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Quantification of spontaneous initiation in radical polymerization of styrene in aqueous miniemulsion at high temperature[☆]

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Abstract

The spontaneous (thermal) initiation rate ($R_{i,th}$; no added initiator) in radical polymerization of styrene in aqueous miniemulsion at 110 and 125 °C with sodium dodecylbenzenesulfonate or poly(vinyl alcohol) as surfactants (colloidal stabilizers) has been estimated using a novel approach based on the total number of chains. In qualitative agreement with previous work at lower temperatures, $R_{i,th}$ was found to be 3.1–15.1 times greater than that in bulk. According to the activation energy and conversion dependence of $R_{i,th}$, the radical generation mechanism differs from that in bulk. The experimental evidence is consistent with the enhanced $R_{i,th}$ in miniemulsion being related to the oil–water interface, with radical generation in the aqueous phase playing a negligible role. The implications with regards to nitroxide-mediated radical polymerization in aqueous dispersed systems are discussed.

Keywords: Thermal polymerization; Kinetics; Miniemulsion

1. Introduction

It is well established that styrene (S) undergoes spontaneous (thermal) polymerization [1–7], i.e. the pure monomer polymerizes on heating in the absence of a radical initiator, the rate of radical generation being third order with respect to monomer [8]. The two most widely accepted mechanisms are the Mayo mechanism [2,9] and the biradical mechanism proposed by Flory [1,9]. In an aqueous dispersed system of S, radical generation is expected to occur in the dispersed phase according to the same mechanism as in bulk S. However, experimental evidence suggests that there are additional contributions to the radical generation rate. The rate of spontaneous generation of radicals in an aqueous S emulsion polymerization at 50 °C with a particle diameter of approximately 100 nm is greater than that in the corresponding bulk system [10–12]. At such a low temperature, the rate of spontaneous initiation in bulk/solution is extremely low [8]. The mechanism and the nature of the initiating species in such S emulsion polymerization systems remain unknown, although it has been reported that radical generation occurs in all three phases (i.e. monomer droplets, particles, and the aqueous phase) [13].

The development of controlled/living radical polymerization (CLRP) [14,15] has revolutionized the field of radical polymerization over the past 15 years. Not only does CLRP provide us with means of synthesizing well-defined polymers and block copolymers with narrow molecular weight distributions (MWDs) as well as other complex architectures, it is also increasingly being utilized as a tool to deepen our understanding of fundamental kinetic/mechanistic aspects of radical polymerization in ways that have hitherto not been possible [16,17].

The application of controlled/living radical polymerization (CLRP) [14,15] in aqueous heterogeneous systems is an active area of research [18–27]. In nitroxide-mediated polymerization (NMP) [28,29] (one of the most frequently employed CLRP techniques), temperatures significantly higher than those normally employed for conventional emulsion polymerizations

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are required (generally > 90 °C depending on the nitroxide/monomer) [14]. The rate of spontaneous initiation plays an important role in NMP [14,30], and a quantitative understanding of spontaneous initiation in high temperature aqueous dispersed systems is thus desirable. Adding to the complex picture of these systems, Cunningham et al. [31,32] recently proposed that the surfactant sodium dodecylbenzenesulfonate (SDBS) is participating in the generation of radicals during 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO)-mediated polymerization of S in aqueous miniemulsion at 135 °C. In the same study, it was also found that changing the concentration of the surfactant Dowfax 8390 (disulfonated alkyl diphenyloxide sodium salt) did not influence the polymerization rate. El-Aasser et al. [33] investigated the rate of spontaneous initiation of S in bulk and aqueous miniemulsion (Dowfax 8390) in the presence of various amounts of TEMPO at 125 °C, reporting that the induction periods were very similar in bulk and miniemulsion, which suggests that the rates of spontaneous initiation were also similar in both systems. Spontaneous initiation in TEMPO-mediated polymerization of S is complicated by the fact that the presence of TEMPO affects the rate of initiation [3,34–36].

In the present contribution, spontaneous initiation in the conventional (non-living) radical polymerization of S in aqueous miniemulsion at high temperature (110 and 125°C) using SDBS or poly(vinyl alcohol) as surfactants (colloidal stabilizers) has been quantitatively investigated by employing a novel approach based on analysis of the total number of chains in the system as a function of time. It is shown that the spontaneous radical generation rates in aqueous miniemulsion are significantly higher than in the corresponding bulk systems. The implications of the results with regards to the implementation of NMP in aqueous miniemulsion are discussed.

2. Experimental and methodology

2.1. Materials

Styrene (S) and methyl methacrylate (MMA) were purified by distillation under reduced pressure in a nitrogen atmosphere. Linear polystyrene (PS; Wako Pure Chemical Industries, Ltd., Japan), sodium dodecylbenzenesulfonate (SDBS; Nacalai Tesque Inc., Kyoto, Japan), hexadecane (HD; Nacalai Tesque Inc., Kyoto, Japan) and special-grade (Aldrich) poly(vinyl alcohol) (PVA; Gohsenol GH-17: degree of polymerization, 1700; degree of saponification, 88%; Nippon Synthetic Chemical Co., Ltd., Japan) were used as received. Analytical grade potassium persulfate (KPS, Nacalai Tesque, Kyoto, Japan) was purified by recrystallization.

2.2. Polymerization procedures

Miniemulsion polymerizations (5.0 wt% solids content based on 100% monomer conversion): A solution of S (0.75 g), HD (26.25 mg) and linear PS (0.75 mg; DP = 2000) was mixed with an aqueous solution of SDBS (45 mg; 6 wt% rel. to S). The recipe for the miniemulsion polymerization containing PVA was the same except that PVA (45 mg; 6 wt% rel. to S) was used instead of SDBS. Bulk polymerization with SDBS: S (4 g) was mixed with SDBS (16 mg; 0.4 wt% rel. to S).

Emulsification was carried out using ultrasonication (Ultrasonic Homogenizer, Nissei, US-600 T) for 12 min at 0 °C. The resulting emulsion was transferred to a glass ampule (approximately 4 mL), degassed using several N_2/vacuum cycles and sealed off under vacuum. The polymerizations were carried out at 110 and 125 °C shaking the ampules horizontally at a rate of 110 cycles $\min^{-1}$.

Polymerizations of monomer-saturated aqueous solutions: S (15 g) was mixed with water (200 g) in a glass beaker followed by vigorous magnetic stirring for 5 h at room temperature. The mixture was transferred to a separable flask and left standing at room temperature until complete phase separation had occurred (1 h). The aqueous phase solution (15 g) was transferred to a glass ampule, degassed using several N_2/vacuum cycles and sealed off under vacuum, and subsequently heated at 125 °C for 24 h shaking the ampule horizontally at a rate of 110 cycles $\min^{-1}$. Polymerizations of monomer-saturated aqueous solutions containing KPS were carried out as above except that KPS (2.5 mg; 9.2×10^{-3} mmol) was added and the polymerizations were conducted at 70 °C for 5 h.

