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# Propagation and termination kinetics in high conversion free radical co-polymerization of styrene/divinylbenzene investigated by electron spin resonance and Fourier-transform near-infrared spectroscopy

Per B. Zetterlund*, Hirotomo Yamazoe, Bunichiro Yamada*

*Department of Applied Chemistry, Graduate School of Engineering, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan*

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## Abstract

The bulk co-polymerization of styrene (St) and divinylbenzene (DVB; 0–0.20 M) has been monitored by electron spin resonance and FT near infrared spectroscopy to high conversion at 70 °C. The molecular weight and polydispersity started to increase at lower conversion than the radical concentration and the rate of polymerization, indicating that a significant fraction of pendant unsaturations had reacted at the onset of the gel-effect. The propagation rate coefficient ($k_p$) remained approximately constant until 80% conversion for all DVB contents, where it fell dramatically. The values of $k_t$ exhibited an initial plateau region, then decreased by approximately two orders of magnitude between approximately 20 and 60% conversion. The decrease was more significant, and the onset of the decrease occurred at lower conversion, with increasing DVB content. At very high conversion levels ($>80\%$), both $k_p$ and $k_t$ decreased with increasing DVB content at a given conversion, consistent with reaction diffusion being the dominant termination mechanism. © 2002 Published by Elsevier Science Ltd.

*Keywords:* Propagation rate coefficient; Reaction diffusion; Cross-linking

## 1. Introduction

The quantification of propagation ($k_p$) and termination rate coefficients ($k_t$) in free-radical polymerization by means of electron spin resonance (ESR) [1] and pulsed-laser polymerization (PLP) techniques [2,3] has seen significant progress in recent years [4]. However, investigations focusing on the middle and high conversion ranges still remain relatively scarce, especially for cross-linking systems. The ESR method is based on direct quantification of the propagating radical concentration, and may be employed over the entire conversion range with the additional advantage of being applicable to cross-linking systems. The information available on $k_p$ and $k_t$ as functions of conversion in cross-linking free-radical polymerization systems has been obtained mainly from ESR data [5–9] and conversion measurements of photo-polymerizations combining steady state and non-steady state conditions to decouple $k_p$ and $k_t$ [10–14].

The development of the polymer network in cross-linking free radical polymerizations involving monovinyl and divinyl compounds proceeds in a non-ideal manner [15–18], deviating from the classical Flory–Stockmeyer theory [19,20] due to intramolecular cyclization, reduced reactivity of pendant unsaturations, intramolecular cross-linking and microgelation [15]. There is considerable evidence that the reactivity of vinyl groups decreases upon incorporation in the polymer network [17,18,21–23]. In the co-polymerization of styrene (St) and divinylbenzene (DVB), the ratio of the reactivity of pendant to monomer vinyls has been reported to decrease with increasing DVB content. During the bulk polymerization of St and methyl methacrylate (MMA), the value of $k_p$ has been shown to remain close to constant up to approximately 75% conversion, where it falls dramatically [24–27]. In the case of cross-linking systems, $k_p$ often starts to decrease at lower conversions depending on the cross-linking density as a result of lower rates of monomer diffusion in a cross-linked matrix [9–14].

It is generally believed that termination is usually

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* Corresponding authors. Tel./fax: +81-6-6605-2189/2797.
*E-mail addresses:* pbzetterlund@a-chem.eng.osaka-cu.ac.jp (P.B. Zetterlund),
yamada@a-chem.eng.osaka-cu.ac.jp (B. Yamada).

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diffusion controlled from zero conversion onwards [2, 28–30] except for sterically hindered monomers [31,32], exhibits chain-length dependence in the conversion range where the rate determining step is translational diffusion [28,33,34], and that reaction diffusion becomes the dominant reaction mechanism when the chains become sufficiently immobile [29,35–37]. The conversion dependence of $k_t$ up to intermediate conversion levels in cross-linking polymerizations has been addressed in several studies mainly for methacrylate based systems [6,9,11,13]. ESR studies of radical decay at conversion levels close to the limiting conversion have shown that higher cross-link density leads to a reduction in $k_t$ for MMA/dimethacrylate polymerization [5,8]. It has been reported that in the polymerization of MMA [25], in the co-polymerization of MMA and ethylene glycol dimethacrylate (EGDMA) [8] and for various dimethacrylates [5], $k_t$ decreases with time during the after-effect. The origin has been proposed to be physical trapping in the polymer network [5,8,38] or ‘short-long’ termination in an entangled system [39].

