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Gel formation and primary chain lengths in nitroxide-mediated radical copolymerization of styrene and divinylbenzene in miniemulsion

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Abstract

Gelation in 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO)-mediated cross-linking copolymerization of styrene and divinylbenzene (8.2 mol%) in aqueous miniemulsion at 125 °C has been investigated. The rate of gel formation relative to monomer conversion was the same in miniemulsion and the corresponding solution polymerization when the organic phase contained 6 vol% tetradecane (TD; hydrophobe) and 48 vol% toluene. However, at 54 vol% TD and no toluene (the same total monomer concentration), the conversion at the gel point was lower in miniemulsion than in solution, consistent with our previous results describing enhanced apparent pendant reactivity related to the presence of TD in the present system. The primary chain lengths were higher in miniemulsion with 54 vol% TD than in miniemulsion with 6 vol% TD and in solution (6 and 54 vol% TD). It was deduced via application of Flory–Stockmayer gelation theory that this difference in primary chain lengths, although significant with regards to gelation, was insufficient to explain the rapid gel formation in the miniemulsion containing 54 vol% TD, which is speculated to be related to specific effects of the heterogeneity of the miniemulsion system.

Keywords: Controlled/living radical polymerization; Cross-linking; Nitroxide

1. Introduction

Cross-linked polymer particles have been the subject of intense research for several decades, resulting in a multitude of commercial materials, and much work has been devoted to elucidation of mechanistic/kinetic features of network formation in aqueous heterogeneous systems [1–12]. During the course of our research [1–7], micron-sized, cross-linked hollow polymer particles have been successfully prepared by seeded polymerization using the SaPSeP method. We have discovered a range of factors that have a profound influence on network formation, for instance, the role of hexadecane (inert non-solvent) on phase separation in conventional (i.e. not controlled/living) radical polymerization of divinylbenzene (DVB) [5], as well as effects of particle viscosity [7]. The above examples illustrate the complexity of conventional cross-linking radical polymerization in aqueous heterogeneous systems.

The recent advent of controlled/living radical polymerization (CLRP) [13,14] enables synthesis of linear polymers of predefined molecular weights (MW) with low polydispersities, as well as polymers with other more complex architectures by free radical means. CLRP was initially developed for bulk/solution polymerizations, but in recent years significant progress has been made on CLRP in aqueous heterogeneous systems [15–21]. Attention has also been directed towards the use of CLRP techniques in connection with cross-linking systems [22–31]. Ide and Fukuda [22,23] reported that the apparent pendant reactivity was much lower in the 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO)-mediated radical bulk copolymerization of styrene (S) and 4,4′-divinylbiphenyl than

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in the corresponding conventional system. This is believed to be mainly a local concentration effect of the pendant unsaturations, caused by the (normally) much higher primary chain lengths associated with a conventional system compared to a CLRP system. This local concentration effect, which leads to intramolecular cross-linking dominating at low conversion in a typical conventional system, is much less pronounced in CLRP, resulting in more homogeneous network formation without microgels, higher swelling and anticipated superior mechanical properties [23]. Similar results have been obtained for atom transfer radical polymerization (ATRP) [24–27,31–33] and reversible addition fragmentation chain transfer (RAFT) polymerization [29,34,35] of cross-linking systems.

Cross-linking CLRP in heterogeneous systems remains fairly unexplored, with only a few papers published to date [32,36,37]. We recently reported the controlled/living radical cross-linking copolymerization of S/DVB initiated by a PS-TEMPO macroinitiator in aqueous miniemulsion at 125 °C [36,37]. The development of the cross-linked network in miniemulsion was markedly different from that in bulk, as evidenced mainly by significantly lower apparent pendant reactivities in miniemulsion. Based on these findings, and considering that a quantitative mechanistic understanding of network formation is essential in order to optimize cross-linked polymer particle synthesis for a given application, we embarked on an investigation of gel formation in the TEMPO-mediated radical copolymerization of S/DVB in aqueous miniemulsion at 125 °C.

2. Experimental section

2.1. Materials

S was purified by distillation under reduced pressure in a nitrogen atmosphere. Benzoyl peroxide (BPO) was recrystallized using chloroform/methanol. DVB (32% *p*-DVB, 68% *m*-DVB; Nippon Steel Chemical; purity 96%) was washed with 1 N NaOH and deionized water to remove inhibitors. TEMPO (Aldrich Chem. Co. Ltd.), sodium dodecylbenzenesulfonate (SDBS), toluene, tetrahydrofuran (THF), *p*-xylene, *n*-tetradecane (TD), and methanol (Nacalai Tesque Inc., Kyoto, Japan) were used as received.

