

# Free-radical crosslinking copolymerization of styrene and divinylbenzene: real time monitoring of the gel effect using fluorescence probe

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## Abstract

The steady-state fluorescence and dilatometric techniques were used to study the free-radical crosslinking copolymerization of styrene (S) and commercial divinylbenzene (DVB) in bulk. Pyrene (Py) was used as a fluorescence probe for the in situ polymerization experiments. The time required for a sudden increase in the fluorescence intensity of Py was recorded for various DVB content and temperature. The monomer conversions and the gel points were recorded by dilatometry. To interpret the experimental data, a kinetic model was developed for the S-DVB copolymerization system. It was shown that both the pendant vinyl groups and Py molecules are affected by the reaction medium in a similar way, their mobility decreases as the DVB concentration increases or the temperature decreases. The reaction time at which the Py intensity in the fluorescence spectra exhibits a sudden increase corresponds to the reaction time at which the rate of polymerization becomes maximum resulting from the gel effect. The results show that the fluorescence technique can be used to follow the onset of the gel effect in S-DVB copolymerization. © 1999 Elsevier Science Ltd. All rights reserved.

*Keywords:* Steady-state fluorescence technique; Free-radical crosslinking copolymerization; Gel effect

## 1. Introduction

Steady state fluorescence spectra of many chromophores are sensitive to the polarity of their environment. The interactions between the chromophore and the solvent molecules in the environment affect the energy difference between the ground and the excited states. This energy difference is called the Stokes shift, and depends on the refractive index and dielectric constant of the solvent. Recently, by measuring the Stokes shift of a polarity sensitive fluorescence molecule, the gelation during epoxy curing was monitored as a function of cure time [1]. Time-resolved and steady-state fluorescence techniques were employed to study isotactic polystyrene in its gel state. Excimer spectra were used to monitor the existence of two different conformations in the gel state of polystyrene. A pyrene derivative was used as a fluorescence molecule to monitor the polymerization, aging and drying of aluminosilicate gels. These results were interpreted in terms of the chemical changes

occurring during the sol–gel process and the interactions between the chromophores and the sol–gel matrix.

The gel effect also called the Trommsdorff effect in free-radical polymerization of vinyl monomers is a well-known phenomenon that is accompanied by an increase in both rate and degree of polymerization [2–4]. Analysis of the gel effect was the subject of continued investigations for many years. Methyl methacrylate (MMA) polymerization in bulk also shows a very pronounced gel effect caused by the diffusion control of the termination reaction [5]. This is a result of increased viscosity of the reaction solution of poly(methyl methacrylate) (PMMA) in MMA monomer. Thus, during the free-radical polymerization of MMA, the monomer conversion first increases only slightly but then it accelerates because of the gel effect. Compared to MMA, the diffusion control of the termination reactions and the resulting gel effect is less obvious in styrene polymerization [6].

Recently, we have shown that the quenching properties of the excited state of a fluorescing molecule can be used to measure the time for the onset of the gel effect and the corresponding activation energy in linear MMA polymerization [7]. However, using the same experimental technique in crosslinking copolymerization of MMA with ethylene glycol dimethacrylate (EGDM) as a crosslinker,

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we monitored, instead of the gel effect, the sol–gel transitions [8–10]. In the present work, we attempt to study the free-radical crosslinking copolymerization (FCC) of styrene (S) and commercial divinylbenzene (DVB) using both the steady state fluorescence and dilatometric techniques. Our aim was primarily to answer the question, which critical time, the time required for the onset of gelation or that for the onset of the gel effect, can be monitored using the steady-state fluorescence technique in S-DVB copolymerization. It was also of inherent interest to present new measurements on this classical FCC system, which will enable us to estimate the magnitude of non-idealities, such as the reactivity of pendant vinyl groups, depending on the reaction conditions.

The copolymerization reactions were carried out in bulk using the monomers S and commercial DVB, a mixture of *para* and *meta*-isomers of DVB and ethylstyrene, at various temperatures and with various amounts of DVB as the crosslinker. Benzoyl peroxide and pyrene (Py) were used as the initiator and the fluorescence probe for the in situ polymerization experiments, respectively. The monomer conversions up to the onset of gelation and the gel points were recorded by dilatometry, whereas the critical times required for a drastic increase in the fluorescence intensity of Py were monitored by the in situ fluorescence experiments. The experimental data obtained from both experimental techniques were organized and studied within the framework of a kinetic model developed for S-DVB copolymerization.

## 2. Theoretical considerations

### 2.1. Fluorescence method

Fluorescence and phosphorescence intensities of aromatic molecules are affected by both radiative and non-radiative processes [11]. Whereas the radiative probabilities are relatively independent of the environment and even of molecular species, non-radiative transitions are affected by the environmental effects [12]. The role of the solvent in such a picture is to add the quasi-continuum of states needed to satisfy energy resonance conditions. The solvent acts as an energy sink for rapid vibrational relaxation, which occurs after the rate limiting transition from the initial state.

Birks et al. studied the influence of solvent viscosity on fluorescence characteristics of pyrene (Py) solutions in various solvents and observed that the rate of monomer internal quenching is affected by solvent quality [13]. Kamioka et al. reported the solvent dependence of energy trapping in phenanthrene block polymers and explained the decrease in fluorescence yield with the static quenching, caused by the solvent induced trapping states [14]. As the temperature of the liquid solution is varied, the environment about the molecule changes and much of the change in absorption spectra and fluorescence yields in solution can

be related to the changes in solvent viscosity. A matrix that changes little with temperature will enable one to study molecular properties themselves without changing environmental influence. Poly(methyl methacrylate) (PMMA) was used as such a matrix in many studies [15]. Recently we have reported viscosity effects on low frequency, intramolecular vibrational energies of excited naphthalene in swollen PMMA latex particles [16]. In the present work, these properties of aromatic molecules were used to monitor the physical changes occurring during the free-radical crosslinking copolymerization of styrene and divinylbenzene.

