

Formation of Macroporous Styrene–Divinylbenzene Copolymer Networks: Theory vs. Experiments

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ABSTRACT: A kinetic–thermodynamic model is presented to predict the total porosities of macroporous copolymer networks formed by free-radical crosslinking copolymerization of styrene (S) and commercial divinylbenzene (DVB, a mixture of meta and para DVB isomers and ethylstyrene). The kinetic part of the model predicts, based upon the method of moments, the concentration of the reacting species, the gel, and sol properties as a function of the monomer conversion. The thermodynamic part of the model describes the phase equilibria between the gel and separated phases during the S–DVB copolymerization and predicts the volume of the separated phase, which is the pore volume of the crosslinked material, as a function of the monomer conversion. Calculation results show that the porosity of S–DVB networks increases as the polymer–diluent interaction parameter increases, or as the initial monomer concentration decreases. Porosity also increases on increasing the DVB content of the monomer mixture. Both the polymerization temperature and the initiator concentration affect significantly the kinetics of S–DVB copolymerization. However, the final porosity of S–DVB copolymers is largely insensitive to the amount of the initiator and to the polymerization temperature. All calculation results are in accord with the experimental data published previously. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2181–2195, 1999

Key words: porosity formation; phase separation; macroporous styrene–divinylbenzene copolymer networks; kinetic–thermodynamic modeling; free-radical crosslinking copolymerization

INTRODUCTION

Heterogeneous (macroporous) styrene–divinylbenzene (S–DVB) copolymer networks have a wide range of applications as ion-exchange resins and absorbents. These materials are prepared mainly by free-radical crosslinking copolymerization (henceforth referred as FCC) of S and DVB monomers in the presence of an inert diluent.^{1–3} 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 these crosslinked materials.²

Heterogeneities in the network structure appear if the diluent separates out of the gel phase during the crosslinking copolymerization.^{3–7} 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 S–DVB network consisting of network and

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diluent phases is obtained. Removal of the diluent from the network creates voids (pores) of sizes 1 nm up to 1 μ m in the glassy state. Relationships between the synthesis conditions and the structure of heterogeneous S–DVB networks have been the subject of intensive studies during the last four decades.^{4–24} Experiments showed that the volume of the separated diluent phase, i.e., the pore volume increases as the concentration of the divinyl monomer or that of the diluent increases, or as the solvating power of the diluent decreases.

Recently, we developed a model combining both the 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 reaction conditions.²⁵ This model takes into account all the kinetic features of FCC of vinyl/divinyl monomers. In the present paper, we apply this model to the FCC of S and commercial DVB, a mixture of meta and para DVB isomers and ethylstyrene, in the presence of dibenzoyl peroxide as an initiator. Due to the importance of the crosslinked materials obtained in this copolymerization system, a large number of experimental works has been reported, but no theoretical work can be found in the literature. As will be shown below, the model presented here successfully predicts the porosity of S–DVB copolymers depending on the synthesis conditions. The effects of the polymerization temperature and the initiator concentration on the pore structure formation of S–DVB copolymers, which have not been studied previously, are also described.

THEORY

Here are the main assumptions of the model that 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; and (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.

THERMODYNAMICS

The reaction system in FCC beyond the gel point involves the unreacted monomers, solvent or non-

solvent, soluble polymers, and a polymer network. For the following analysis, we will refer to the mixture of the unreacted monomers and the (non)solvent as “the diluent” (single liquid approximation). The FCC system at a given degree of monomer conversion can thus be considered a ternary system consisting of the diluent, network, and the soluble polymer. 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. We can thus analyze the system as a network immersed in polymer solution. Swelling of a nonionic polymer network in such a system is governed by two free energy terms,^{26,27} i.e., the changes in the free-energy of mixing ΔG_m and in the free energy of elastic deformation ΔG_{el} :

$$\Delta G = \Delta G_m + \Delta G_{el} \quad (1)$$

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

$$\Delta G_m = RT \left(\sum_i n_i \ln v_i + \sum_{i < j} n_i v_j \chi_{ij} \right) \quad (1a)$$

where n_i is the moles of the species i ($i = 1, 2$, and 3), v_i is its volume fraction, χ_{ij} is the interaction parameter between the species i and j , R is the gas constant, and T is 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 in FCC system²⁸:

$$\Delta G_{el} = (3/2)(RT/NV_s)((v_2^0/v_2)^{2/3} - 1 - \ln(v_2^0/v_2)^{1/3}) \quad (1b)$$

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. Substitution of eqs. (1a) and (1b) 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_i of the components 1 and 3 in both network and separated phases:

$$\frac{\Delta\mu_1}{RT} = N^{-1}(v_2^{1/3}v_2^{o2/3} - v_2/2) + \ln v_1 + (1 - v_1) - v_3/y + (\chi_{12}v_2 + \chi_{13}v_3)(1 - v_1) - \chi_{23}v_2v_3 \quad (2a)$$

$$\frac{\Delta\mu'_1}{RT} = \ln v'_1 + v'_3(1 - 1/y) + \chi_{13}v'^2_3 \quad (2b)$$

$$\begin{aligned} \frac{\Delta\mu_3}{yRT} &= N^{-1}(v_2^{1/3}v_2^{o2/3} - v_2/2) \\ &+ (1/y)\ln v_3 + (1/y)(1 - v_3) - v_1 \\ &+ (\chi_{13}v_1 + \chi_{23}v_2)(1 - v_3) - \chi_{12}v_1v_2 \quad (3a) \end{aligned}$$

$$\frac{\Delta\mu'_3}{yRT} = (1/y)\ln v'_3 - v'_1(1 - y^{-1}) + \chi_{13}v'^2_1 \quad (3b)$$

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.

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, 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.³ Thus, at the incipient phase separation during FCC, the swelling capacity of the network becomes equal to its degree of dilution in the reaction system, i.e.,

$$v_2 = v_2^0 \quad (4)$$

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 (component 1) and the soluble polymers (component 3) inside the network phase are in thermodynamic equilib-

rium with those in the separated phase. This equilibrium state is described by the equality of the chemical potential μ_i of these components in both phases. Thus, at swelling equilibrium, we have

$$\Delta\mu_1 - \Delta\mu'_1 = 0 \quad (5)$$

$$\Delta\mu_3 - \Delta\mu'_3 = 0 \quad (6)$$

Substitution of eqs. (2) and (3) 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:

$$\begin{aligned} 0.5N^{-1}v_2^o + \ln\left(\frac{v_1}{v'_1}\right) + (1 - v_1 - v'_3) \\ - (v_3 - v'_3)/y + \chi_{12}v_2^{o2} + \chi_{13}(v_3^2 - v'^2_3) \\ + (\chi_{12} + \chi_{13} - \chi_{23})v_2^0v_3 = 0 \quad (7) \end{aligned}$$

$$\begin{aligned} -\ln\left(\frac{v_1}{v'_1}\right) + (1/y)\ln(v_3/v'_3) + 2\chi_{13}(v'_3 - v_3) \\ + (\chi_{23} - \chi_{12} - \chi_{13})v_2^0 = 0 \quad (8) \end{aligned}$$

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

$$v_1 + v_2^0 + v_3 = 1 \quad (9)$$

$$v'_1 + v'_3 = 1 \quad (10)$$

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:

$$v_2^0 = \bar{v}_p W_g / v_g \quad (11)$$

$$\bar{v}_p(1 - W_g) = v_3v_g + v'_3(1 - v_g) \quad (12)$$

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

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

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 15 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, three parameters (W_g , N , and y) change continuously with the monomer conversion α . These three conversion-dependent parameters are the output of the kinetic model of S-commercial DVB copolymerization system given in the following section. Thus, knowing these 8 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' , v_3' .

KINETICS

Vinyl Group Conversions

In the kinetic treatment of S-commercial DVB copolymerization, we made the following additional assumptions: (i) Commercial DVB consists of DVB isomers (m-DVB : p-DVB ratio = 3 : 1) and ethylstyrene. Due to the equal reactivity of the vinyl groups on ethylstyrene and styrene monomers,²⁹ ethylstyrene is taken as styrene. (ii) Both meta- and para-type pendant vinyl groups have equal reactivity. (iii) Chain transfer reactions are dismissed from the kinetic treatment.