Copolymerizations of S and MMA in aqueous solutions were carried out after mixing individual monomer-saturated aqueous solutions of each monomer (1:1 volume ratio; total mass of water = 15 g) prepared as above, with and without KPS (2.5 mg; 9.2×10^{-3} mmol).

2.3. Measurements

S conversions were determined by gas chromatography (Shimadzu Corporation, GC-18A) with helium as carrier gas, employing *N*,*N*-dimethylformamide as solvent and *p*-xylene as internal standard. Molecular weights (MW) were obtained by gel permeation chromatography (GPC) employing a Tosoh GPC system equipped with two TSK gel columns (GMHHR-H, 7.8 mm i.d. × 30 cm) using tetrahydroforan (THF) as eluent at 40 °C at a flow rate of 1.0 mL $\min^{-1}$, and a refractive index detector (RI-8020). The column was calibrated against five standard PS samples (1.05×10^3–5.48×10^6). Particle size distributions were measured using dynamic light scattering (FPAR-1000, Otsuka Electronics, Osaka, Japan) at the light scattering angle of 160° at room temperature. Number-average (d_n) and weight-average (d_w) droplet diameters were obtained using the Marquadt analysis routine. The values given are average values over the course of the polymerizations.

2.4. Estimation of rate of spontaneous initiation

The rate of spontaneous (thermal) initiation ($R_{i,th}$) was estimated experimentally from MW data (GPC). It was assumed that chains are initiated by thermal radicals (R•) and monomeric radicals (M•) generated by chain transfer to monomer. In the following, the subscripts R and M denote chains initiated by thermal radicals and monomeric radicals, respectively, and P• and PH denote propagating radicals and chains having undergone chain transfer to monomer, respectively. The chain-stopping events are:

Chain transfer to monomer:

$$\mathrm{P_R\bullet + M \overset{k_{tr,M}}{\rightarrow} P_RH + M\bullet} \tag{1}$$

$$\mathrm{P_M\bullet + M \overset{k_{tr,M}}{\rightarrow} P_MH + M\bullet} \tag{2}$$

Bimolecular termination:

$$\mathrm{P_R\bullet + P_R\bullet \overset{k_t}{\rightarrow} P_RP_R} \tag{3}$$

$$\mathrm{P_M\bullet + P_M\bullet \overset{k_t}{\rightarrow} P_MP_M} \tag{4}$$

$$\mathrm{P_R\bullet + P_M\bullet \overset{k_t}{\rightarrow} P_RP_M} \tag{5}$$

There are thus five types of dead chains in the system, and their concentrations are denoted as C_{RH} ($\mathrm{P_RH}$), C_{MH} ($\mathrm{P_MH}$), C_{RR} ($\mathrm{P_RP_R}$), C_{MM} ($\mathrm{P_MP_M}$), and C_{RM} ($\mathrm{P_RP_M}$). The concentration of R end groups derived from R• ([R end group]$_{\mathrm{th}}$) by spontaneous initiation is equal to:

$$[\mathrm{R\,end\,group}]_{\mathrm{th}} = C_{\mathrm{RH}} + 2C_{\mathrm{RR}} + C_{\mathrm{RM}} \tag{6}$$

(the “2” accounting for one chain containing two R end groups) and it follows that the rate of spontaneous generation of radicals ($\mathrm{M\,s^{-1}}$) is given by:

$$R_{\mathrm{i,th}} = \mathrm{d}[\mathrm{R\,end\,group}]_{\mathrm{th}}/\mathrm{d}t \tag{7}$$

Now, the task at hand is to calculate the value of [R end group]$_{\mathrm{th}}$ from [chains]$_{\mathrm{tot}}$, where the latter is readily obtained from GPC data according to:

$$[\mathrm{chains}]_{\mathrm{tot}} = \alpha[\mathrm{M}]_0(\mathrm{MW})_0/M_{\mathrm{n}} \tag{8}$$

where $[\mathrm{M}]_0$ is the initial monomer concentration, α is fractional monomer conversion, $(\mathrm{MW})_0$ is the MW of the monomer, and M_{n} is the number-average MW of the polymer.

The total concentration of chains is:

$$[\mathrm{chains}]_{\mathrm{tot}} = C_{\mathrm{RH}} + C_{\mathrm{MH}} + C_{\mathrm{RR}} + C_{\mathrm{MM}} + C_{\mathrm{RM}} \tag{9}$$

Assuming that $C_{\mathrm{tr,M}}$ remains constant with conversion [37], the concentration of chains having undergone chain-stopping by chain transfer to monomer is [38]:

$$[\mathrm{chains}]_{\mathrm{tr,M}} = C_{\mathrm{RH}} + C_{\mathrm{MH}} = \alpha[\mathrm{M}]_0C_{\mathrm{tr,M}} \tag{10}$$

where α is the fractional monomer conversion, $[\mathrm{M}]_0$ is the initial monomer concentration, and $C_{\mathrm{tr,M}} = 2.34 \times 10^{-4}$ at 110 °C [38]. It follows from Eqs. (9) and (10) that the concentration of chains derived from bimolecular termination is given by:

$$[\mathrm{chains}]_{\mathrm{tot}} - [\mathrm{chains}]_{\mathrm{tr,M}} = C_{\mathrm{RR}} + C_{\mathrm{MM}} + C_{\mathrm{RM}} \tag{11}$$

Each chain transfer to monomer event generates one M•, which reinitiates a new chain. Thus, by counting M end groups, we can write:

$$[\mathrm{chains}]_{\mathrm{tr,M}} = \alpha[\mathrm{M}]_0C_{\mathrm{tr,M}} = C_{\mathrm{MH}} + 2C_{\mathrm{MM}} + C_{\mathrm{RM}} \tag{12}$$

Equating Eqs. (10) and (12) and rearranging yields:

$$C_{\mathrm{MM}} = 0.5(C_{\mathrm{RH}} - C_{\mathrm{RM}}) \tag{13}$$

Insert Eq. (13) into Eq. (11):

$$\begin{aligned}[\mathrm{chains}]_{\mathrm{tot}} - [\mathrm{chains}]_{\mathrm{tr,M}} &= C_{\mathrm{RR}} + 0.5(C_{\mathrm{RH}} - C_{\mathrm{RM}}) + C_{\mathrm{RM}} \\ &= C_{\mathrm{RR}} + 0.5C_{\mathrm{RH}} + 0.5C_{\mathrm{RM}}\end{aligned} \tag{14}$$

Eqs. (6) and (14) give:

$$\begin{aligned}[\mathrm{R\,end\,group}]_{\mathrm{th}} &= C_{\mathrm{RH}} + 2C_{\mathrm{RR}} + C_{\mathrm{RM}} \\ &= 2([\mathrm{chains}]_{\mathrm{tot}} - [\mathrm{chains}]_{\mathrm{tr,M}})\end{aligned} \tag{15}$$

where $[\mathrm{chains}]_{\mathrm{tot}}$ and $[\mathrm{chains}]_{\mathrm{tr,M}}$ are evaluated from Eqs. (8) and (10), respectively. The slope of a plot of [R end group]$_{\mathrm{th}}$ vs. time subsequently yields $R_{\mathrm{i,th}}$ (Eq. (7)) as a function of time.