### 2.2. Kinetic modeling of styrene-commercial divinylbenzene copolymerization

Although several theories of gel formation were developed in the past half century, kinetic approaches are widely used to describe the gel formation process in free-radical crosslinking copolymerization (FCC) [17–22]. This is mainly resulting from the fact that kinetic models take into account all the kinetic features of FCC and so offer a more realistic approach to the microscopic phenomena occurring during the free-radical polymerization reactions.

In the kinetic treatment that follows, we made the following assumptions: (i) steady-state approximation for the concentration of each radical species; (ii) cyclization and multiple crosslinking reactions occur at constant rates; (iii) commercial DVB consists of DVB isomers (*m*-DVB: *p*-DVB ratio = 3:1) and ethylstyrene. Resulting from the equal reactivity of the vinyl groups on ethylstyrene and styrene monomers [23], ethylstyrene is taken as styrene; (iv) both *meta* and *para* type pendant vinyl groups have equal reactivity; and (v) chain transfer reactions are dismissed from the kinetic treatment because of the very low transfer constant to the monomer and the absence of a polymerization solvent in our experiments.

S-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 centre, namely, those with S unit at the end ( $M_{1*}$ ), *m*-DVB or *p*-DVB units with one unreacted vinyl (pendant vinyl) at the end ( $M_{2'*}$  or  $M_{2''*}$ , respectively), and the 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 ( $k_{p1}$ ,  $k_{p2'}$ ,  $k_{p2''}$ ), crosslinking ( $k_{p3}$ ), and termination reactions ( $k_t^0$ ) are defined as follows:

$$k_{pi} = \sum_j k_{pji}x_j \quad (1a)$$

$$k_{tc}^0 = \sum_i \sum_j k_{tcij}x_i x_j \quad (1b)$$

$$k_{td}^0 = \sum_i \sum_j k_{tdij} x_i x_j \quad (1c)$$

$$k_t^0 = k_{tc}^0 + k_{td}^0 \quad (1d)$$

( $i, j = 1, 2', 2''$  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. However, termination rates of polymer radicals are diffusion controlled. Many models were proposed to calculate the diffusion controlled termination rate constant  $k_t$  during the linear and crosslinking polymerizations [24–33]. The resulting expressions involve, however, parameters which are not available for the present system. Tobita and Hamielec suggested the following empirical equations for the diffusion controlled termination in FCC [18,34]:

$$k_t = k_t^0 \text{ for } x < Z_2 \quad (1e)$$

$$k_t = k_t^0 \exp\{-Z_1(x - Z_2)\} \text{ for } x > Z_2 \quad (1f)$$

where  $x$  is the monomer conversion,  $Z_1$  and  $Z_2$  are adjustable parameters. As will be shown in the next section, the termination reactions in S-DVB copolymerization are chemically controlled prior to gelation. Thus, the parameter  $Z_2$  equals to the monomer conversion at the gel point  $x_c$ . However, the termination rate constant  $k_t$  becomes diffusion controlled beyond gelation in S-DVB copolymerization [35]. In Ref. [35], the parameter  $Z_1$  describing the variation of  $k_t$  with the monomer conversion  $x$  was evaluated by fitting Eq. (1f) to the experimental time-conversion data of the bulk S-DVB copolymerization system. Curve fitting results give  $Z_1 = 15 \pm 1$ , independent of the level of DVB (4%–8%) and on the polymerization temperature (70°C–90°C) [35]. We set  $Z_1 = 15$  in our simulations.

Applying Eqs. (1a)–(1f), one may derive the rate equations for the concentration of the initiator  $I$  and vinyl groups  $M_i$  as follows:

$$r_I = -k_d[I] \quad (2)$$

$$r_{M_i} = -k_{p1}[R^*][M_1] \quad (3)$$

$$r_{M_{2'}} = -2k_{p2'}[R^*][M_{2'}] \quad (4)$$

$$r_{M_{2''}} = -2k_{p2''}[R^*][M_{2''}] \quad (5)$$

$$r_{M_3} = (1 - k_{cyc})(k_{p2'}[M_{2'}] + k_{p2''}[M_{2''}])[R^*] \\ - (1 + k_{mc})k_{p3}[R^*][M_3] \quad (6)$$

where

$$[R^*] = (2fk_d[I]/k_t)^{0.5} \quad (7)$$

$f$  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.

In the characterization of gel forming systems, an important property is the distribution of molecular weights of polymer molecules. Let  $[P_r]$  be the concentration of polymer molecules composed of  $r$  structural units, normalization gives

$$Q_n = \sum_{r=1}^{\infty} r^n [P_r]$$

where  $Q_n$  is the  $n$ th moment of the polymer distribution ( $n = 0, 1, 2, \dots$ ). Using the rate equations for  $P_r$  given in Ref. 19, one obtains the following equations for the first and second moments of the polymer distribution in S-DVB copolymerization:

$$r_{Q_1} = (k_{p1}[M_1] + k_{p2'}[M_{2'}] + k_{p2''}[M_{2''}])[R^*] \quad (8)$$

$$r_{Q_2} = (2k_t + k_{tc})Y_1^2 \quad (9)$$

where

$$Y_1 = \left( k_{p1}[M_1] + k_{p2'}[M_{2'}] + k_{p2''}[M_{2''}] + k_{p3}[M_3]Q_2/Q_1 \right) / k_t \quad (10)$$

