)–(12), contains 16 parameters. Five of these parameters (v_2^{00}, χ_{12}, χ_{13}, χ_{23} and ε) are system specific and therefore, they are fixed by the experimental conditions. However, four parameters (W_g, N, y, N_i) change continuously with the monomer conversion. These four conversion-dependent parameters are the output of the kinetic model of FCC given in the Appendix. Thus, knowing these 9 parameters and taking α as the independent variable, Eqs. (7)–(12) can be solved numerically for the six remaining unknowns: v_g, v_1, v_2^0, v_3, v'_1 and v'_3.

3. Results and discussion

The kinetic–thermodynamic model was solved for the crosslinking copolymerization of styrene (S) and *m*-divinylbenzene (*m*-DVB) at 60°C using 2,2′-azobisisobutyronitrile (AIBN) as an initiator. The values of the kinetic constants and the parameters used in the calculation of the conversion-dependent gel and sol properties are presented in Table 1. For the present simulation, we neglected cyclization and multiple crosslinking reactions ($k_{cyc} = k_{mc} = 0$) and the gel effect during the reactions. We first calculated the gel point conversion α_{cr} and the values of W_g, y, and N using the kinetic rate equations as a function of the volume conversion α. Then, these data were used for the solution of the thermodynamic Eqs. (7)–(12) to predict the critical conversion for the onset of a phase separation in FCC, the volume fraction of the gel phase v_g, as well as the distribution of soluble polymers between the gel and separated phases v_3/v_3'.

The most common methods to produce heterogeneous S/DVB copolymers are to work at a high DVB concentration (v-induced syneresis), or to use a poor solvent as the inert diluent [3] (χ-induced syneresis). Here, theoretical results are presented showing the effect of these parameters on the development of the heterogeneity in S/*m*-DVB copolymers. All calculations were performed up to a volume conversion of $\alpha = 0.98$. Since the sol molecules and the gel have the same chemical composition, it was assumed that $\chi_{23} = 0$ and $\chi_{12} = \chi_{13}$.

In Fig. 2A, the dependencies of the weight fraction of gel

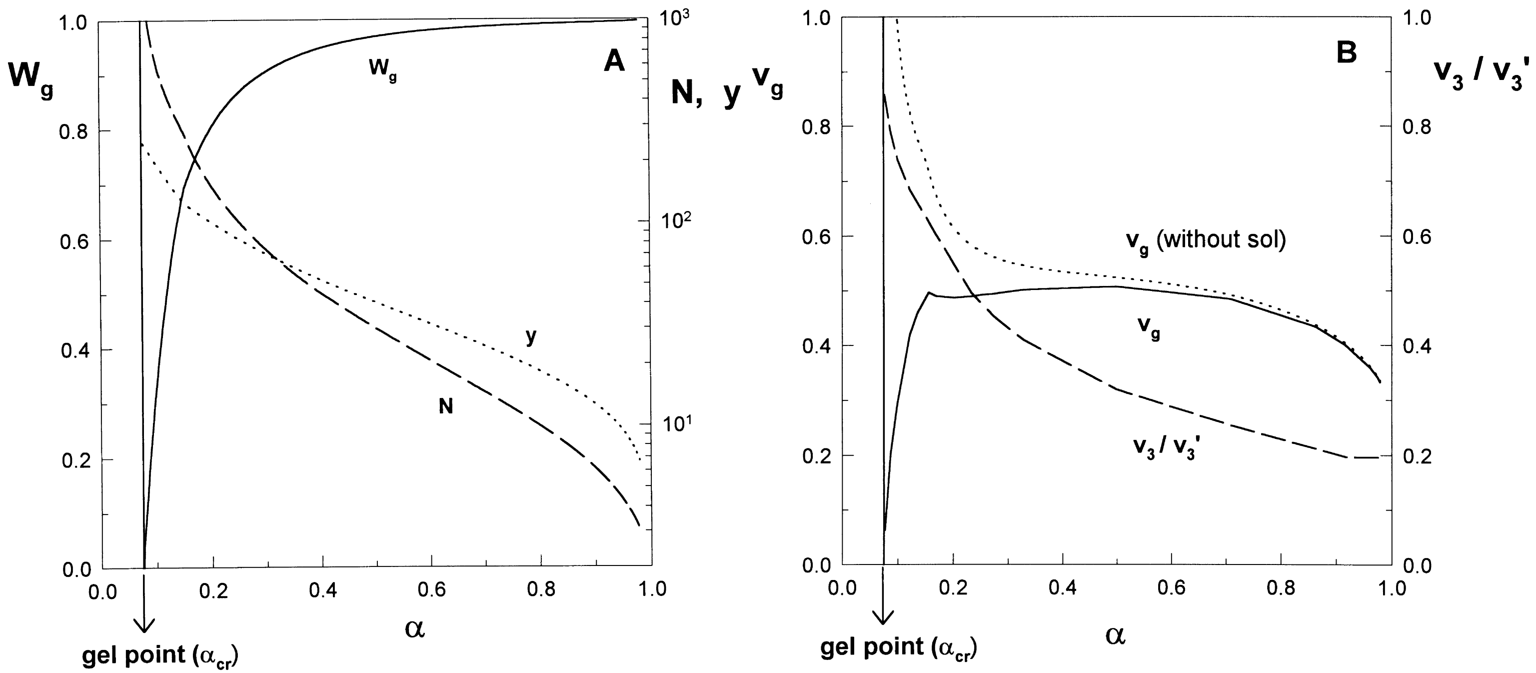

Fig. 2. (A) The weight fraction of gel W_g the number-average degree of polymerization of sol polymers y *and* the number of segments in the network chains N shown as a function of the volume conversion α in S/*m*-DVB copolymerization with AIBN as an initiator. The calculations were for 67 mol% *m*-DVB in the initial monomer mixture and for $v_2^{00} = 0.20$. The solid vertical line represents the location of the kinetic gel point. (B): The volume fraction of the network phase v_g and the distribution of the soluble polymers between the gel and separated phases v_3/v_3' shown as a function of the monomer conversion α. Calculations were fox $\chi_{12} = 0.46$. The solid curve represents the v_g values calculated using the present model, whereas the dotted curve is the result of v_g calculations with neglected sol fraction.

