

Kinetic investigation of the free-radical crosslinking copolymerization of styrene with a mixture of divinylbenzene isomers acting as the crosslinker

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The objective of this paper is to study the crosslinking copolymerization of styrene (S) with a mixture of *para*- and *meta*-divinylbenzenes (mixed-DVBs). The crosslinking copolymerization, initiated with benzoyl peroxide (BPO), was performed at temperatures of 70, 80, and 90°C. The mole ratio of DVB to S was kept small, i.e. within 4–8%. At various stages of the polymerization the overall conversion of the monomers to sol and gel were measured by gravimetry. The sol and gel formations with time were also measured. The gels were characterized by equilibrium swelling measurements as a function of the overall degree of conversion. The experimental data were then incorporated into the kinetic model developed by Tobita and Hamielec. The kinetic parameters involved in the crosslinking copolymerization of S/DVB were also estimated. A satisfactory agreement of the results obtained from the experimental measurements with the predictions of the model was observed. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Most modern ion-exchange resins consist of a synthetic polymer backbone to which is attached a functional group that gives each ion exchanger its specific properties. The polymer matrices are usually crosslinked to make them insoluble and to give them mechanical strength and stability. The most common matrices are styrene-divinylbenzene (S/DVB) copolymers in which DVB is the crosslinking agent, and is typically present in 4–12% concentration.

The copolymerization of DVB with S was first studied by Staudinger and Heuer¹, who demonstrated that crosslinking does occur for S/DVB systems. Storey² compared the initial rates of the S/*p*-DVB copolymerization with those measured for S and *p*-DVB homopolymerization and concluded that crosslinking results in an increase in the reaction rate. Gel times were measured and it was concluded that the higher the content of crosslinker, then the less would be the conversion required to reach the gelation point. The overall first-order rate constants for S/*p*-DVB copolymerization over a broad range of compositions, initiated by 1% BPO at temperatures of 70 and 90°C, were calculated. The conversion-time curves obtained from dilatometric measurements for 4, 10, and 20% *p*-DVB at 70°C were also reported. It was postulated that all of the double bonds in the S/*p*-DVB system are of equal reactivity.

Hild and Okasha³ studied the kinetics of the free-radical copolymerization of S and commercial DVB (*para*- and *meta*-isomers) in the presence of carbon tetrachloride as a chain transfer agent. In further work they investigated the kinetics of free-radical crosslinking copolymerization of S with *p*-DVB or *m*-DVB in benzene solution at 60°C⁴. The DVB proportions were kept small with respect to styrene, in order to reduce the importance of the DVB radicals in the reaction media. The consumptions of S and DVB isomers were measured as a function of time. The radical reactivity ratios of S with respect to both *m*-DVB and *p*-DVB were also obtained.

Malinsky *et al.*⁵ evaluated the copolymer composition of S with *p*-DVB or *m*-DVB, and indicated that after one of the vinyl groups in the DVB isomers has reacted, the reactivity of the remaining vinyl group then falls. It was also concluded that the pendant double bonds in both the *p*-DVB and *m*-DVB units have the same reactivity. They also evaluated the effect of concentration of the DVB isomers on the conversion at the gel point. This conversion was found to depend on the concentration of DVB at lower values of the latter (< 20%).

Wiley *et al.*⁶ measured the reactivity ratios of S/*m*-DVB and S/*p*-DVB at low conversion by differential analysis. In further work, they used the integrated form of the copolymerization equation to determine the reactivity ratios⁷. This method was claimed to avoid errors encountered in the low-conversion data that was required for the differential analysis.

Hild and Okasha⁸ investigated the crosslinking copolymerization of S/*p*-DVB and S/*m*-DVB in the post-gel state, and determined the swelling degree and

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the modulus of the swollen networks as a function of conversion. It was established that the delay in gelation originates from the lower reactivity of the pendant double bond and not from formation of the many intramolecular cyclizations.

To date, no experimental data have been reported on the S/mixed-DVB (mixture of *para*- and *meta*-isomers) crosslinking copolymerization. In this present research work, a set of experimental data on sol and gel formation versus time, elastic crosslinking density, reaction rate, and network structure under different temperatures, for the system of S and mixed-DVBs is presented. In order to fit the experimental data, several models were studied. The modelling attempts for free-radical crosslinking copolymerization may be classified as statistical, percolation, and kinetic⁹. The statistical approaches, which have originated from the classical work of Flory and Stockmayer, have been widely proposed for crosslinking copolymerization. Several statistical methods have been reported by Gordon and coworkers^{10,11}, Maćosko and Miller^{12,13}, Durand and Bruneau^{14,15}, Williams and Vallo¹⁶ and finally Landina and Maćosko¹⁷. Although the more recent statistical models are very advanced, they suffered from complexity which limits their use for practical purposes. Percolation models which are based on random walks have been proposed by Boots *et al.*¹⁸, Bansil *et al.*¹⁹, and Herman and coworkers^{20,21}. This method is still at an early development stage and is far from being of practical use. Few reports have appeared on kinetic approaches^{22,23}. This method, which is based on the true chemical reactions occurring in crosslinking copolymerization, is more understandable. Mikos *et al.*²² used the moment equations to describe the pre-gel region in the crosslinking copolymerization of S/*p*-DVB and S/*m*-DVB. However, no experimental data were reported. Recently, a very basic kinetic approach has been developed by Tobita and Hamielec (TH)²³⁻³¹. This model can predict important properties such as the onset of gelation, weight fraction of sol and gel, number- and weight-average molecular weights, crosslinking density in sol and gel fractions, number of pendant double bonds, etc. The model considers the history of growth for polymer chains which at present the statistical models cannot account for. The TH model has been widely used by its authors to describe the crosslinking copolymerization of methyl methacrylate (MMA)/ethylene glycol dimethacrylate (EGDMA) and polyacrylamide networks³⁰. Some limited modelling attempts on S/DVB systems were also reported, based on kinetic data in the open literature^{25,32}. The model was extended to cover the network structure in emulsion crosslinking copolymerization²⁸. The control of network structure in emulsion and bulk free-radical crosslinking copolymerization by a semi-batch policy was also reported^{29,31}.