2.2. Polymerization procedures

Miniemulsion copolymerizations (30 wt% organic phase): A solution of S (4.5 g), DVB (0.5 g), TEMPO (37.6 mg; 0.02 M), BPO (46.3 mg; 0.016 M), toluene (5.0 g; 48 vol% rel. to organic phase) and TD (0.526 g; 6 vol% rel. to organic phase) was mixed with an aqueous solution of SDBS (4 wt% rel. to organic phase). Miniemulsion polymerizations were also carried out as above but with 4.94 g TD (54 vol% rel. to organic phase) in the absence of toluene, i.e. at the same total monomer concentration. The resulting mixtures were emulsified by ultrasonication (Ultrasonic Homogenizer, Nissei, US-600T, set at "Power 9") for 12 min at 0 °C. The miniemulsions were subsequently transferred to glass ampules, degassed using several N_2/vacuum cycles and sealed off under vacuum. Polymerizations were carried out at 125 °C shaking the ampules (approx. 8 g/ampule) horizontally at 100 cycles/min. The corresponding solution polymerizations (i.e. as above but without water and SDBS) were also performed in glass ampules (approx. 3 g/ampule) as above.

2.3. Measurements

Conversions were measured by both gravimetry and gas chromatography (Shimadzu Corporation, GC-18A, with helium as carrier gas, employing THF as solvent and *p*-xylene as internal standard) with good agreement in all cases, except for the solution polymerizations containing 54 vol% TD above 27% conversion, which were measured by gravimetry only.

Polymer (for subsequent gel fraction measurement) was recovered using various procedures depending on the particular polymerization. The miniemulsions were poured into methanol and the polymer was collected by filtration. 6 vol% TD solution polymerization: The polymer sample was (partially) dissolved in toluene during vigorous stirring/mixing with a glass rod for approx. 10 min, after which the polymer was precipitated in methanol and subsequently collected by filtration. 54 vol% TD solution polymerization: A small amount of toluene was added to the polymer sample (causing swelling), which was transferred to a mortar and ground to a fine powder-like state. The powder was subsequently mixed with methanol for 10 min with intermittent stirring with a glass rod (to remove unreacted monomer and TD), followed by collection of the polymer by filtration. The polymer powders thus obtained from all four polymerizations were mixed with methanol for 10 min with intermittent stirring with a glass rod for 10 min, followed by filtration and drying under vacuum to ensure complete removal of TD.

Gel fractions were determined as follows: polymer (obtained as described above) was immersed in excess toluene as a good solvent to extract soluble parts. The thus obtained solution (toluene containing dissolved polymer) was replaced with new toluene three times during one week. The remaining insoluble polymer (gel) was weighed after drying to constant weight under vacuum.

Molecular weight distributions (MWDs) were measured by gel permeation chromatography (GPC) using two S/DVB gel columns (TOSOH Corporation, TSK gel GMH_{HR}-H, 7.8 mm i.d. × 30 cm, separation range per column: approx. 50–4×10^8 g/mol (exclusion limit)) using THF as eluent at 40 °C at a flow rate of 1.0 mL/min with UV detection (TOSOH UV-8020). The columns were calibrated with six standard linear PS samples (1.05×10^3 to 5.48×10^6, $M_w/M_n = 1.10–1.15$).

Particle size distributions were measured by dynamic light scattering (FPAR-1000RK, Otsuka Electronics, Osaka, Japan) at the light scattering angle of 90° at room temperature after dilution using deionized water. Number-average (d_n) and weight-average (d_w) particle diameters were obtained using the Marquadt Analysis routine. The particle sizes remained approximately constant throughout the polymerizations (average values given).

3. Results and discussion

3.1. Rate of polymerization

Fig. 1 shows conversion–time data for TEMPO-mediated copolymerization of S/DVB with the organic phase containing 6 and 54 vol% of the hydrophobe TD (with 48 and 0 vol% toluene, respectively) in solution and miniemulsion at 125 °C (TD was added for reasons explained later). The monomer concentration in the organic phase (based on the recipes) was the same as in the solution polymerizations for both miniemulsion polymerizations. The rates of polymerization (R_p) were similar, although not identical, in all cases. The particle size was deliberately chosen to be large enough ($d_n \approx 190$ nm and $d_w \approx 250$ nm in both miniemulsion polymerizations) so that compartmentalization effects (segregation and confined space effects) [38] and possibly other less understood interfacial effects [39] would not be significant. Theoretical work shows that partitioning of TEMPO to the aqueous phase does not significantly influence the polymerization in the present system [40]. Cunningham and coworkers [41] very recently reported that the presence of SDBS itself in TEMPO-mediated polymerization of S results in an increase in R_p in both miniemulsion (volume-average diameter = 115–129 nm) and bulk at 135 °C. However, no such effects were detected in the present work (R_p in miniemulsion was essentially the same as in solution).