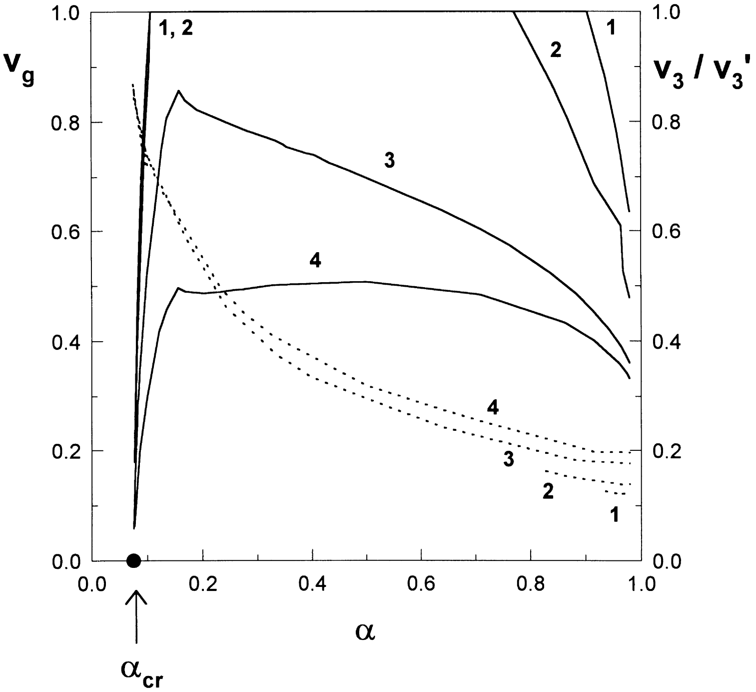

Fig. 3. Variations of v_g (solid curves) and v_3/v'_3 (dotted curves) with the monomer conversion α in S/*m*-DVB copolymerization. *m*-DVB = 67 mol%. $v_2^{00} = 0.20$, $\chi_{23} = 0$, $\chi_{12} = \chi_{13} = 0$ (1), 0.20 (2), 0.40 (3) and 0.46 (4).

W_g, the number-average degree of polymerization of sol polymers y, and the number of segments in the network chains N are shown as a function of the volume conversion α. The calculations were for 67 mol% *m*-DVB in the initial monomer mixture and for $v_2^{00} = 0.20$ (volume fraction of the monomers in the initial reaction mixture). The solid vertical line represents the location of the gel point, at which the second moment of the polymer distribution goes to infinity. This critical point corresponds to $\alpha_{cr} = 0.075$. Beyond the gel point, the amount of the network W_g increases and the number of segments between successive crosslinks N decreases as the polymerization and crosslinking reactions proceed. At the same time, the size of soluble polymers, represented by y, rapidly decreased because of the predominant crosslinking reactions between the sol molecules of larger sizes and the gel. Fig. 2A also shows that, even at high monomer conversions, soluble polymers with y of the order of 10^1 are present in the reaction mixture. Previous experimental works carried out on the same system also support this prediction and provided good agreement with the kinetic calculations [36].

For the same copolymerization system (67 mol% *m*-DVB, $v_2^{00} = 0.20$), variations of the volume fraction of the network phase v_g and the distribution of the soluble polymers between the gel and separated phases v_3/v'_3 are shown Fig. 2b as a function of the monomer conversion α. Calculations were for $\chi_{12} = 0.46$, the value reported for S/DVB–toluene system [37]. The solid curve in the figure represents the v_g values calculated using the present model, which takes into account the effect of soluble polymers on the phase equilibria in FCC system. The dotted curve is the result of v_g calculations with neglected sol fraction ($v_3 = v'_3 = 0$, i.e. $W_g = 0$), as was done by Dusek [23]. It is seen that the calculation results with neglected sol fraction become a reasonable approximation only if $\alpha \cong 1$. At high conversions, since both the amount and the size of soluble polymers are small (Fig. 2A), the effect of sol polymers on phase equilibria becomes insignificant so that both approaches match each other. However, significant deviations appear at low conversions ($\alpha = \alpha_{cr} - 0.6$) on account of the existence of a large number of soluble chains in the reaction system.

One of the remarkable results of the present simulation method is that the volume of the gel is not equal to the reaction volume at the gel point predicted by the kinetic theory. It is seen that, at a high crosslinker content, a phase separation sets in at the gel point, even in the presence of a good solvent as a diluent. This is because of the fact that the crosslink density of the first formed network (N^{-1}) increases much more rapidly than its amount in the reaction mixture ($\alpha v_2^{00} W_g$). As a result, the ‘‘infinite network’’ cannot absorb the whole unreacted monomers and the diluent, i.e. it cannot occupy the whole available volume, and becomes a micronetwork. Thus, the kinetic gel point corresponds to the microgelation rather than the macrogelation point and results in the formation of a microgel solution in monomer + diluent mixture. The volume fraction of the gel phase v_g, which is zero at the gel point, rapidly increases with increasing conversion up to $\alpha = 0.15$ as a result of the