In this present work, the copolymerization of S with a mixture of DVB isomers was performed and a set of experimental data was produced. The TH model was then used to fit the experimental data.

THEORY

The details of the TH model are beyond the scope of this present paper. Only a very brief review of the substantial features of the TH model is therefore presented. The

interested reader is referred to several publications on this topic for further information.

According to the model, the crosslinking density of a primary molecule, which is an imaginary molecule with a linear structure, consists of two parts, as follows:

$$\rho_a(\theta, \Psi) = \rho_i(\theta) - \rho_a(\theta, \Psi) \quad (1)$$

where ρ_i is the instantaneous crosslinking density during the growth of the primary molecules; $\rho_a(\theta, \Psi)$ is the additional crosslinking experienced in the conversion interval θ to Ψ by a primary molecule born at conversion θ . The additional crosslinking density may be calculated by a balance equation on crosslinking density in an interval Ψ to $\Psi - \Delta\Psi$, as follows:

$$N_\theta [\rho_a(\theta, \Psi - \Delta\Psi) - \rho_a(\theta, \Psi)] = k_p^* [F_2(\theta) - \rho_a(\theta, \Psi) - \rho_c(\theta, \Psi)] N_\theta R \Delta t \quad (2)$$

where N_θ is the total number of monomer units bound in the primary chains born at $x = \theta$ and $F_2(\theta)$ is the mole fraction of divinyl monomer at $x = \theta$; $\rho_c(\theta, \Psi)$ may be defined as the cyclization density distribution for the primary molecules born at $x = \theta$. Now, k_p^* , which is the propagation rate constant for the pendant double bonds, is defined by the following:

$$k_p^* = k_{p14}^* \phi_1 - k_{p24}^* \phi_2 - k_{p34}^* \phi_3 - k_{p44}^* \phi_4 \quad (3)$$

where ϕ_1 , ϕ_2 , ϕ_3 , and ϕ_4 are the ratios of S, *m*-DVB, *p*-DVB, and pendant double bond radicals to the total radicals, respectively. Since the DVB content was kept less than 8%, it may be assumed that $\phi_1 = 1$ and $\phi_2 = \phi_3 = \phi_4 = 0$.

The fundamental equation for the additional crosslinking density is obtained as follows:

$$\frac{\sigma \rho_a(\theta, \Psi)}{\sigma \Psi} = \frac{k_p^* [F_2(\theta) - \rho_a(\theta, \Psi) - \rho_c(\theta, \Psi)]}{k_p (1 - \Psi)} \quad (4)$$

where $\rho_c(\theta, \Psi)$ is the cyclization density at $x = \Psi$ for the primary molecule born at $x = \theta$. The cyclization reactions are divided into two groups, namely primary and secondary cyclization. Primary cyclization occurs when the cycle forms within one primary molecule. Hence it is solely a function of a birth conversion. Secondary cyclization exists when a cycle is formed between two or more primary molecules, and has both the function of birth and present conversion.

The primary cyclization density was assumed to be proportional to the mole fraction of divinyl monomers bound in the polymer chains:

$$\rho_{cp}(\theta) = k_{cp} F_2(\theta) \quad (5)$$

The secondary cyclization may be defined, similar to equation (1), as follows:

$$\rho_{cs}(\theta, \Psi) = \rho_{cs,i}(\theta) + \rho_{cs,a}(\theta, \Psi) \quad (6)$$

where $\rho_{cs,a}(\theta, \Psi)$ is the additional secondary cyclization density and $\rho_{cs,i}(\theta)$ is the instantaneous secondary cyclization.

The instantaneous crosslinking density is given by the integration over all of the birth conversions, as follows:

$$\rho_i(x) = \int_0^x \frac{\partial \rho_a(\theta, x)}{\partial x} d\theta \quad (7)$$

A similar relationship is applicable to instantaneous secondary cyclization, as follows:

$$\rho_{cs,i}(x) = \int_p^x \frac{\partial \rho_{cs,a}(\theta, x)}{\partial x} d\theta \quad (8)$$

The fundamental equation for additional secondary cyclization is as follows:

$$\frac{\partial \rho_{cs,a}(\theta, x)}{\partial x} = \eta(\theta, \Psi) \frac{\partial \rho_a(\theta, x)}{\partial x} \quad (9)$$

where $\eta(\theta, \Psi)$ is the average number of secondary cycles per crosslink, which is a function of the mole fraction of the pendant double bonds, chain length of the primary molecules, etc.