Fig. 2 shows the relative monomer consumption rates by plotting ln[DVB]$_0$/[DVB] vs. ln[S]$_0$/[S], revealing no significant differences between the systems. According to our previous work on the system S/DVB/TEMPO/125 °C in aqueous miniemulsion, the relative consumption rate of DVB was lower in miniemulsion than in bulk when the initial mol% DVB (rel. to S and DVB) was 1% [36,37] for reasons that are currently not clear. However, in the present system (8.2 mol% DVB rel. total monomer), no such differences were detected, suggesting that the origin of this phenomenon is closely related to the DVB content. Thus, at a given conversion, the gel contents of the various systems can be directly compared without having to consider different levels of DVB incorporation. The entire data set (all four polymerizations) were fitted according to Eq. (1) [36].

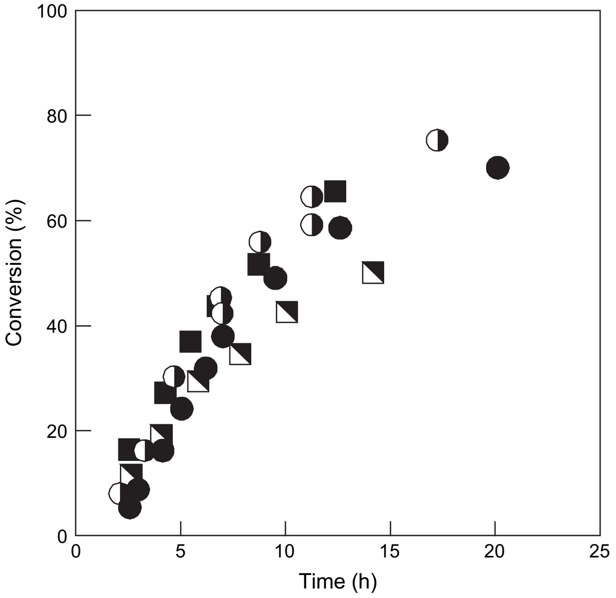

Fig. 1. Conversion–time plots for TEMPO-mediated radical copolymerizations of S (91.8 mol%) and DVB (8.2 mol%) in solution (◪,■) and miniemulsion (◑,●) containing 6 vol% tetradecane (TD) and 48 vol% toluene (◪,◑) and 54 vol% TD and 0 vol% toluene (■,●) at 125 °C.

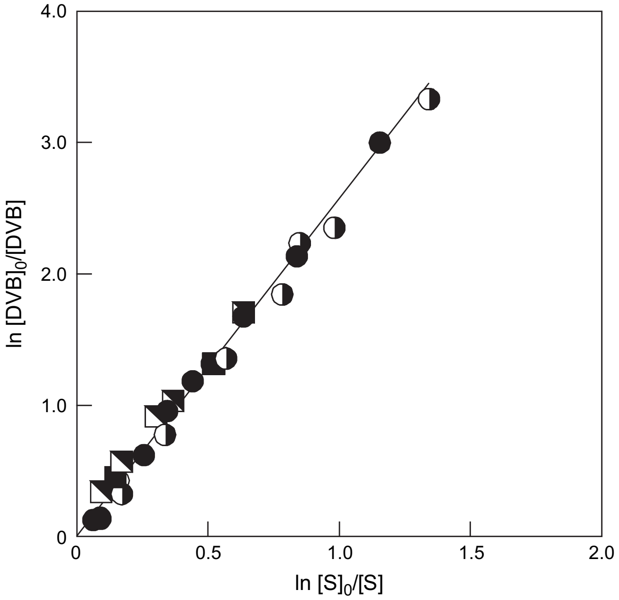

Fig. 2. Relative rates of consumption of DVB and S for TEMPO-mediated radical copolymerizations of S (91.8 mol%) and DVB (8.2 mol%) in solution (◪,■) and miniemulsion (◑,●) containing 6 vol% TD and 48 vol% toluene (◪,◑) and 54 vol% TD and 0 vol% toluene (■,●) at 125 °C.

$$\ln\frac{[\mathrm{DVB}]_0}{[\mathrm{DVB}]} = \frac{k_{\mathrm{SDVB}}}{k_{\mathrm{SS}}}\ln\frac{[\mathrm{S}]_0}{[\mathrm{S}]} \tag{1}$$

where k_{SS} is the propagation rate coefficient for S and k_{SDVB} is the rate coefficient for addition of a PS radical to DVB, yielding $k_{\mathrm{SS}}/k_{\mathrm{SDVB}} = r_{\mathrm{S}} = 0.39$, which lies well within the reported range [42]. Use of Eq. (1) for estimation of r_{S} is based on the assumption that the rates of S and DVB consumption by DVB-terminated radicals are negligible ([S] ≫ [DVB]).