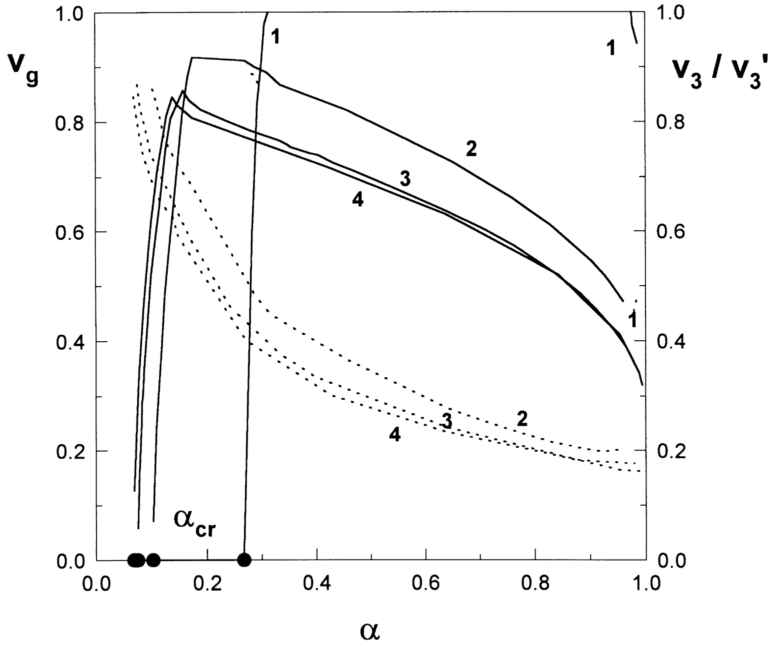

Fig. 4. Variations of v_g (solid curves) and v_3/v'_3 (dotted curves) with the monomer conversion α in S/*m*-DVB copolymerization. $\chi_{12} = \chi_{13} = 0.40$, $\chi_{23} = 0$. $v_2^{00} = 0.20$. *m*-DVB = 10 (1), 37.5 (2), 67 (3) and 90 mol% (4).

simultaneous increase of the amount of the network W_g (Fig. 2A). The rate of change of W_g decreases after $\alpha = 0.15$, as seen in Fig. 2A, which is reflected in the cessation of the growth of the gel phase in the reaction system. At high conversions, the rate of change of W_g becomes negligible but the crosslink density of the gel (N^{-1}) continues to increase owing to the intermolecular reactions of pendant vinyl groups, which results in a decrease in the gel volume v_g. After polymerization, 67% of the volume of the heterogeneous network consists of the separated pure diluent phase.

In Fig. 2B, the dashed curve shows the variation of v_3/v'_3 ratio with the monomer conversion α. v_3/v'_3 represents the ratio of the volume fraction of sol polymers in the network phase (v_3) to that in the separated diluent phase (v'_3); thus $v_3/v'_3 = 1$ means that the sol polymer concentration inside the network is equal to that in the separated phase, whereas $v_3/v'_3 = 0$ means that the network excludes al the sol molecules. Fig. 2B indicates that a large amount of sol polymers can penetrate into the gel phase at conversions close to the microgel point α_{cr}. This is as a result of the loosely crosslinked structure of the gel phase (microgels) in the vicinity of the gel point so that the soluble chains can easily enter in the gel without an essential loss in their conformational entropy. As polymerization proceeds, the v_3/v'_3 ratio decreases monotonically, i.e., the gel phase becomes less accessible for the soluble chains because of the increased crosslink density N^{-1} of the gel. The concentration difference of soluble chains between the inside and outside the gel phase creates an additional osmotic pressure compressing the network. This additional osmotic pressure is responsible for the different results of calculations of v_g with and without neglecting sol fraction at low conversions (dotted and solid curves).

For the same reaction conditions (67 mol% *m*-DVB, $v_2^{00} = 0.20$), effect of the solvating power of the diluent on the volume of the gel phase v_g and on the sol polymer distribution v_3/v'_3 is shown in Fig. 3. Here, the solvating power of the diluent is represented by χ_{12} which is varied between 0 and 0.46. It is seen that, even for athermal interactions between the network segments and diluent molecules ($\chi_{12} = 0$), the reaction system becomes heterogeneous at the kinetic gel point owing to the high crosslinker and diluent concentrations, which limit the swellability of the network. For $\chi_{12} \leq 0.2$, polymerization-induced heterogeneities at the gel point disappear again within a few conversion intervals as a result of the high growth rate of the network; but at high monomer conversions, the reaction system again phase separates owing to the presence of a large amount of diluent. As the solvating power of the diluent decreases, i.e. as χ_{12} increases, the volume of the gel phase decreases, indicating increasing heterogeneity (porosity) in the final network. Another feature shown in Fig. 3 is that, for a given monomer conversion, v_3/v'_3 ratio decreases as the solvating power of the diluent increases. Since the separated diluent phase becomes a better solvent for the soluble polymers with decreasing χ_{12} their concentration in the separated phase v'_3 increases, which shifts the v_3/v'_3 ratio toward smaller values.