Equations (1), and (4–9), by using a suitable approximation for $\eta(\theta, \Psi)$, may be solved simultaneously to give the crosslinking density distribution as a function of the birth conversion θ of the primary polymer molecule at any conversion Ψ . As a first approximation, $\eta(\theta, \Psi)$ may be considered as a constant ($\eta(\theta, \Psi) = \eta = \text{constant}$). This assumption seems valid only at low conversion levels.

Equations (1), (4)–(6), and (9) may be solved analytically³³ to give $\rho_a(\theta, \Psi)$ and $\rho_{cs,a}(\theta, \Psi)$ as follows:

$$\rho_a(\theta, \Psi) = \frac{(1 - k_{cp})F_2(\theta)}{(1 - \eta)} \left[1 - \left(\frac{1 - \Psi}{1 - \theta} \right)^{c(1+\eta)} \right] \quad (10)$$

$$\rho_{cs,a}(\theta, \Psi) = \eta \rho_a(\theta, \Psi) \quad (11)$$

where $c = k_p^*/k_p$. Substituting equations (10) and (11) into equations (7) and (8), and then integrating gives the following:

$$\rho_{cs,i}(x) = c(1 - k_{cp})(1 - x)^{c(\eta+1)-1} \int_0^x \frac{F_2(\theta)}{(1 - \theta)^{c(\eta+1)}} d\theta \quad (12)$$

$$\rho_i(x) = \eta \rho_i(x) \quad (13)$$

As a second approximation, $\eta(\theta, \Psi)$ was defined as the average number of pendant double bonds on a primary polymer molecule, born at $x = \theta$.

$$\eta(\theta, \Psi) = k_{cs} [F_2(\theta) - \rho_a(\theta, \Psi) - \rho_{cs,a}(\theta, \Psi) - \rho_{cp}(\theta)] P_{np}(\theta) \quad (14)$$

where $P_{np}(\theta)$ is the number-average of the chain lengths of the primary polymer molecules formed at $x = \theta$.

Equations (1), (4)–(6), (9) and (14) may be solved analytically³³ to give the exact solution for $\rho_a(\theta, \Psi)$ and $\rho_{cs,a}(\theta, \Psi)$ as follows:

$$\rho_a(\theta, \Psi) = H(\theta) [K(\theta)(1 - C_2(1 - \Psi)^c)] \quad (15)$$

$$\rho_{cs,a}(\theta, \Psi) = \frac{1}{k_{cs}\nu(\theta)} \left\{ \ln \left[\frac{1}{1 - C_2(1 - \Psi)^c} \right] - \left[\frac{1}{1 - C_2(1 - \Psi)^c} \right] \right\} + C_1 \frac{1}{k_{cs}\nu(\theta)} \quad (16)$$

where $\nu(\theta)$, $K(\theta)$, C_1 , and C_2 are defined as follows:

$$\nu(\theta) = 1/(\tau(\theta) + \beta(\theta)) \quad (17)$$

$$K(\theta) = (1 - k_{cp})F_2(\theta)k_{cs}\nu(\theta) + 1 \quad (18)$$

$$C_1 = K(\theta) - \ln(K(\theta)) \quad (19)$$

$$C_2 = \left[\frac{(1 - k_{cp})F_2(\theta)k_{cs}\nu(\theta)}{(1 - k_{cp})F_2(\theta)k_{cp}\nu(\theta) - 1} \frac{1}{[(1 - \theta)^c]} \right] \quad (20)$$

$\rho_1(x)$ and $\rho_{cs,1}(x)$ were obtained by use of equations (7) and (8) as follows:

$$\rho_1(\Psi) = \int_0^\Psi \frac{\sigma \rho_a(\theta, \Psi)}{\sigma \Psi} d\theta = \int_0^\Psi \frac{c}{(1 - \Psi)} \omega(\theta, \Psi) d\theta \quad (21)$$

$$\begin{aligned} \rho_{cs,1}(\Psi) &= \int_0^\Psi \frac{\sigma \rho_{cs,a}(\theta, \Psi)}{\sigma \Psi} d\theta \\ &= \int_0^\Psi \frac{c}{(1 - \Psi)H(\theta)} \bar{\omega}^2(\theta, \Psi) d\theta \end{aligned} \quad (22)$$

where:

$$\omega(\theta, \Psi) = \left(\frac{1}{k_{cs}\nu(\theta)} \left(\frac{C_2(1 - \Psi)^c}{(1 - C_2(1 - \Psi)^c)} \right) \right) \quad (23)$$

The accumulated values of $\rho_a(\theta, \Psi)$ and $\rho_{cs,a}(\theta, \Psi)$ were given by their integration over all values of the birth conversion. For example, the accumulated value of $\rho_{cs,a}(\theta, \Psi)(\rho_{cs,a}(x))$ was defined as follows:

$$\bar{\rho}_{cs,a}(\Psi) = \frac{1}{\Psi} \int_0^\Psi \rho_{cs,a}(\theta, \Psi) d\theta \quad (24)$$

In the pre-gel region, the accumulated sol fraction is obtained by birth conversions between 0 and Ψ , as follows:

$$\omega_s(\Psi) = \frac{1}{\Psi} \int_0^\Psi w_s(\theta, \Psi) d\theta \quad (25)$$

where $w_s(\theta, \Psi)$, which is the weight fraction of the sol at conversion Ψ for primary molecules which were formed at conversion θ , is given by the following:

$$w_s(\theta, \Psi) = AG_1(T + ABG_1) \quad (26)$$

where $T = \tau(\theta)$, $B = \beta(\theta)$, $A = T + B$, and $G_1 = 1 - \rho(\theta, \Psi)W_g(\theta, \Psi)$. The parameters τ and β are the ratios of the rate of transfer plus disproportionation, and combination reactions, to propagation reactions, respectively.