We have thus developed a very simple means of estimating $R_{\mathrm{i,th}}$, which relies only on experimental GPC data and the value of $C_{\mathrm{tr,M}}$.

3. Results and discussion

3.1. Rate of polymerization

Fig. 1a shows conversion vs. time data for spontaneously initiated (no initiator added) polymerizations of S at 110 °C in miniemulsion with SDBS ($d_{\mathrm{n}} \approx 61$ nm) and PVA ($d_{\mathrm{n}} \approx 250$ nm), as well as in bulk. The initial rates of polymerization (R_{p}) were much higher in both miniemulsion polymerizations than in bulk, in agreement with previous reports [39,40]. At 110 °C, the initial R_{p} in the miniemulsion with $d_{\mathrm{n}} \approx 61$ nm was approximately 68 times greater than for the corresponding bulk system, while that of the miniemulsion with $d_{\mathrm{n}} \approx 250$ nm was 4.4 times greater than that of the bulk system (Table 1).

Fig. 2a shows conversion vs. time data for spontaneously initiated polymerizations of S at 125 °C in miniemulsion with SDBS ($d_{\mathrm{n}} \approx 64$ nm) and the corresponding bulk polymerization. Again, R_{p} was much higher in miniemulsion than in bulk, by a factor of approximately 34.

The number of propagating radicals per particle ($\overline{n}$) was calculated from Eq. (16):

$$\overline{n} = \frac{N_{\mathrm{A}}V_{\mathrm{p}}}{k_{\mathrm{p}}}\left\{\frac{\mathrm{d}\left(\ln\left([\mathrm{S}]_0/[\mathrm{S}]\right)\right)}{\mathrm{d}t}\right\} \tag{16}$$

where N_{A} is Avogadro’s number, V_{p} is the average particle volume ($V_{\mathrm{p}} = (1/6)\pi d_{\mathrm{v}}^3$, where d_{v} is the volume average particle diameter; d_{v} was approximated with d_{w}), k_{p} is the propagation rate coefficient (1580 and 2320 $\mathrm{M^{-1}\,s^{-1}}$ at 110 and 125 °C, respectively [41]), and $[\mathrm{S}]_0$ and $[\mathrm{S}]$ are the initial and instantaneous S concentrations in the organic phase, respectively. Based on the initial slopes of the first-order plots

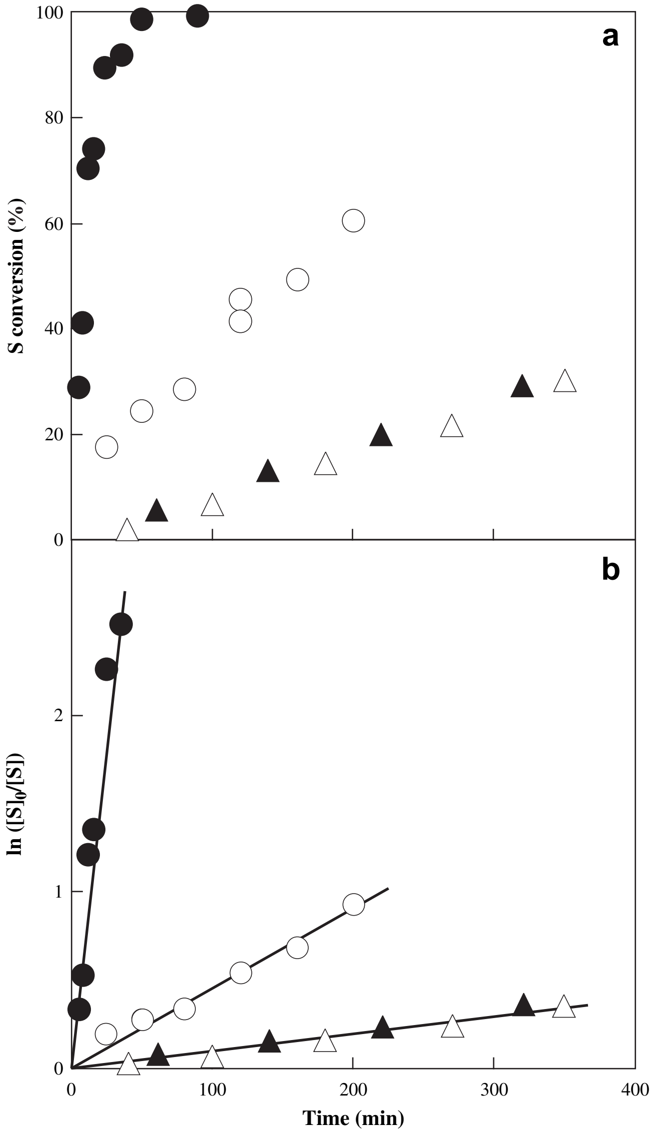

Fig. 1. (a) Conversion–time and (b) first-order plots for spontaneously initiated polymerizations of S at 110 °C in bulk without (△) and with (▲) 0.4 wt% SDBS, and in miniemulsions with PVA (○; $d_n \approx 250$ nm) and SDBS (●; $d_n \approx 61$ nm).