Effects of the *m*-DVB concentration and the initial degree of dilution of the monomers (v_2^{00}) on v_g and v_3/v'_3 versus α dependencies are shown in Figs. 4 and 5, respectively. The kinetic gel points, shown in the figures as filled circles, shift

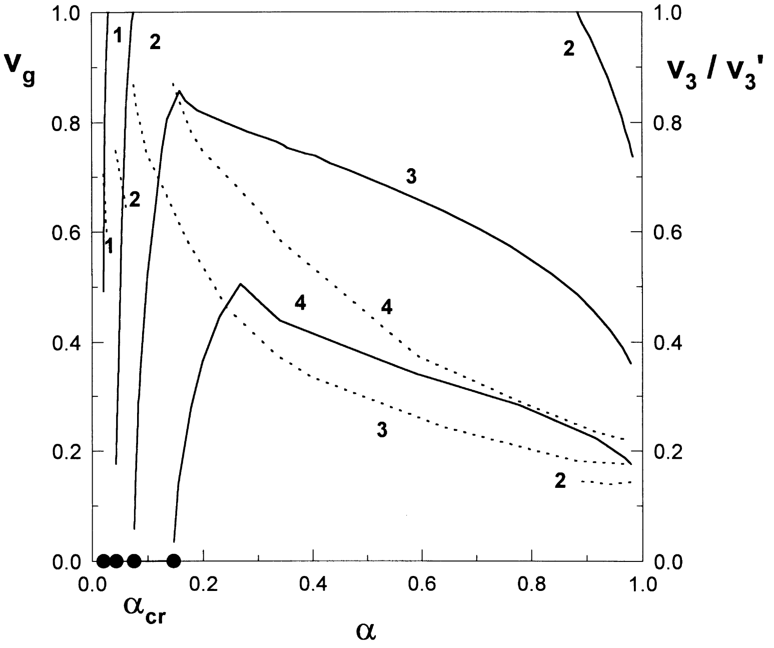

Fig. 5. Variations of v_g (solid curves) and v_3/v_3' (dotted curves) with the monomer conversion α in S/*m*-DVB copolymerization. $\chi_{12} = \chi_{13} = 0.40$. $\chi_{23} = 0$. *m*-DVB = 67 mol% $v_2^{00} = 1.00$ (1), 0.40 (2), 0.20 (3) and 0.10 (4).

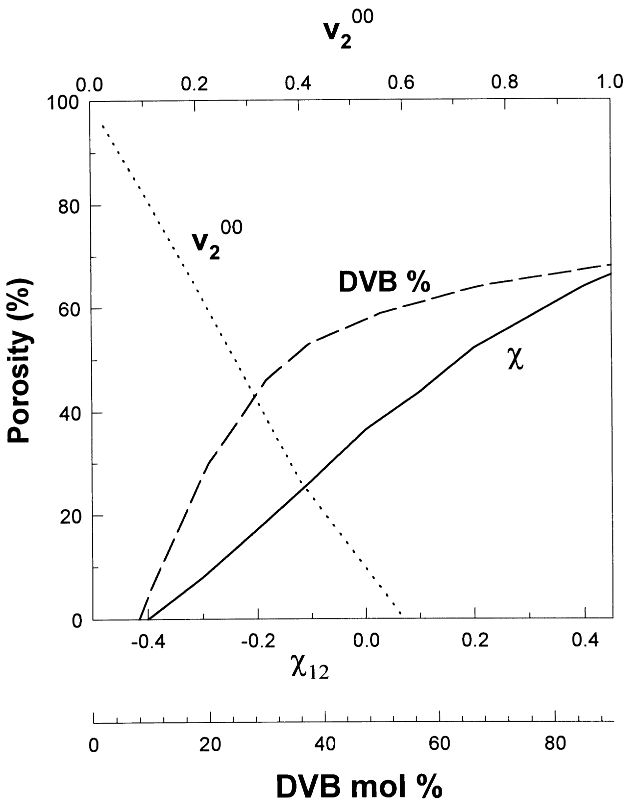

Fig. 6. The total porosity of S/*m*-DVB copolymer networks shown as a function of the *m*-DVB concentration, initial degree of dilution of the monomers(v_2^{00}) and χ_{12} parameter. Solid curve: *m*-DVB mol% = 67,$v_2^{00} = 0.20$. Dashed curve: $\chi_{12} = 0.40$, $v_2^{00} = 0.20$. Dotted curve: *m*-DVB mol% = 67, $\chi_{12} = 0.40$.

toward higher monomer conversions as the crosslinker or total monomer concentration decreases. Under the selected reaction conditions, the reaction mixture always phase separates at the kinetic gel point because of the high degree of initial dilution (20 v/v% initial monomer concentration, Fig. 4), or owing to the high crosslinker concentration (67 mol % *m*-DVB, Fig. 5). Even under bulk polymerization condition ($v_2^{00} = 1$, curve 1 in Fig. 5), the system separates into two phases at the gel point but it rehomogenize immediately and remains homogeneous during the course of the reaction. The appearance of a turbidity in highly crosslinked FCC systems even in a bulk state is an experimental fact and indicates the scattering of light from the spatial inhomogeneities of the system refractive index [38,39]. As was reported by Horie et al. [39], bulk methyl methacrylate–ethylene glycol dimethacrylate (EGDM) copolymerization with >20% EGDM content leads to the formation of opaque polymers in the first stage of the reaction. But as the reaction proceeds, these microgels are connected with one another and the opaque polymer turns to a polymer which is transparent and homogeneous in appearance [39]. Thus, the simulation results are in accord with the experiments. At a given monomer conversion, the volume of the gel phase decreases as the DVB concentrations increase or the initial monomer concentration decreases. The higher the *m*-DVB concentration, the higher the crosslink density of the gel at a given monomer conversion, which implies that the volume of the gel phase decreases on rising the *m*-DVB concentration, as shown in Fig. 4. Further, at a given *m*-DVB concentration, the lower the monomer concentration represented by v_2^{00}, the higher the volume of the diluent, which results that the volume of the separated diluent phase increases on

