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High-Conversion Free-Radical Bulk Polymerization of Styrene: Termination Kinetics Studied by Electron Spin Resonance, Fourier Transform Near-Infrared Spectroscopy, and Gel Permeation Chromatography

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ABSTRACT: The free-radical bulk polymerization of styrene initiated by dimethyl 2,2′-azobisisobutyrate at 70 °C has been studied employing the techniques of Fourier transform near-infrared spectroscopy, electron spin resonance spectroscopy and gel permeation chromatography. The initiator efficiency (f) as a function of monomer conversion was estimated via an equation relating the instantaneous and the cumulative number average degrees of polymerization. The result was subsequently employed to calculate the conversion dependence of the termination rate coefficient (k_t) from zero to the limiting conversion for different initiator concentrations. Over the course of the reaction, k_t decreases by 5 orders of magnitude (10^7−10^2 M^{-1} s^{-1}). At conversion levels approaching the limiting value, k_t shows a marked dependence on initiator concentration; higher initiator concentration shifts the k_t vs conversion curves toward higher conversion levels. The reaction diffusion constant was found to decrease with increasing conversion in the high-conversion regime.

Introduction

The field of high-conversion free-radical bulk polymerization has been the subject of intense research over several decades. In recent years, the development of laser-based techniques[1−3] and improvements in the electron spin resonance (ESR) method[4] for the determination of propagation (k_p) and termination rate coefficients (k_t) have brought about a dramatic increase in the amount of reliable rate coefficient data available.[5] However, accurate rate coefficient and initiator efficiency (f) data at high conversion remain relatively scarce in the literature. Termination kinetics is of fundamental importance when attempting to understand free radical polymerization processes. The dependence of k_t on various factors is believed to be the main cause of the gel effect[6] and is also one of the key factors that determine the molecular weight and molecular-weight distribution.[7]

The pulsed laser polymerization−size exclusion chromatography (PLP−SEC)[1,3] technique can be used to determine k_p at low monomer conversions. The determination of k_t is more troublesome; it involves the use of pulsed laser techniques which yield some combination of k_p and k_t, and a knowledge of k_p from PLP−SEC measurements subsequently renders k_t accessible.[1,2] This approach relies on k_p being independent of the level of conversion, which holds up to approximately 75% monomer conversion[8−10] in the case of styrene (St).

The ESR technique makes it possible to directly quantify the propagating radical concentration as a function of conversion over the entire conversion range.[4] With regards to the determination of k_t employing ESR, three separate methods can be distinguished: (i) calculation of k_t at low conversion from the steady-state propagating radical concentration, (ii) calculation of k_t from the propagating radical concentration as a function of conversion, including the term for the rate of change of radical concentration, if necessary, (iii) determination of k_t from the radical decay as the UV-irradiation is interrupted during polymerization with UV-induced initiator decomposition. Methods i and ii yield the quantity k_t/f (and thus k_t if f is known), whereas method iii is independent of f. The value of k_t up to high conversion for St in the temperature range 75−85 °C has been estimated by Shen et al.[10] employing ESR and dilatometry (method ii). Method iii was employed by Otsu et al.[11] to determine k_t as a function of conversion up to high conversion levels for the bulk polymerization of St at 70 °C. ESR has also been applied to obtain information on k_t up to high conversion for methyl methacrylate (MMA),[12−17] as well as for cross-linking systems.[18,19] The ESR technique is thus extremely valuable because it is in principle possible to estimate k_p and k_t (or at least k_t/f) even as the conversion approaches its limiting value.

The aim of the present work has been to investigate the bulk polymerization of St up to high conversion combining the techniques of ESR spectroscopy, gel permeation chromatography (GPC), and Fourier transform near-infrared (FT-NIR) spectroscopy. In a previous publication,[9] we focused on the dependence of k_p for St and the propagating radical concentration on conversion. Here, we turn our attention to k_t and f. It is a well-known dilemma that it is difficult to separate k_t and f in the quantity k_t/f as obtained from monomer conversion and propagating radical concentration data.[20] In this paper, k_t and f were decoupled by use of a novel approach, which has allowed estimation of both quanti-

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ties as functions of conversion throughout the entire polymerization process up to the limiting level of conversion. The implications of the results with regards to termination by reaction diffusion[21] are discussed.