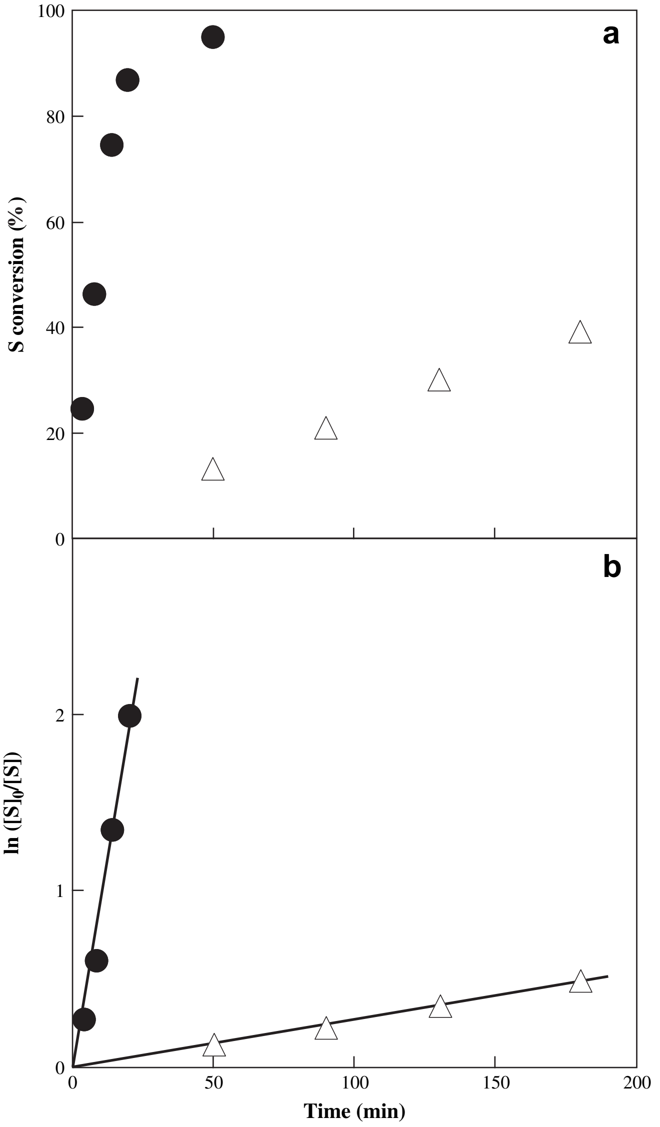

Fig. 2. (a) Conversion–time and (b) first-order plots for spontaneously initiated polymerization of S at 125 °C in bulk without SDBS (△) and in miniemulsion with SDBS (●; $d_n \approx 64$ nm).

(Figs.1b and 2b), $\bar{n} \approx 0.11$ (SDBS; 110 °C; $d_n = 61$ nm), $\bar{n} \approx 0.44$ (PVA; 110 °C; $d_n = 250$ nm), and $\bar{n} \approx 0.10$ (SDBS; 125 °C; $d_n = 64$ nm), consistent with significant compartmentalization effects in all cases.

Emulsion polymerizations are normally faster than their homogenous counterparts as a result of compartmentalization (segregation) of propagating radicals which reduces the termination rate [12], consistent with R_p(miniemulsion) ≫ R_p(bulk) as well as the miniemulsion with smaller particles exhibiting the highest R_p at 110 °C (Fig. 1). However, R_p is also affected by the rate of spontaneous initiation, which may differ between the miniemulsion and bulk systems, as well as between the two miniemulsion systems (effects of

Table 1
Spontaneously initiated miniemulsion polymerizations of styrene

System	Emulsifier	T (°C)	d_n (d_w) (nm)	$R_{i,th} \times 10^7$ (mol/L s)	$R_p \times 10^4$ (mol/L s)	$R_p/(R_{i,th})^{1/2}$	$M_n \times 10^{-5a}$ (g mol^{-1})
Bulk	–	110	–	0.90	1.44	0.48	2.01 (7)
Bulk	SDBS	110	–	0.90	1.49	0.50	2.00 (6)
Bulk	–	125	–	2.42	3.92	0.80	1.61 (13)
Miniemulsion	PVA	110	250 (310)	4.41	6.37	0.96	1.35 (24)
Miniemulsion	SDBS	110	61 (76)	13.6	97.6	8.37	2.48 (28)
Miniemulsion	SDBS	125	64 (80)	18.2	134.5	9.96	2.33 (24)

[a] Numbers in brackets indicate S conversions (%).

surfactant and/or particle size). As stated in the Section 1, the rate of spontaneous generation of radicals in an aqueous S emulsion polymerization at 50 °C for 100 nm diameter particles exceeds that of the corresponding bulk system [10–12], and this is also considered likely to be the case at the much higher temperatures in the present study.

3.2. Rate of spontaneous initiation

In a homogeneous system (bulk/solution), the rate of spontaneous initiation ($R_{i,th}$ ($M\,s^{-1}$)) can be estimated from R_p provided that the fundamental rate coefficients are known. However, in an aqueous dispersed system, the relationship between $R_{i,th}$ and R_p is very complex due to the influence of compartmentalization and entry/exit, and also because it is not clear in which phase(s) radical generation occurs.

Therefore, $R_{i,th}$ in the present study has been obtained using a novel approach, whereby the total concentration of polymer chains in the system is estimated as a function of time from GPC data (see Section 2). The approach involves differentiating between the number of chains initiated by spontaneous initiation from the total number of chains, which entails accounting for the change in the number of chains due to bimolecular termination by combination (most studies indicate that the extent of termination by disproportionation for S is approximately 10% [9]) and chain transfer to monomer followed by reinitiation by monomeric radicals (it has been proposed that chain transfer to monomer may in fact be to the Diels–Alder dimer formed by reaction of two S units [9,42]).

Chain transfer to surfactant would cause overestimation of $R_{i,th}$ as obtained in the present study. The MWDs obtained in the bulk polymerizations of S at 110 °C in the presence and absence of SDBS were, however, close to identical (Fig. 1), thus ruling out chain transfer to SDBS as a significant pathway to new chains.

Fig. 3 shows the concentrations of R end groups derived from R• ([R end group]$_{th}$) by spontaneous initiation as functions of time for the spontaneously initiated polymerizations of S in Figs. 1 and 2. The slope of [R end group]$_{th}$ vs. time corresponds to $R_{i,th}$ according to Eq. (7), and the resulting $R_{i,th}$ values are listed in Table 1 (the error in $R_{i,th}$ is expected to be less than 50%). $R_{i,th}$ was markedly higher in miniemulsion than in bulk at both 110 and 125 °C. The value of $R_{i,th}$ for the miniemulsion with the smaller particle size (SDBS; $d_n \approx 61$ nm) at 110 °C was 15.1 times greater than that for the bulk system, and the miniemulsion at 125 °C (SDBS; $d_n \approx 64$ nm) had a value of $R_{i,th}$ 7.5 times greater than that in the bulk system at the same temperature. At 110 °C, $R_{i,th}$ of the miniemulsion with the smaller particle size (SDBS; $d_n \approx 61$ nm) was greater than that of the miniemulsion with larger particles (PVA; $d_n \approx 250$ nm) by a factor of 3.1, indicating that $R_{i,th}$ is a function of particle size and/or surfactant type. The absolute values of $R_{i,th}$ in bulk S as estimated in the present work are in relatively good agreement with the literature values of Hui and Hamielec [8]; $R_{i,th} = 9.0 \times 10^{-8}\ M\,s^{-1}$ (Hui and Hamielec: 2.8×10^{-8}) at 110 °C and $2.4 \times 10^{-7}\ M\,s^{-1}$ (Hui and Hamielec: 1.1×10^{-7}) at 125 °C. It should be borne in mind that the accuracy of the literature values of Hui and Hamielec is compromised by assumptions in the model employed when fitting experimental data to obtain $R_{i,th}$.