3.2. Gelation

We have previously proposed that the interface between the aqueous and the organic phase may exert some influence on the apparent pendant reactivity in the TEMPO-mediated copolymerization of S and DVB in aqueous miniemulsion at 125 °C [37]. Poly(DVB) is known to migrate to the interface of monomer/toluene droplets in an aqueous emulsion, and this process is promoted by the presence of a hydrophobe such as linear PS or hexadecane [5]. This is the basis of the self-assembling of phase separated polymer (SaPSeP) method for hollow polymer particle synthesis [1–6]. For the system S/DVB (1 mol% rel. to total monomer)/TEMPO/125 °C in aqueous miniemulsion, our previous results showed that the apparent pendant reactivity increased upon addition of 30 wt% TD, and a pronounced high MW shoulder appeared [37]. Prompted by these results, the gelation behavior was investigated at two different TD levels: 6 and 54 vol% (the total volume of toluene and TD was kept constant).

Gel fractions vs. conversion are displayed in Fig. 3a for solution and miniemulsion polymerizations containing 6 vol% TD. Within experimental error, the gelation behaviors were the same in miniemulsion and solution. This was somewhat surprising, because at a lower DVB content (1 mol% rel. to 8.2 mol% in the present study), the apparent pendant reactivity was considerably lower in miniemulsion than in the corresponding bulk system [36,37]. However, the rate of gel formation cannot be directly related to the overall apparent pendant reactivity, but must also be correlated with the extents of inter- and intramolecular reaction of the pendant unsaturations.

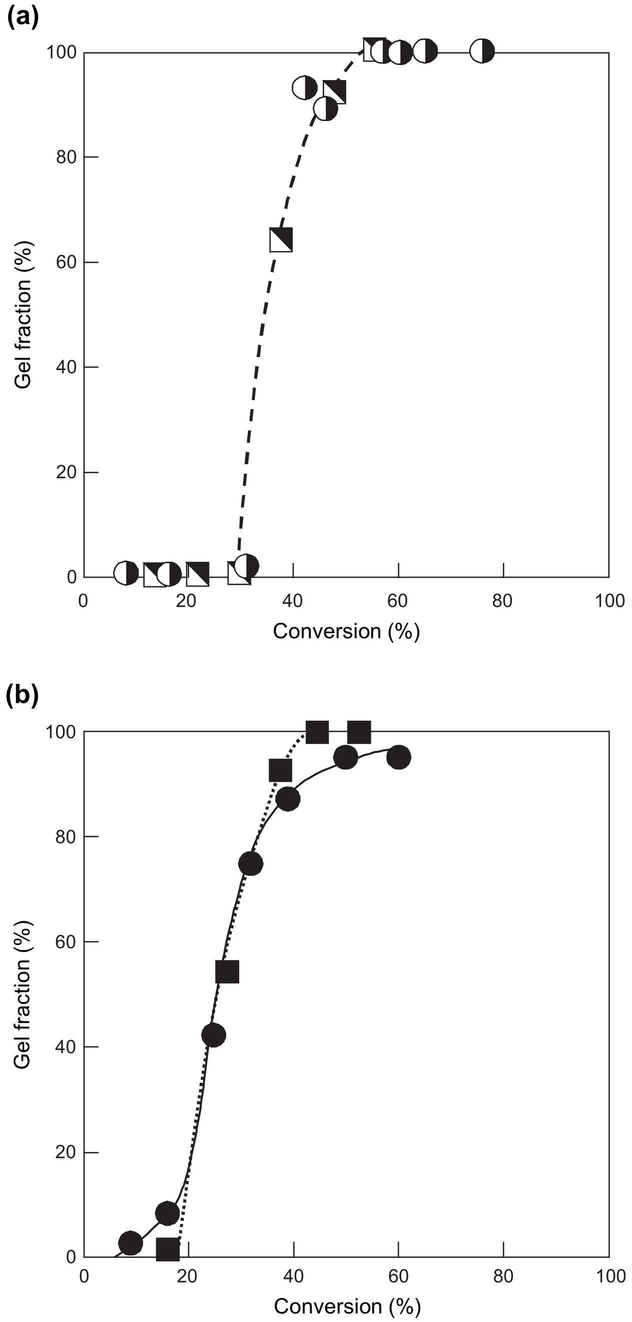

Fig. 3. Gel fraction vs. total conversion for TEMPO-mediated radical copolymerizations of S (91.8 mol%) and DVB (8.2 mol%) at 125 °C containing (a) 6 vol% TD and 48 vol% toluene (◪, ◑) and (b) 54 vol% TD and 0 vol% toluene (■, ●) in solution (◪, ■) and miniemulsion (◑, ●) at 125 °C. The lines are guides to the eye only.