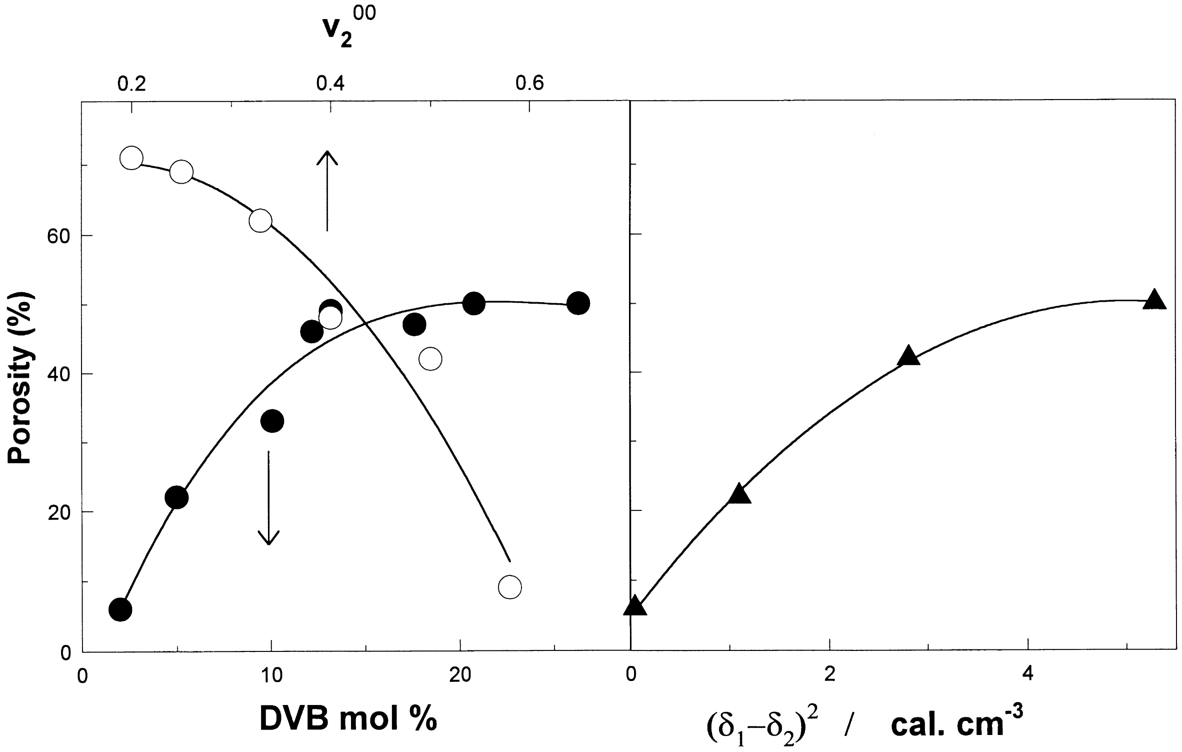

Fig. 7. The total porosity of S/commercial DVB copolymer networks shown as a function of the DVB concentration, initial degree of dilution of the monomers (v_2^{00}) and the diluent quality $(\delta_1 - \delta_2)^2$. Experimental data points are from Okay [13,15]. The curves only show the trend of the data. Experiments were for various DVB concentrations at $v_2^{00} = 0.50$ with cyclohexanol as a diluent (filled circles), for various initial monomer concentrations (v_2^{00}) at 17 mol% DVB with cyclohexanol/toluene mixture (75/25 v/v) as a diluent (empty circles) and for various types of diluent at 20 mol% DVB and $v_2^{00} = 0.50$ (filled triangles). The diluent quality is represented by $(\delta_1 - \delta_2)^2$ where δ_1 and δ_2 are the solubility parameters of the diluent and the polymer, respectively [15].

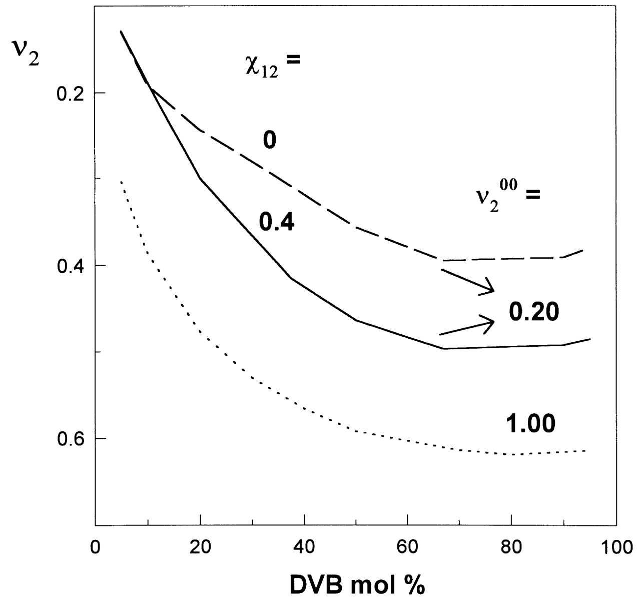

Fig. 8. The equilibrium swelling ratio of S/m-DVB copolymer networks, in terms of v_2, shown as a function of the m-DVB concentration. $\chi = 0.46$. Calculations were for $v_2^{00} = 1.00$ (dotted curve), $v_2^{00} = 0.20$; $\chi_{12} = 0$ (dashed curve) and $v_2^{00} = 0.20$; $\chi_{12} = 0.40$ (solid curve).

increasing dilution of the monomers. Figs. 4 and 5 also show that the concentration of sol polymers inside the gel phase decrease on increasing m-DVB or total monomer concentration. Since the crosslink density of the gel phase increase on rising DVB or monomer concentration, it becomes less accessible for the soluble chains.