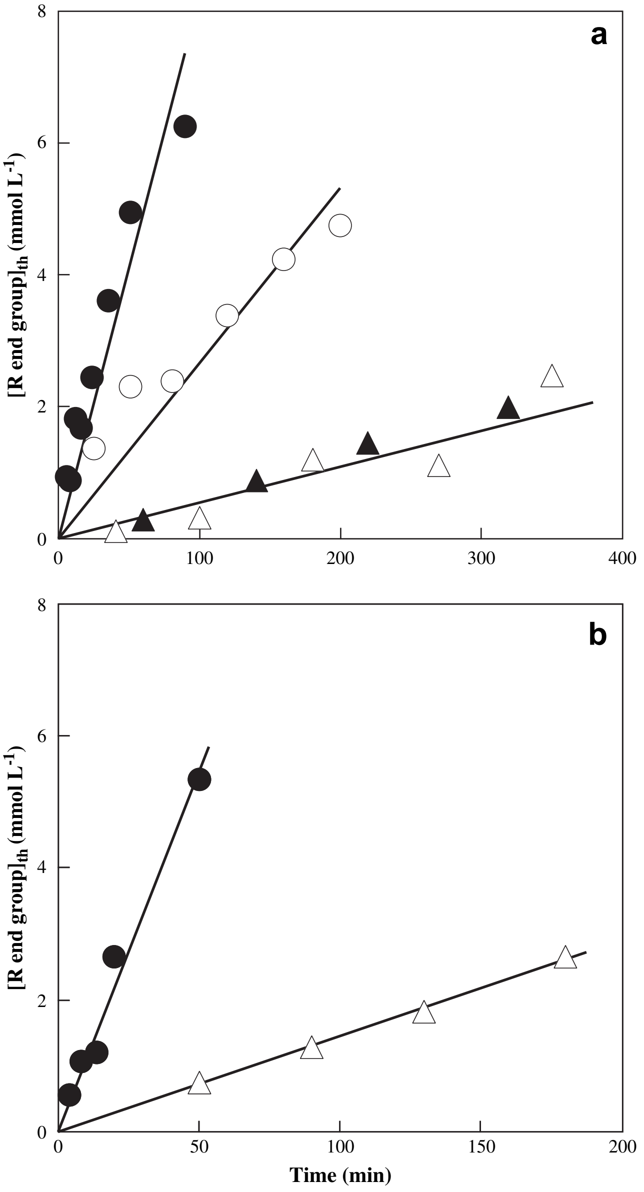

Fig. 3. Concentration of R end groups derived from R• ([R end group]$_{th}$) by spontaneous initiation vs. time for spontaneously initiated polymerization of S; (a) bulk without (△) and with (▲) 0.4 wt% SDBS, and miniemulsion with PVA (○; $d_n \approx 250$ nm) and SDBS (●; $d_n \approx 61$ nm) at 110 °C; (b) bulk without SDBS (△), and miniemulsion with SDBS (●; $d_n \approx 64$ nm) at 125 °C.

3.3. Kinetic analysis

Figs. 4 and 5 show the MWDs for spontaneously initiated polymerizations of S at 110 and 125 °C in miniemulsion and the corresponding bulk polymerizations. In all cases, the MWDs remained approximately constant with conversion. This is consistent with chain transfer to monomer playing a major role as an end-forming event. According to theory, the chain transfer constant ($k_{tr,M}/k_p$) is expected to be

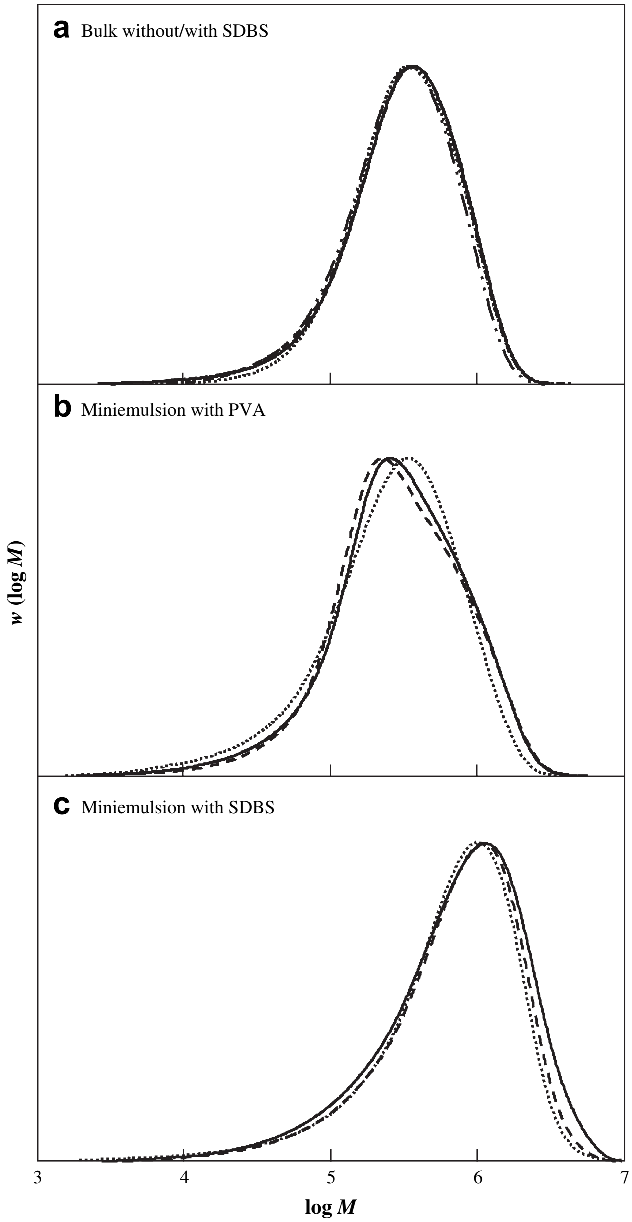

Fig. 4. MWDs at various conversions for spontaneously initiated (no added initiator) polymerization of S at 110 °C in (a) bulk without (conversions: dotted line: 7%; broken line: 22%; full line: 37%) and with SDBS (conversions: broken-dotted line: 20%), and (b) miniemulsion with PVA ($d_n \approx 250$ nm) (conversions: dotted line: 28%; broken line: 41%; full line: 50%) and (c) miniemulsion with SDBS ($d_n \approx 61$ nm) (conversions: dotted line: 29%; broken line: 41%; full line: 90%).

independent of conversion [37], and thus the MWDs should remain the same throughout the polymerization in a system dominated by chain transfer to monomer, with the number-average MW (M_n) equal to $(k_p/k_{tr,M}) \times (MW)_0$, where $(MW)_0$ is the MW of monomer. In the case of S, the chain transfer to monomer limits are approximately $M_n = 4.5 \times 10^5$ and 3.3×10^5 g mol^{-1} at 110 and 125 °C, respectively [38,41], close to the experimentally obtained values in bulk and miniemulsion in the present study (Table 1).