The co-polymerization of St and DVB is widely employed for the preparation of cross-linked co-polymer gels for applications such as size exclusion chromatography and ion exchange resins. Although the St/DVB system has been extensively investigated over the years [16,21,23,30, 40–42], the absolute values and conversion-dependences of $k_p$ and $k_t$ have not been experimentally determined for any cross-linking co-polymerization involving St. In our previous papers [26,43], extensive kinetic analysis of the bulk polymerization of St up to the limiting conversion was carried out by gel permeation chromatography (GPC), FT-NIR and ESR spectroscopy. In particular, it was revealed that the initiator concentration affects both $k_p$ and $k_t$ in the very highest conversion range, and the mechanistic implications were discussed with regards to termination by reaction diffusion. The current paper deals with the kinetic aspects of the co-polymerization of St in the presence of small amounts of DVB to high conversion, and compares the results with those obtained for the homopolymerization of St by considering the effects of the introduction of cross-links on monomer and macroradical mobility [26,43].

## 2. Experimental

### 2.1. Materials

Commercially available St and DVB were purified by distillation under reduced pressure before use. DVB consisted of the *p*- and *m*-isomers of DVB (50.8%) and ethyl styrene (49.2%) according to $^1$H NMR analysis. The initiator dimethyl 2,2′-azobisisobutyrate (MAIB) was purified by recrystallization from *n*-hexane.

### 2.2. Methods

Polymerizations were carried out in bulk St containing 0.05, 0.10 and 0.20 M DVB initiated by 0.10 M MAIB at 70 °C. Samples for molecular weight analysis in the pre-gel region were obtained by polymerization in vacuum-sealed glass ampoules after repeated freeze-thawing. The polymer was precipitated in a large amount of methanol, and isolated by filtration. The conversion range within which gelation occurred was determined by observing when cross-linked polymer was formed. Molecular weights were measured on a Tosoh-800 series HPLC equipped with GPC columns calibrated against polystyrene standards.

Conversion as a function of time was measured by use of FT-NIR spectroscopy, carried out using a Jasco INT-400 Spectrometer equipped with a MCT detector in 5 mm o.d. Pyrex tubes in a custom-made aluminum furnace maintained at 70 °C. The consumption of St was monitored by the absorbance at 6150 cm$^{-1}$, which has been assigned to the overtone absorption of $\nu_{C=C-H}$.

The free radical concentration was determined by ESR spectroscopy during polymerization in a 5 mm o.d. quartz ampoule sealed under vacuum after several freeze-thaw cycles. 2,2,6,6-Tetra methyl piperidinyl-1-oxyl in benzene was employed for calibration of the relationship between ESR spectral signal intensity and free radical concentration. It has been established that due to the non-polar nature of St and polystyrene, the ESR sensitivity remains constant over the entire conversion range [1,44].

The temperature of the polymerization mixture was measured in specially designed glass ampoules of o.d. 18 mm with a 3 mm wide thermometer in a glass jacket located in the center of the ampoule [26] using 0.01, 0.02, 0.05, 0.10, 0.20 M DVB in bulk St.

## 3. Results and discussion

### 3.1. Rate of polymerization and final conversion

The conversion-time data show that the rate of polymerization ($R_p$) is approximately independent of the DVB concentration up to around 20% conversion (Fig. 1). The extent of reaction undergone by pendant unsaturations, which are present in much lower concentration than monomer, is insufficient to affect $R_p$ via the formation of branched and cross-linked structures. A gradual increase in $R_p$ can be observed when the gel-effect [30,45] sets in as the conversion goes beyond 20%. The gel-effect starts at lower conversion and becomes more pronounced with increasing DVB content resulting from increased restriction of chain mobility. The maximum $R_p$ increases with DVB content, but is reached at approximately 70% conversion for all DVB contents. Shortly after the maximum has been reached, $R_p$ decreases relatively abruptly at approximately 85% conversion at all DVB contents.

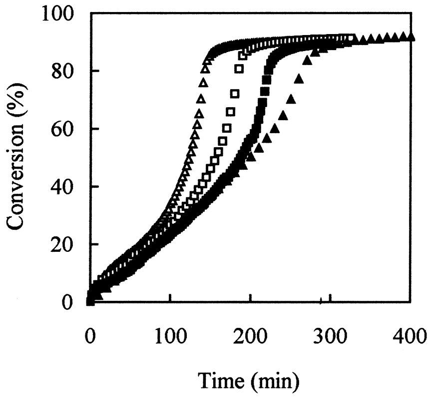

Fig. 1. Conversion-time plots for the co-polymerization of St and DVB initiated with 0.10 M MAIB at 70 °C. $[DVB]_0 = 0.20$ (△), 0.10 (□), 0.05 (■) and 0 (▲) M.

The final level of conversion was not significantly affected by the DVB content (including when $[DVB]_0 = 0$ M). The same observation has been made previously by gravimetric means for slightly higher DVB contents than in the present study (4, 6 and 8 wt%) in the temperature range 70–90 °C [23]. The limiting conversion for the co-polymerization of MMA/EGDMA has been reported to decrease as the EGDMA content was increased from 0 to 100% [8]. However, within the more narrow range of 0–25 wt% EGDMA, no systematic trend in the final conversion with monomer feed could be found [46].