In a batch isothermal S-DVB copolymerization, the reaction volume  $V$  will also change during the reactions because of the differences in the densities of the monomer  $d_M$  (monomer densities are assumed to be equal) and the polymer  $d_P$ . If  $S$  represents the concentration of species  $I$ ,  $M_i$ , and the moments of the polymer distribution  $Q_n$ , a mass balance requires:

$$r_s = \frac{d(VS)}{Vdt} = \frac{dS}{dt} + \frac{S}{V} \frac{dV}{dt} \quad (11)$$

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

$$\frac{dV}{dt} = -\epsilon V \sum_i r_{M_i} \bar{V}_i \quad (i = 1, 2', \text{ and } 2'') \quad (12)$$

Table 1  
Kinetic constants and parameters for S-DVB copolymerization in bulk using benzoyl peroxide as an initiator

Constant	Reference
$k_d = 6.38 \times 10^{13} \text{ s}^{-1} \exp[-124.3 \text{ kJ mol}^{-1}/(\text{RT})]$	34
$k_{p11} = 2.4 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1} \exp[-37.5 \pm 1.6 \text{ kJ mol}^{-1}/(\text{RT})] = 176\text{--}560^a (343/60^\circ\text{C})^b; 266\text{--}818^a (480/70^\circ\text{C})^b; 393\text{--}1169^a (614/80^\circ\text{C})^b; 567\text{--}1637^a (944/90^\circ\text{C})^b$	39
$k_{ic11} = 1.26 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1} \exp[-7.03 \text{ kJ mol}^{-1}/(\text{RT})]$	34
$k_{id11} = 0$	34
$r_{12'} = 0.88$	40
$r_{12''} = 1.18$	40
$Z_1 = 15$	35
$d_M = 924\text{--}0.918(\text{T}-273)\text{gL}^{-1}$	6
$d_p = 1084.8\text{--}0.605(\text{T}-273)\text{gL}^{-1}$	6

<sup>a</sup> The range of  $k_{p11}$  from the Arrhenius equation of Ref. [39].

<sup>b</sup>  $k_{p11}$  value used in the simulation. Calculated from the initial rate of polymerization using the equation  $k_{p11} = (dx/dt)_0/[R^*]_0$ , where the subscript 0 means value at zero conversion.

where

$$\bar{V}_i$$

is the molar volume of the monomer with the vinyl group of type  $i$ , and  $\epsilon$  is the contraction factor, i.e.

$$\epsilon = 1 - d_M/d_p \quad (13)$$

Up to the onset of gelation, all molecules present in the S-DVB copolymerization system are finite. Thus, if the rate constants and the parameters are known, the mass balance equations of the kinetic model represented by Eq. (11) can be solved numerically 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:

$$\lim_{t \rightarrow t_c} Q_2 = \infty \quad (14)$$

where  $t_c$  is the time required for the onset of gelation. To predict the gel point, Eqs. (1a)–(10) can be solved until the condition of Eq. (14) is achieved. Beyond the gel point, Eqs. (1a)–(9) still hold giving the concentration of species as a function of the post-gelation time. The independent variable reaction time  $t$  can be replaced with the fractional monomer conversion  $x$  using the equation:

$$x = \frac{Q_1 V}{[M]_0 V_0} \quad (15)$$

where  $[M]_0$  and  $V_0$  represent initial concentration of the total monomers and the initial reaction volume, respectively.

### 3. Calculations

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.  $k_{p11} =$

$k_{p21} = k_{p31}$ ; (ii) previous experimental data indicates that the extent of cyclization and multiple crosslinking reactions during the bulk S-DVB copolymerization is small. Therefore, we assume  $k_{cyc} = k_{mc} = 0$ . It must be pointed out that the use of  $k_{cyc}$  and  $k_{mc}$  values reported in the literature for dilute polymerization systems [36–38] does not affect the result of the present study; (iii) the initiator efficiency is 0.5; and (iv) 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 60°C to 90°C.

The values of the kinetic constants and the parameters used in the calculations are collected in Table 1. It can be seen that all parameters are available in the literature with one exception, namely the rate constant of crosslinking reactions  $k_{p3}$ . Our previous work on MMA-EGDM copolymerization systems showed that  $k_{p3}$  is actually not a constant, but dependant on the reaction conditions [41,42]. Moreover, instead of the absolute value of  $k_{p3}$ , its relative value with respect to  $k_{p2'}$  and  $k_{p2''}$  is more informative for understanding the formation mechanism of polymer structure during FCC. Therefore, we define the unknown parameter of the model as the average pendant vinyl group reactivity,  $\bar{r}_{32}$ , which is the reactivity ratio of pendant vinyl to monomeric vinyl on DVB:

$$\bar{r}_{32} = \frac{k_{p3}}{k_{p2'}x_{M_2'} + k_{p2''}(1 - x_{M_2'})} \quad (16)$$

where  $x_{M_2'}$  is the mole fraction of  $m$ -DVB in the DVB isomer mixture. According to Eq. (16),  $\bar{r}_{32} = 1$  means that the reactivity of pendant vinyl groups for intermolecular reactions is equal to that of the monomeric vinyls, from which they are formed.

The equations of the kinetic model represented by Eq. (11) can be solved to predict the monomer conversions, the moments, and the gel points, if information concerning the reactivity of pendant vinyls  $\bar{r}_{32}$  for intermolecular links is available. In the present study, the question was reversed and one asks what  $\bar{r}_{32}$  would be in order to reproduce the experimental measured gel point data. In order to adjust the theoretical gel point to the experimental one, the parameter  $\bar{r}_{32}$  was varied until the calculated gel point becomes identical to the experimental. After finding  $\bar{r}_{32}$ , the whole conversion versus time histories with the gel effect included can be simulated and compared with the experimental data of the in situ polymerization experiments.