Methodology

***k_t/f*.** The rate of change of the propagating radical concentration ([St•]) is given by eq 1:

$$\frac{d[\mathrm{St}\bullet]}{dt} = 2fk_d[\mathrm{I}]_0 \exp(-k_d t) - 2k_t[\mathrm{St}\bullet]^2 \qquad (1)$$

where $[\mathrm{I}]_0$ is the initial initiator concentration. Rearrangement yields

$$k_t = \frac{2fk_d[\mathrm{I}]_0 \exp(-k_d t) - \frac{d[\mathrm{St}\bullet]}{dt}}{2[\mathrm{St}\bullet]^2} \qquad (2)$$

Despite the presence of a distinct maximum in [St•] vs time,[9] $2fk_d[\mathrm{I}]_0 \exp(-k_d t)$ is much greater than $d[\mathrm{St}\bullet]/dt$ under the current experimental conditions for this system, and eq 2 reduces to eq 3:

$$\frac{k_t}{f} = \frac{k_d[\mathrm{I}]_0 \exp(-k_d t)}{[\mathrm{St}\bullet]^2} \qquad (3)$$

Because the conversion-time dependence is available from FT-NIR measurements and [St•] has been obtained from ESR experiments,[9] the value of k_t/f can be calculated over the entire conversion range.

Initiator Efficiency. The parameter f, i.e., the fraction of primary radicals formed upon initiator decomposition that initiate a polymer chain, can be calculated from the rate of polymerization (R_p), the rate of decomposition of the initiator (k_d[I]) and the instantaneous number average degree of polymerization ($\overline{P_n}$) by use of eq 4:[22]

$$f = \frac{R_p}{\overline{P_n} k_d[\mathrm{I}]} \qquad (4)$$

In the case of St free-radical polymerization, termination occurs almost exclusively by combination,[20] and hence, eq 4 can be applied without the use of a correction term for the mode of termination.

The rate of chain transfer to St[23] (or to the Diels–Alder adduct[24,25]) up to high conversion was estimated, taking into account the fact that $k_{tr,M}$ and k_p exhibit the same conversion dependences.[26] Invoking the k_p conversion dependence from our previous publication,[9] the rate of chain transfer to monomer was found to be negligible compared to the rate of initiation over almost the entire conversion range, as expected under the present conditions using high concentrations of dimethyl 2,2′-azobisisobutyrate (MAIB). It cannot be excluded, however, that chain transfer to monomer may result in a slight overestimation of f (and thus also k_t) at very high conversion where f falls dramatically.[13,15,27] Chain transfer to polymer, which may become significant at high levels of conversion, was not accounted for when applying eq 4.

Cumulative and Instantaneous Degrees of Polymerization. The cumulative number average degrees of polymerization ($\overline{\overline{P_n}}$) in a chain polymerization, obtained readily from GPC data, can be converted into the instantaneous values ($\overline{P_n}$) by use of the relationship derived by Schulz:[22,28]

$$\overline{P_n} = \overline{\overline{P_n}}\left(1 - \frac{x}{\overline{\overline{P_n}}}\frac{d\overline{\overline{P_n}}}{dx}\right)^{-1} \qquad (5)$$

where x is the monomer conversion. In principle, it is possible to experimentally evaluate $\overline{P_n}$ by subtracting GPC curves corresponding to different conversion levels,[29] provided that the sampling interval is sufficiently short. However, this technique can in practice at best provide semi-instantaneous values because of experimental limitations.

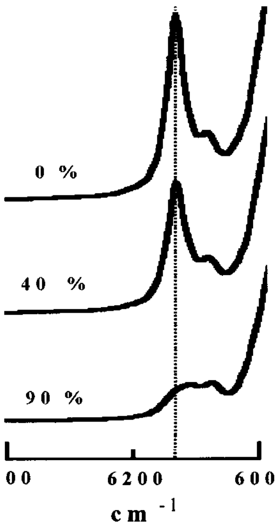

Figure 1. FT-NIR spectra recorded at different conversions during the bulk free-radical polymerization of St at 70 °C. The dotted line indicates the peak assigned to the overtone absorption of $\nu_{C=C-H}$, which was used to monitor St conversion.