S-commercial DVB copolymerization reactions thus involve four types of vinyl groups: those (i) on S (M_1), (ii) on m-DVB ($M_{2'}$), (iii) on p-DVB ($M_{2''}$), and (iv) on polymer chains, i.e., pendant vinyls (M_3). Copolymerization of these four types of vinyl groups results in the formation of four types of growing radicals, depending on the location of the radical center, namely, those with S unit at the end (M_{1*}), m-DVB and p-DVB units with one unreacted vinyl (pendant vinyl) at the end ($M_{2'*}$ and $M_{2''*}$, respectively), and DVB 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 (k_{p1} , $k_{p2'}$, $k_{p2''}$), intermolecular crosslinking (k_{p3}), and termination reactions (k_t^0) are defined as follows:

$$k_{pi} = \sum_j k_{pji} x_j \quad (14a)$$

$$k_{tc}^0 = \sum_i \sum_j k_{tcij} x_i x_j \quad (14b)$$

$$k_{td}^0 = \sum_i \sum_j k_{tdij} x_i x_j \quad (14c)$$

$$k_t^0 = k_{tc}^0 + k_{td}^0 \quad (14d)$$

where $i, j = 1, 2', 2'',$ and 3 . Here, k_{pji} is the propagation rate constant between radicals M_{j*} and vinyls M_i , k_{tcij} and k_{tdij} 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 $[R^*] = \sum_j [M_{j*}]$.

In FCC, the propagation rate constants of the elementary reactions for monomeric vinyls are reaction controlled up to about 80% of the monomer conversion. Therefore, it is reasonable to assume constant propagation rate constants during the reactions. The termination reactions in S-DVB copolymerization are also chemically controlled prior to gelation, but become diffusion controlled beyond gelation. In order to account the diffusion controlled termination, an empirical equation was used^{30,31}:

$$k_t = k_t^0 \quad (x < x_c) \quad (14e)$$

$$k_t = k_t^0 \exp[-A(x - x_c)] \quad (x > x_c) \quad (14f)$$

where x_c is the monomer conversion at the gel point and A is an empirical constant describing the variation of the termination rate constant with the monomer conversion x .

Applying eqs. (14a)–(14f), one may derive the rate equations for the concentration of the initiator I , vinyl groups M_i , and intermolecular crosslinks μ as follows:

$$r_I = -k_d[I] \quad (15)$$

$$r_{M_1} = -k_{p1}[R^*][M_1] \quad (16)$$

$$r_{M_{2'}} = -2k_{p2'}[R^*][M_{2'}] \quad (17)$$

$$r_{M_{2''}} = -2k_{p2''}[R^*][M_{2''}] \quad (18)$$

$$r_{M_3} = (1 - k_{cyc})(k_{p2'}[M_{2'}] + k_{p2''}[M_{2''}])[R^*] - (1 + k_{mc})k_{p3}[R^*][M_3] \quad (19)$$

$$r_\mu = k_{p3}[M_3][R^*] \quad (20)$$

where

$$[R^*] = (2fk_d[I]/k_t)^{0.5} \quad (21)$$

f is the initiator efficiency, k_d is the decomposition rate constant of the initiator, k_{cyc} is the fraction of DVB units consumed by cyclization reactions, and k_{mc} is the average number of multiple crosslinks formed per intermolecular link. Previous experimental studies on S-DVB and methyl methacrylate-ethylene glycol dimethacrylate copolymerization systems showed that the rate constant of the crosslinking reactions k_{p3} is not a constant, but depends on the reaction conditions.³²⁻³⁴ This is due to the conversion-dependent structural changes of the polymer chains, to which the pendant vinyl groups are attached. Therefore, instead of a "rate constant," it is reasonable to consider the pendant vinyl group reactivity for intermolecular crosslinking reactions. Here, we define the average pendant vinyl group reactivity $\bar{r}_{32}$ as the reactivity ratio of pendant vinyl to monomeric vinyl on DVB, and is related to k_{p3} using the equation:

$$\bar{r}_{32} = \frac{k_{p3}}{[k_{p2}x_{M_2'} + k_{p2''}(1 - x_{M_2'})]} \quad (22)$$

where $x_{M_2'}$ is the instantaneous mole fraction of m-DVB in the DVB isomer mixture.

Molecular Weight Distribution

In the characterization of gel-forming systems, an important property is the distribution of molecular weights of soluble polymer molecules. The kinetic model presented here distinguishes, depending on the location, two types of molecules: those in the sol and those in the gel. The symbols with a superscript s are used to denote species in the sol, whereas those without this superscript refer to species in the whole polymerization system. Let $[P_r^s]$ be the concentration of polymer molecules composed of r structural units; normalization gives $Q_n^s \equiv \sum_{r=1}^{\infty} r^n [P_r^s]$, with $n = 0, 1, 2, \dots$, where Q_n^s represents the n th moment of the polymer distribution. From the moments of the polymer distribution, the n th average polymerization

degree of polymer molecules defined as $\bar{X}_n^s \equiv Q_n^s / Q_{n-1}^s$ ($n = 1, 2, 3, \dots$) can be calculated. Kinetic calculations can also be performed by considering the "primary molecules" as the reacting species, i.e., the molecules that would result if all crosslinks in the reaction system were cut. In the following treatment, symbols with a superscript dot ($\bullet$) relate to the primary molecules, whereas those without this superscript relate to the branched molecules. Using the rate equations for P_r^s given in ref. 35, one obtains the following equations for the n th moment of the primary molecules in free-radical crosslinking copolymerization of S and commercial DVB:

$$r_{Q_n^s} = \left(k_{td}/\phi_s + \frac{n+1}{2} k_{tc} \right) Y_0^{s\bullet} Y_n^{s\bullet} \quad (n = 0, 1, 2, \dots) \quad (23)$$

where

$$Y_0^{s\bullet} = \phi_s [R^*] \quad (23a)$$

$$Y_1^{s\bullet} = \phi_s^2 \sum_i k_{pi} [M_i] / k_t \quad (i = 1, 2', \text{ and } 2'') \quad (23b)$$

$$Y_n^{s\bullet} = n! (Y_1^{s\bullet} / Y_0^{s\bullet})^n Y_0^{s\bullet} \quad (n = 2, 3, 4, \dots) \quad (23c)$$

and ϕ_s is the fraction of radicals belonging to the sol fraction, i.e.,:

$$\phi_s = \left(1 + \frac{k_{p3}[M_3]W_g}{k_t[R^*]} \right)^{-1} \quad (24)$$

Solution of eqs. (23) and (24) for $n = 1$ give the weight fraction of soluble polymers W_s as

$$W_s = 1 - W_g = \phi_s^2 \left\{ 1 - \frac{k_{tc}}{k_t} (1 - \phi_s) \right\} \quad (25)$$

In contrast to the primary molecules, the polymerization degree of a branched molecule changes upon the reaction of pendant vinyl groups belonging to it with the radicals. The first three moments of branched molecules in the sol can be expressed as follows³⁵:

$$r_{Q_0^s} = r_{Q_0^{s\bullet}} - k_{p3}[M_3]Y_0^{s\bullet}W_s \quad (26)$$

$$r_{Q_1^s} = r_{Q_1^{s\bullet}} \quad (27)$$

$$r_{Q_2^s} = 2(k_{td}/\phi_s + 1.5k_{tc})(Y_1^s)^2 \quad (28)$$

where

$$Y_1^s = Y_1^{s*} + \phi_s^2(k_{p3}[M_3]W_s/k_t)\bar{X}_2^s \quad (29)$$

In a batch isothermal S–DVB copolymerization, the reaction volume V will also change during the reactions due to the differences in the densities of the monomer and the polymer. If S represents the concentration of species I , M_i , μ , and the moments of the polymer distribution Q_n^s and Q_n^{s*} , a mass balance requires

$$r_s = \frac{d(VS)}{V dt} = \frac{dS}{dt} + \frac{S}{V} \frac{dV}{dt} \quad (30)$$

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

$$\frac{dV}{dt} = -\varepsilon V \sum_i r_{M_i} \bar{V}_i \quad (31)$$

where $i = 1, 2'$, and $2''$, and $\bar{V}_i$ is the molar volume of the monomer with vinyl group of type i .