## 4. Experimental

### 4.1. Materials

Styrene (S, Merck) and commercial DVB (DVB, Merck) were shaken with 10% NaOH, washed with water, dried with anhydrous  $\text{CaCl}_2$ , and finally distilled under reduced pressure. Purity was checked by gas chromatography. Various batches of DVB solution were used. Batch analyses

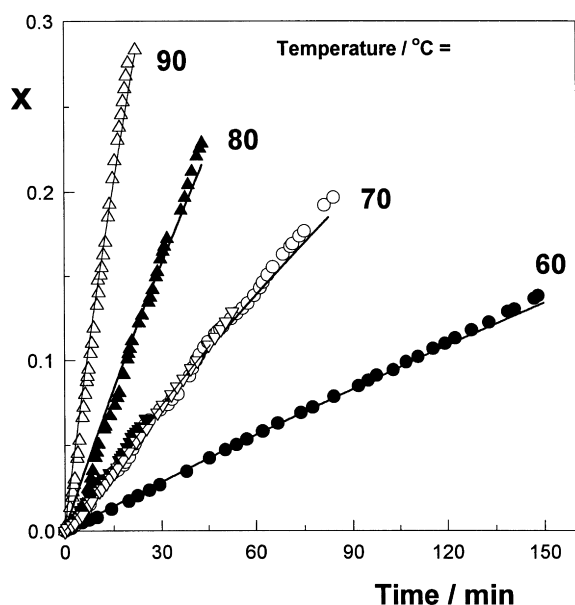


Fig. 1. Monomer conversion  $x$  versus time  $t$  histories in bulk S-DVB copolymerization up to the onset of gelation. The curves were calculated using the kinetic model and with the parameters listed in Table 1.  $[I]_0 = 0.100$  M. DVB = 1.6 mol%; temperature = 60 (●); 70 (○); 80 (▲); and 90°C (△). Temperature = 70°C; DVB = 1.6 (○); 3.2 (▽) and 8.3 mol% (▼).

ranged between 50%–60% DVB isomers (m-DVB: p-DVB ratio = 3–3.2:1), the rest being ethylstyrene. Benzoyl peroxide (BP, Merck) was recrystallized from acetone solution.

#### 4.2. Methods

The free-radical crosslinking copolymerization (FCC) of S and DVB was performed in bulk in the presence of BP as an initiator. The initiator concentration was held constant at  $[I]_0 = 0.100$  M. The reaction mixtures were prepared by dissolving BP in the selected S-DVB monomer mixture and flushing with nitrogen 10 min prior to polymerization. In this work, mainly two sets of FCC experiments were performed; in the first set, different DVB content in the range 0.8 to 12 mol% was used for each FCC experiment at a constant temperature (70°C). In the second experimental set, FCC reactions were performed separately at various temperatures between 60°C and 90°C for constant DVB content (1.6 mol%). In both sets of experiments gelation was monitored against the reaction time  $t$ .

Dilatometric and in situ steady state fluorescence techniques were used to monitor S-DVB copolymerization. The conversion of the monomers up to the onset of gelation and the gel points were followed by dilatometry. The dilatometers constructed in this laboratory consisted of a blown glass bulb, approximately 25 ml in volume connected to a 30 cm length of 1.5 mm precision-bore capillary tubing with a ground-glass joint. In our experiments, after the dilatometer was immersed in the thermostated tank, the reaction solution rose in the dilatometer capillary because of the thermal expansion of the solution. The zero reaction time

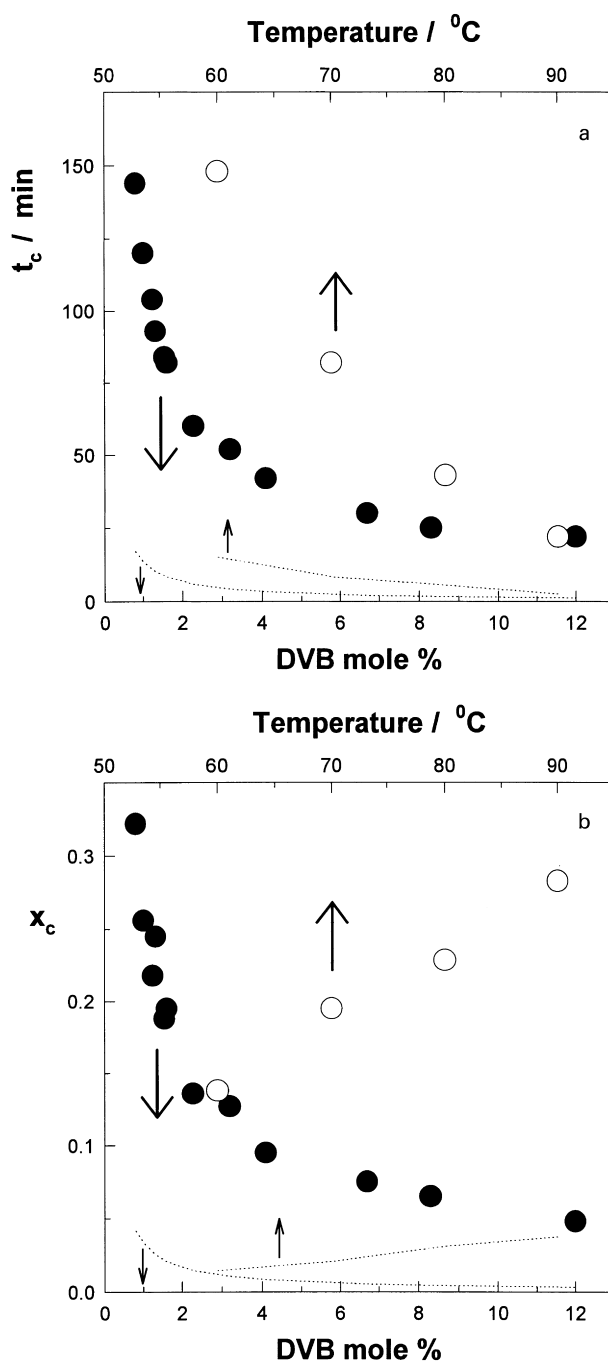


Fig. 2. Gel points in terms of the reaction time  $t_c$  (a) and monomer conversion  $x_c$  (b) shown as a function of the DVB content (●) and the polymerization temperature (○). The curves were calculated for equal reactivity of pendant vinyls and monomeric vinyls on DVB.