The crosslinking density of accumulated polymer in each fraction is given by the following:

$$\bar{\rho}^{\text{sol}}(\Psi) = \frac{1}{\Psi w_s(\Psi)} \int_0^\Psi \rho^{\text{sol}}(\theta, \Psi) w_s(\theta, \Psi) d\theta \quad (27)$$

$$\bar{\rho}^{\text{gel}}(\Psi) = \frac{1}{\Psi w_g(\Psi)} \int_0^\Psi \rho^{\text{gel}}(\theta, \Psi) w_g(\theta, \Psi) d\theta \quad (28)$$

where $\rho^{\text{sol}}(\theta, \Psi)$ and $\rho^{\text{gel}}(\theta, \Psi)$ are the crosslinking densities of the sol and gel fractions, respectively, and are given by the following:

$$\rho^{\text{sol}}(\theta, \Psi) = \rho(\theta, \Psi) w_s(\theta, \Psi) \quad (29)$$

$$\rho^{\text{gel}}(\theta, \Psi) = \rho(\theta, \Psi)(1 + w_s(\theta, \Psi)) \quad (30)$$

The number- and weight-average chain lengths of the sol fraction ($\bar{P}_n^{\text{sol}}(\Psi)$ and $\bar{P}_w^{\text{sol}}(\Psi)$, respectively) can be measured with conventional experimental methods and are given by the following expressions:

$$\bar{P}_n^{\text{sol}}(\Psi) = \frac{1}{(1/P_{np}^{\text{sol}}(\Psi) - \rho^{\text{sol}}(\Psi)/2)} \quad (31)$$

$$\bar{P}_w^{\text{sol}}(\Psi) = \frac{P_{\text{wp}}^{\text{sol}}(\Psi)(1 + \rho^{\text{sol}}(\Psi))}{1 - \rho^{\text{sol}}(\Psi)(P_{\text{wp}}^{\text{sol}}(\Psi) - 1)} \quad (32)$$

where $P_{\text{np}}^{\text{sol}}(\Psi)$ and $P_{\text{wp}}^{\text{sol}}(\Psi)$ are the accumulated number- and weight-average chain lengths of the primary polymer molecules, respectively.

The pseudo-kinetic method is used to follow the reaction rate and molecular-weights development during the course of polymerization. The reaction rate for total mole monomer content can be written as follows:

$$\frac{d(v[\text{M}])}{vdt} = \left(\frac{k_p^2}{k_t}\right)^{1/2} (2fk_a[\text{I}])^{1/2}[\text{M}] \quad (33)$$

where k_a and k_t are the pseudo-kinetic propagation and termination rate constants, respectively, and $[\text{I}]$ and $[\text{M}]$ are, respectively, the initiator concentration and the concentration of the total monomers in the reaction media.

EXPERIMENTAL

Commercial styrene was purified prior to use; it was treated with 5% NaOH solution twice, then washed twice with distilled water, and dried over sodium sulfate. It was then distilled under reduced pressure, and the middle cut was chosen to represent 'pure' styrene. The refractive index of the distilled styrene was checked with that of pure styrene, up to a level of four decimal places (1.5468). Benzoyl peroxide was recrystallized twice from chloroform. The crosslinker, a mixture of divinylbenzene isomers (Merck), was washed and distilled similarly, and then analysed by gas chromatography. It consisted of 26.3% *p*-DVB and 41.5% *m*-DVB, with the rest being mostly monovinyl derivatives of ethylstyrene. In formulating the design of the experiments, only the DVB content was regarded as the crosslinker, with the remainder being assumed to react as styrene. The copolymerization reactions were conducted in Pyrex glass ampoules which were sealed under vacuum (1 mmHg). The ampoules had a surface/volume ratio of $2/9 \text{ mm}^{-1}$, and internal diameter of 9 mm and a thickness of 1 mm.

The polymerization reactions were conducted at three different temperatures, i.e. 70, 80, and 90°C. In all of the experiments the temperature was maintained constant within 0.1°C of the desired temperature. All runs were carried out by employing 0.1 wt% BPO as initiator (with respect to the weight of total monomers). The DVB contents were assigned as 4, 6, and 8 wt%. In all of the experiments, the composition of the DVB isomer mixture was found to be constant.

At the desired conversion, the reaction was quenched by placing the ampoules in liquid nitrogen. The reaction mixture was then dissolved in toluene containing a very small amount of hydroquinone to prevent further polymerization taking place. After being shaken for at least 24 h, the gel was removed by filtration. The solution was then added to a 40-fold excess of chilled methanol to precipitate out the sol. The precipitated polymer was filtered and washed several times with fresh methanol, and was then dried at 40°C under vacuum for at least 48 h. The swollen gels were extracted (Soxhlet) with toluene for 48 h to remove the trapped non-consumed

Table 1 Kinetic parameters for the styrene-divinylbenzene copolymerization crosslinking reaction²²

$d_p = 1084.8 - 0.605(T - 273) \text{ g l}^{-1}$
$d_{\text{ms}} = 924 - 0.918(T - 273) \text{ g l}^{-1}$
$d_{\text{mDVB}} = 913 - 916(20^\circ\text{C}/4^\circ\text{C}) \text{ g l}^{-1}$
$k_{\text{p11}} = 1.06 \times 10^7 \exp(-7.07/RT) \text{ l mol}^{-1} \text{ s}^{-1}$
$k_{\text{ic11}} = 1.26 \times 10^6 \exp(-1.68/RT) \text{ l mol}^{-1} \text{ s}^{-1}$
$k_{\text{id11}} = 0$
$r_{12} = 0.2 \text{ (S/p-DVB)}$
$r_{13} = 1.11 \text{ (S/m-DVB)}$

monomers and the polymer species which had not been incorporated into the networks. They were then dried in vacuum to constant weight. The amount of soluble polymer in the gel was also measured by non-solvent treatment, as previously described for the sol fraction.