### 3.2. Free radical concentrations

The free radical concentration as a function of conversion for different contents of DVB are depicted in Fig. 2. The radical concentrations remain approximately constant and independent of the DVB content up to about 20% conversion, as was the case for $R_p$. As the conversion increases further, the radical concentrations begin to gradually increase. This can be explained by considering the dependence of $k_t$ on conversion, and the fact that a matrix with higher cross-link density (i.e. higher DVB content) would be expected to result in higher diffusion resistance for propagating radicals, thereby reducing $k_t$ and causing the radical concentration to rise. The DVB containing samples reach a maximum in the radical concentration at approximately 70% conversion, coinciding with the maximum in $R_p$. After the maximum, the radical concentration once again increases as the final conversion is approached. A detailed analysis of the conversion dependence of $k_t$, which largely determines the free radical concentration profiles in combination with the initiator efficiency ($f$), will be presented later in this paper.

### 3.3. Gel-effect

The conversion at the gel-point decreased with increasing DVB concentration as has been well established for

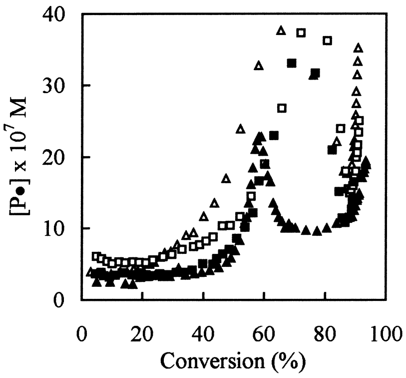

Fig. 2. Free radical concentration versus conversion (polymerization conditions as in Fig. 1). $[DVB]_0 = 0.20$ (△), 0.10 (□), 0.05 (■) and 0 (▲) M.

St/DVB and other free radical cross-linking systems [15,30,47]. Gelation occurred in the conversion ranges of 38–45, 16–23 and 8–15% for $[DVB]_0 = 0.05$, 0.10 and 0.20 M, respectively. The values of $M_n$ and $M_w/M_n$ in the pre-gel stage increased with conversion for all samples containing DVB, whereas both $M_n$ and $M_w/M_n$ remained close to constant for the homopolymerization of St up to at least 30% conversion (Fig. 3). The increase with conversion in $M_n$ and $M_w/M_n$ in the co-polymerization of St/DVB can be ascribed to the gel-effect and/or the reaction of the pendant vinyl groups of the primary chains resulting in branched, and eventually cross-linked structures. It is no trivial task to experimentally define the onset of the gel-effect, and several different ways have been proposed [48]. We have here chosen to define the onset as the conversion at which the increase in the free radical concentration leading up to the maximum begins. This is consistent with an earlier definition as the conversion where the polymerization kinetics begin to deviate from the classical steady state expression for $R_p$ [48]. According to this definition, the gel-effect begins at the approximate conversion levels of 43, 32, 24 and 17% (for $[DVB]_0 = 0$, 0.05, 0.10 and 0.20 M, respectively), roughly correlating with the increase in $R_p$ (Fig. 1). The free radical concentrations thus begin to

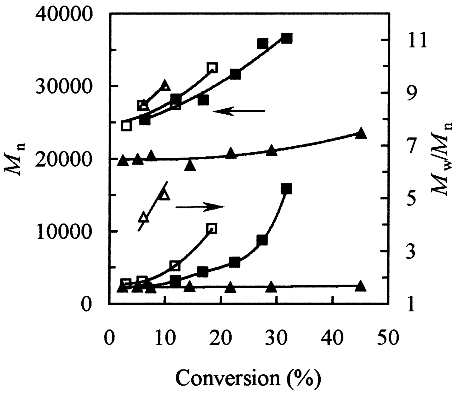

Fig. 3. $M_n$ and $M_n/M_w$ versus conversion in the pre-gel region (polymerization conditions as in Fig. 1). $[DVB]_0 = 0.20$ (△), 0.10 (□), 0.05 (■) and 0 (▲) M.

increase during or just after the conversion range when gelation occurs for $[\mathrm{DVB}]_0 = 0.20$ and 0.10 M, and slightly before gelation in the case of $[\mathrm{DVB}]_0 = 0.05$ M. The increases in $M_n$ and $M_w/M_n$ that occur before the onset of the gel-effect can thus be attributed to reaction of pendant groups leading to branched polymer. Higher DVB contents result in a more significant increase in both $M_n$ and $M_w/M_n$ as a consequence of an increased number of reacting pendant groups per primary chain (Fig. 3). The $M_n$ of the polymer formed in the limit of 0% conversion was estimated by extrapolation to be approximately 22,000 for all DVB concentrations investigated. This molecular weight corresponds to primary chains with all pendant groups remaining unreacted, and the value agrees with that of the homopolymerization of St.