was taken as the time at which the solution in the capillary starts to drop. The meniscus of the polymerizing solution was measured throughout the experiment with a millimetric paper to 0.2 mm. The polymerization technique used was described in detail elsewhere [43]. The reproducibility of the kinetic data was checked by repeating the experiments. The deviation in the data points between two runs was always less than 3%. The non-isothermal condition during

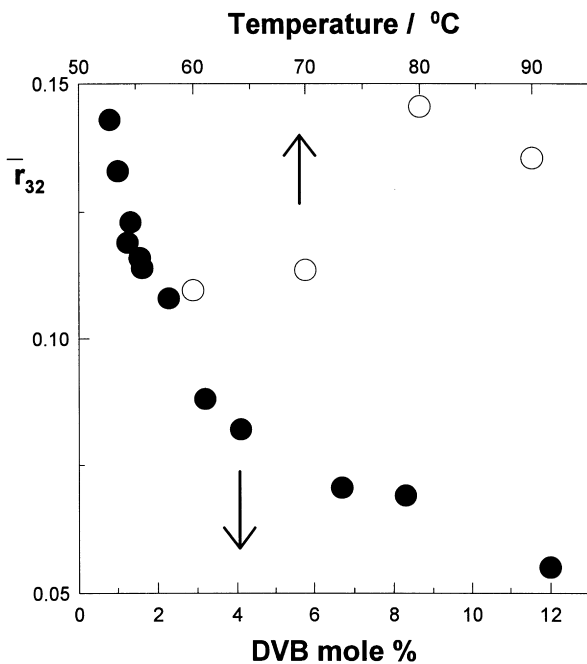


Fig. 3. Variation of the average reactivity ratio of pendant to monomeric vinyls for intermolecular reactions,  $\bar{r}_{32}$ , with the DVB content (●) and polymerization temperature (○).

the warm up period of the reaction solution must be mentioned as the main source of error in the dilatometric studies. For the gel point measurements, dilatometers containing a steel sphere of 4.8 mm diameter were used. The midpoint between the last time at which the sphere moves magnetically and that at which it stops moving is taken as the gel point. We reported previously the consistency in the gel points determined using dilatometric and gravimetric methods [42]. Standard deviations were 7%.

Pyrene (Py) was used as a fluorescence probe at  $10^{-4}$  M concentration for the in situ steady-state polymerization experiments, where styrene and mobile polymer chains act as an energy sink for the excited Py during polymerization. Later, the formation of bulk polystyrene provides an ideal, unchanged environment for the excited Py molecules. Naturally, from these experiments one may expect a substantial increase in fluorescence intensity,  $I$ , of Py at a certain time interval. For the fluorescence measurements, reaction mixtures were transferred into round glass tubes of 15 mm internal diameter and they were deoxygenated by bubbling nitrogen for 10 min. The copolymerization of S and DVB was performed in the fluorescence accessory of the spectrometer. The Py molecule was excited at 363 nm during the in situ experiments, and the variation in the fluorescence emission intensity,  $I$ , was monitored with the time-drive mode of the spectrometer, by staying at the 393 nm peak of the Py spectra. In situ steady-state fluorescence measurements were carried out using the Model LS-50 spectrometer of Perkin Elmer, equipped with a temperature controller. All measurements were made at  $90^\circ$  position and slit widths were kept at 7 mm.

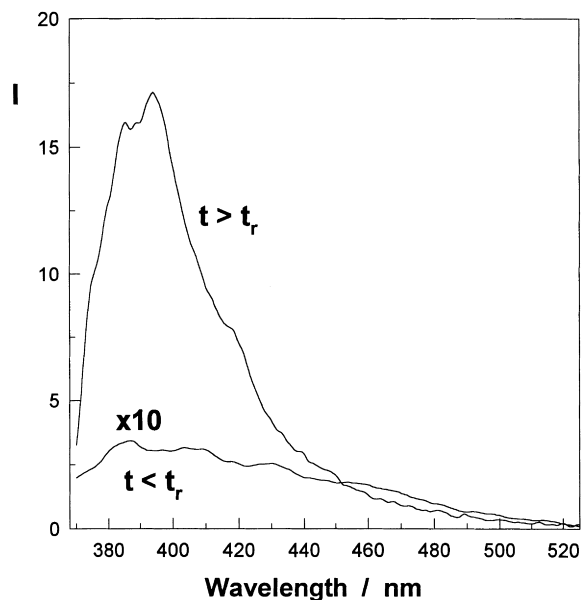


Fig. 4. A typical fluorescence emission spectra of Py before and after  $t_r$  in bulk free-radical copolymerization of S and DVB. Py molecules are excited at 363 nm.