The crosslinking density of the gels was determined by equilibrium swelling. To attain the equilibrium degree of swelling, the gels were immersed in cyclohexanol for at least 48 h at a temperature of 34°C. The equilibrium swelling process was tested by occasional weighing of the samples. The gels were then weighed in the swollen state and dried under vacuum to constant weight.

Parameter estimation

In order to predict the polymerization rate and chain length development up to the gel point, all of the initial kinetic rate constants and their variation with conversion due to diffusion-controlled reactions must be known. The kinetic parameters necessary for the calculations were obtained from the literature and are listed in *Table 1*. Since the level of DVB crosslinker was maintained at a low level, it may be assumed that the sole radical existing in the reaction media is the styrenic radical. It is well understood that the termination rate constant, k_t , is diffusion controlled in free-radical bulk polymerization, even from zero conversion. Furthermore, the propagation rate constant, k_p , also becomes diffusion controlled at high conversion levels. Several theoretical models have been proposed to account for the variation of the reaction rate constants with conversion in free-radical polymerization. However, few of these have been applied to crosslinking copolymerization. Mikos *et al.*²² used the model of Cardenos and Driscoll³⁴ for the simulation of S/DVB copolymerization. Chern and Poehlein³⁵ used the model of Soh and Sundberg³⁶⁻³⁹ for studying the kinetics of vinyl crosslinking polymerization. However, the nature of the motion of a branched polymer in a viscous medium is not well understood at the present time. Hence, the empirical correlations proposed by Tobita and Hamielec²⁵ were used in this present work to incorporate the effect of diffusion-controlled reactions into the model as follows:

$$k_p/k_t^{0.5} = k_{\text{p0}}/k_{\text{t0}}^{0.5} \quad (x < z_2) \quad (34)$$

$$= k_{\text{p0}}/k_{\text{t0}}^{0.5} \exp(z_1(x - z_2)) \quad (z_2 < x < z_4) \quad (35)$$

$$= k_{\text{p0}}/k_{\text{t0}}^{0.5} \exp(z_1(x - z_2) - z_3(x - z_4)) \quad (z_4 < x) \quad (36)$$

Where z_1 , z_2 , z_3 , and z_4 are adjustable parameters and were calculated by fitting equation (33) to the

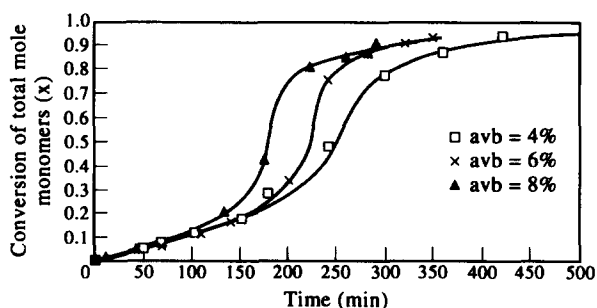


Figure 1 Conversion profiles of S/mixed DVB copolymerization at 70°C for various DVB concentrations (points represent the data; lines represent model simulations); BPO = 0.1 wt%: 4 wt% DVB ($z_1 = 7$, $z_2 = 0.12$, $z_3 = 10$, $z_4 = 0.55$); 6 wt% DVB ($z_1 = 8$, $z_2 = 0.11$, $z_3 = 14$, $z_4 = 0.6$); 8 wt% DVB ($z_1 = 8.1$, $z_2 = 0.07$, $z_3 = 15$, $z_4 = 0.56$)

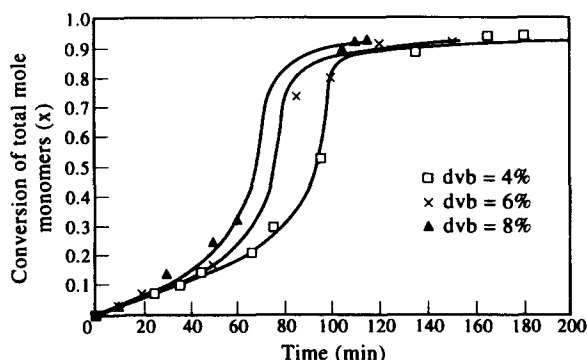


Figure 2 Conversion profiles of S/mixed DVB copolymerization at 80°C for various DVB concentrations (points represent the data; lines represent model simulations); BPO = 0.1 wt%: 4 wt% DVB ($z_1 = 7.4$, $z_2 = 0.11$, $z_3 = 37$, $z_4 = 0.775$); 6 wt% DVB ($z_1 = 8$, $z_2 = 0.075$, $z_3 = 19$, $z_4 = 0.63$); 8 wt% DVB ($z_1 = 7$, $z_2 = 0.04$, $z_3 = 15.56$, $z_4 = 0.64$)