Experimental Section

Bulk polymerization of St, distilled under reduced pressure before use, initiated by 0.05, 0.10, and 0.20 M MAIB (supplied by Wako Pure Chemicals and recrystallized from hexane) was conducted in glass ampules sealed under vacuum at 70 °C. The polymer formed was isolated by pouring the contents of the ampule into a large amount of methanol and collecting the precipitate. FT-NIR measurements were carried out in a 5 mm o.d. Pyrex tube 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 $\nu_{C=C-H}$, employing a Jasco INT-400 spectrometer equipped with a MCT detector (Figure 1). Molecular weights were measured with a Tosoh-800 series HPLC equipped with GPC columns. ESR spectra were recorded on a Bruker ESP300 during polymerization in the cavity in a 5 mm o.d. quartz tube which was sealed under vacuum. A series of spectra recorded using the same ESR conditions at different conversions (0.20 M MAIB) show how the line width and apparent splitting pattern change with conversion as a result of increasing viscosity[11] (Figure 2). The ESR spectra in this study were recorded under conditions that favor accurate free-radical concentration measurement (high-modulation amplitude) at the expense of finer spectral patterns due to poor resolution. The values of the hyperfine coupling constants of the poly(St) radical have been reported previously.[4] 2,2,6,6-Tetramethylpiperidinyl-1-oxyl in benzene was used as a stable free radical for calibration of the relationship between ESR spectral signal intensity and radical concentration. Benzene was used instead of St in the calibration procedure because it has been reported that the signal from 2,2,6,6-tetramethylpiperidinyl-1-oxyl decays relatively rapidly in St solutions above room temperature.[30] The use of toluene instead of St has a relatively small effect on the ESR detector response (approximately 10%),[30] and this in combination with the nonpolar nature of both St and benzene supports the use of benzene. The sensitivity of the ESR instrument is known to change with conversion during polymerization of polar monomers such as MMA.[29] It has previously been established that because of the nonpolar nature of St the sensitivity remains constant over the entire conversion range,[4,29] and thus no correction was required in the quantification procedure.

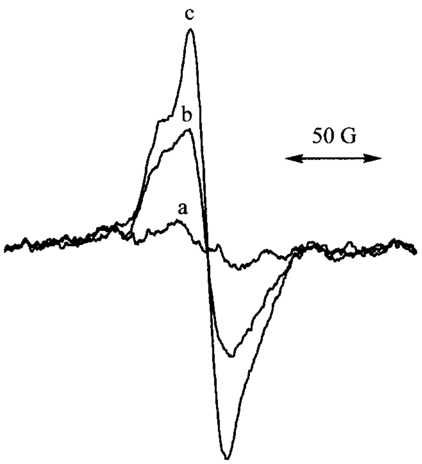

Figure 2. ESR spectra recorded at different conversions during the bulk free-radical polymerization of St initiated with 0.20 M MAIB at 70 °C: (a) 24% conversion (60 min), (b) 91% (250 min), (c) 95% (410 min).

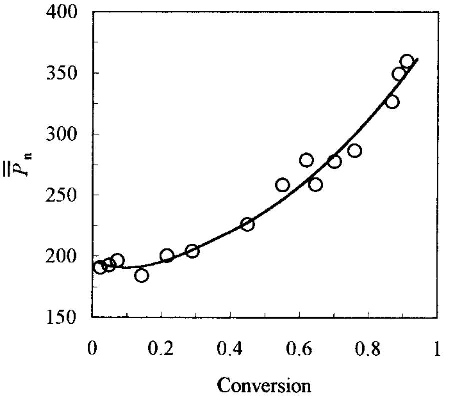

Figure 3. Cumulative number average degree of polymerization vs conversion. The line is a polynomial best fit.

Results and Discussion

$\overline{\overline{P}}_n$ and $\overline{P}_n$. $\overline{\overline{P}}_n$ as a function of monomer conversion is depicted in Figure 3 for the bulk polymerization of St initiated by 0.10 M MAIB at 70 °C. It is noteworthy that a slight minimum appears around 15% conversion; this is a result of the decreasing monomer concentration, while k_p, k_t, and f still remain roughly constant. The differential of the polynomial fitted to the data points, $d\overline{\overline{P}}_n/dx$, was substituted into eq 5 for the computation of $\overline{P}_n$ (Figure 4). The $\overline{P}_n$ data points displayed in Figure 4 were obtained by the GPC subtraction technique,[29] and the agreement between the two methods is surprisingly good. $\overline{\overline{P}}_n$ exhibits a smooth increase with increasing conversion after the slight minimum. This increase is, as expected, more pronounced for the quantity $\overline{P}_n$, which increases sharply at approximately 80% conversion, coinciding with the conversion level where the final dramatic decrease of k_t, by several orders of magnitude, sets in as will be shown later (Figure 6).

k_t and f. The value of f vs conversion as obtained from eq 4, using $\overline{P}_n$ from Schulz's eq[27] 5 and k_d from the literature,[31] is displayed in Figure 5. Extrapolation to zero conversion yields an initial value for f of 0.65, well within the range previously reported.[23] The value of f decreases gradually to about 0.50 as the conversion reaches approximately 75%, at which point it falls dramatically by several orders of magnitude as expected in free-radical bulk polymerization.[13,15,27]