Up to the onset of gelation, all molecules present in S–DVB copolymerization system are finite. Thus, the mass balance equations of the kinetic model represented by eq. (30) can be solved numerically for the condition $W_s = 1$ and $\phi_s = 1$ to predict the vinyl group conversions and the moments of the polymer distribution prior to gelation. At the incipient formation of infinite structures, which is called the gel point, the second moment of the polymer distribution diverges:

$$\lim_{t \rightarrow t_c} Q_2^s = \infty \quad (32)$$

where t_c is the time required for the onset of gelation. To predict the gel point in terms of the reaction time t_c , eqs. (14)–(31) can be solved until the condition of eq. (32) is achieved. Beyond the gel point, both an infinite network (gel) and finite molecules (sol) coexist in the polymerization system. Analytical solution of eqs. (23)–(29) predicts the weight fraction of gel W_g and the molecular weight averages ($\bar{X}_1^s$, $\bar{X}_2^s$, $\bar{X}_1^{s*}$, $\bar{X}_2^{s*}$) of soluble molecules.^{35,36} The number of repeat units between two successive crosslinks N is calculated as³⁵

$$N = \{2\mu(2 - W_g)/Q_1^s - 2/\bar{X}_2^{s*}\}^{-1} \quad (33)$$

The independent variable reaction time t in the above equations can be replaced with the fractional monomer conversion x or with the volume conversion α of the monomers using

$$x = \frac{Q_1^s V}{[M]_0 V_0} \quad (34)$$

$$\alpha = 1 - \left(\frac{1 + f_2 \Delta \bar{V}/\bar{V}_1}{1 + f_{20} \Delta \bar{V}/\bar{V}_1} \right) (1 - x) \quad (35)$$

where $[M]_0$ and V_0 represent initial concentration of the total monomers and the initial reaction volume, respectively, $\Delta \bar{V} = \bar{V}_2 - \bar{V}_1$, and f_2 and f_{20} are the mole fractions of DVM at conversion x and at zero conversion, respectively.

Calculations for S–Commercial DVB System

The model is solved for a batch isothermal S–commercial DVB copolymerization in the presence of dibenzoyl peroxide as the initiator. For the solution of the kinetic model, the following reasonable approximations were also made: (i) The propagation, crosslinking, and termination rate constants are independent of the type of the radical end, i.e., $k_{p11} = k_{p21} = k_{p31} = k_{p1}$, etc. (ii) The initiator efficiency is 0.5. (iii) The reactivity ratio of S with the first double bond of *m*- and *p*-DVB ($r_{12'}$ and $r_{12''}$, respectively) are temperature independent in the temperature range from 50 to 100°C. (iv) Previous experimental studies indicate that, in a wide range of crosslinker concentration, the pendant vinyl group reactivity is ten-to hundredfold smaller than the reactivity of the vinyl groups on divinyl monomers.³⁴ For the present simulation we assume that $\bar{r}_{32} = 1/10$ in S–DVB copolymerization system in the presence of inert diluents.

The values of the kinetic constants and the parameters used in the calculations are collected in Table I. We first calculated the gel point conversion x_c and the values of W_g , $\gamma(\bar{X}_1^s)$, and N using the kinetic rate equations as a function of the monomer conversion x . 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 as well as the volume fraction of the separated phase ($1 - v_g$), which corresponds to, assuming isochoric conditions, the total porosity P of the final copolymer network. Solution of the thermodynamic equations require the values of the interaction param-

Table I Kinetic Constants and Parameters for S-Commercial DVB Copolymerization Using Dibenzoyl Peroxide as an Initiator

Constant	Reference
$f = 0.5$	
$k_d = 6.38 \times 10^{13} \text{ s}^{-1} \exp[-124.3 \text{ kJ mol}^{-1}/(RT)]$	31
$k_{p1} = 2.4 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1} \exp[-37.5 \text{ kJ mol}^{-1}/(RT)]$	37
$k_{p2'} = k_{p1}/0.88$	38
$k_{p2''} = k_{p1}/1.18$	38
$\bar{r}_{32} = 1/10$	34
$k_{cyc} = 0.3$	39
$k_{mc} = 0$	
$k_{tc}^0 = 1.26 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1} \exp[-7.03 \text{ kJ mol}^{-1}/(RT)]$	31
$k_{td}^0 = 0$	31
$A = 15$	40
$d_M = 924 - 0.918(T - 273) \text{ g L}^{-1}$	41
$d_P = 1084.8 - 0.605(T - 273) \text{ g L}^{-1}$	41

eters χ_{12} , χ_{13} , and χ_{23} . Since the sol molecules and the gel have the same chemical composition, it was assumed that $\chi_{23} = 0$. The diluent in S-DVB copolymerization (component 1) consists of the unreacted monomers and of the (non)solvent (pore-forming agent), which changes its composition depending on the monomer conversion. As a result, the overall solvating power of the component 1 for the polymer changes as the monomers are consumed in the polymerization. Thus, χ_{12} can be calculated from the monomer-polymer (χ_{12}^{mon}) and solvent-polymer (χ_{12}^{sol}) interaction parameters as

$$\chi_{12} = \chi_{12}^{\text{mon}} + (\chi_{12}^{\text{sol}} - \chi_{12}^{\text{mon}})\Phi_s \quad (36)$$

where Φ_s is the volume fraction of the (non)solvent in the diluent mixture, i.e.,

$$\Phi_s = \frac{1 - v_2^{00}}{1 - \alpha v_2^{00}} \quad (36a)$$

χ_{12}^{mon} is reported to be 0.42 and χ_{12}^{sol} represents the thermodynamic quality of the pore-forming agent, which is one of the independent variables of the model.

The most common methods to produce heterogeneous S-DVB copolymers are to work at a high DVB concentration (v -induced syneresis²). As will be shown in the following section, under these reaction conditions gelation occurs at a low monomer conversion and the sol fraction in the reaction mixture approaches to zero at $x > 0.3$. Respective calculations showed that, under these

conditions, the effect of soluble polystyrene chains on the phase equilibria in S-DVB copolymerization is negligible. This is mainly due to the strong gel effect in S-DVB copolymerization, which leads to a rapid consumption of the soluble polymers in the reaction system.⁴⁰ Therefore we assumed that $v_3 = v_3' = 0$.

RESULTS AND DISCUSSION

Figure 1(A) shows the sol and gel properties as a function of the monomer conversion x in S-DVB copolymerization at 70°C in the presence of 0.1M dibenzoyl peroxide as the initiator. Initial monomer mixture contains 70 mol % DVB isomers and the total monomer concentration is 20 vol % ($v_2^{00} = 0.20$). The weight-average polymerization degree of branched polymers, $\bar{X}_2^s$, goes to infinity at $x = 0.073$, which corresponds to the critical conversion x_c for the onset of gelation. Beyond the gel point, the amount of polystyrene chains incorporated into the network W_g increases and the number of segments between successive crosslinks N decreases abruptly; At the same time, the size of the soluble polymers rapidly decreases due to the predominant crosslinking reactions between the sol molecules of larger sizes and the gel. At $x > 0.3$, the gel fraction approaches to unity and the size of soluble polymers ($\bar{X}_1^s$ and $\bar{X}_2^s$) decreases to the size of the primary molecules ($\bar{X}_1^{s*}$ and $\bar{X}_2^{s*}$). These are the well-known features of S-DVB copolymerization carried out in the presence of a high amount of DVB.