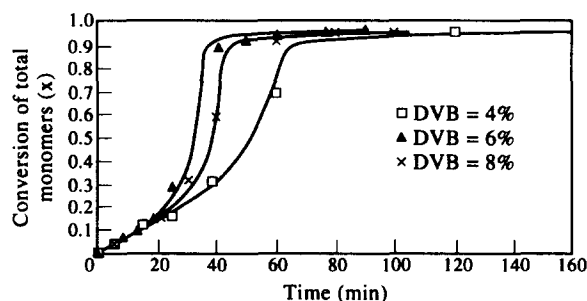


Figure 3 Conversion profiles of S/mixed DVB copolymerization at 90°C for various DVB concentrations (points represent the data; lines represent model simulations); BPO = 0.1 wt%: 4 wt% DVB ($z_1 = 5.1$, $z_2 = 0.13$, $z_3 = 40$, $z_4 = 0.85$); 6 wt% DVB ($z_1 = 7$, $z_2 = 0.1$, $z_3 = 40$, $z_4 = 0.81$); 8 wt% DVB ($z_1 = 7.1$, $z_2 = 0.07$, $z_3 = 40$, $z_4 = 0.82$)

experimental conversion data by using the least-squares method⁴⁰. The parameters z_2 and z_4 represent the conversions at the onset of gel and glass formation, respectively. As shown in *Figures 1–3* z_2 decreases with increasing DVB content of the initial monomer feed; z_1 and z_3 represent the strength and importance of the gel and glass effects, respectively²⁵.

A dilute monomer solution with a low mole fraction of DVB favours primary cyclization, while a high mole fraction of DVB results in enhancement of the secondary cyclization. Furthermore, the primary cyclization is expected to remain constant as the reaction proceeds,

while the secondary cyclization should increase with conversion. The value of $k_{cp} = 0.23$ was obtained by fitting the data for solution copolymerization of S/*p*-DVB²⁵. The effect of secondary cyclization also increases as the primary molecule chain length builds up, due to the fact that the probability that a growing primary chain can find two or more pendant double bonds increases. The parameter, k_p^* , the reactivity of the pendant double bonds, is a function of the network structure, chain length and reaction medium viscosity. It is obvious that k_p^* varies during the course of polymerization. However, it may be considered constant for simplicity²⁵. Furthermore, the decreasing reactivity of the pendant double bonds occurs simultaneously with the increase in secondary cyclization²⁵. Hence, k_p^* may be defined as a function of the crosslinker concentration and temperature, and increases with both parameters. Although the increasing temperature simultaneously, increases the reactivity of the pendant double bonds and secondary cyclization, the effect on the latter is expected to be less significant due to the subsequent decrease in the primary molecule chain length. It was assumed that both the *meta*- and *para*-type pendant double bonds have the same reactivity⁵. In order to find k_p^* and k_{cs} , the experimental data for sol and gel fractions *versus* time were fitted to the model.

RESULTS AND DISCUSSION

Figures 1–3 show the effect of the DVB content on the conversion with time. It is apparent from these figures that there is an auto-acceleration in the conversion rate which decreases with the increase in divinyl monomer content. This is due to the stronger gel effect caused by the more restricted chain segments when a higher concentration of DVB is used. The maximum rate is obtained with the highest level of crosslinker.

Temperature has the same effect on the conversion–time profiles. Increasing the temperature also results in an auto-acceleration in the conversion rate, as depicted in *Figures 1–3*. The maximum rate is obtained with the highest temperature. The sudden decrease in the conversion rate at high conversions, which was reported for the MMA–EGDMA system⁴¹ was not observed in the S–DVB systems.

At a fixed temperature, it was expected that the limiting conversion would be higher for a lower amount of crosslinker, due to the lower T_g of the crosslinked polymer. However, no distinct difference in the limiting conversions was observed in any of the experiments. The unusual variation of limiting conversion with crosslinker level has also been reported for MMA–EGDMA crosslinking copolymerization⁴².

At a fixed amount of crosslinker, there was also no detectable difference in limiting conversion for different temperatures. The limiting conversion variation with temperature was reported to be negligible for MMA/EGDMA copolymerization⁴³. It is generally accepted that the glass effect is delayed as the reaction temperature reaches the T_g of the polymer. Nielsen⁴⁴ indicated that the shift in the glass transition temperature due to crosslinking is inversely proportional to the number-average molecular weight between the crosslink points,

which is a decreasing function of the temperature. Hence, this ambiguity can be probably addressed to the counterbalancing effects of the temperature on the glassy behaviour of the crosslinked copolymer.