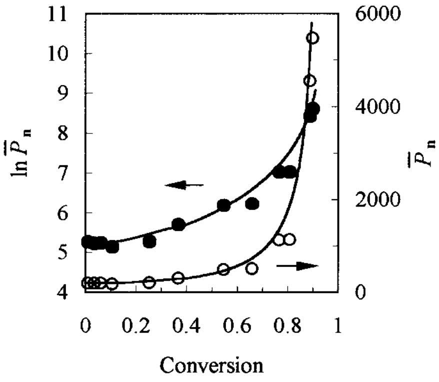

Figure 4. Instantaneous number average degree of polymerization vs conversion. The points were obtained from GPC using the "subtraction technique"; the lines are from eq 5 using the differential of the polynomial of Figure 3.

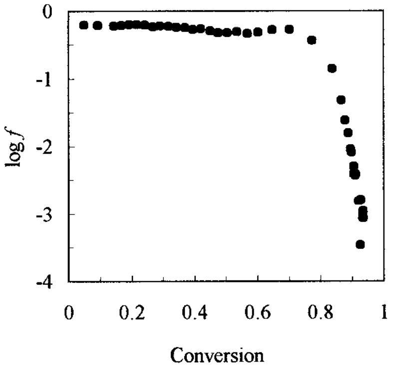

Figure 5. Initiator efficiency vs conversion for dimethyl 2,2′-azobisisobutyrate ([MAIB] = 0.10 M) at 70 °C in bulk St calculated from eq 4.

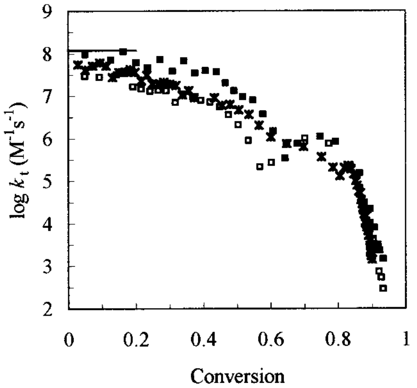

Figure 6. The termination rate coefficient vs conversion calculated from eqs 3 and 4 for different initiator concentrations; [MAIB] = 0.20 (■), 0.10 (□), 0.05 (*). The line refers to the PLP value reported in ref 36.

When f has been obtained as a function of conversion for [MAIB] = 0.10 M, it is possible to calculate k_t from k_t/f using eq 3 for this particular initiator concentration. If it can be assumed that f vs conversion forms a master curve for different initiator concentrations, then the obtained conversion dependence of f can be used to calculate k_t vs conversion for different initiator concentrations. Independence of f on the initiator concentration is supported by experimental data of Sack et al.[22] for the bulk free-radical polymerization of MMA initiated by azobis(cyclohexanenitrile). The presence of such a master curve has also been advocated by Russell et al.,[27]

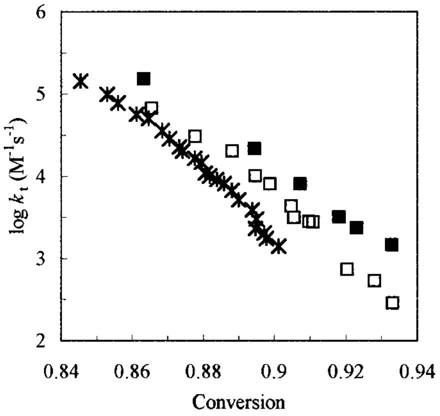

Figure 7. The termination rate coefficient vs conversion in the highest-conversion regime calculated from eqs 3 and 4 for different initiator concentrations: [MAIB] = 0.20 (■), 0.10 (□), 0.05 (∗).

who calculated f vs conversion (from k_p and conversion data combined with values of k_t deduced from emulsion polymerization free-radical concentrations ($x < 0.75$) and a model of k_t ($x > 0.75$)) for the bulk polymerization of MMA at 50 °C using different concentrations of azobis(isobutyronitrile) as initiator. It has however been shown that f decreases with increasing viscosity,[32,33] and it follows that if an increase in initiator concentration caused a sufficient decrease in viscosity (higher initiator concentration leads to lower molecular weight), f would be expected to increase with increasing initiator concentration at constant conversion. If no master curve exists for this reason, then multiplication of k_t/f by f (f thus increases with increasing initiator concentration) would lead to an even greater increase in k_t with increasing initiator concentration than that displayed in Figure 7. It can therefore be concluded that the k_t dependence on initiator concentration obtained here at high conversion is not caused by the f vs conversion master curve assumption, should this assumption in fact not hold.