## 5. Results and discussion

### 5.1. Gel points and the pendant vinyl group reactivity

Fig. 1 shows typical plots of fractional monomer conversion  $x$  versus time  $t$  up to the onset of gelation in S-DVB copolymerization. The experimental data from dilatometry were for various polymerization temperatures and DVB contents. The curves were calculated using the kinetic model with the parameters listed in Table 1. The predictions of the model are in good agreement with the experimental data. This indicates that, up to the gel point, the gel effect does not appear in bulk S-DVB copolymerization. Experimental determined gel points, in terms of both the reaction time,  $t_c$ , and monomer conversion,  $x_c$ , are shown in Fig. 2(a) and (b), respectively, plotted as a function of the DVB concentration (filled symbols) and the polymerization temperature (empty symbols). The expected inverse dependence of the gel point on crosslinker concentration is seen in the figures up to 12 mol% DVB content [37–44]. Experimental data also show the drastic dependence of the gel point on the polymerization temperature; at a given DVB content, gelation occurs at a lower conversion but, it requires a longer reaction time as the temperature of the experiment is decreased.

Using the experimental gel point data, the pendant vinyl group reactivity for intermolecular reactions can now be calculated. If one assumes equal reactivity of monomeric and pendant vinyls ( $\bar{r}_{32} = 1$ , i.e. no substitution effect), theory predicts the gel points shown in Fig. 2(a) and (b) as the dotted curves. It can be seen that gelation occurs

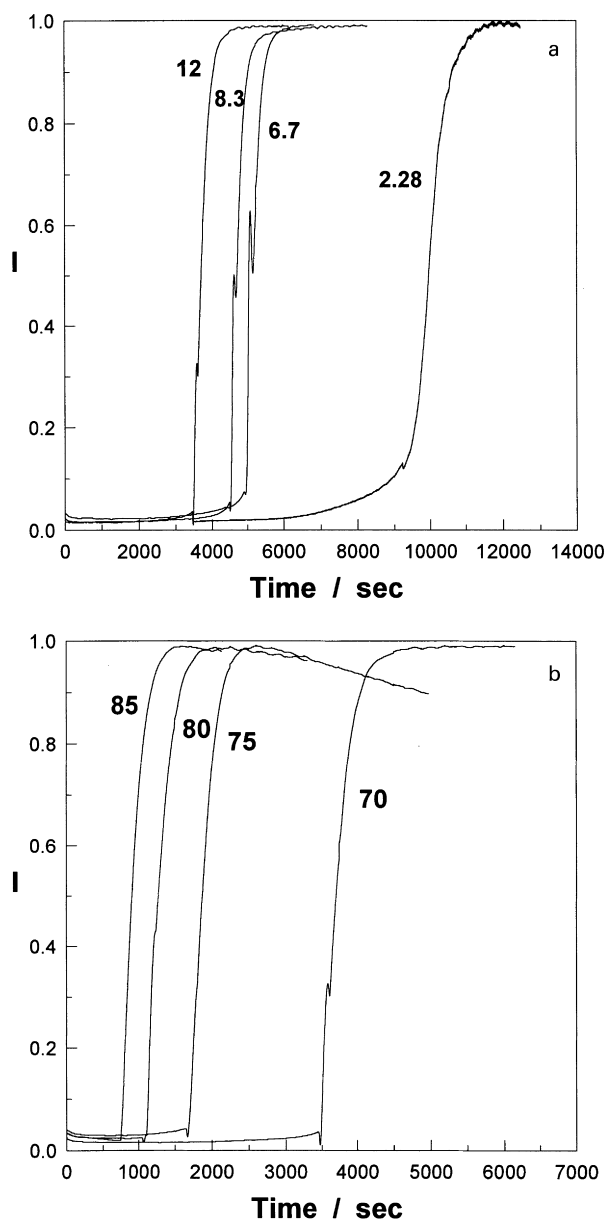


Fig. 5. Plots of smoothed Py fluorescence intensity  $I$  against reaction time  $t$  during S-DVB copolymerization in bulk at various DVB content (a) and temperature (b). Time drive mode of the spectrometer was employed and the maximum intensity peak at 393 nm was monitored for data collection. Numbers above the curves indicate the DVB contents in mol% (a) and the polymerization temperatures in °C (b), respectively.

much later than predicted for  $\bar{r}_{32} = 1$ . The kinetic model predicts the actual gel points if the reactivity ratio  $\bar{r}_{32}$  is much less than unity. The calculated  $\bar{r}_{32}$  values are plotted versus DVB content and temperature in Fig. 3. The pendant vinyl group reactivity for intermolecular links,  $\bar{r}_{32}$ , decreases as the DVB concentration increases or the temperature decreases. This decrease in the pendant vinyl group reactivity may predominantly be caused by a decrease in the mobility of polymer segments by increasing cross-linking or decreasing temperature.