Figures 4–6 show the weight fraction of sol at predetermined temperatures and crosslinker concentrations. The value of k_p^* , estimated by the application of the TH model to the experimental data, is in the range 0.1 to 0.2, depending on the level of crosslinker concentration and temperature. This indicates a very large decrease in the pendant double-bond reactivities in S/DVB

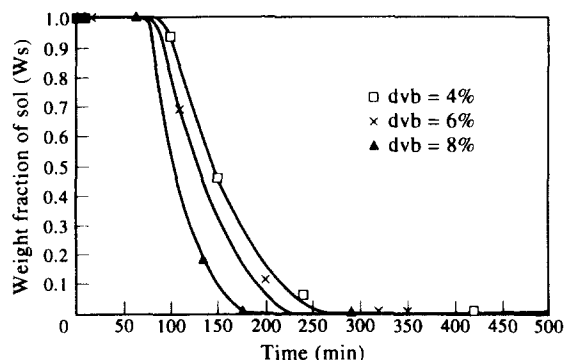


Figure 4 Weight fraction of sol versus time at 70°C for various DVB concentrations; BPO = 0.1 wt%: 4 wt% DVB ($c = k_p^*/k_p = 0.132$, $k_{cp} = 0.23$); 6 wt% DVB ($c = 0.099$, $k_{cp} = 0.23$); 8 wt% DVB ($c = 0.08$, $k_{cp} = 0.23$)

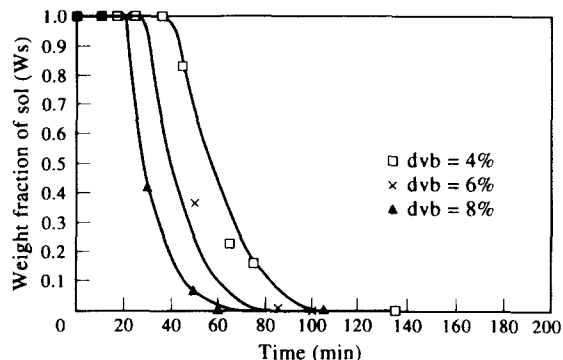


Figure 5 Weight fraction of sol versus time at 80°C for various DVB concentrations; BPO = 0.1 wt%: 4 wt% DVB ($c = 0.19$, $k_{cp} = 0.23$); 6 wt% DVB ($c = 0.181$, $k_{cp} = 0.23$); 8 wt% DVB ($c = 0.171$, $k_{cp} = 0.23$)

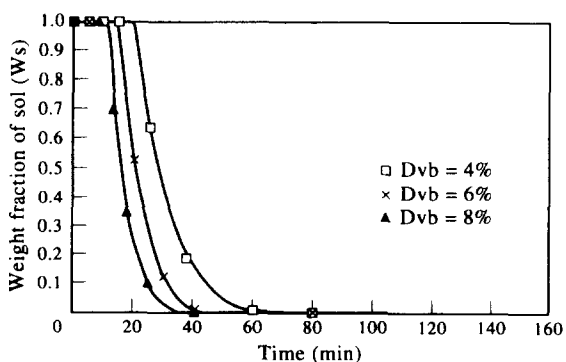


Figure 6 Weight fraction of sol versus time at 90°C for various DVB concentrations; BPO = 0.1 wt%: 4 wt% DVB ($c = 0.219$, $k_{cp} = 0.23$, $k_{cs} = 0.008$); 6 wt% DVB ($c = 0.205$, $k_{cp} = 0.23$, $k_{cs} = 0.04$); 8 wt% DVB ($c = 0.298$, $k_{cp} = 0.23$, $k_{cs} = 0.08$)

copolymerization, which is consistent with the published data⁵. The experimental results indicate that the pendant double-bond reactivities increase with temperature, but decrease with the level of crosslinker concentration. At a constant temperature, the sol fraction starts to decrease at a lower conversion as the crosslinker concentration increases. The gel point is reached more rapidly as the temperature increases. However, the degree of conversion at the gel point may be obtained by extrapolating the curves to zero gel conversion. At a fixed amount of crosslinker, a delay in reaching the gel point with respect to conversion was observed with increasing temperature.

The procedure for measurement of the elastic crosslinking density was adapted from Tobita and Hamielec²⁵. The swelling equilibrium between solvent and swollen gel can be described by the following equation⁴⁵:

$$-\left[\ln(1 - v_{2m}) + v_{2m} + \chi_1 v_{2m}^2\right] = z(v_1 d_2 / M_c) \left(\zeta_0^{2/3} v_{2m}^{1/3} - v_{2m} / 2\right) \quad (37)$$

where v_{2m} is the equilibrium volume fraction of polymer in the swollen gel and χ is the Flory interaction parameter. M_{np} is the number-average molecular weight of the primary molecules incorporated into the gel fraction. This property cannot be measured; however, it may be calculated by using the model. M_c is the number-average molecular weight between crosslinks, d_2 and v_1 are the

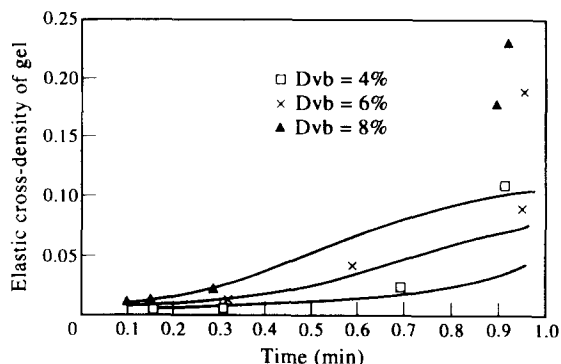


Figure 7 Crosslinking density versus time for various amounts of DVB at 70°C; BPO = 0.1 wt%: 4 wt% DVB ($c = 0.132$, $k_{cp} = 0.23$); 6 wt% DVB ($c = 0.099$, $k_{cp} = 0.23$); 8 wt% DVB ($c = 0.08$, $k_{cp} = 0.23$)