The conversion dependence of k_t over the entire conversion range is displayed in Figure 6 for three different initiator concentrations. The minima that appear in the log k_t vs conversion curves for [MAIB] = 0.20 and 0.10 M, and to a lesser extent also for 0.05 M, are believed to be experimental artifacts caused by different heat-transfer characteristics, resulting in different temperatures and hence different conversions of the FT-NIR and ESR samples at the same reaction times.[9,34] This problem would be accentuated at high rates of polymerization, i.e., at high initiator concentrations, and this is the trend that can be observed in the present data.

In agreement with previous k_t measurements for St by Yamada et al.[11] (ESR), Shen et al.[10] (ESR), and Buback et al.[35,36] (PLP), k_t remains close to constant up to approximately 20% conversion. This conversion range has been assigned to termination rate control by segmental diffusion.[35,37–39] The absolute value obtained by Buback et al.[35,36] is in reasonable agreement with the value obtained here at low conversion. The value of k_t at low conversion has been proposed to be proportional to $\overline{P_n}^{-a}$ as a result of chain-length dependence (a is a positive constant).[40] However, because of scatter (originating from the ESR data as a result of the free-radical concentration being considerably lower in this conversion regime than at high conversion), it cannot be concluded whether the initiator concentration, and thereby the radical chain length, is affecting the k_t value in this conversion range. It is noteworthy that the initial conversion range in which k_t remains approximately constant is considerably shorter for St than for some monomers such as, for example, dodecyl methacrylate and dodecyl acrylate.[41,42] This has been proposed to have its origin in the fact that steric hindrance in the termination step (controlled by steric effects with possible contributions from segmental diffusion[41]) results in lower k_t values than those for St and therefore the effect of increasing bulk viscosity on k_t is not observed until higher conversion levels.[43]

In the conversion range in which the center of mass diffusion is the rate-determining step, the initiator concentration is believed to affect the termination kinetics in two different ways: (i) it affects the average chain length of the propagating radicals; a higher initiator concentration leads to shorter propagating radicals with higher diffusion coefficients resulting in a higher k_t;[2,32,44,45] (ii) it affects the medium; a higher initiator concentration results in the formation of dead polymer of shorter chain length, resulting in higher free volume of the system,[27] which leads to lower diffusion resistance and hence a higher k_t. As the conversion increases beyond approximately 20%, center of mass diffusion of macroradicals becomes the rate-determining step, and k_t decreases as the viscosity of the system increases. In the conversion range of 20−40%, the highest initiator concentration results in significantly higher k_t values than the two lower initiator concentrations, indicating that any dependence of k_t on the initiator concentration may be stronger in this conversion range than at lower conversions. This is in agreement with previous PLP studies,[35] in which the pulse repetition rate (higher pulse repetition rate gives shorter chain lengths) has been reported to have a significantly larger effect on k_t in the conversion range of 20−50% than at lower conversion levels.

Termination by Reaction Diffusion. Examination of the high-conversion regime (Figure 7) reveals a marked increase in k_t with increasing initiator concentration; at $x \approx 0.89$, $k_t([\text{MAIB}]_0 = 0.20\ \text{M}):k_t([\text{MAIB}]_0 = 0.10\ \text{M}):k_t([\text{MAIB}]_0 = 0.05\ \text{M}) \approx 5.6:2.6:1$. At intermediate to high conversion levels, the dominating termination mode is believed to be reaction diffusion.[1,21,46,47] The overall termination rate coefficient can be described by

$$k_t = k_{t,D} + k_{t,RD} \tag{6}$$

where $k_{t,D}$ is the diffusion-controlled rate coefficient and $k_{t,RD}$ is the rate coefficient for reaction diffusion. At sufficiently high conversion, the macroradicals become so immobile that they are unable to diffuse together for bimolecular termination to occur ($k_{t,D} \approx 0$). The only way termination can take place under such circumstances is when the radical center is moved by the propagation reaction. It then follows that k_t becomes proportional to the monomer concentration (expressed in terms of the fraction of unreacted monomer $(1 - x)$) multiplied by k_p. The rate coefficient for termination by reaction diffusion is given by eq 7, where C_{RD} is an empirical constant, the reaction diffusion constant.[21,46,47]

$$k_{t,RD} = C_{RD}k_p(1 - x) \tag{7}$$

It would thus appear as if any dependence on the initiator concentration in the reaction diffusion regime