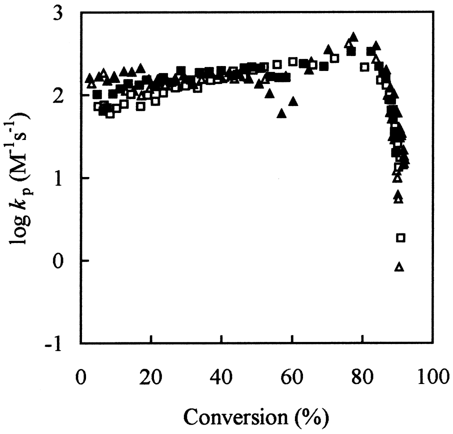

Fig. 4. Propagation rate coefficient ($k_p$) versus conversion (polymerization conditions as in Fig. 1). $[\mathrm{DVB}]_0 = 0.20$ (△), 0.10 (□), 0.05 (■) and 0 (▲) M.

### 3.4. Propagation rate coefficient

The initial reaction mixture contains four different types of polymerizable double bonds; *m*-DVB, *p*-DVB, ethyl styrene and St. As the polymerization proceeds, there will be an even greater number of different double bonds present as various macromolecular structures containing pendant unsaturations are formed. The overall propagation rate coefficient can be expressed in terms of the total concentrations of polymerizable double bonds ([M]) and propagating radical species ($[\mathrm{P}^\cdot]$) and $R_p$ according to Eq. (1):

$$k_p = \frac{R_p}{[\mathrm{P}^\cdot][\mathrm{M}]} \tag{1}$$

Since [M], $[\mathrm{P}^\cdot]$ and $R_p$ have been obtained as functions of conversion from ESR and FT-NIR data, $k_p$ can be estimated over the entire conversion range. The value obtained for $k_p$ in this manner represents some average value containing contributions from the different types of propagation reactions occurring. The values of $k_p$ as a function of conversion for different DVB concentrations are displayed in Fig. 4.

The minimum and maximum values of $k_p$ that appear in the homopolymerization of St have been discussed previously [26], and is believed to be related to slightly different conversion levels at a given reaction time during the ESR and FT-NIR measurements, originating from differences in heat transfer characteristics between the two experiments [49,50]. It can also be seen that the values obtained for $k_p$ for the DVB-containing samples in fact increase from 0 to 80% conversion. This is also believed to have its origin in non-isothermal conditions due to inefficient heat transfer [26,49,50]. The temperature as a function of time was measured in separate experiments during polymerization in specially designed glass ampoules [26], revealing a significant temperature rise with its maximum value close to the maximum in $R_p$ and the free radical concentration (Fig. 5). The increase was as large as 30 °C for the highest DVB concentration. However, since the surface/volume ratio of the reaction mass was considerably lower in the experiments where the temperature was measured, the detected temperature increase will exceed that of the ESR and FT-NIR experiments [26,49,50]. Nonetheless, according to the IUPAC recommended Arrhenius parameters for $k_p$ of St [51], the increase in $k_p$ obtained in Fig. 4 corresponds to a temperature increase that is of similar magnitude as that recorded.

The value of $k_p$ falls dramatically by several orders of magnitude at approximately 80% conversion. It appears as if the propagation step remains under chemical control and is not diffusion-controlled even at conversion levels considerably higher than the gel-point, which occurred at approximately 8–15% conversion for the sample with the highest DVB content. The effect of increasing the DVB content on $k_p$ within the concentration range investigated here (including the homopolymerization of St) is relatively small over the entire conversion range, in agreement with findings by Carswell et al. [9] at low conversion for MMA containing small amounts of EGDMA (< 10%). This

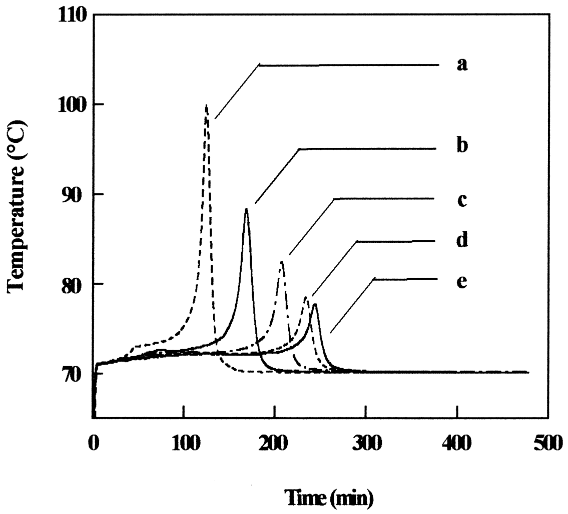

Fig. 5. Temperature as a function of time during the co-polymerization of St and DVB initiated with MAIB at 70 °C. $[\mathrm{DVB}]_0 = 0.20$ M (a), 0.10 M (b), 0.05 M (c), 0.02 M (d) and 0.01 M (e).