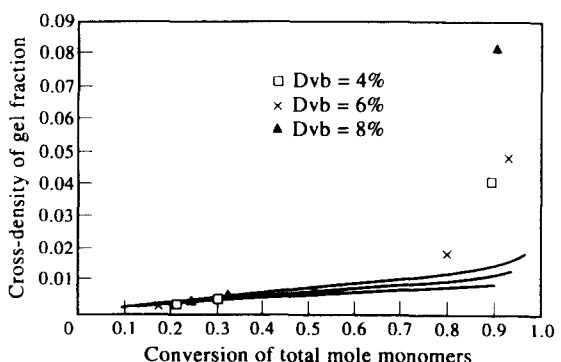


Figure 8 Crosslinking density versus time for various amounts of DVB at 80°C; BPO = 0.1 wt%: 4 wt% DVB ($c = 0.219$, $k_{cp} = 0.23$, $k_{cs} = 0.008$); 6 wt% DVB ($c = k_p^*/k_p = 0.205$, $k_{cp} = 0.23$, $k_{cs} = 0.04$); 8 wt% DVB ($c = 0.298$, $k_{cp} = 0.23$, $k_{cs} = 0.08$)

density of the polymer and the molar volume of the solvent, respectively, while z is an empirical constant and an indicator of physical crosslinkage in the gel, which actually increases with conversion. However, for our modelling purposes it was considered to be constant and equal to one²⁵. The parameter ζ_0 is the volume fraction of polymer which is formed, and can be replaced by the monomer conversion x , due to the low mole fraction of crosslinker in the system.

The elastic crosslinker densities as a function of time for the S/DVB system at different temperatures and crosslinker concentrations are shown in Figures 7–9. It is obvious from the results that the crosslinking density increases as both the temperature and the fraction of the monomer capable of forming crosslinks increase. The agreement of the experimental data with the calculated results at low conversion is satisfactory. However, the deviations at high conversions are appreciable. This may be attributed to the high physical crosslinkage density of tight gels at high conversion. The same deviation was also reported for the MMA–EGDMA system²⁵. The elastic crosslinking density in the sol fraction increases to a maximum value, and then abruptly decreases at a fixed temperature and crosslinker concentration.

The macromolecules which are formed in the initial stage of the polymerization are essentially linear. However, as the polymerization proceeds, more branched macromolecules are formed. Figure 10 shows

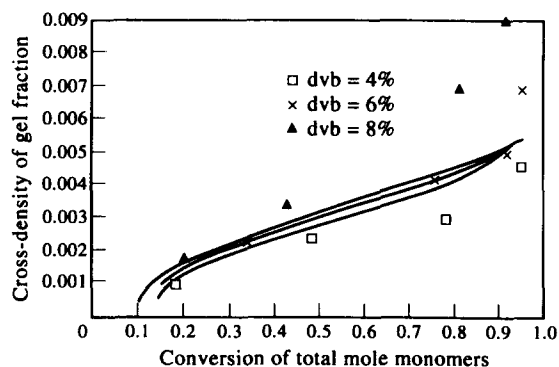


Figure 9 Crosslinking density versus time for various amounts of DVB at 90°C; BPO = 0.1 wt%: 4 wt% DVB ($c = 0.219$, $k_{cp} = 0.23$, $k_{cs} = 0.008$); 6 wt% DVB ($c = 0.205$, $k_{cp} = 0.23$, $k_{cs} = 0.04$); 8 wt% DVB ($c = 0.298$, $k_{cp} = 0.23$, $k_{cs} = 0.08$)

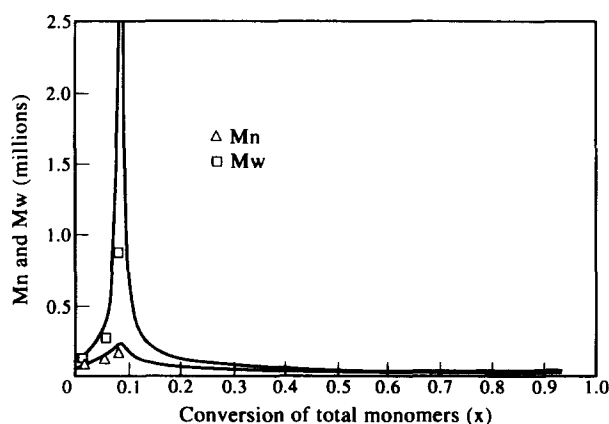


Figure 10 Molecular-weight development in sol fraction at 70°C; BPO = 0.1 wt%; DVB = 8 wt%

the variation of the molecular weight with time for a DVB content of 8 wt% at 70°C. No correction was made to the data for branching. It is apparent from the figure that M_w increases hyperbolically and becomes infinite at the gel point, whereas the M_n values fluctuate at around 50 000–100 000 in both the pre-gel and post-gel regions. The increasing amount of crosslinker caused the molecular weight at a given conversion to increase and the gel point to shift to a lower conversion.

CONCLUSIONS

A rather comprehensive set of experimental data on the kinetics of S/mixed-DVB crosslinking copolymerization has been reported. A study was made of the effects of DVB crosslinker concentration and temperature on the reaction rates, sol and gel formation, molecular weights at the initial stages of polymerization, and the network structure in S/DVB copolymerization. The reaction rates increase both with temperature and the level of crosslinker. The same effects were also observed for the pendant double-bond reactivities. The secondary cyclization was also found to increase with the temperature and the crosslinker content, although the effect of the latter was not fully understood. The kinetic model of Tobita and Hamielec which describes the network structure development during free-radical crosslinking copolymerization was fitted to the experimental data.

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