After complete conversion of the monomers, the heterogeneous network formed consists of a gel phase of volume fraction v_g with the rest being the separated diluent phase. Removing of the diluent from the network creates pores of various sizes. Although the present model does not yield the size distribution of the separated diluent droplets, it predicts the volume of the whole diluent phase using the equation:

$$p\% = (1 - v_g) \times 100 \tag{14}$$

where $p\%$ is the total porosity of the final material. The calculated porosities of S/m-DVB copolymers are shown in Fig. 6 as a function of the χ_{12} parameter, initial m-DVB and total monomer concentrations. It is seen that, a porous structure in the copolymer starts to appear after crossing a critical m-DVB or diluent concentration, or after a critical value of χ_{12}. The porosity increases first abruptly but then slightly on rising m-DVB concentration. Increasing initial dilution of the monomers or, decreasing solvating power of the diluent also increases the porosity m S/m-DVB copolymers. These model predictions are in good agreement with

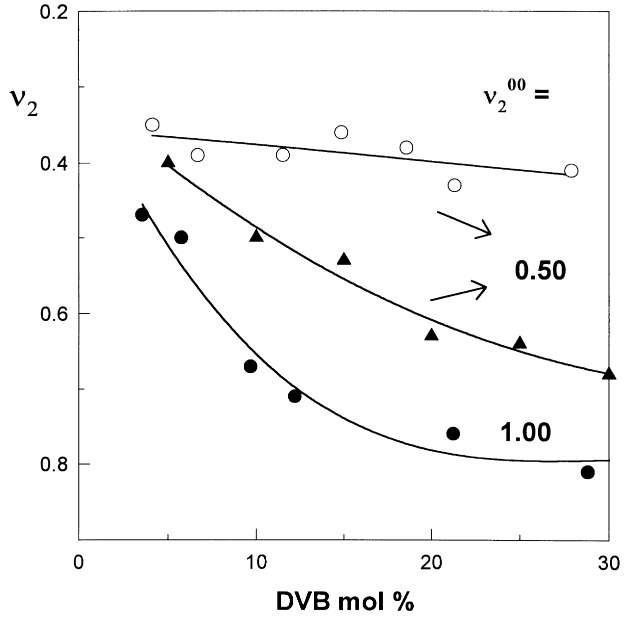

Fig. 9. The equilibrium swelling ratio of S/commercial DVB copolymer networks in toluene, in terms of v_2, shown as a function of the DVB concentration. Experimental data are from Okay [13,15]. The curves only show the trend of the data. $v_2^{00} = 1.00$ (●); $v_2^{00} = 0.50$, diluent = toluene (○) and $v_2^{00} = 0.50$, diluent = toluene/cyclohexanol (50/50 v/v) mixture (▲).

the experimental data reported in the literature [3]. For comparison, some of the reported porosity data of S/commercial DVB copolymers [13,15] are collected in Fig. 7 as a function of the reaction conditions. Experiments were for various DVB concentrations at $v_2^{00} = 0.50$ with cyclohexanol as a diluent (filled circles), for various initial monomer concentrations at 17 mol% DVB with cyclohexanol/toluene mixture (75/25 v/v) as a diluent (empty circles), and for various types of diluent at 20 mol% DVB and $v_2^{00} = 0.50$ (filled triangles). The diluent quality is represented by $(\delta_1 - \delta_2)^2$ where δ_1 and δ_2 are the solubility parameters of the diluent and the polymer, respectively [15]. Comparison of Figs. 6 and 7 shows that the model correctly predicts all the trends observed by experiments.

One of the characteristics of heterogeneous networks is their volume swelling ratio in solvents. According to the Flory's swelling equation, the equilibrium volume swelling ratio of a polymer network q_v is related to its crosslink density through the following equation [28]:

$$\ln(1 - v_2) + v_2 + \chi v_2^2 + N^{-1}\left(v_2^{1/3} v_2^{02/3} - v_2/2\right) = 0 \qquad (15)$$

where $v_2 = 1/q_v$ and χ is the interaction parameter between the polymer network and the swelling agent. Using the N and v_2^0 values, calculated using the present model at $\alpha = 0.98$, and for $\chi = 0.46$, the equilibrium v_2 values of S/m-DVB networks were calculated using Eq. (15). Calculation results are presented in Fig. 8. Here, the dotted curve represents $v_2$versus DVB mol% dependence for S/m-DVB copolymer networks prepared without using a diluent ($v_2^{00} = 1.00$), which we call thereafter standard networks. The dashed and solid curves were calculated for networks prepared in the presence of a diluent ($v_2^{00} = 0.20$) with $\chi_{12} = 0$ and 0.4, respectively. One can see that the network prepared in the presence of a good solvent as a diluent ($\chi_{12} = 0$) swells much more than the corresponding standard network. As the solvating power of the diluent decreases ($\chi_{12} = 0.4$), the swelling capacity of the network decreases and it approaches to that of the standard network. According to the model calculations, the heterogeneity in the network structure appears as a result of the separation of the diluent out of the gel phase during the reactions. Therefore, the distribution of the diluent between the gel and the separated phases determines the heterogeneity as well as the volume swelling ratio of the networks. The diluent separated out of the gel phase act as a pore forming agent, whereas the other part remains in the network structure and increases its volume swelling ratio, i.e., decreases its v_2 value. According to Fig. 8, the good solvent present during the network formation process mostly remains in the network throughout the copolymerization and thus, increases its volume swelling ratio, i.e. decreases the v_2 value of the final network. As the diluent quality decreases, i.e. as χ_{12} increases, increasing amount of the diluent separates out of the gel phase and therefore, it mainly acts as a pore forming agent and so the volume swelling ratio decreases. In Fig. 9, experimental v_2 versus DVB mol% dependencies are shown for S-commercial DVB copolymers swollen in toluene. Experimental data were taken from the literature [13,15]. It is seen that the networks prepared in the presence of toluene as a diluent remain in the swollen state, whereas those prepared with cyclohexanol as a diluent deswell on rising DVB concentration and their swelling ratio approaches to that of the standard networks. Thus, the present model fully describes the behavior of heterogeneous networks.