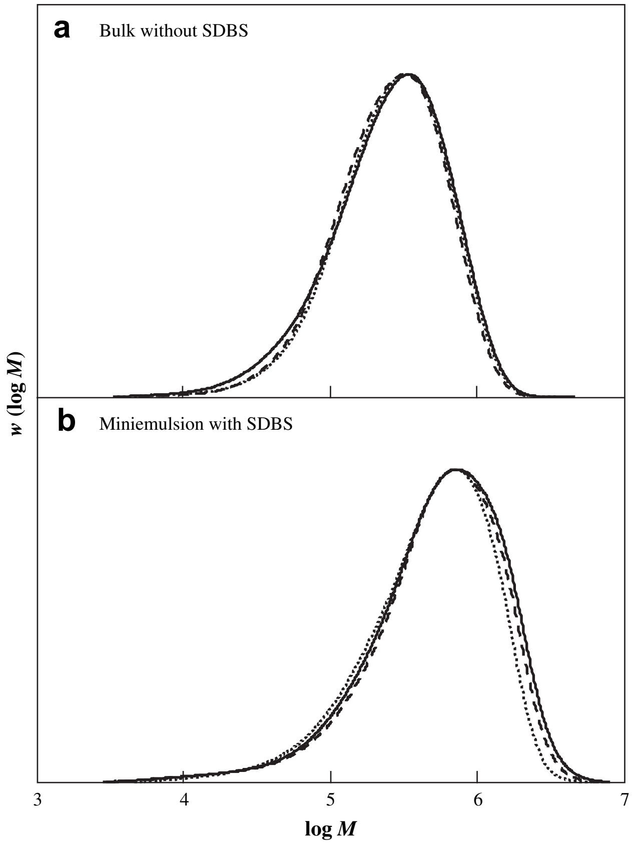

Fig. 5. MWDs at various conversions for spontaneously initiated polymerizations of S at 125 °C in (a) bulk (conversions: dotted line: 13%; broken line: 21%; full line: 39%) and (b) miniemulsion with SDBS ($d_n \approx 264$ nm) (conversions: dotted line: 24%; broken line: 46%; full line: 86%).

The MWs in the miniemulsions with small particles [(SDBS; 110 °C; $d_n \approx 61$ nm) and (SDBS; 125 °C; $d_n \approx 64$ nm)] were greater than in the corresponding bulk systems (Table 1 and Figs. 4 and 5). The MW in the miniemulsion with large particles (PVA; 110 °C; $d_n \approx 250$ nm) was similar to that in bulk at the same temperature (Fig. 4). In a S emulsion polymerization with sufficiently small particles ($d < 140$ nm [43]), one is dealing with a so called Limit 2a zero–one system [12]. Under such conditions, the main end-forming event is chain transfer to monomer, and the vast majority of the thus generated monomeric radicals reinitiate within the particle rather than exit. Monomeric radicals that do undergo exit are most likely to undergo re-entry. This results in a MWD governed by chain transfer to monomer, where bimolecular termination only makes a limited contribution because it is suppressed by compartmentalization (segregation of radicals). The differences in MWs in Figs. 4 and 5 originate in the different contributions of bimolecular termination to the chain end-forming process. In the absence of bimolecular termination, chains grow until the chain transfer to monomer limit is reached. Bimolecular termination acts as to reduce the MW, preventing the chain transfer limit to be reached (although this effect is counteracted by the increase in MW by termination by combination). The smaller the particles, the smaller is the contribution of termination due to compartmentalization. At 110 °C (Fig. 4), more extensive termination in bulk and the miniemulsion with large particles (PVA; $d_n \approx 250$ nm) led to a lower MW than the miniemulsion with small particles (SDBS; $d_n \approx 61$ nm). In the same way, more significant termination in bulk than miniemulsion (SDBS; 125 °C; $d_n \approx 64$ nm) at 125 °C resulted in higher MW in miniemulsion (Fig. 5). Based on the particle sizes and the MWs, it is likely that (SDBS; 110 °C; $d_n \approx 61$ nm) and (SDBS; 125 °C; $d_n \approx 64$ nm) are zero–one systems, whereas (PVA; 110 °C; $d_n \approx 250$ nm) is not.

According to classical kinetics of radical polymerization, R_p in a homogeneous system (bulk/solution) is proportional to $R_i^{0.5}$, where R_i is the rate of initiation. In the present study, if the only factor that sets the polymerizations apart from a kinetic point of view is $R_{i,th}$, then the ratio $R_p/R_{i,th}^{0.5}$ should be a constant at each temperature. The data in Table 1 show that at 110 °C, $R_p/R_{i,th}^{0.5}$ increases in the order bulk < (PVA; $d_n \approx 250$ nm) < (SDBS; $d_n \approx 61$ nm). In other words, compared to R_p(bulk), R_p(SDBS; $d_n \approx 61$ nm) is higher than expected based only on the enhanced $R_{i,th}$. The same qualitative trend can be seen at 125 °C. The additional R_p enhancement is partly or entirely due to compartmentalization, i.e. segregation of radicals leading to lower termination rate, the effect of which increases with decreasing particle size. The values of $R_p/R_{i,th}^{0.5}$ are relatively similar for bulk and the miniemulsion with large particles (PVA; 110 °C; $d_n \approx 250$ nm), indicating that compartmentalization is not important in this case, and that close to pseudo-bulk kinetics are obeyed, as expected based on the particle size [12,43]. This is also consistent with the MWs being similar in these two systems (Fig. 4).

3.4. Origin of spontaneous initiation

The origin of the enhanced $R_{i,th}$ in miniemulsion, and the apparent dependence of $R_{i,th}$ on particle size and/or surfactant type, are presently not understood. The values of $R_{i,th}$ in bulk yield an activation energy ($E_{i,th}$) of 84 kJ mol^{-1} (based on $R_{i,th}$ being proportional to $\exp(-E_{i,th}/RT)$). The values of $R_{i,th}$ corresponding to the miniemulsions with small particle sizes [(SDBS; 110 °C; $d_n \approx 61$ nm) and (SDBS; 125 °C; $d_n \approx 64$ nm)] yield a much lower $E_{i,th}$ of 25 kJ mol^{-1}. Hui and Hamielec [8] obtained $E_{i,th} = 115.2$ kJ mol^{-1} for spontaneous initiation of S in bulk. The values of $E_{i,th}$ in our study are likely to contain significant error because they were derived from only two temperatures covering a narrow temperature range. However, the significant difference in $E_{i,th}$ between miniemulsion and bulk is consistent with the mechanisms of spontaneous initiation being different.