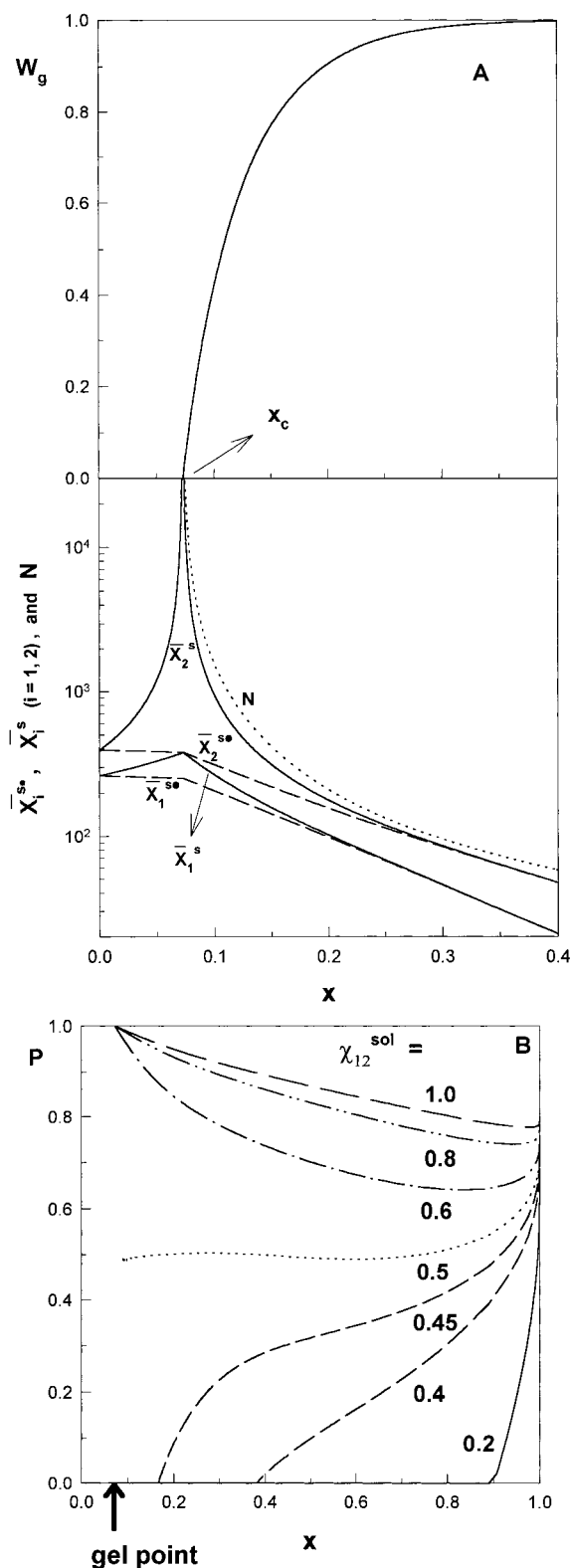


Figure 1 (A) The weight fraction of gel W_g , the number- and weight-average degrees of polymerization of primary molecules ($\bar{X}_1^s$ and $\bar{X}_2^s$), of branched molecules ($\bar{X}_1^s$ and $\bar{X}_2^s$), and the number of segments in the

For the same reaction conditions, the effect of the thermodynamic quality of the diluent represented by χ_{12}^{sol} on the porosity development in S-DVB copolymers is shown in Figure 1(B). For $\chi_{12}^{sol} < 0.5$, i.e., in the presence of good solvating diluents, the reaction system phase separates beyond the gel point due to the crosslink density (v)-induced syneresis. Thus, in accord with the experimental observations,^{16,18} porous S-DVB networks can be prepared even in the presence of good solvents as a diluent. As the monomer conversion increases, the porosity also increases due to the simultaneous increase of the crosslink density of the network N^{-1} . For $\chi_{12}^{sol} \geq 0.5$, i.e., in the presence of precipitating diluents, the polymerization system is discontinuous at the gel point because of the repulsive interactions between the polymer segments and solvent molecules (χ -induced syneresis) which induce phase separation prior to gelation. Thus, the kinetic gel point x_c , at which the second moment of the polymer distribution diverges, does not correspond to a macrogelation point; it rather corresponds to a critical point, at which microgel or macrogel particles start to appear in the reaction system containing unreacted monomers, precipitating diluent, and soluble polymers. Beyond this point, the porosity decreases on increasing the monomer conversion. This is due to the fact that as the gel grows, that is, as the weight fraction of the gel W_g increases, the volume of the separated phase necessarily decreases. The porosity starts to increase at high monomer conversions due to the predominant crosslinking reactions, which reduces the volume of the gel phase.

Effect of the initial monomer concentration (v_2^0) on the kinetics of S-DVB copolymerization is shown in Figures 2(A) and 2(B). The gel point conversions x_c calculated from $\bar{X}_2^s$ vs x curves [Fig. 2(B)] are illustrated in Figure 2(A) as filled circles. Under the selected reaction conditions (50 mol % DVB, 70°C, $[I]_0 = 0.1M$), as the initial monomer concentration increases from 5 to 80 v/v %, the gel point conversion x_c at which $\bar{X}_2^s$ goes to

network chains N shown as a function of the monomer conversion x in S-DVB copolymerization. DVB = 70 mol %. $v_2^0 = 0.20$. Temperature = 70°C. $[I] = 0.1M$. (B) Variation of the total porosity P of S-DVB networks with the monomer conversion x in the presence of various diluents. The diluent-polymer interaction parameter values χ_{12}^{sol} used in the calculations are indicated in the figure. See legend to A for the reaction conditions.

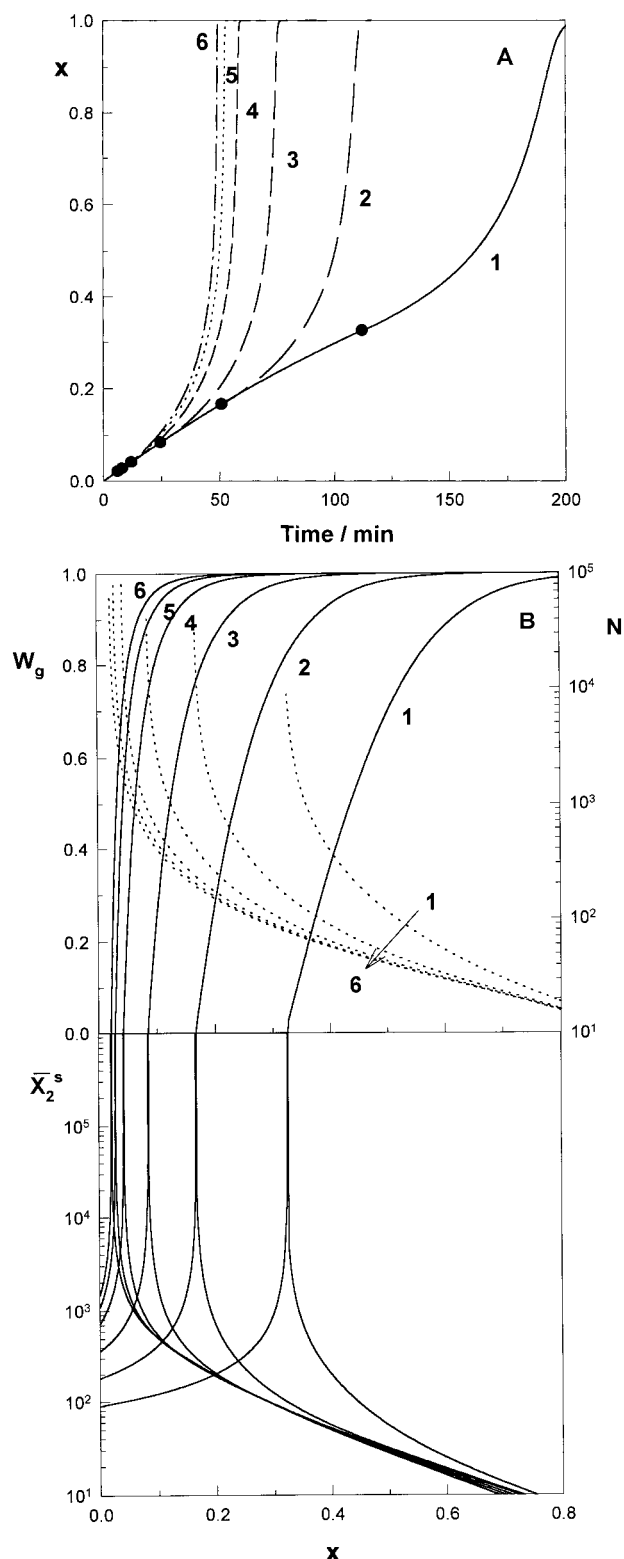


Figure 2 (A) Variation of monomer conversion x with the reaction time in S-DVB copolymerization at various initial monomer concentrations. The gel points are shown as filled circles. DVB = 50 mol %. $[I]_0 = 0.1M$. Temperature = 70°C. Volume fraction of the monomers

infinity decreases from 0.326 to 0.022. The acceleration of the polymerization and crosslinking reactions becomes significant on increasing the monomer concentration due to the earlier gelation. Also, the growth rate of the gel in terms of its mass (W_g) and its crosslink density (N^{-1}) increases significantly on increasing the monomer concentration in the initial reaction mixture.