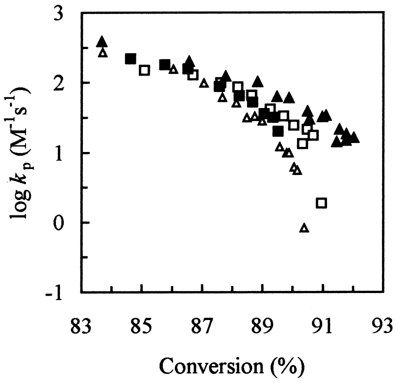

Fig. 6. Propagation rate coefficient ($k_p$) versus conversion at high conversion (polymerization conditions as in Fig. 1). $[DVB]_0 = 0.20$(△), 0.10 (□), 0.05 (■) and 0 (▲) M.

suggests that the differences in $R_p$ between the samples (Fig. 1) are mainly caused by different termination kinetics as reflected in the free radical concentrations, which increase substantially with increasing DVB content (Fig. 2). The point at 80% conversion, where the drastic decrease in $k_p$ commences is where the propagation reaction becomes diffusion controlled as a result of the continuous increase in viscosity with increasing conversion [26]. At very high conversion levels the system may undergo vitrification, i.e. the system becomes glassy as the glass transition temperature exceeds the reaction temperature. Examination of the highest conversion range (Fig. 6) reveals that $k_p$ increases with decreasing DVB content at a given conversion level. At 90% conversion, the $k_p$ value for the homopolymerization of St is approximately one order of magnitude greater than for the sample containing 0.20 M DVB. This is likely to be a direct result of higher cross-link densities leading to lower rates of monomer diffusion.

### 3.5. Termination rate coefficient and initiator efficiency

The propagating radical concentrations versus time obtained from ESR measurements for different DVB contents are displayed in Fig. 7. Under the current experimental conditions, $d[P^\cdot]/dt \ll 2fk_d[I]_0 \exp(-k_d t)$ ($k_d$ is the rate constant for initiator decomposition and $[I]_0$ is the initial initiator concentration), and thus the ratio $k_t/f$ can be obtained as a function of time (or coupled with FT-NIR data, the conversion dependence) from Eq. (2):

$$\frac{k_t}{f} = \frac{k_d[I]_0 \exp(-k_d t)}{[P^\cdot]^2} \tag{2}$$

It follows that the propagating radical concentration is given by Eq. (3):

$$[P^\cdot] = \left(\frac{f}{k_t}\right)^{1/2} (k_d[I]_0 \exp(-k_d t))^{1/2} \tag{3}$$

The change in the term $(k_d[I]_0 \exp(-k_d t))^{1/2}$ over the course of the polymerization was small compared to that measured for $[P^\cdot]$ (the term $(k_d[I]_0 \exp(-k_d t))^{1/2}$, calculated using a literature value of $k_d$ [52], decreased by approximately 65% in 1200 min), and thus the time-dependence of $[P^\cdot]$ can be ascribed mainly to changes in the ratio $f/k_t$. The general increase in the free radical concentration that is observed with time is thus caused by the relative decrease in $k_t$ being greater than the relative decrease in $f$. The pronounced maximum occurring at all DVB contents, which coincides with the maximum in $R_p$, is a result of the balance between the relative rates of decrease of $k_t$ and $f$ with increasing conversion [26,43]. After the maximum has been reached, the relative rate of decrease in $f$ is greater than that of $k_t$, thus causing a maximum as opposed to a continuous increase in radical concentration. In the case of an initial concentration of DVB of 0.10 and 0.20 M, the radical concentration at the maximum was about ten times higher than at the initial stage of the polymerization. Similar maxima have been observed for other linear and cross-linking systems such as the bulk polymerizations of St [43], MMA [7] and MMA/EDGMA [7].

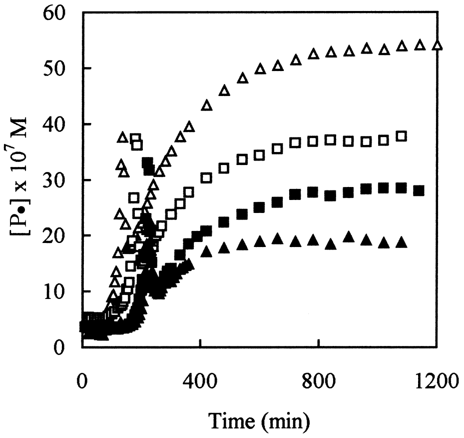

Fig. 7. Free radical concentration versus time (polymerization conditions as in Fig. 1). $[DVB]_0 = 0.20$ (△), 0.10 (□), 0.05 (■) and 0 (▲) M.

The radical concentration at the maximum appears to reach a limiting value at $[DVB]_0 \approx 0.10$ M (Fig. 8). This observation may be rationalized by considering that the value at the peak will be strongly influenced by the conversion level at which $f$ starts to decrease more rapidly than $k_t$. Assuming that the value of $k_t$ decreases with increasing DVB content at a given conversion level, the fact that the free radical concentration at the peak appears to reach a maximum suggests that $f$ starts to decrease more rapidly than $k_t$ at a somewhat lower conversion at higher $[DVB]_0$, otherwise the increase in radical concentration at the peak with $[DVB]_0$ would not be expected to level off.