Fig. 3b shows the gel fractions vs. conversion in solution and miniemulsion at the higher level of TD (54 vol%). In both cases, gelation occurred at considerably lower conversion than for 6 vol% TD (Fig. 3a). Moreover, at 54 vol% TD, gel formed at a lower conversion in miniemulsion than in solution, consistent with the effect of TD on apparent pendant reactivity and MWDs in the system S/DVB (1 mol% rel. to total monomer)/TEMPO/125 °C in aqueous miniemulsion [36,37]. It is noteworthy that even though the primary chain lengths were only approx. 3400 (M_n) at 8.7% conversion (discussed below), insoluble polymer had nonetheless formed. However, the effect of TD cannot solely be ascribed to effects specifically related to the heterogeneous nature of the miniemulsion system, because gelation occurred at a lower conversion at the higher TD level also in solution (Fig. 3a and b). It has previously been reported that gelation is delayed as the solvent quality is increased [10,43], consistent with the present results (PS is insoluble in TD).

Fig. 4a shows the MWDs of the soluble fraction of the polymer at different conversion levels for the miniemulsion polymerization with 6 vol% TD, revealing a gradual shift to higher MWs as well as the emergence of a high MW shoulder with increasing conversion (these experimental MWs are linear PS equivalents and are thus underestimated due to branching/cross-linking). The gel point of this system was approx. 31% (Table 1). The reason the high MW shoulder is more prominent at 31% than 42% conversion is that gelation results in removal of a significant amount of high MW polymer, and the MWDs displayed correspond to soluble polymer only. The MWDs at 16% conversion for the miniemulsion polymerizations containing 6 and 54 vol% TD are displayed in Fig. 4b. The 6 vol% TD sample corresponds to total polymer, whereas that of the 54 vol% sample corresponds to the sol part only, i.e. the complete (sol plus gel) MWD contains more high MW polymer than that displayed. The level of TD had a marked effect on the MWDs, with a higher TD content leading to both a higher primary chain length (addressed below) as well as a much more prominent high MW shoulder, indicative of more intermolecular cross-linking, and consistent with earlier gelation (Fig. 3).

3.3. Primary chain lengths

In a CLRP cross-linking system, the primary chains grow over the entire course of the polymerization. This is in stark contrast to the situation in a non-living cross-linking radical polymerization, where primary chains are initiated throughout the polymerization and usually reach their final length (i.e. terminate) within a few seconds. In a CLRP cross-linking system,

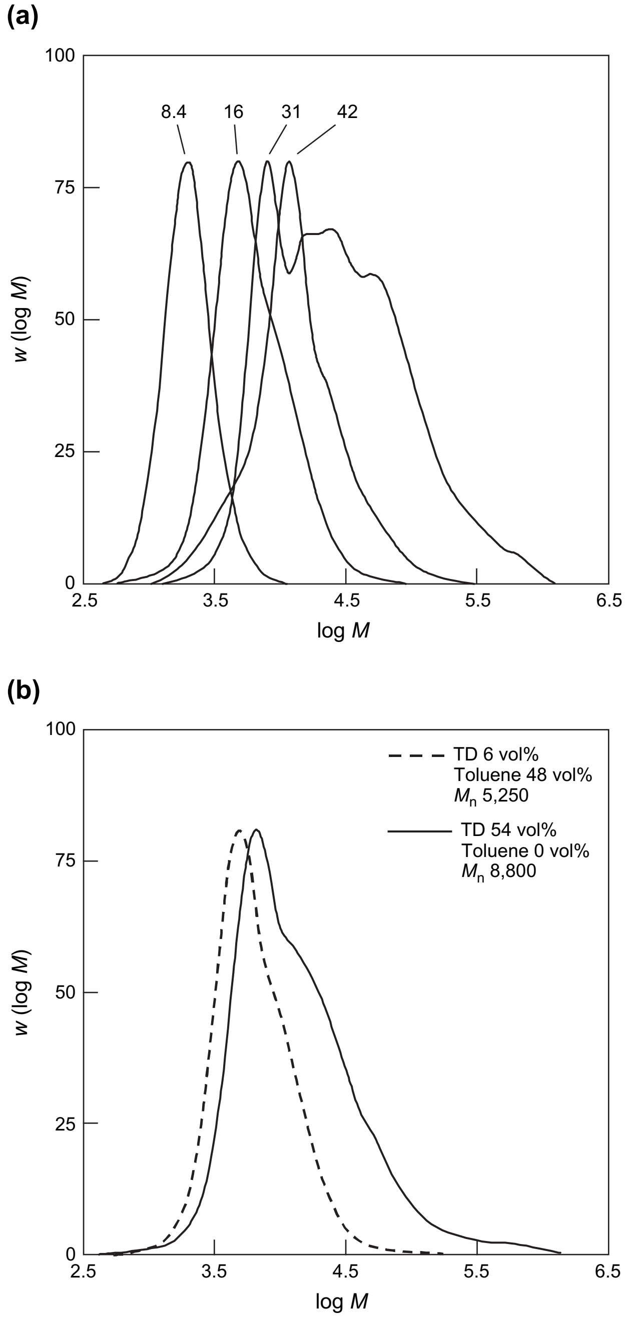

Fig. 4. (a) Molecular weight distributions at different conversions (%) as indicated for TEMPO-mediated radical copolymerizations of S (91.8 mol%) and DVB (8.2 mol%) in solution containing 6 vol% TD and 48 vol% toluene at 125 °C. (b) Molecular weight distributions at 16% conversion for TEMPO-mediated radical copolymerizations of S (91.8 mol%) and DVB (8.2 mol%) in miniemulsion containing 6 vol% TD and 48 vol% toluene (dotted line) and 54 vol% TD and 0 vol% toluene (full line).