Figure 3 illustrates the variation of porosity P of S-DVB networks with conversion x for various initial monomer concentrations. The monomer concentration affects significantly the porosity of the copolymer networks. In the presence of a good solvent ($\chi_{12}^{sol} = 0.4$), the reaction system phase separates at or beyond gelation; the higher the initial degree of dilution of the reaction system, the higher the porosity of the resulting copolymer network. The porosity increases on increasing the monomer conversion due to the simultaneous increase of the crosslink density. However, in the presence of a poor solvent ($\chi_{12}^{sol} = 0.6$), the porosity first decreases with monomer conversion due to increased volume of the gel phase, but then it increases again due to the crosslinking reactions.

The results shown in Figures 1(B) and 3 demonstrate that the networks prepared in nonsolvating diluents or in more diluted solutions exhibit larger porosity values. These dependencies are collected in Figure 4 for a wide range of parameter values, which shows the variation of porosity P as a function of the quality and the amount of the diluent present during the polymerization. Calculations were for 70 mol % DVB in the initial monomer mixture and for a monomer conversion of $x = 0.99$. It is seen that the final porosity of S-DVB networks strongly depends both on the degree of dilution v_2^{00} and on the extent of the thermodynamic interactions between the diluent and network segments χ_{12}^{sol} . For comparison, some of the reported porosity data of S-DVB copolymer networks^{2,11,16,18,19} are collected in Figures 5 and 6 as a function of the quality and the amount of the diluent, respectively. Experimental data shown in Figures 5 and 6 are for different di-

in the initial monomer mixture $v_2^{00} = 0.05$ (1), 0.10 (2), 0.20 (3), 0.40 (4), 0.60 (5), and 0.80 (6). (B) The weight fraction of gel W_g , the number of segments in the network chains N (dotted curves), and the weight-average degree of polymerization of branched molecules $\bar{X}_2^s$ shown as a function of the monomer conversion x at various initial monomer concentrations. See legend to A for the reaction conditions.

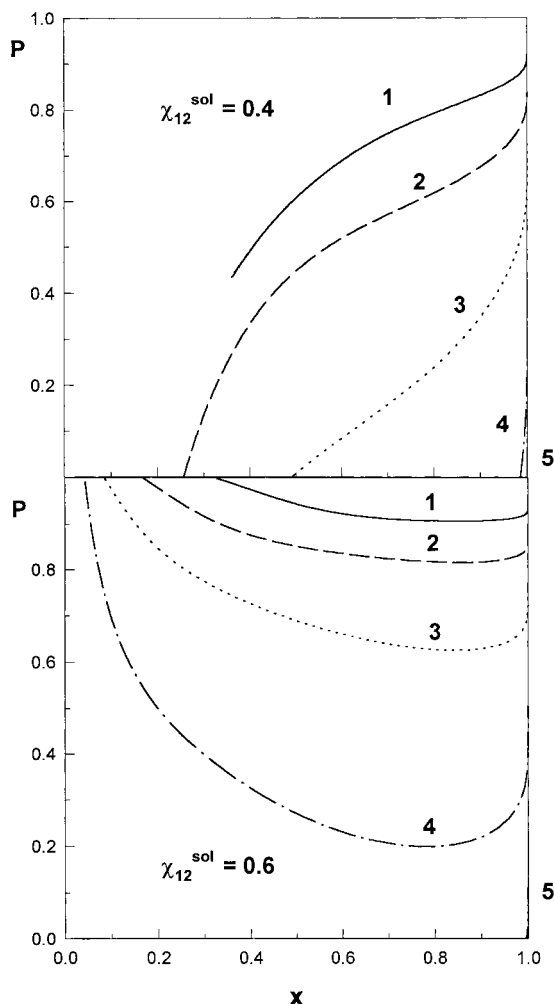


Figure 3 Variation of the total porosity P of S-DVB networks formed in S-DVB copolymerization with the monomer conversion x for various initial monomer concentrations v_2^{00} . DVB = 50 mol %, $[I]_0 = 0.1M$. Temperature = 70°C . χ_{12}^{sol} values used in the calculations are indicated in the figure. Volume fraction of the monomers in the initial monomer mixture $v_2^{00} = 0.05$ (1), 0.10 (2), 0.20 (3), 0.40 (4), and 0.60 (5).

luents, i.e., aliphatic alcohols of various chain length, toluene/cyclohexanol and *n*-heptane/toluene mixtures of various compositions. Since the χ_{12}^{sol} parameter values of these polymer-solvent systems are unknown, the diluent quality was represented as $\Delta\delta^2 = (\delta_1 - \delta_2)^2$, where δ_1 and δ_2 are the solubility parameters of the diluent and the polymer, respectively.¹⁸ Both the simulation results and the experimental data in Figure 5 indicate that, for a fixed monomer dilution v_2^{00} , porosity P increases on worsening the polymer-solvent interactions during the gel formation process. This increase in P is first rapid but then it

slightly increases on increasing χ_{12}^{sol} (or $\Delta\delta^2$) parameter value of the diluent. Thus, the theory predicts all the trends observed by experiments. Both simulation and experimental results also indicate that the porosity increases with increasing degree of monomer dilution (Fig. 4 vs Fig. 6). Theory predicts a continuous increase in P with increasing monomer dilution. This stands in contrast to the experimental data obtained at lower concentration of the monomers (Fig. 6); in the region of $v_2^{00} < 0.3$, experimental data indicate that the rate of increase of porosity slows down on further increase of the monomer dilution. This difference is probably due to the fact that the copolymer networks formed at a low monomer concentration, i.e., at $v_2^{00} < 0.30$, cannot hold the isochoric condition due to the loose network structure.⁴² Therefore, the pores in such copolymers may collapse upon drying or upon the removal of the diluent, and result in lower porosity values than expected in the limit of high dilution degrees.

The effect of the DVB concentration on the kinetics of S-commercial DVB copolymerization at 70°C is shown in Figures 7(A) and 7(B). The monomer and initiator concentrations were $v_2^{00} = 0.20$ and $[I]_0 = 0.1M$, respectively. The filled symbols in Figure 7(A) represent the gel points. As the DVB concentration increases from 5 to 90

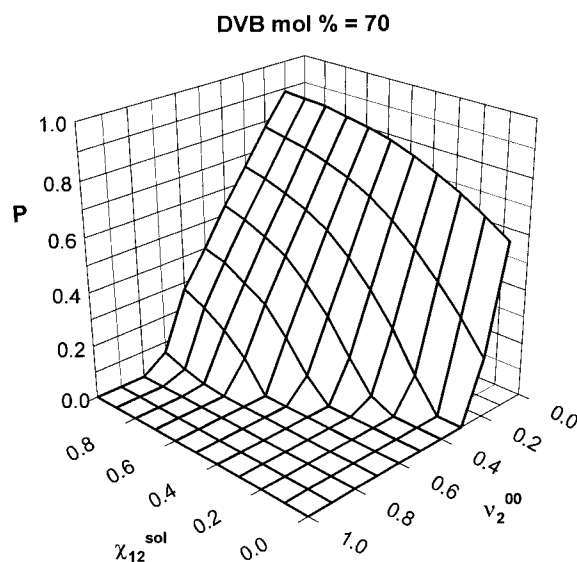


Figure 4 The total porosity P of S-DVB networks formed at $x = .99$ plotted as a function of the quality χ_{12}^{sol} and the amount v_2^{00} of the diluent present during the polymerization. DVB = 70 mol %, $[I]_0 = 0.1M$. Temperature = 70°C .