As the limiting conversion is approached, the free radical concentration keeps increasing and finally reaches a plateau value. The final level of radical concentration at long reaction times increases steadily with increasing DVB content; the increase compared to $[DVB]_0 = 0$ M is linear with $[DVB]_0$ (Fig. 8). This suggests that at these high conversion levels, the gradual relative reduction in $k_t$ with increasing cross-link density is greater than that in $f$.

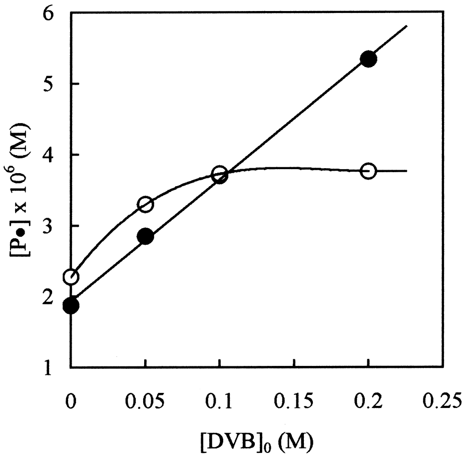

Fig. 8. Free radical concentration at the maximum point (○) and at the final level of conversion (●) as function of DVB content.

Coupled with the fact that $f$ is known to be very low at these high conversion levels [43,53,54], it is apparent that termination is extremely slow. It has been shown previously by ESR measurements that propagating radicals exhibit extremely long life-times at high conversion in cross-linking [5,8] and also in linear polymerizations of St [24,43].

The value of $k_t/f$ as a function of conversion, obtained from Eq. (2) using a literature value for $k_d$ [52], is displayed in Fig. 9 for various DVB contents. The quantity $k_t/f$ decreases approximately two orders of magnitude during the course of the polymerization. The sharp maxima in the radical concentration versus time plots correspond to the minima in the $k_t/f$ plots. From zero to approximately 20% conversion, the value of $k_t/f$ remains close to constant for all DVB contents investigated. The most striking differences between the samples can be found in the medium conversion range of 20–60%, where a clear trend with DVB content can be observed. Between 20 and 60% conversion, the values of $k_t/f$ decrease by almost two orders of magnitude. Hill et al. [6] reported that the initiator efficiency for the initiator *tert*-butyl peroxy-2-ethyl hexanoate during the cross-linking polymerization of siloxane modified DVB prepolymers and DVB at 70 °C decreased by less than 50% as the monomer conversion increased from zero to 70%, at which point the initiator efficiency fell dramatically. Their results suggest that the decrease in $k_t/f$ observed here over the conversion range of 20–60% mainly has its origin in changes in $k_t$. A clear trend with DVB content is also evident in the very highest conversion range of above 85% (Fig. 10); at approximately 91% conversion, $k_t/f$ decreases by a factor of six as [DVB]$_0$ is increased from 0 to 0.20 M.

Although it is possible to make certain assumptions regarding the relative contributions of $k_t$ and $f$ to the trends observed in Figs. 9 and 10, it is difficult to quantitatively compare experiments, since any differences may in principle be ascribed to $k_t$ and/or $f$. In our previous publication [43], it was assumed that $f$ forms a master curve versus conversion for

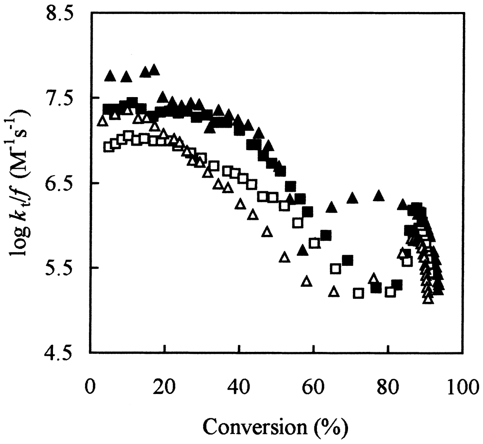

Fig. 9. The value of $k_t/f$ as a function of conversion (polymerization conditions as in Fig. 1). [DVB]$_0$ = 0.20 (△), 0.10 (□), 0.05 (■) and 0 (▲) M.