Table 1
Comparison of theoretical ($\alpha_{c,th}$) and experimental ($\alpha_{c,exp}$) gel points in copolymerizations of S/DVB (NMP)

Sample	Diluent composition (vol%)				
	TD	Toluene	$\alpha_{c,exp}$	$\alpha_{c,th}$[a]	$\alpha_{c,exp}/\alpha_{c,th}$
Solution	6	48	30	16.3	1.8
Solution	54	0	16	16.3	0.98
Miniemulsion	6	48	31	14.4	2.2
Miniemulsion	54	0	8.7[b]	12.0	0.73

TD: tetradecane.

[a] Calculated using Flory–Stockmayer equation.

[b] Maximum value of gel point (gel existed in real experiment).

it is often possible to identify the primary chains in the MWDs as a narrow peak located in the low MW region of the MWD, with the cross-linked/branched polymer chains appearing as a high MW shoulder (4a) [30,44].

The number-average MW (M_n) of the primary chains in the present study was estimated as the M value at the point left of the peak corresponding to the primary chains where the y-axis value was 88% of the maximum value (estimated by examination of the position of M_n in the homopolymerizations of S at approx. 15% conversion ($M_w/M_n \approx 1.2$)). This is admittedly a somewhat crude approach, but it does adequately serve the purpose of roughly comparing the primary chain lengths in different systems.

Fig. 5a shows that M_n increased close to linearly with conversion in all polymerizations, consistent with a controlled/living system. However, the primary chain lengths in the miniemulsion with 54 vol% TD were approx. 30% higher than the theoretical M_n ($M_{n,th} = (\alpha[M]_0 M_M)/[TEMPO]_0$), where α is the total monomer conversion, $[M]_0$ denotes the total monomer concentration, and M_M was approximated as the MW of S, whereas M_n of the other polymerizations agreed relatively well with $M_{n,th}$. As emphasized above, these M_n values are merely semi-quantitative. However, the trend is real, as evidenced by the MWDs in Fig. 4b which clearly show that the low MW segment of the MWD (as well as the peak) was higher for the miniemulsion with 54 vol% TD.

The primary chain lengths were further investigated by carrying out solution and miniemulsion polymerizations at both TD levels in the absence of DVB. Fig. 5b shows that also in the absence of DVB, the miniemulsion system with 54 vol% TD exhibited M_n values approximately a factor 1.8 greater than $M_{n,th}$. This indicates that the number of chains in this system was 44% lower than theory predicts, and the linearity of the data shows that the number of chains remained approximately constant with conversion. In other words, a significant number of chains were lost at the very initial stage of the polymerization. The miniemulsion with 6 vol% TD also exhibited M_n values somewhat higher than $M_{n,th}$, although the deviation was much smaller (approx. 24%) than for the miniemulsion with 54 vol% TD. The fact that increasing the amount of TD in solution does not appear to alter the primary chain lengths suggests that the effect in miniemulsion is specifically related to the heterogeneous character of the system. The exact origin of this phenomenon is presently unclear, but forms the subject of ongoing work in our laboratory.

3.4. *Effect of primary chain lengths on gelation*

The primary chain length is an important factor with regards to gelation. The higher the primary chain length, the lower is the conversion at the gel point as a result of a higher number of pendant unsaturations (DVB units) per primary