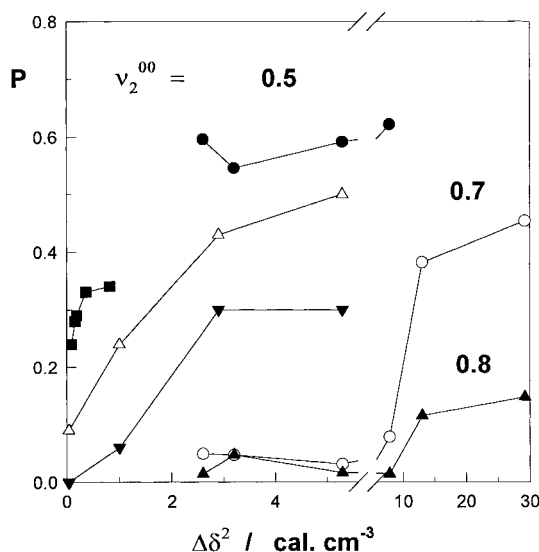


Figure 5 The total porosity P of S-DVB copolymer networks shown as a function of the diluent quality $\Delta\delta^2 = (\delta_1 - \delta_2)^2$, where δ_1 and δ_2 are the solubility parameters of the diluent and the polymer, respectively.¹⁸ The initial volume fraction of the monomer v_2^{00} is shown in the figure. Experimental data points are from Seidl et al.,² Wiczeorek et al.,¹¹ and Okay.^{16,18} The curves only show the trend of the data. Diluent = aliphatic alcohols of various chain length,² DVB = 20%, $v_2^{00} = 0.50$ (●), 0.70 (○), and 0.80 (▲). Diluent = toluene/cyclohexanol mixtures,^{16,18} $v_2^{00} = 0.50$, DVB = 10 (▼) and 25% (△). Diluent = *n*-heptane/toluene mixtures,¹¹ $v_2^{00} = 0.50$, DVB = 50% (■).

mol %, the gel point conversion x_c decreases from 0.555 to 0.066. The gel effect that starts at the gel point becomes significant on raising the DVB concentration; at DVB concentrations above 10 mol %, all the monomers completely react within a few minutes after the gel point due to the strong gel effect. Increase in the DVB concentration also increases the rate of change of W_g , i.e., the growth rate of the gel due to the simultaneous increase of the pendant vinyl group concentration in the reaction mixture [Fig. 7(B)].

Figure 8 shows the variation of porosity P with monomer conversion x for various levels of DVB. The calculation results are for two differed solvents with $\chi_{12}^{sol} = 0.5$ and 0.6. The results illustrate that the porosity in the network increases on increasing DVB concentration up to 70 mol % and then levels off. For the reaction system in a solvent with χ_{12}^{sol} close to χ_{12}^{mon} (upper curves), the system phase separates at or beyond the gel point. Thereafter, the porosity does not change much over a wide range of the monomer conver-

sion but it increases at high conversions due to the simultaneous increase of the network crosslink density N^{-1} . Even at low DVB contents (curves 1 and 2), the network becomes heterogeneous at high monomer conversions or by curing the reaction system at complete monomer conversion due to the increasing crosslinking density [Fig. 7(B)]. In a poor solvent as a diluent (lower curves), porosity first decreases with increasing conversion because of the increased gel fraction. At high monomer conversions porosity increases again due to the crosslinking reactions.

The calculated porosities of S-DVB networks formed at a monomer conversion $x = 0.99$ are collected in Figure 9 as a function of the DVB and the initial monomer concentration. It is seen that the porosity of S-DVB networks increases with increasing DVB content of the monomer mixture. In the presence of sufficient amount of DVB, the porosity does not change with a further increase in the DVB concentration. The maximum value of porosity obtained at high DVB contents is close to the amount of the diluent present during the reactions. Moreover, Figure 9 also indicate that, to

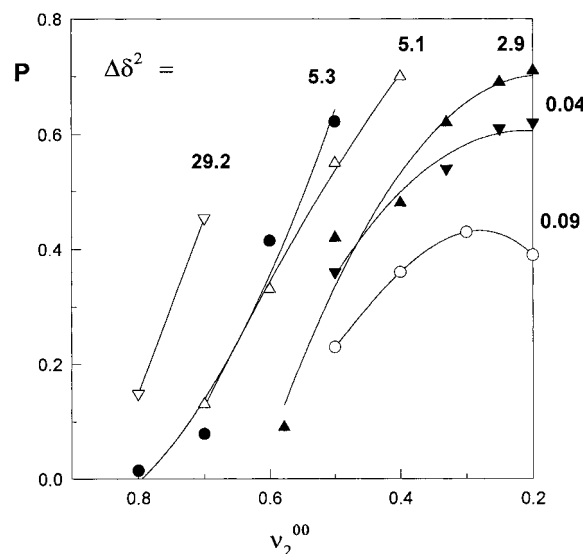


Figure 6 The total porosity P of S-DVB copolymer networks shown as a function of the monomer dilution v_2^{00} . The difference between the solubility parameters of the diluent and the polymer is shown in the figure. Experimental data points are from Seidl et al.,² Wiczeorek et al.,¹¹ Okay,¹⁸ and Jun et al.¹⁹ The curves only show the trend of the data. DVB = 20%, diluent = methanol² (▽), *n*-butanol² (●), isooctane² (△), and toluene/cyclohexanol (1/3) mixture¹⁸ (▲). DVB = 50%, diluent = *n*-heptane/toluene (1/9) mixture¹¹ (○). DVB = 98.4%, diluent = toluene¹⁹ (▼).