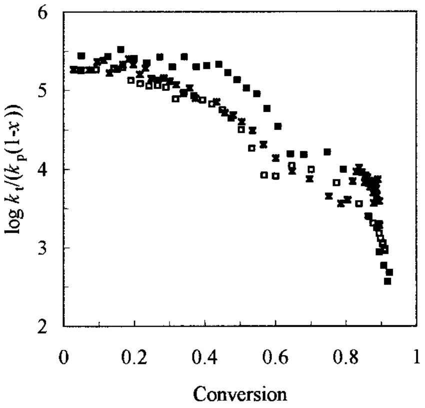

Figure 8. The quantity $k_t/(k_p(1 - x))$ vs conversion, which is equal to the reaction diffusion constant (C_{RD}) when reaction diffusion is the dominant mode of termination: [MAIB] = 0.20 (■), 0.10 (□), 0.05 (∗).

would have its origin in changes in the medium that depend on the initiator concentration, because the rate-determining diffusion process is now monomer diffusion (at conversion levels where the rate of propagation is diffusion controlled), i.e., it is *not* related to diffusion characteristics of macroradicals. The value of k_p at a given conversion level increases with initiator concentration in the diffusion-controlled regime in which the rate-determining step is monomer diffusion.[9] It can therefore be expected that k_t will be affected qualitatively the same as k_p by a change in initiator concentration at high conversion where reaction diffusion is the dominant mode of termination.

The quantity log $k_t/\{k_p(1 - x)\}$ vs conversion is displayed in Figure 8, using k_p data from our previous publication.[9] There is a significant decrease in log $k_t/\{k_p(1 - x)\}$ over the conversion range of 40−60% as the center of mass diffusion resistance increases, after which a plateau value appears to be reached. It is believed that at this point termination by reaction diffusion becomes the dominant termination mechanism.[35] For linear free-radical polymerization systems, C_{RD} has been found to be of the order of 10^2−10^3.[35,47] The parameter C_{RD} is thought to be a measure of the mobility of the radical center,[47] and it is conceivable that the radical chain end mobility will become more restricted as the glassy state is approached at high conversion. It has been suggested that C_{RD} might be a function of conversion at high conversion,[47] and the data obtained in this study support this. As the conversion increases from 60% to the limiting conversion, the estimated value of C_{RD} decreases quite dramatically from approximately 10^4 to $10^{2.5}$ (Figure 8). The parameter C_{RD} has been evaluated for highly cross-linked acrylate and methacrylate systems, and not surprisingly considering the above, values as low as 2−5 have been reported.[48]

The k_p and k_t data of ref 10, corresponding to the temperature range of 75−85 °C for the bulk polymerization of St initiated by benzoyl peroxide, were analyzed using eq 7, revealing the same qualitative trend in C_{RD} with increasing conversion as that in the present study (Figure 9). Furthermore, at high conversion, the value of C_{RD} increases with temperature. However, because the same initiator concentration was used in all experiments, this may also be attributed to higher rates of initiator decomposition (i.e., equivalent to increasing the initiator concentration).

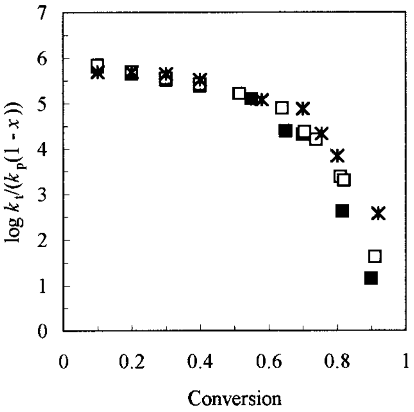

Figure 9. The quantity $k_t/(k_p(1 - x))$ vs conversion, calculated from k_p and k_t data from ref 10 for the bulk polymerization of St initiated by benzoyl peroxide at 75 (■), 80 (□), and 85 °C (∗).

The value of C_{RD} for St at 2000 bar and 40 °C has been reported as 800,[47] lower than the values obtained in this study (and those resulting from analysis of ref 10), except at the highest level of conversion. It is however known that C_{RD} decreases with increasing pressure for butyl acrylate,[49] presumably as a result of more restricted radical chain end mobility. Because of experimental scatter (Figure 8), it is difficult to comment on a possible initiator-concentration dependence of C_{RD}.