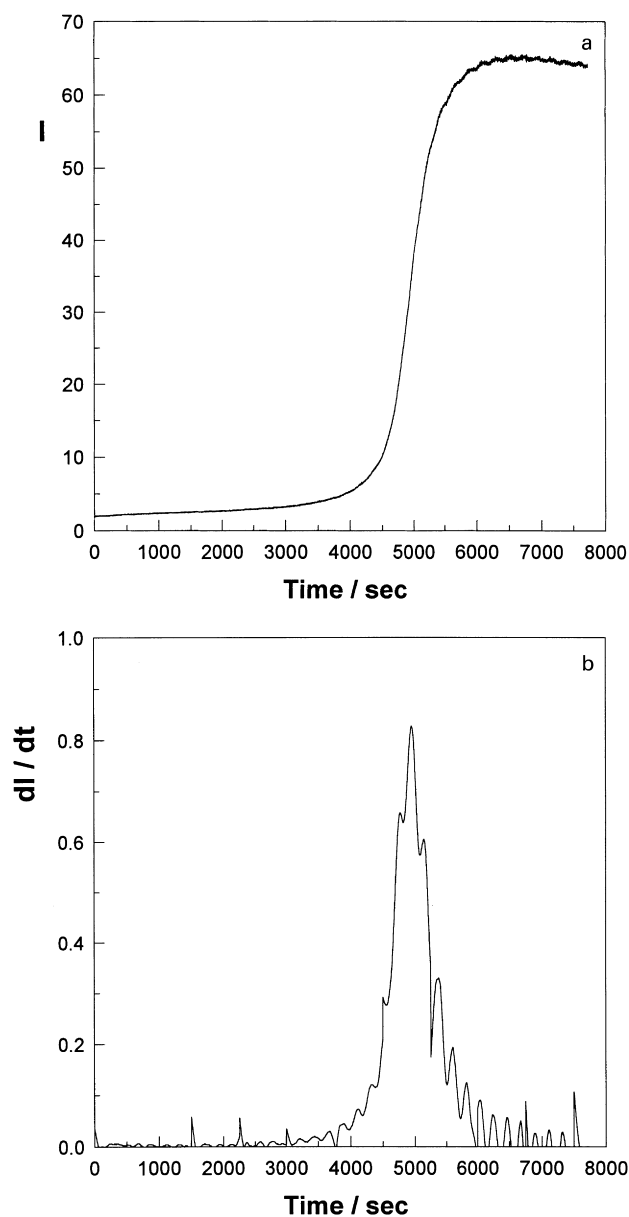


Fig. 6. Determination of  $t_r$  at 70°C. (a) Plot of Py fluorescence intensity  $I$ ; and (b) its first derivative  $dI/dt$  against the reaction time  $t$ . The maximum corresponds to  $t_r$  in  $t$  axis.

## 5.2. In situ fluorescence measurements

During the in situ polymerization experiments with Py as a fluorescence probe, no shift was observed in the wavelength of the maximum intensity of Py and all samples have kept their transparency during the polymerization process. Scattering light from the samples was also monitored during polymerization experiments and no serious variation was detected at 363 nm intensity.

In the experiments, we always observed a sudden increase in the fluorescence intensity of Py after crossing a critical time. Let  $t_r$  be the time needed for an abrupt increase in the Py intensity. In Fig. 4, typical Py spectra are shown before

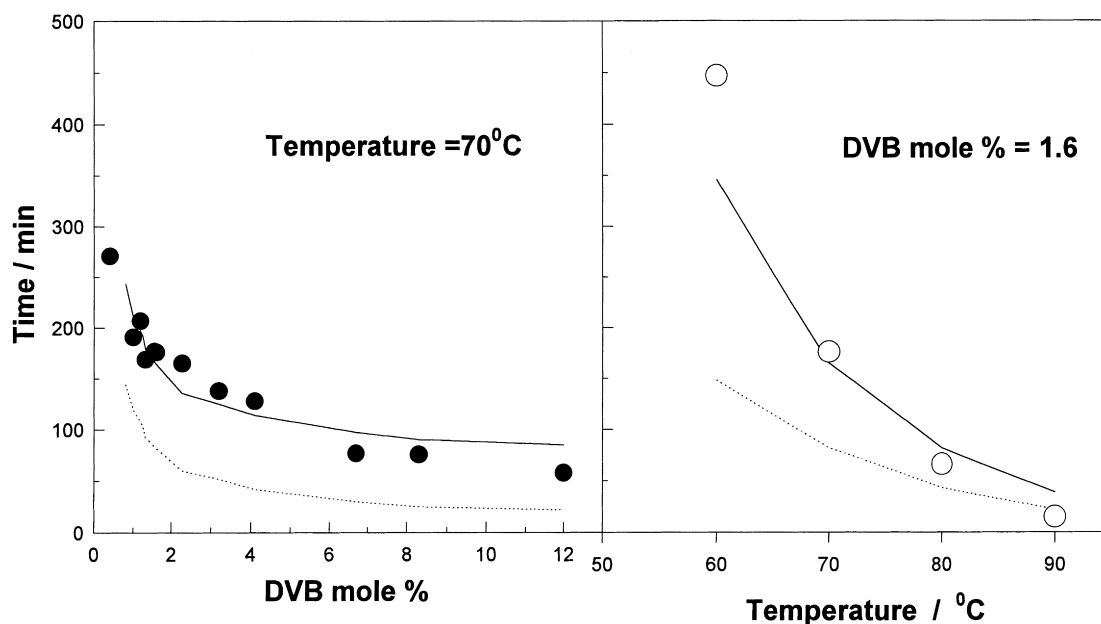


Fig. 7.  $t_r$  values shown as a function of the DVB content (●) and temperature (○). The dotted curves show the experimental gel points  $t_c$ . The solid curves were calculated from the inflection points of conversion versus time plots shown in Fig. 8(a).

and after the critical time  $t_r$ . Normalized Py intensities,  $I$  versus reaction times are plotted in Fig. 5(a) and (b) for various DVB content and temperature, respectively. It is seen that all curves present sudden increases at a given reaction time, and then reach an equilibrium at later times. Below  $t_r$ , since  $I$  presents small values, Py molecules are relatively free, they can interact and be quenched by other molecules. However, above  $t_r$ ,  $I$  gives large values indicating that the reaction mixture is highly viscous and Py molecules are trapped in a polystyrene network. According to Fig. 5(a) and (b), at low DVB content or at low temperature, the increase in  $I$  takes place at longer times, indicating that trapping of Py molecules in the reaction system is delayed. It is seen that both Py and pendant vinyl groups are affected by the reaction medium in a similar way, which we quantify these effects by  $\bar{r}_{32}$  and  $t_r$ , respectively.