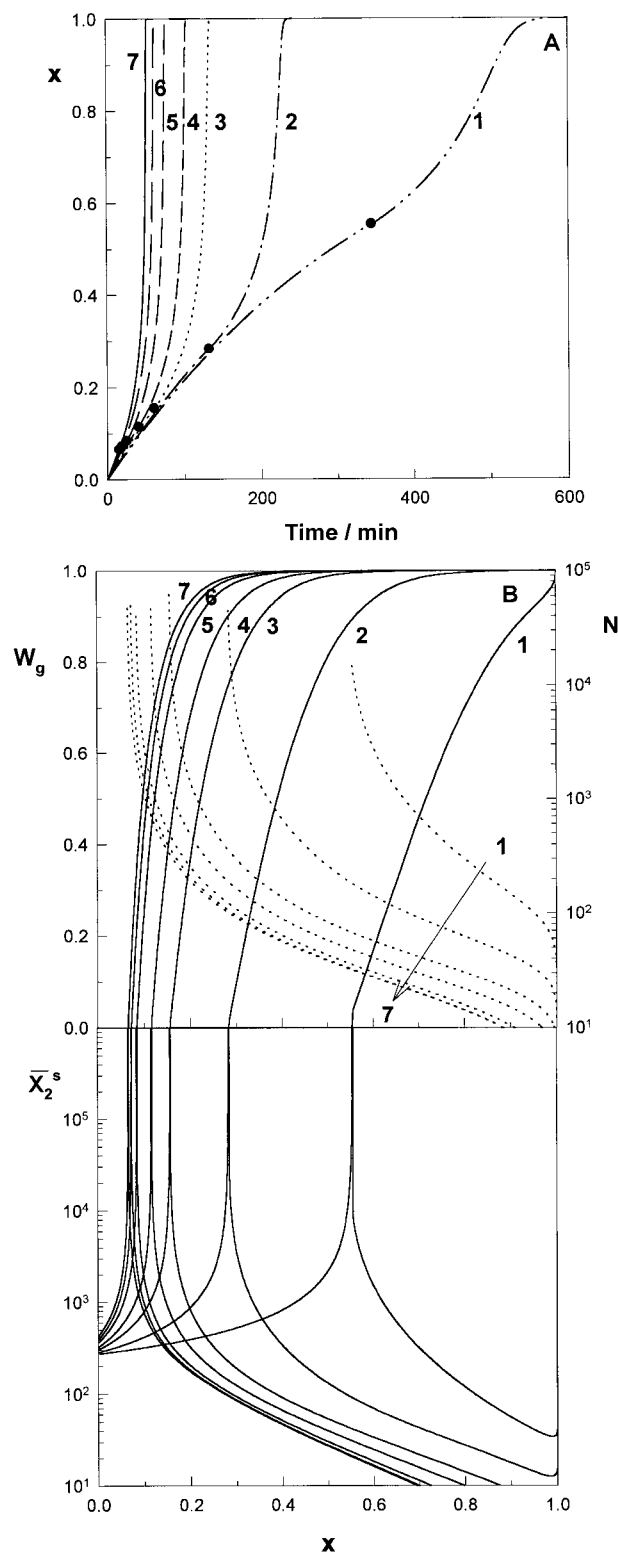


Figure 7 (A) Variation of monomer conversion x with the reaction time in S-DVB copolymerization at various DVB concentration. The gel points are shown as filled circles. $v_2^{00} = 0.20$. $[I]_0 = 0.1M$. Temperature = 70°C . DVB mol % = 5 (1), 10 (2), 20 (3), 30 (4), 50 (5),

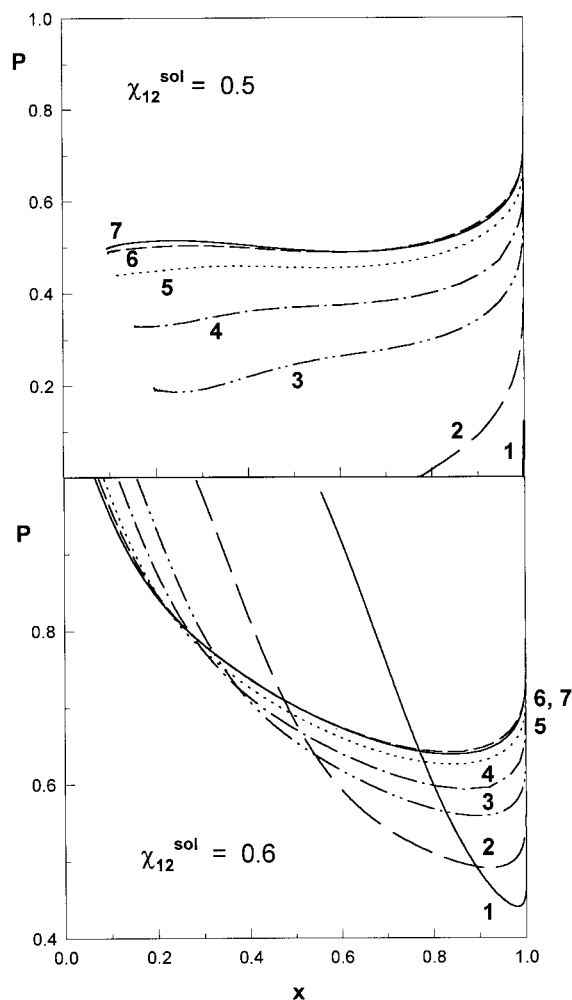


Figure 8 Variation of the total porosity P of S-DVB networks formed in S-DVB copolymerization with the monomer conversion x for various levels of DVB. $v_2^{00} = 0.20$. $[I]_0 = 0.1M$. Temperature = 70°C . DVB mol % = 5 (1), 10 (2), 20 (3), 30 (4), 50 (5), 70 (6), and 90 (7). χ_{12}^{sol} values used in the calculations are indicated.

obtain porous copolymers, a critical amount of DVB, or a critical degree of initial monomer dilution, are required. The critical DVB concentration decreases with increasing degree of dilution of the monomers. In Figure 10, experimental porosity data of S-DVB networks published in the literature^{16,18,43} are collected as a function of the DVB concentration. A comparison of Figures 9 and 10

70 (6), and 90 (7). (B) W_g , N (dotted curves), and $\bar{X}_2^s$ shown as a function of the monomer conversion x in S-DVB copolymerization at various levels of DVB. See legend to A for the reaction conditions.

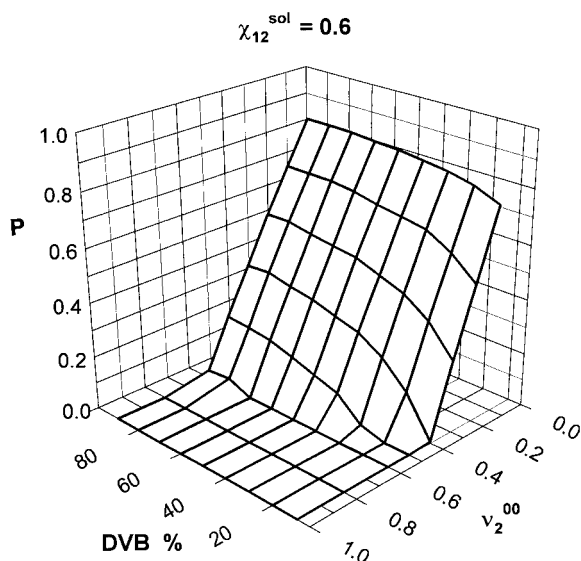


Figure 9 The total porosity P of S-DVB networks formed at $x = .99$ plotted as a function of the initial concentrations of the DVB and the total monomers. $\chi_{12}^{\text{sol}} = 0.60$. $[I]_0 = 0.1M$. Temperature = 70°C .

shows that the predictions of the model are in excellent agreement with the experimental data. The slight decrease in the porosity of S-DVB net-

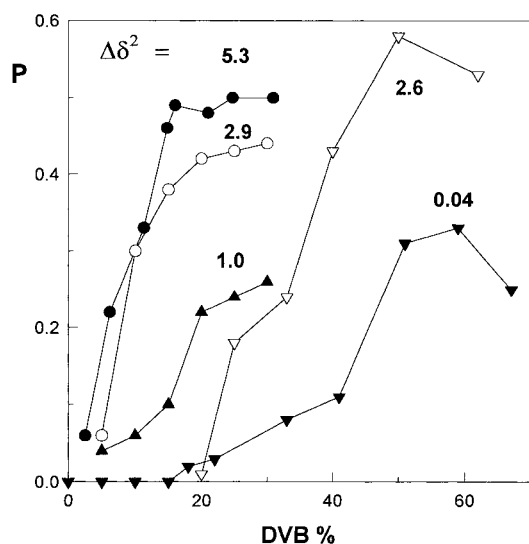


Figure 10 The total porosity P of S-DVB copolymer networks shown as a function of the DVB concentration. The difference between the solubility parameters of the diluent and the polymer is shown. Experimental data points are from Poinescu et al.⁴³ and Okay.^{16,18} The curves only show the trend of the data. $v_2^{00} = 0.50$, diluent = cyclohexanol¹⁶ (●), toluene/cyclohexanol (1/3)¹⁸ (○), toluene/cyclohexanol (1/1)¹⁸ (▲), and toluene¹⁶ (▼). $v_2^{00} = 0.40$, diluent = toluene/gasoline (1/100)⁴³ (V).