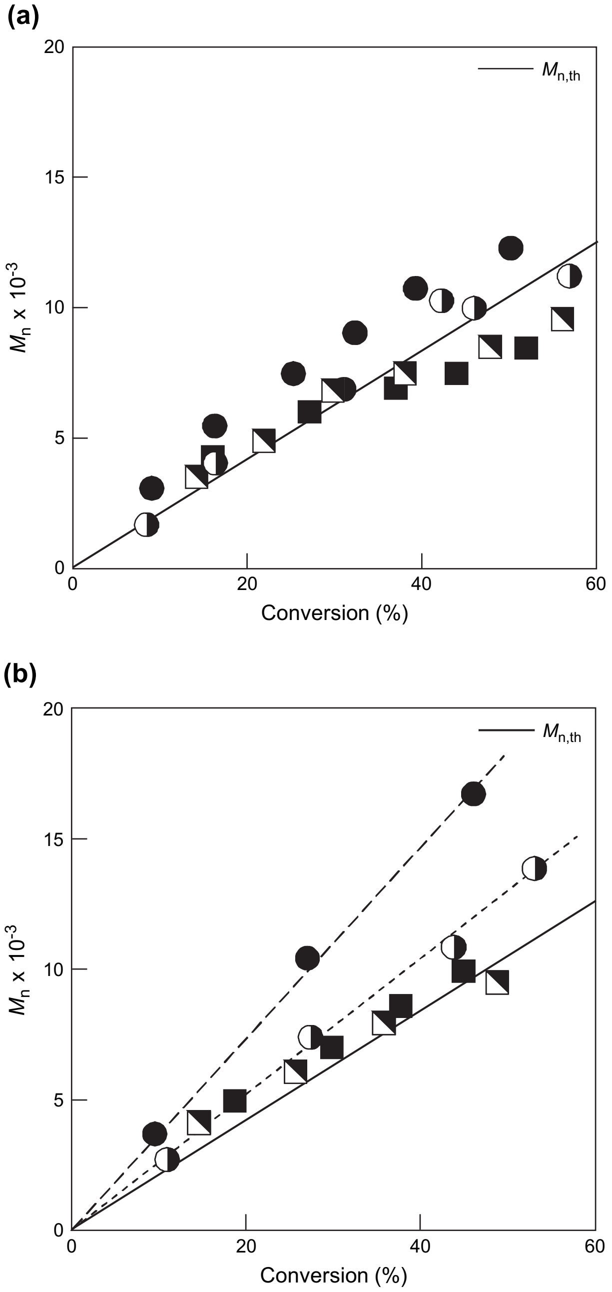

Fig. 5. (a) M_n of primary chains vs. total conversion for TEMPO-mediated radical copolymerizations of S (91.8 mol%) and DVB (8.2 mol%) in solution (◩, ■) and miniemulsion (◑, ●) containing 6 vol% TD and 48 vol% toluene (◩, ◑) and 54 vol% TD and 0 vol% toluene (■, ●) at 125 °C. (b) M_n vs. S conversion for TEMPO-mediated radical polymerizations of S (in the absence of DVB) in solution (◩, ■) and miniemulsion (◑, ●) containing 6 vol% TD and 48 vol% toluene (◩, ◑) and 54 vol% TD and 0 vol% toluene (■, ●) at 125 °C. Full line: Theoretical M_n ($M_{n,th}$); dotted lines: guides to the eye only.

chain [10]. The higher primary chain length in the 54 vol% TD miniemulsion is therefore anticipated to be a contributing factor towards this system having a lower gel point than the miniemulsion with 6 vol% TD (and the two solution polymerizations). The miniemulsion with 54 vol% TD contained on the average 3.9 DVB units per primary chain at approx. 8.5% conversion, to be compared with 2.2 for the miniemulsion with 6 vol% TD (based on data in Figs. 2 and 5(a)).

The Flory–Stockmayer (FS) gelation theory [45,46] provides a framework for quantitative analysis of the effect of primary chain length on gelation. It is however difficult to quantify the effect of primary chain length on the rate of gelation based on FS theory due to deviations from "ideal network formation" (e.g. intramolecular cyclization, intramolecular cross-linking). Eq. (2) describes the relationship between the conversion and the primary chain length at the gel point for ideal network formation [45]:

$$\alpha_c = \frac{1}{\rho(\overline{P}_w - 1)} \tag{2}$$

where α_c is the total vinyl group conversion at the gel point, ρ is the fraction of vinyl groups residing on divinyl units before polymerization, and $\overline{P}_w$ is the weight-average degree of polymerization of primary chains at the gel point.

In an attempt to semi-quantitatively estimate whether the effect of the increased primary chain lengths in the 54 vol% TD system is significant with regards to gelation, Eq. (2) was employed to calculate the gel point (α_c) as a function of M_n of the primary chains based on $M_w/M_n = 1.3$ (a typical value for the S/TEMPO system at 125 °C). The result obtained as well as the straight line describing the relationship between $M_{n,th}$ of the primary chains (calculated as described in Section 3.3) and the total vinyl group conversion, and the experimentally obtained M_n values in the miniemulsion polymerizations with 6 and 54 vol% TD (in the absence of DVB; Fig. 5b), are shown in Fig. 6. The total vinyl group conversion (as appearing in Eq. (2)) is not the same as the total monomer conversion