In miniemulsion, the values of $R_{i,th}$ (i.e. the slopes in Fig. 3) appeared to decrease somewhat with increasing conversion, although there is considerable scatter. In bulk/solution, $R_{i,th}$ is proportional to $[S]^3$ [8], and thus decreases dramatically with increasing conversion. In Fig. 3, $R_{i,th}$ in bulk appears to remain relatively constant. However, the levels of conversion were low (<30%), thus not clearly exposing the conversion dependence. This also suggests that the mechanism of spontaneous initiation is not the same in bulk and miniemulsion.

In a zero–one system, radicals generated in pairs are expected to terminate rapidly as a result of the confined space effect [22,44–46] (spontaneous initiation of S in bulk/solution generates radicals in pairs), unless significant exit of such radicals occurs [47]. Therefore one would expect that in a miniemulsion system, the contribution of spontaneous initiation according to the bulk mechanism would decrease with decreasing particle size. According to the present data (Table 1), however, $R_{i,th}$ increased with decreasing particle size, although it cannot be excluded that the surfactant type (SDBS vs. PVA) exerts some influence on $R_{i,th}$ (see below). This also suggests that a significant fraction of radicals in the system are generated in such a manner that geminate termination within particles is not a main factor in determining $R_{i,th}$, i.e. suggesting the mechanism is different from that in bulk.

In order to investigate whether significant radical generation occurs in the aqueous phase, a S-saturated aqueous solution was held at 125 °C for 24 h. The solution remained transparent (Fig. 6a), and gas chromatography revealed that the S conversion was zero within experimental error. The S concentration in water at saturation at 25 °C is as low as 3.22×10^{-3} M [48], and it is thus conceivable that even if radical generation

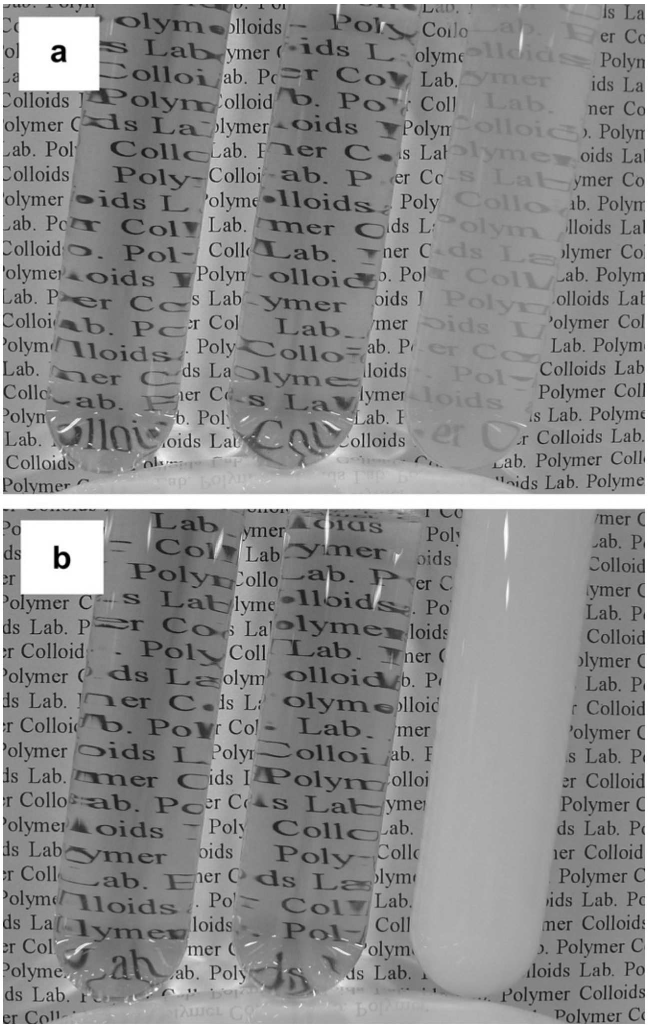

Fig. 6. Photographs of S (a) and S/MMA (b) saturated aqueous phase polymerization systems; (a) left: S/water/125 °C/24 h, middle: S/water/SDBS/125 °C/24 h, right: S/water/KPS/70 °C/5 h; (b) left: S/MMA/water/125 °C/24 h, middle: S/MMA/water/SDBS/125 °C/24 h, right: S/MMA/water/KPS/70 °C/5 h. See text for details.

occurs, the efficiency of initiation (i.e. radical addition to S) is very low due to the low S concentration. To increase the monomer concentration, two saturated aqueous solutions of S and MMA were mixed in a 1:1 volume ratio, and held at 125 °C for 24 h (the MMA concentration in water at saturation at 60 °C is 0.256 M [49]). This also resulted in a transparent solution, with zero conversion of both S and MMA (Fig. 6b). In the miniemulsion systems, the aqueous phase contains a small amount of the emulsifier SDBS. To mimic the actual miniemulsions, SDBS in low concentration ([SDBS] = 0.334 mM; the critical micelle concentration (cmc) at 50 °C is 3.34 mM [50]) was added to the S-saturated aqueous solution and the S/MMA aqueous solution, and the solutions were held at 125 °C for 24 h. Again, transparent solutions were obtained with zero monomer conversions (Fig. 6a and b). Finally, separate experiments using the S-solution and the S/MMA-solution (no SDBS) were conducted at 70 °C for 5 h in the presence of KPS (0.617 mM). In both cases, polymerization occurred, as evidenced by the solutions turning turbid due to particle formation (Fig. 6a and b). The above experiments provide convincing evidence that the rate of radical generation in the aqueous phase in the present miniemulsion systems is negligible within the context of the present work.

There are several reports in the literature on the spontaneous radical polymerization of S in aqueous dispersed systems. Hawkett et al. [11] found that the spontaneous polymerization rate in seeded emulsion polymerization of S at 50 °C (surfactant: sodium dodecylsulfate, SDS; particle diameters 88–158 nm) was approximately 350 times greater than in the corresponding bulk system. Rigorous investigations suggested that impurities in S and/or water were not the source of the spontaneous radical generation. Moreover, changing the surfactant from SDS to sodium dioctyl sulphosuccinate (Aerosol MA 80) resulted in comparable, but not identical, polymerization rates. Ab initio emulsion polymerization under the same conditions produced a latex, which strongly suggests that spontaneous radical generation is occurring in the aqueous phase. This is supported by the work of Lacik et al. [51], who found that spontaneous radical seeded emulsion polymerization of S at 50 °C under zero–one conditions did not proceed in the presence of an aqueous phase radical scavenger (Fremy's salt), thus suggesting that radical formation occurs in the aqueous phase and/or at the particle/aqueous interface.

Asahara et al. [52] investigated spontaneous initiation of S in an ab initio emulsion polymerization in the presence of the surfactant sodium tetrapropylenebenzenesulfonate at 70–100 °C. The activation energy of the radical generation step was estimated to be 86.2 kJ mol^{-1}, i.e. higher than that obtained in the present study. Note, however, that its value was obtained from the overall energy of activation of the polymerization (no value of $R_{i,th}$ was reported), whereas our estimate was derived directly from $R_{i,th}$. They speculated that radical generation mainly occurred at the interface between micelles (particles) and the aqueous phase.