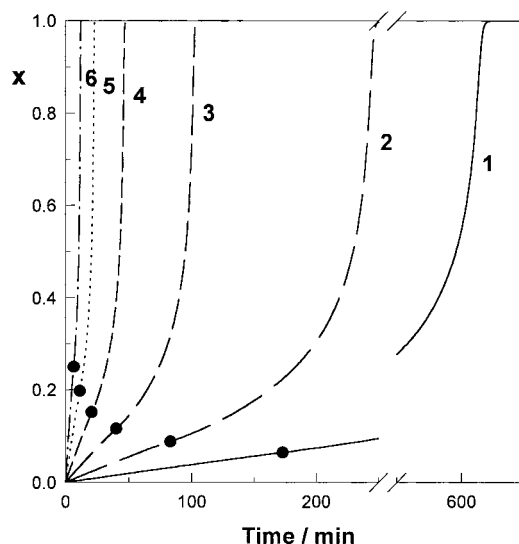


Figure 11 Variation of monomer conversion x with the reaction time in S-DVB copolymerization with 30 mol % DVB at various polymerization temperatures. The gel points are shown as filled circles. $v_2^{00} = 0.20$, $[I]_0 = 0.1M$. Polymerization temperature = 50 (1), 60 (2), 70 (3), 80 (4), 90 (5), and 100°C (6).

works above 60 % DVB (Fig. 10) is due to the destruction of the rigid pore structure during the polymerization or during the measurements.^{13,16}

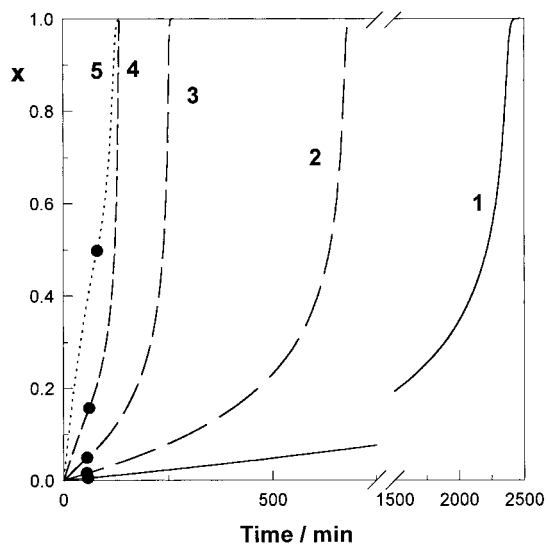


Figure 12 Variation of monomer conversion x with the reaction time in S-DVB copolymerization with 20 mol % DVB at various initiator concentrations. The gel points are shown as filled circles. $v_2^{00} = 0.20$, Temperature = 70°C . Initiator concentration $[I] = 10^{-4}$ (1), 10^{-3} (2), 10^{-2} (3), 10^{-1} (4), and 10^0M (5).

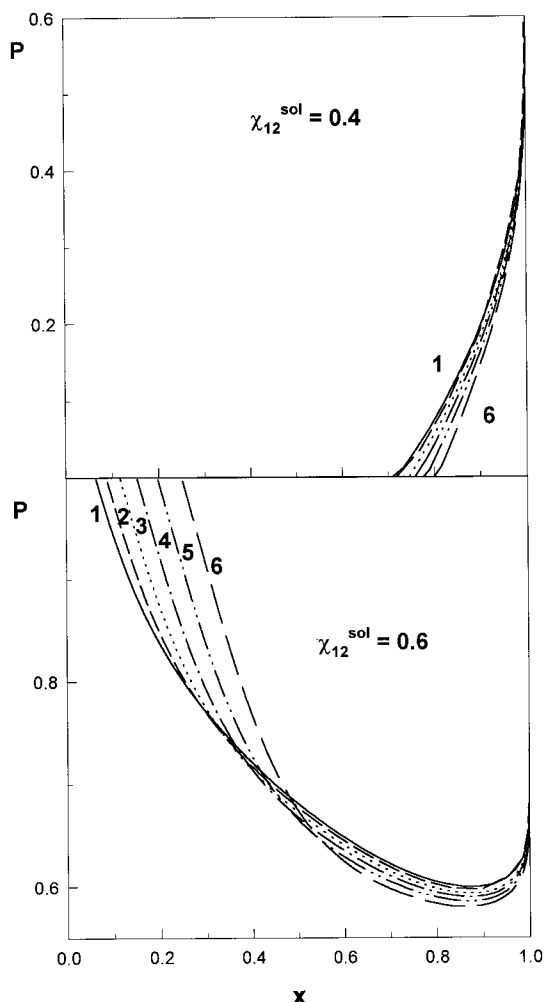


Figure 13 Variation of the total porosity P of S-DVB networks formed in S - DVB copolymerization with the monomer conversion x for various polymerization temperatures. DVB = 30 mol %, $v_2^{00} = 0.20$, $[I]_0 = 0.1M$. χ_{12}^{sol} values used in the calculations are indicated. Polymerization temperature = 50 (1), 60 (2), 70 (3), 80 (4), 90 (5), and 100°C (6).

The effects of the polymerization temperature and the initiator concentration on the porosity of S-DVB networks have, to our knowledge, not been studied previously. Figure 11 shows the effect of temperature on conversion-time history of S-DVB copolymerization, while Figure 12 shows similar plots but at various initiator levels.¹¹⁻¹² As the temperature decreases, gelation occurs at earlier monomer conversions but at later reaction times (Fig. 11). For example, as the polymerization temperature decreases from 100 to 50°C, the gel point conversion decreases from 0.250 to 0.064, but the gelation time increases from 6.4 to 173 min. This is due to the fact that, at a low

temperature, the polymerization and crosslinking reactions slow down, which shift the gel point toward longer reaction times. On the other hand, since low polymerization temperature facilitates formation of long primary chains, the gel point with respect to monomer conversion becomes shorter on decreasing the temperature. Figure 12 shows that, as the initial concentration of the initiator increases, gelation occurs at higher monomer conversions due to the formation of short primary chains that delays gelation. But the gel point with respect to time is largely insensitive to the amount of the initiator.

Figures 13 and 14 illustrate how the porosity varies depending on the polymerization temperature and the initiator concentration. The porosity of partially formed networks ($x < 0.5$) increases with increasing temperature or with increasing initiator concentration. Thus, the partially formed networks obtained at higher temperatures or at higher initiator concentrations should exhibit higher porosities due to the delayed gelation and lower gel fractions. Calculations also indicate that the final porosity of the networks slightly increases on decreasing the polymerization temperature or the initiator concentration. However, this effect is, compared to the other effects shown in Figures 4 and 9, insignificant.

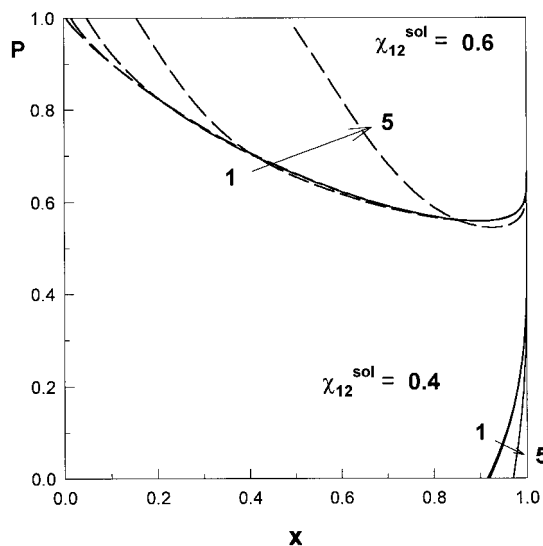


Figure 14 Variation of the total porosity P of S-DVB networks formed in S - DVB copolymerization with the monomer conversion x for various initiator concentrations. DVB = 20 mol %, $v_2^{00} = 0.20$. Temperature = 70°C. χ_{12}^{sol} values used in the calculations are indicated. Initiator concentration $[I] = 10^{-4}$ (1), 10^{-3} (2), 10^{-2} (3), 10^{-1} (4), and 10^0M (5).

CONCLUSIONS

A kinetic-thermodynamic model for the formation of macroporous copolymer networks was presented and applied to the free-radical crosslinking copolymerization of S and commercial DVB. S-DVB copolymerization system at a high DVB concentration, or at a low monomer concentration, phase separates during polymerization and results in the formation of macroporous networks. The results presented demonstrate that the networks prepared in more diluted solutions, at a high DVB concentration, or in the presence of nonsolvating diluents exhibit larger porosity values. The porosity of S-DVB copolymer networks increases on increasing DVB or the diluent concentration, or on decreasing the solvating power of the diluent. It was also found that the porosity of partially formed networks increases with increasing polymerization temperature, or with increasing concentration of initiator. However, the final porosity of S-DVB networks is largely insensitive to both the amount of the initiator and the polymerization temperature. Comparison of the simulation results with the experimental data indicates that the model predicts all the trends observed by experiments.

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