4. Conclusions

A new kinetic–thermodynamic model for the heterogeneous network formation in FCC was presented. The model can predict the formation conditions of heterogeneities during the FCC of vinyl/divinyl monomers and the properties of the resulting heterogeneous networks. The model takes into account all the kinetic features of FCC system and uses conversion-dependent sol and gel properties (the weight fraction and the crosslink density of the gel, the molecular weight of soluble chains) as input data for the solution of thermodynamic equations. Thermodynamic equations describe the phase equilibria between the gel and the separated phases and predict the volume of the gel phase as well as the distribution of soluble chains between the phases as a function of the monomer conversion. Calculation results were presented for S/m-DVB copolymerization system in the presence of diluents. S-*m*-DVB copolymerization system at a high *m*-DVB concentration, or, at a low monomer concentration phase separates at the gel point and results in the formation of a microgel solution. The calculation results also show that the heterogeneity in S/*m*-DVB copolymer networks increases on increasing DVB or diluent concentration, or, on decreasing the solvating power of the diluent, in accord with the experimental data published previously. The model also correctly predicts the equilibrium swelling ratio of heterogeneous networks.

It must be pointed out that in real systems, the equilibrium condition during the course of FCC process may not be fulfilled. For example, if the relaxation rate of the network chains is slower than the rate of copolymerization and crosslinking reactions, kinetically frozen structures may appear and they become fixed with further polymerization. Moreover, the volume of the separated diluent phase may not necessarily correspond to the pore volume in the final material because of the collapse of the network structure on drying or on post-treatment [13]. However, the present model gives at least qualitative informations regarding the phenomena occurring during the FCC of vinyl/divinyl monomers in dilute solutions.

Acknowledgements

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Appendix. Kinetics of free-radical crosslinking copolymerization (FCC)

Vinyl-group conversions: FCC of vinyl/divinyl monomers involves three types of vinyl groups: those on monovinyl monomer MVM (M_1), on divinyl monomer DVM (M_2), and on polymer chains, i.e. pendant vinyls (M_3). Copolymerization of these three types of vinyl groups results in the formation of three types of growing radicals, depending on the location of the radical center, namely, those with MVM unit at the end (M_1*), DVM unit with one unreacted vinyl (pendant vinyl) at the end (M_2*), and DVM unit with both reacted vinyls at the end (M_3*). In order to simplify the kinetic treatment of the reaction system, the instantaneous rate constants for propagation, crosslinking, and termination reactions are defined as follows [35]:

$$k_{\mathrm{p}i} = \sum_{j=1}^{3} k_{\mathrm{p}ji} x_j \qquad (i = 1, 2, 3), \tag{A1a}$$

$$k_{\mathrm{tc}} = \sum_{i=1}^{3} \sum_{j=1}^{3} k_{\mathrm{tc}ij} x_i x_j, \tag{A1b}$$

$$k_{\mathrm{td}} = \sum_{i=1}^{3} \sum_{j=1}^{3} k_{\mathrm{td}ij} x_i x_j, \tag{A1c}$$

$$k_{\mathrm{t}} = k_{\mathrm{tc}} + k_{\mathrm{td}}. \tag{A1d}$$

Here, $k_{\mathrm{p}ji}$ is the propagation rate constant between radicals M_j* and vinyls M_i, $k_{\mathrm{tc}ij}$ and $k_{\mathrm{td}ij}$ are the termination rate constants between radicals of types M_i* and M_j* by coupling (c) and by disproportionation (d) respectively, x_j is the instantaneous mole fraction of the radical M_j*, i.e. $x_j = [M_j*]/[R*]$, where $[R*]$ is the total radical concentration defined by $[R*] \equiv \sum_{j=1}^{3}\left[M_j*\right]$.

Applying Eqs. (Ala)–(Ald) and neglecting chain transfer reactions, one may derive the rate equations for the concentration of the initiator I, vinyl groups M_i, crosslinks μ and the nth moment of the primary molecules $Q_n^{\cdot}$ defined as $Q_n^{\cdot} \equiv \sum_{r=1}^{\infty} r^n [P_r^{\cdot}]$, where $P_r^{\cdot}$ represents the primary molecules of chain length r, as follows [35]:

$$r_{\mathrm{I}} = -k_{\mathrm{d}}[I], \tag{A2}$$

$$r_{M_1} = -k_{p1}[R*][M_1], \tag{A3}$$

$$r_{M_2} = -2k_{p2}[R*][M_2], \tag{A4}$$

$$r_{m_1} = -r_{M_1}, \tag{A5}$$

$$r_{m_2} = -0.5 r_{M_2}, \tag{A6}$$

$$r_{\mu} = k_{p3}[R*][M_3], \tag{A7}$$

$$r_{M_3} = (1 - k_{\mathrm{cyc}}) r_{m_2} - (1 + k_{\mathrm{mc}}) r_{\mu}, \tag{A8}$$

$$r_{Q_n^{\cdot}} = \left(k_{\mathrm{td}} + \frac{n+1}{2} k_{\mathrm{tc}}\right) Y_0^{\cdot} Y_n^{\cdot} \qquad (n = 0, 1, 2, \ldots) \tag{A9}$$

where

$$Y_0^{\cdot} = [R*] = (2fk_{\mathrm{d}}[I]/k_{\mathrm{t}})^{0.5}, \tag{A10}$$

$$Y_1^{\cdot} = \left(k_{p1}[M_1] + k_{p2}[M_2]\right)/k_t, \tag{A11}$$

$$Y_n^{\cdot} = n!(Y_1^{\cdot}/Y_0^{\cdot})^n Y_0^{\cdot} \tag{A12}$$

f is the initiator efficiency, k_d is the decomposition rate constant of the initiator, m_1 and m_2 are the structural units formed from MVM and DVM respectively, k_{cyc} is the fraction of DVM units consumed by cyclization reactions, and k_{mc} is the number of multiple crosslinks formed per intermolecular link. Note that (A1a–A1d; A2–A12) hold during the course of the whole polymerization process.