The critical time  $t_r$  can be determined by taking the first derivative of the experimentally obtained  $I$  curve with respect to  $t$ . Fig. 6(a) and (b) present a typical intensity curve and its derivative ( $dI/dt$ ) against  $t$ , respectively. The maximum in the  $dI/dt$  curve corresponds to  $d^2I/dt^2$ , i.e. to the inflection point in curve  $I$ , which gives the  $t_r$  on the time axis. The  $t_r$  values obtained in this way are collected in Fig. 7 as symbols, plotted as a function of the DVB content and temperature. For comparison, the experimental gel point data,  $t_c$ , obtained by dilatometry are also included in the figure and shown as the dotted curves. One can see that  $t_r$  does not correspond to  $t_c$ . Py molecules are starting to be trapped in the rigid polymer environment much later than at the time of the sol–gel phase transitions. Thus, we can conclude that, in bulk S-DVB copolymerization, the fluorescence technique does not monitor the sol–gel transitions.

In order to quantify the above results, we simulated the

whole monomer conversion profiles of S-DVB copolymerization reactions using the kinetic model. The parameters in Table 1 together with the  $\bar{r}_{32}$  values calculated in the previous section were used for this simulation. Calculated monomer conversion  $x$  versus time  $t$  plots are shown in Fig. 8 for various DVB content. In Fig. 8(b), the calculated rates of polymerization ( $dx/dt$ ) are plotted as a function of the reaction time. The maxima of these curves correspond to the inflection points in  $x$  versus  $t$  curves. Similar calculations were also carried out for a fixed DVB content but for various polymerization temperatures. The reaction times at these inflection points are shown in Fig. 7 as the solid curves. Good agreement between theory and fluorescence experiments can be seen from the figure. This indicates that  $t_r$  in the fluorescence spectra corresponds to the reaction time at which the rate of S-DVB copolymerization reaches a maximum value.

## 6. Conclusions

A kinetic model for S-DVB copolymerization was developed and applied to the experimental data obtained using both dilatometric and in situ fluorescence techniques. It was shown that both the pendant vinyl groups and Py molecules are affected by the reaction medium in a similar way, their mobility decreases as the DVB concentration increases or the temperature decreases. The reaction time at which the Py intensity in the fluorescence spectra exhibits a sudden increase does not correspond to the gel point but it corresponds to the time for the onset of the gel effect. It was shown that the time at the inflection point in the Py intensity curve matches the reaction time at which the rate of



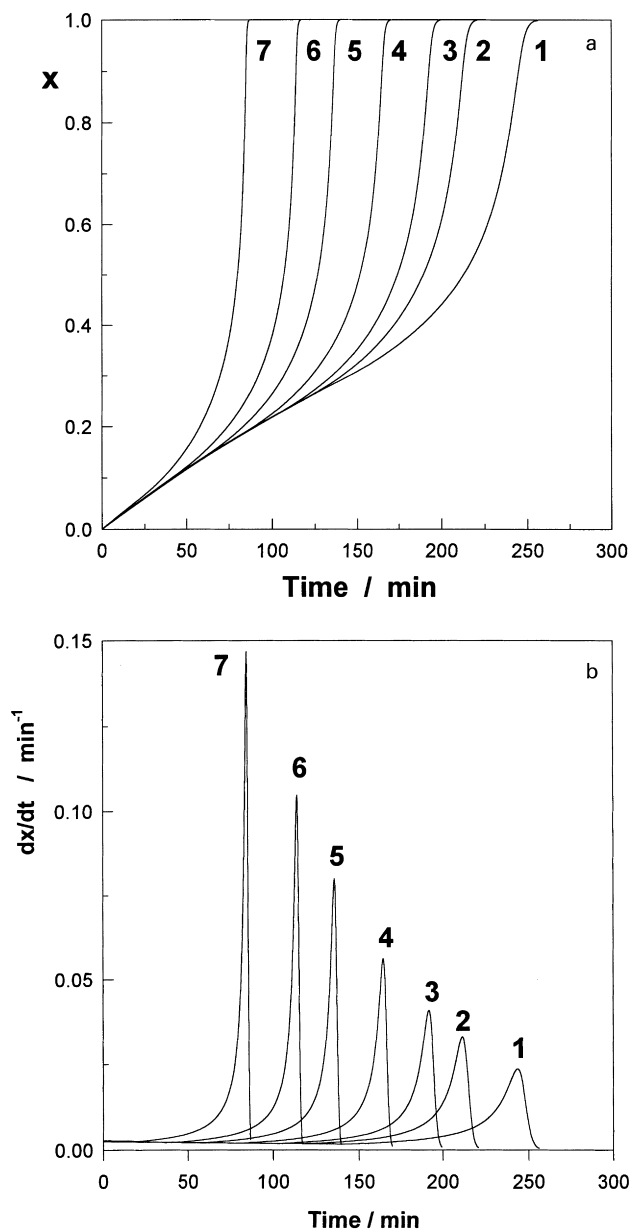


Fig. 8. Variation of (a) monomer conversion  $x$ ; and (b) rate of polymerization in  $\text{min}^{-1}$  ( $dx/dt$ ) with the reaction time  $t$  in FCC of S and DVB in bulk at various DVB contents. The calculations were using the kinetic model and with the parameters listed in Table 1. The maxima in (b) gives the theoretical  $t_r$  values from which the theoretical curve in Fig. 7 was derived. Temperature =  $70^\circ\text{C}$ ;  $[I]_0 = 0.100 \text{ M}$ ; DVB = 0.8 (1), 1 (2), 1.25 (3), 1.61 (4), 2.28 (5), 4.1 (6), and 12 mol% (7).

polymerization becomes maximum because of the gel effect. At present, the kinetics of diffusion controlled termination reactions in FCC are not fully understood. The technique introduced here provides a simple experimental tool to monitor these reactions.

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