a series of different initiator concentrations in the bulk polymerization of St at 70 °C initiated by 0.10 M MAIB. It has been reported that $f$ appears to be independent of initiator concentration in the bulk polymerization of MMA initiated by azobis(cyclohexanenitrile) [55] and AIBN [54]. In this case, however, the experimental variable is the cross-linker content, and to our knowledge, there is no support available for such an assumption with regard to cross-linker content; indeed, one may expect $f$ to decrease with increasing cross-link density, since it is well established that an increase in viscosity reduces the value of $f$ [56,57]. However, it is important to point out that if indeed $f$ at a given conversion does increase with decreasing cross-linker content, then multiplication of $k_t/f$ by the true value of $f$ would result in an even greater increase in $k_t$ with decreasing cross-linker concentration than by assuming that $f$ is independent of the cross-linker concentration. In other words, the qualitative trend in $k_t$ with [DVB]$_0$ that is observed would not be altered. In view of these considerations, it was decided to attempt to decouple $k_t$ and $f$ by use of the values of $f$ versus conversion obtained in our previous paper for the homopolymerization

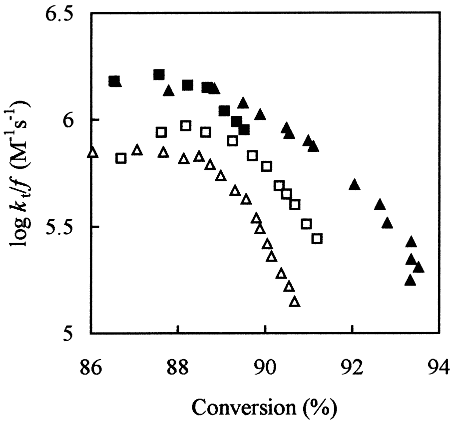

Fig. 10. The value of $k_t/f$ in the highest conversion range (polymerization conditions as in Fig. 1). [DVB]$_0$ = 0.20 (△), 0.10 (□), 0.05 (■) and 0 (▲) M.

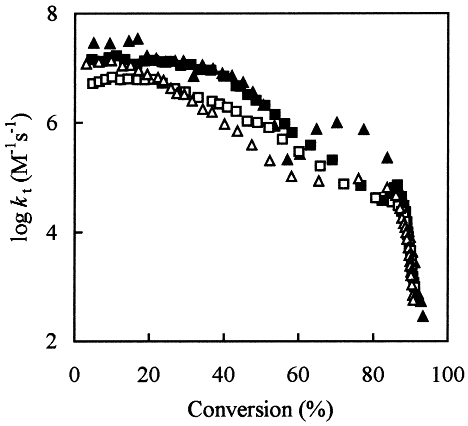

Fig. 11. The value of $k_t$ as a function of conversion (polymerization conditions as in Fig. 1). $[DVB]_0 = 0.20$ (△), 0.10 (□), 0.05 (■) and 0 (▲) M.

of St. The results obtained are displayed in Fig. 11. The values of $k_t$ remain close to constant in the conversion range 0–20%; this initial plateau region has been assigned to termination being controlled by segmental diffusion in the case of linear polymerization [2,29]. This is followed by a decrease of approximately two orders of magnitude between 20 and 60% monomer conversion. The decrease is more significant, and the onset of the decrease occurs at lower conversion with increasing DVB content; the value of $k_t$ for the homopolymerization of St is approximately one order of magnitude greater than for the co-polymerization with 0.20 M DVB in this conversion regime (20–60%). In linear free radical polymerization, the rate of termination is believed to be controlled by translational diffusion of macroradicals in this conversion range [2,29]. The conversion levels at which $k_t$ starts to decrease roughly correlate with the gel-points of the respective samples. The addition of DVB results in branched and eventually cross-linked structures, and the more significant and earlier decrease in $k_t$ observed with increasing DVB content indicates the constraints of free radical diffusion imposed by branched and network structures. A plateau value in $k_t$ appears to be reached at around 60% conversion, which is followed by a sharp decrease of more than two orders of magnitude from 85% conversion up to the final conversion. The value of $k_t$ in the highest conversion range (85–95% conversion) displays a clear dependence on DVB content; at a given conversion level, $k_t$ increases with decreasing DVB content (Fig. 12). It cannot be excluded that some primary radical termination may contribute to the rate of radical loss in the highest conversion range. It is however expected that this contribution is small since primary radical termination cannot compete favorably with reaction diffusion when the value of $f$ falls dramatically.

### 3.6. Termination by reaction diffusion

With increasing conversion, the macroradicals will eventually become sufficiently immobile so that the predominant mode of termination is reaction diffusion [29,35,36], i.e. the macroradical centers move as a result of monomer addition. It then follows that $k_t$ would be expected to be proportional to the product of $k_p$ and the fraction of unreacted monomer remaining according to Eq. (4)

$$k_{t,RD} = C_{RD}k_p(1-x) \tag{4}$$

where $k_{t,RD}$ is the termination rate coefficient for termination by the mechanism of reaction diffusion, $x$ is the fractional monomer conversion, and $C_{RD}$ is the reaction diffusion constant [29,35,36]. The onset of reaction diffusion as the dominant termination mechanism occurs at approximately 60% conversion in the bulk polymerizations of St and MMA [2,43], but often at considerably lower conversion levels for cross-linking systems [10,11,13,37,58]. The fact that the same qualitative trend with increasing DVB content at a given conversion level can be observed for the values of $k_t$ (Fig. 12) and $k_p$ (Fig. 6) in the highest conversion range is consistent with termination occurring predominantly by reaction diffusion. It has previously been reported that both $k_p$ and $k_t$ increase with initiator concentration in the highest conversion range of 80–95%, where both the rate of propagation and termination decrease by orders of magnitude in the case of St bulk polymerization initiated by MAIB at 70 °C [26,43]. The sharp decrease over approximately two orders of magnitude in the values of $k_t$ in the highest conversion range corresponds to the decrease in $k_p$ as a result of the propagation step becoming diffusion controlled.