Could the observed decrease in C_{RD} with increasing conversion at very high conversion simply be a result of the level of conversion measured by FT-NIR being slightly different from that of the ESR samples at the same reaction time? An alternative expression for C_{RD} can be derived from eqs 3, 4, and 7:

$$C_{RD} = \frac{[St]_0}{\bar{P}_n[St\bullet]} \qquad (8)$$

where $[St]_0$ is the initial St concentration. Both quantities in the denominator increase with increasing conversion at high conversion in the data of the present study, suggesting that any discrepancy in the conversion levels between the ESR and FT-NIR experiments would not be the cause of the observed behavior of C_{RD} at high conversion.

Conclusions

The termination rate coefficient, k_t, for the free-radical bulk polymerization of St initiated by MAIB at 70 °C has been estimated as a function of conversion over the entire conversion range from conversion (FT-NIR), propagating radical concentration (ESR), and molecular weight data (GPC). It has been found that k_t exhibits a significant dependence on initiator concentration at high conversion, a higher initiator concentration resulting in a higher k_t. The reaction diffusion constant, C_{RD}, was found to decrease with increasing conversion at high conversion (assuming that termination at high conversion predominantly occurs by reaction diffusion). The results obtained in this study have demonstrated the potential of the ESR technique, especially because it can be applied up to high conversion, where also the propagation reaction becomes diffusion-controlled.

References and Notes

(1) Beuermann, S.; Buback, M. Pulsed Laser Experiments Directed Toward the Detailed Study of Free-Radical Poly-