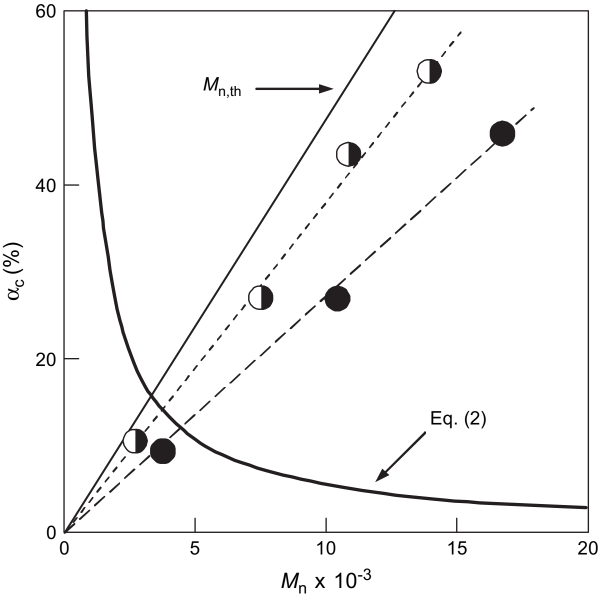

Fig. 6. Relationship between total vinyl group conversion (α_c) and M_n of the primary chains at the gel point based on the Flory–Stockmayer (FS) theory (Eq. (2); thick curve). The thin full line shows the theoretical M_n ($M_{n,th}$) of the primary chains in the polymerizations detailed in the caption of Fig. 1. The data points correspond to the TEMPO-mediated radical polymerization of S in miniemulsion containing 6 vol% TD and 48 vol% toluene (◑) and 54 vol% TD and 0 vol% toluene (●) at 125 °C (both in the absence of DVB).

(the conversion upon which $M_{n,th}$ is based); the two quantities differ due to each DVB unit containing two vinyl groups. However, at a pendant conversion of 50% at 32% total monomer conversion, the difference between the two "conversions" is merely 0.09 percentage points, i.e. negligible within the current context. According to Eq. (2), the gel point decreases from 16.3% to 12.0% as a result of the increase in primary chain length in the miniemulsion with 54 vol% TD (in Fig. 6, the gel points correspond to the intersections of the corresponding straight line and the curve describing Eq. (2)). The same analysis applied to the miniemulsion with 6 vol% TD gives a reduction in gel point from 16.3% to 14.4%. This analysis thus suggests that the increase in primary chain length due to the presence of 54 vol% TD in the miniemulsion system (Fig. 5) does have a significant effect on gelation.

The gel points predicted by Eq. (2) and the actual gel points are listed in Table 1. The primary chain lengths in the solution polymerizations (i.e. $\overline{P}_w$ in Eq. (2)) were calculated from $M_{n,th}$ and $M_w/M_n = 1.3$. For 6 vol% TD, gelation occurred later than theory predicts both in solution and miniemulsion ($\alpha_{c,exp}/\alpha_{c,th} > 1$), as is normally observed for non-living radical cross-linking polymerization (due to cross-links being "wasted" by e.g. intramolecular cyclization and intramolecular cross-linking) [10,47]. However, the conversion at the gel point in the miniemulsion with 54 vol% TD was lower than predicted by theory, suggesting that the rate of gelation is influenced by specific factors related to the heterogeneity of the system.

Overall, the ratios between the experimental gel points and the theoretical gel points are much lower than the ratios frequently reported for non-living cross-linking systems [10,43]. Similar findings have been reported for ATRP of allyl methacrylate in bulk [31]. This may be related to the fact that the relative level of intermolecular cross-linking (compared to intramolecular cross-linking) is expected to be higher in a CLRP system than a non-living system (mainly due to the primary chain length being much greater in a non-living system) [22,23], and thus less pendant unsaturations are consumed in intramolecular reactions, which contribute less to gelation than intermolecular reactions. This is also consistent with the observation that the extent of delay of gelation compared to FS theory decreased with decreasing primary chain length [10,31].

The graphic representation in Fig. 6 effectively illustrates the very different nature of a controlled/living cross-linking system compared to a conventional, non-living system. In a non-living system, the primary chain length is much higher than in a controlled/living system, and remains close to constant up to intermediate conversion levels [48].

4. Conclusions

Depending on the particular experimental conditions, gel formation in the TEMPO-mediated cross-linking copolymerization of S and DVB (8.2 mol%) in aqueous miniemulsion at 125 °C proceeded differently from the corresponding solution polymerization. Consistent with our previous findings that the addition of relatively high levels of TD to the present system resulted in enhanced apparent pendant reactivity [37], the rate of gel formation relative to monomer conversion increased at high levels of TD. Part of the reason for the gel formation at lower conversion in the miniemulsion system with the higher level of TD (54 vol% in the organic phase) was that the primary chain lengths in this system (unlike miniemulsion polymerization with a lower level of TD and the corresponding solution polymerizations) were higher than the theoretical chain lengths based on an ideal controlled/living polymerization. However, comparison of the experimental gel points with the theoretical predictions based on Flory–Stockmayer gelation theory indicates that the increase in the primary chain lengths is not sufficient to explain the rapid gel formation in the miniemulsion containing 54 vol% TD. The results thus indicate that factors specifically related to the heterogeneity of the system may significantly influence the build up of the polymer network.

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