Gel point: up to the gel point all molecules present in the reaction system are finite. At the incipient formation of infinite structures, which is called the gel point, the second moment of the branched polymer distribution Q_2 goes to infinity:

$$\lim_{t \to t_g} (Q_2)^{-1} = 0 \tag{A13}$$

where Q_2 is defined as $Q_2 \equiv \sum_{r=1}^{\infty} r^2 [P_r]$ and P_r represents the branched polymer molecules of chain length r. Application of the method of moments to the kinetic model of the reactions given in Ref. [35] yields the rate equation for Q_2 as follows:

$$r_{Q_2} = (2k_t + k_{tc}) \left\{ Y_1^{\cdot} + \left(k_{p3}[M_3]/k_t \right) \left(Q_2 / Q_1^{\cdot} \right) \right\}^2. \tag{A14}$$

Eqs. (A13) and (A14) together with the previous equations predict the gel point at which the system changes from liquid to solid-like state.

Post-gelation period: Beyond the gel point, both an infinite network (gel) and finite molecules (sol) coexist in the polymerization system. Henceforth, the superscripts (s) and (g) will be used to denote the species in the sol and in the gel, respectively, whereas those without any primes refer to species in the whole polymerization system. The kinetic treatment of the post-gelation period assumes a steady state concentration for the radical concentration in the sol and in the whole reaction system. For instance, invoking the steady state approximation for the radical concentration in the sol, i.e.

$$\frac{d[R^s*]}{dt} = 2fk_d[I] - \left(k_t[R*] + k_{p3}[M_3^g] \right)[R^s*] \cong 0, \tag{A15}$$

one obtains the fraction of radicals belonging to the sol fraction (ϕ_s) as:

$$\phi_s = \left(1 + \frac{k_{p3}[M_3^g]}{k_t[R*]} \right)^{-1} \tag{A16}$$

Using this approach, the moment equations for sol molecules were derived previously [40]. The equations needed for the present simulations are:

$$W_s = 1 - W_g = \phi_s^2 \left[1 - \frac{k_{tc}}{k_t}(1 - \phi_s) \right], \tag{A17}$$

$$y = \left\{ (\phi_s Q_1^{\cdot} / Q_0^{\cdot})^{-1} - \mu W_s / Q_1^{\cdot} \right\}^{-1}, \tag{A18}$$

$$N = \left\{ \frac{2\mu}{Q_1^{\cdot}}(1 + W_s) - \frac{2Q_1^{\cdot}}{Q_2^{\cdot}} \right\}^{-1} \tag{A19}$$

where W_s is the weight fraction of sol. If MVM has an ionic substituent with a degree of ionization α_i (ratio of ionic groups to the total number of MVM units), the concentration of ions per network chain N_i is obtained as:

$$N_i = \alpha_i N \frac{m_1}{Q_1^{\cdot}} \tag{A20}$$

In order to solve the equations given above, one needs to know the concentrations of pendant vinyl groups in the gel M_3^g. The rate equations for the formation of pendant vinyl groups on the gel molecule is given as [40]:

$$\begin{aligned} r_{M_3^g} = {} & \left(1 - k_{cyc} \right) \\ & \times \left(k_{p2}[R*][M_2] \right)_0 + \left\{ k_{p2}[M_2] - (1 + k_{mc}) k_{p3} [M_3^g] \right\} \\ & \times [R*](1 - \phi_s) \end{aligned}$$

$$(t < 2t_g), \tag{A21a}$$

$$r_{M_3^g} = k_{p2}[R*][M_2] - (1 + k_{mc}) k_{p3} [M_3^g][R*](1 - \phi_s)$$

$$(t > 2t_g) \tag{A21b}$$

where the subscript 0 denotes the initial concentrations.

Calculations: The kinetic model is solved for a batch isothermal copolymerization of vinyl/divinyl monomers. Owing to the differences in the densities of the monomer and the polymer the reaction volume V will change during the polymerization. If S represents the concentration of species I, M_i, m_i, Q_n and μ, a mass balance requires:

$$r_S = \frac{d(VS)}{V dt} = \frac{dS}{dt} + \frac{S}{V}\frac{dV}{dt}, \tag{A22}$$

where dV/dt is the rate of volume change, which, assuming ideal solutions, is given by:

$$\frac{dV}{dt} = -\varepsilon V \sum_{i=1}^{2} r_{m_i} \bar{V}_i, \tag{A23}$$

where $\bar{V}_i$ is the molar volume of the monomer with vinyl group of type i.

The mass-balance equations of the kinetic model represented by Eq. (A22) can be solved numerically to predict the vinyl group conversions, gel points, chain length averages and the gel crosslink density as a function of the reaction time. The independent variable reaction time t can be replaced with the mole conversion x or the volume conversion α of the monomers using the equations:

$$x = \frac{Q_1^{\cdot} V}{M_0 V_0}, \tag{A24}$$

$$\alpha = 1 - \left(\frac{1 + f_2 \Delta\bar{V}/\bar{V}_1}{1 + f_{20} \Delta\bar{V}/\bar{V}_1} \right)(1 - x) \tag{A25}$$

where V_0 is the initial volume, M_0 is the initial monomer concentration, $\Delta\bar{V} = \bar{V}_2 - \bar{V}_1$, f_2 and f_{20} are the mole fractions of DVM at conversion x and at zero conversion, respectively.

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