merizations. In *Controlled Radical Polymerization*; Matyjaszewski, K., Ed.; ACS Symposium Series 685; American Chemical Society, Washington, DC, 1998; Chapter 6.
(2) Olaj, O. F.; Zoder, M.; Vana, P. *Macromolecules* **2001**, *34*, 441.
(3) Olaj, O. F.; Bitai, I.; Hinkelmann, F. *Makromol. Chem*. **1987**, *188*, 1689.
(4) Yamada, B.; Westmoreland, D. G.; Kobatake, S.; Konosu, O. *Prog. Polym. Sci*. **1999**, *24*, 565.
(5) Kamachi, M.; Yamada, B. Propagation and Termination Constants in Free Radical Polymerization. In *Polymer Handbook*, 4th ed.; Brandrup, J., Immergut, E. H., Grulke, E. A., Eds.; Wiley: New York, 1999; p II/77.
(6) O'Neil, G. A.; Torkelson, J. M. *Trends Polym. Sci*. **1997**, *5*, 349.
(7) Clay, P. A.; Gilbert, R. G. *Macromolecules* **1995**, *28*, 552.
(8) Yamada, B.; Kageoka, M.; Otsu, T. *Polym. Bull*. **1992**, *29*, 385.
(9) Yamazoe, H.; Zetterlund, P. B.; Yamada, B.; Hill, D. J. T.; Pomery, P. J. *Macromol. Chem. Phys*. **2001**, *202*, 824.
(10) Shen, J.; Wang, G.; Zheng, Y.; Yang, M. *Makromol. Chem., Macromol. Symp*. **1992**, *63*, 105.
(11) Yamada, B.; Kageoka, M.; Otsu, T. *Macromolecules* **1991**, *24*, 5236.
(12) Shen, J.; Tian, Y.; Zeng, Y.; Qiu, Z. *Makromol. Chem., Rapid Commun*. **1987**, *8*, 615.
(13) Carswell, T. G.; Hill, D. J. T.; Londero, D. I.; O'Donnell, J. H.; Pomery, P. J.; Winzor, C. L. *Polymer* **1992**, *33*, 137.
(14) Zhu, S.; Tian, Y.; Hamielec, A. E.; Eaton, D. R. *Polymer* **1990**, *31*, 154.
(15) Shen, J.; Tian, Y.; Wang, G.; Yang, M. *Makromol. Chem*. **1991**, *192*, 2669.
(16) Garrett, R. W.; Hill, D. J. T.; O'Donnell, J. H.; Pomery, P. J.; Winzor, C. L. *Polym. Bull*. **1989**, *22*, 611.
(17) Zhu, S.; Tian, Y.; Hamielec, A. E. *Macromolecules* **1990**, *23*, 1144.
(18) Zhu, S.; Tian, Y.; Hamielec, A. E.; Eaton, D. R. *Polymer* **1990**, *31*, 154.
(19) Li, W. H.; Hamielec, A. E.; Crowe, C. M. *Polymer* **1989**, *30*, 1513.
(20) Odian, G. In *Principles of Polymerization*, 3rd ed.; John Wiley & Sons: New York, 1991; pp 208, 242.
(21) Schulz, G. V. *Z. Phys. Chem*. **1956**, *8*, 290.
(22) Sack, R.; Schulz, G. V.; Meyerhoff, G. *Macromolecules* **1988**, *21*, 3345.
(23) Moad, G.; Solomon, D. H. In *The Chemistry of Free Radical Polymerization*, 1st ed.; Pergamon Press: Elmsford, NY, 1995; p 63, 255.
(24) Olaj, O. F.; Kauffmann, H. F.; Breitenbach, J. W. *Makromol. Chem*. **1976**, *177*, 3065.
(25) Olaj, O. F.; Kauffmann, H. F.; Breitenbach, J. W. *Makromol. Chem*. **1977**, *178*, 2707.
(26) Casey, B. S.; Mills, M. F.; Sangster, D. F.; Gilbert, R. G.; Napper, D. H. *Macromolecules* **1992**, *25*, 7063.
(27) Russell, G. T.; Napper, D. H.; Gilbert, R. G. *Macromolecules* **1988**, *21*, 2141.
(28) Schulz, G. V.; Harborth, G. *Makromol. Chem*. **1947**, *1*, 106.
(29) Yamada, B.; Kageoka, M.; Otsu, T. *Polym. Bull*. **1992**, *28*, 75.
(30) Tonge, M. P.; Kajiwara, A.; Kamachi, M.; Gilbert, R. G. *Polymer* **1998**, *39*, 2305.
(31) Dixon, K. W. Decomposition Rates of Organic Free Radical Initiators. In *Polymer Handbook*, 4th ed; Brandrup, J., Immergut, E. H., Grulke, E. A., Eds.; Wiley: New York, 1999; p II/12.
(32) Matsumoto, A.; Mizuta, K. *Macromolecules* **1994**, *27*, 5863.
(33) Moad, G.; Rizzardo, E.; Solomon, D. H.; Johns, S. R.; Willing, R. I. *Makromol. Chem., Rapid Commun*. **1984**, *5*, 793.
(34) Armitage, P. D.; Hill, S.; Johnson, A. F.; Mykytiuk, J.; Turner, J. M. *Polymer* **1988**, *29*, 2221.
(35) Buback, M.; Kuchta, F.-D. *Macromol. Chem. Phys*. **1997**, *198*, 1455.
(36) Buback, M.; Kowollik, C.; Kurz, C.; Wahl, A. *Macromol. Chem. Phys*. **2000**, *201*, 464.
(37) Moore, P. W.; Clouston, J. G.; Chaplin, R. P. *J. Polym. Sci., Polym. Chem. Ed*. **1981**, *19*, 1659, 1671.
(38) Benson, S. W.; North, A. M. *Trans. Faraday Soc*. **1959**, *81*, 1339.
(39) Benson, S. W.; North, A. M. *Trans. Faraday Soc*. **1962**, *84*, 935.
(40) O'Driscoll, K. F. In *Comprehensive Polymer Science*; Allen, G., Bevington, J. C., Eastmond, G. C., Eds.; Pergamon Press: Elmsford, NY, 1989; Vol. 3, p 161.
(41) Buback, M.; Kowollik, C. *Macromol. Chem. Phys*. **1999**, *200*, 1764.
(42) Buback, M.; Kowollik, C. *Macromolecules* **1999**, *32*, 1445.
(43) Buback, M. Initiation and Termination Rates Associated with Free-Radical Polymerization in Extended Ranges of Temperature and Pressure. In *Controlled/Living Radical Polymerization. Progress in ATRP, NMP and RAFT*; Matyjaszewski, K., Ed.; ACS Symposium Series 768; American Chemical Society, Washington, DC, 2000; Chapter 3.
(44) Sheren, P. A. G. M.; Russell, G. T.; Sangster, D. F.; Gilbert, R. G.; German, A. L. *Macromolecules* **1995**, *28*, 3637.
(45) Buback, M.; Busch, M.; Kowollik, C. *Macromol. Theory Simul*. **2000**, *9*, 442.
(46) Buback, M. *Macromol. Chem. Phys*. **1990**, *191*, 1575.
(47) Buback, M.; Huckestein, B.; Russell, G. T. *Macromol. Chem. Phys*. **1994**, *195*, 539.
(48) Young, J. S.; Bowman, C. N. *Macromolecules* **1999**, *32*, 6073.
(49) Buback, M.; Degener, B. *Makromol. Chem*. **1993**, *194*, 2875.

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