Lansdowne et al. [10] estimated the activation energy of the rate coefficient for radical entry during spontaneous seeded emulsion polymerization of S (surfactant: SDS; particle diameter 96 nm) at 30–65 °C to be 87 kJ mol^{-1}. This value is anticipated to correspond to that of the radical generation process, which is likely to be the rate determining step [10]. It was argued by Lansdowne et al. that this value suggests that radical generation occurs via a process involving bond fission, but most likely not peroxides in the aqueous phase, because the activation energy of the latter process would be expected to be higher [53] (approximately 140 kJ mol^{-1}). Christie et al. [13] investigated the seeded spontaneously initiated polymerization of S (surfactant: SDS; particle diameter = 124 nm) and concluded that radical generation occurs in the monomer droplets, the aqueous phase, and the particles.

An additional factor which may play a role in spontaneous initiation of S in aqueous dispersed systems is the so called "hydrophobic effect" [54], which is the tendency of nonpolar species to aggregate in aqueous solution so as to decrease the hydrocarbon–water interfacial area. The hydrophobic effect has been proposed to speed up spontaneous initiation of S by increasing the rate of formation of the Diels–Alder dimer in the aqueous phase (the Diels–Alder dimer is an intermediate in the proposed mechanisms for spontaneous initiation of S in bulk/solution [9]).

Cunningham and coworkers [31,32] recently proposed that the surfactant SDBS is participating in the generation of radicals during TEMPO-mediated polymerization of S in aqueous miniemulsion at 135 °C. To investigate this, spontaneous polymerization of S in bulk at 110 °C was carried out in the present study in the presence of SDBS (Fig. 1). The polymerization rate was not significantly affected by the presence of SDBS, i.e. SDBS does not significantly influence $R_{i,th}$ in bulk. However, it can of course not be excluded that radical generation involving SDBS may occur in the aqueous phase or at the interface between the organic and aqueous phases. Cunningham and coworkers [31] showed that R_p did increase in the presence of SDBS during TEMPO-mediated polymerization of S in bulk (135 °C), which suggests that an SDBS-related increase in $R_{i,th}$ may be related to the presence of TEMPO. Nevertheless, regardless of the possible role of SDBS, it is evident from Fig. 3 that $R_{i,th}$ in miniemulsion is significantly higher than in bulk also using PVA.

In concluding this section, it is apparent that further work is required to elucidate the mechanism(s) of spontaneous radical generation in these systems. The experimental evidence of the present work is consistent with: (i) radical generation at the interface between the aqueous and the organic phases, and (ii) radical generation according to the bulk mechanism within polymer particles and monomer droplets. The contribution from (i) far exceeds that of (ii).

3.5. Implications for nitroxide-mediated polymerization

Spontaneous radical generation plays a central role in NMP of S. In the absence of spontaneous initiation, a stationary state with respect to the propagating radical concentration ([P•]) is never reached, because [P•] keeps decreasing due to bimolecular termination. However, in the presence of spontaneous initiation, a stationary state is reached, where [P•] is governed by the rates of spontaneous initiation and bimolecular termination according to $[\text{P}\bullet] = (R_{\text{i,th}}/k_t)^{0.5}$, where k_t is the termination rate coefficient, i.e. R_p is independent of the alkoxyamine concentration at the stationary state [14]. It is thus evident that a quantitative mechanistic understanding of NMP of S in aqueous dispersed systems requires knowledge of $R_{\text{i,th}}$.

We have previously reported that the TEMPO-mediated polymerization of S in aqueous miniemulsion at 125 °C using SDBS as surfactant depends on particle size in the diameter range 70–170 nm [26,55] (simulations indicate that smaller particles are required for compartmentalization effects to become important in TEMPO-mediated S polymerization [22,46]). As the particle size decreases in this range, R_p increases at the expense of a gradual loss of control/livingness. This has been proposed to have its origin in (i) the interface effect, whereby some fraction of TEMPO is located near/adsorbed at the interface, and/or (ii) enhanced radical generation caused by SDBS [31,32]. We showed by modeling and simulations [26] that for $d_n \approx 70$ nm, a spontaneous initiation rate as high as $R_{\text{i,th}} = 3.2 \times 10^{-4}$ M s^{-1} is required to explain the experimental conversion–time data by enhanced $R_{\text{i,th}}$ only. This value is a factor of 176 greater than that determined experimentally in the present study (last entry in Table 1). The present results thus support our previous conclusions [26] that enhanced spontaneous initiation alone cannot explain the particle size dependence observed in Ref. [55], consistent with explanations (i) and (ii) both playing significant roles.

4. Conclusions

Spontaneous initiation in radical polymerization of S in aqueous miniemulsion at 110 and 125 °C using the surfactants SDBS and PVA has been investigated. For the first time, the rate of spontaneous radical generation ($R_{\text{i,th}}$) was quantified in such high temperature systems. Such systems are becoming increasingly relevant with the recent advent of NMP in aqueous dispersed systems, which is often carried out at high temperature, and where $R_{\text{i,th}}$ plays an important role.

$R_{\text{i,th}}$ was estimated using a novel approach based on the total number of chains in the system, i.e. without making use of the polymerization rate (R_p). By quantitative consideration of the increase in the number of chains based on chain transfer to monomer, the number of spontaneously generated radicals having initiated chains can be extracted based on a simple algebraic procedure.

In agreement with previous work at lower temperatures, $R_{\text{i,th}}$ was found to be much higher than in the corresponding bulk systems. The values of $R_{\text{i,th}}$ in miniemulsion were 3.1–15.1 times greater than in the corresponding bulk systems, depending on the particular system. Based on the activation energy of $R_{\text{i,th}}$ as well as its conversion (monomer concentration) dependence, the mechanism(s) for radical generation is different from that in bulk, also consistent with previous work at lower temperatures. It was established experimentally that radical generation in the aqueous phase is negligible, thus consistent with the enhanced radical generation observed having its origin at the interface between the aqueous and organic phases (spontaneous radical generation according to the bulk mechanism is also expected to occur).

The present results are of relevance with regards to recent experimental findings in the TEMPO-mediated polymerization of S in miniemulsion at 125 °C using SDBS as surfactant. In this system, we have reported that as the particle size decreases in the diameter range 70–170 nm, R_p increases at the expense of a gradual loss of control/livingness [26,55]. The present results support our previous conclusions [26] that enhanced spontaneous initiation alone cannot explain this particle size dependence (although it does play an important role), consistent with an interface effect being operative, whereby some fraction of TEMPO is located near/adsorbed at the interface.

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