The value of $C_{RD}$ was estimated over the conversion range of 60–90% from Eq. (4) using $k_t$ as a function of conversion from Fig. 11 and $k_p$ from Fig. 4. The value of $k_t$ reaches a plateau at approximately 60% conversion (Fig. 11), which is indicative of a change in the dominant termination mechanism from that of translational diffusion to reaction diffusion [59]. The absolute value of $C_{RD}$ has been suggested to be related to the radical chain end

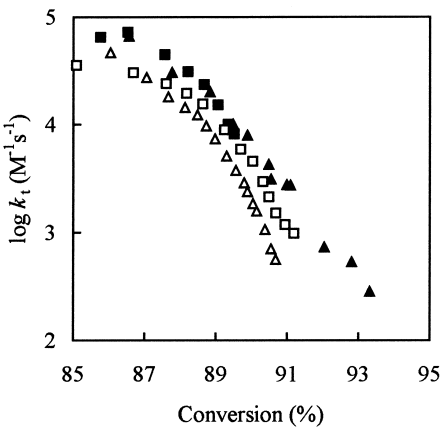

Fig. 12. The value of $k_t$ as a function of conversion in the highest conversion range (polymerization conditions as in Fig. 1). $[DVB]_0 = 0.20$ (△), 0.10 (□), 0.05 (■) and 0 (▲) M.

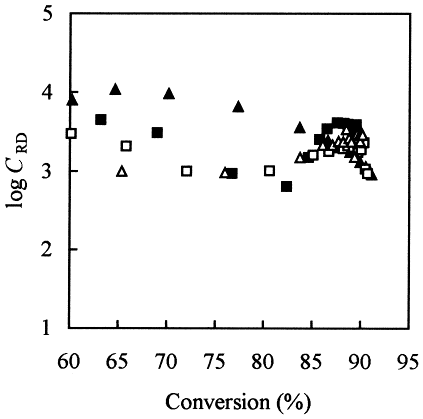

Fig. 13. The reaction diffusion constant ($C_{RD}$) versus conversion calculated from Eq. (3) (polymerization conditions as in Fig. 1). $[DVB]_0 = 0.20$ (△), 0.10 (□), 0.05 (■) and 0 (▲) M.

mobility [36]. The value of $C_{RD}$ is of the order $10^3$–$10^4$, and increases with decreasing DVB content in the conversion range 60–75% (Fig. 13). At conversion levels beyond 80%, the trends between the samples cannot be rationalized. It is likely that *f*-dependence on the DVB content (recall that it was assumed that *f* versus conversion formed a master curve for all DVB concentration investigated) causes overestimation of $C_{RD}$ at high DVB content.

## 4. Conclusions

The free-radical bulk co-polymerization of St and a small amount of DVB at 70 °C has been investigated by ESR, FT-NIR and GPC. The maximum $R_p$ occurred at approximately 70% conversion for all DBV contents investigated, including the homopolymerization of St. A pronounced maximum in the free radical concentration was detected at approximately the same conversion as the maximum $R_p$. The molecular weight and polydispersity began to increase prior to the onset of the gel-effect, indicating that a significant fraction of pendant unsaturations had already reacted. The value of $k_p$ remained constant through the gel-point (which occurred at conversions lower than 50%) until approximately 80% conversion, and only relatively small differences were observed as a function of DVB content. At the very highest conversion levels (>80%), $k_p$ increased with decreasing DVB content at a given conversion, probably as a reflection of higher rates of monomer diffusion in a more loosely cross-linked network.

The value of $k_t$ remained constant up to approximately 20% conversion, and subsequently decreased by approximately two orders of magnitude before leveling off at a plateau value in the conversion range 60–80%. The greatest effect of the DVB content was observed in the conversion range 20–60%; an increase in $[DVB]_0$ from 0 to 0.20 M resulted in a decrease in $k_t$ by approximately one order of magnitude and shortened the initial low conversion plateau region, reflecting the restrictions imposed on radical mobility by network structures. At approximately 80% conversion, $k_t$ decreased dramatically as also the propagation reaction became diffusion controlled. In the very highest conversion range (>80%), the value of $k_t$ decreased with increasing DVB content at a given conversion in a manner corresponding to similar changes in $k_p$, consistent with reaction diffusion being the dominant termination mechanism.

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