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Alam, Md. Nur

Zetterlund, Per B.

Okubo, Masayoshi

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Md. Nur Alam,[1] Per B. Zetterlund,[2] Masayoshi Okubo [1,2]*

[1] Graduate School of Science and Technology, Kobe University, Kobe 657-8501, Japan.

Fax: +81-(0)78-8036161; E-mail: okubo@kobe-u.ac.jp

[2] Department of Chemical Science and Engineering, Faculty of Engineering, Kobe University

Kobe 657-8501, Japan.

* Corresponding author. Fax: +81-(0)78-8036161; E-mail: okubo@kobe-u.ac.jp

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Summary: Polymer network formation in controlled/living radical crosslinking copolymerization of styrene (S)/divinylbenzene (DVB) initiated by a poly(S)-TEMPO macroinitiator in aqueous miniemulsion at 125 °C is investigated. The crosslinking proceeded differently in miniemulsion (heterogeneous system) and in bulk/solution (homogeneous systems), with markedly lower apparent pendant reactivity in miniemulsion. The relative rate of DVB consumption was lower in miniemulsion than in bulk/solution, likely due to DVB partitioning between the two phases. It is proposed that the interface between the particle (monomer droplet at time = 0) and the aqueous phase may play an important role during the crosslinking process. The presence of tetradecane as a hydrophobe in the monomer droplets strongly influenced both pendant reactivity and molecular weight distribution in miniemulsion, whereas only small effects were observed in the corresponding bulk/solution polymerizations. It is believed that this is related to previous results of the hydrophobe promoting migration of poly(DVB) to the interface of toluene droplets in aqueous emulsion. The results suggest novel approaches towards control of polymer network development in crosslinking radical polymerizations.

Introduction

The development of controlled/living radical polymerization (CLRP) has made it possible to prepare polymers of predefined molecular weights (MW) with low polydispersities and various complex architectures by free radical means.[1,2] In recent years, considerable efforts have been directed towards application of these techniques in the industrially important aqueous heterogeneous systems, and aqueous heterogeneous controlled/living radical polymerizations have now been carried out successfully for a range of different systems.[3-9] This is exemplified by our recent work dealing with the synthesis of poly(*i*-butyl methacrylate-*b*-styrene) in aqueous emulsion; miniemulsion atom transfer radical polymerization (ATRP) followed by seeded ATRP.[5,6]

Considering that the success of CLRP is normally evaluated in terms of low polydispersities, predefined MWs and the degree of livingness, it is not immediately obvious what benefits CLRP may offer in connection with crosslinking systems. However, Ide and Fukuda[10,11] showed that the 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO)-mediated radical bulk copolymerization of styrene (S) and 4,4'-divinylbiphenyl proceeded with a considerably lower apparent pendant reactivity than the corresponding conventional system. The MW of the primary chains is normally higher in a conventional system than in CLRP (a primary chain is the imaginary linear chain resulting from breaking all crosslinks connected to it), and this leads to a higher local concentration of pendants around the radical chain end in the conventional system, which in turn manifests itself as a higher apparent pendant reactivity in the conventional system than in CLRP. Consequently, intramolecular crosslinking dominates at low conversion in a typical conventional system. This local concentration effect is much less pronounced in CLRP, resulting in more homogeneous network formation without microgels, higher swelling and anticipated superior mechanical properties.[11] As expected, similar results have been obtained using atom transfer radical polymerization (ATRP) of various crosslinking systems.[12-15] "Iniferter" techniques[16] have also been employed for preparation of crosslinked polymers.[17,18]

A radical polymerization can be carried out as a homogeneous (bulk, solution) or a heterogeneous (*e.g.* emulsion, miniemulsion) process. Heterogeneous polymerizations often proceed in a completely different manner compared to their homogeneous counterparts due to various phenomena associated with heterogeneous systems such as phase transfer events, phase partitioning of reactants, and compartmentalization effects. These differences can be either beneficial in nature, or present a challenge when implementing a process in a heterogeneous system. A well-known example of the former is that it is in general possible to prepare higher MW polymer at higher polymerization rates in emulsion than in bulk due to compartmentalization effects.[19] On the other hand, when implementing ATRP in miniemulsion, a sufficiently hydrophobic ligand must be selected for control of the polymerization to be maintained.[3] There are several reports dealing

with conventional radical crosslinking polymerization in aqueous heterogeneous systems,[20-26] but there is little information available with regards to specific differences between these systems and their homogeneous counterparts in terms of pendant reactivities and gel formation. This topic has however been thoroughly addressed by Tobita et al., whose theoretical and experimental work[27-31] on conventional radical copolymerization of mono- and divinyl compounds has revealed that the network development is entirely different in emulsion polymerization compared to bulk. The crosslink density is higher in emulsion than in a homogeneous system at low and intermediate conversions (Interval II) because the polymer concentration in the polymer particles is higher than in the corresponding homogeneous system at the same conversion. Moreover, the so called "limited space effect" dictates the maximum attainable MW to that of all polymer contained in one particle, and significantly alters the network formation process as manifested in the weight-average molecular weight (M_w) increasing linearly with conversion in some cases.[27-29]

Considering the fact that the heterogeneous nature of a conventional radical crosslinking polymerization can have significant effects on the formation of the polymer network, it appeared worthwhile to thoroughly investigate controlled/living radical crosslinking polymerization in heterogeneous systems with a view to developing novel means of controlling network formation in radical polymerization. The present work deals with the development of the three-dimensional network in terms of the pendant reactivities and molecular weight distributions (MWDs) for the TEMPO-mediated radical miniemulsion copolymerization of S and divinylbenzene. Our previous investigations of this system showed that the apparent pendant reactivities were significantly lower in miniemulsion than in bulk, and that the particle size exerted a marked influence on the polymerization process.[32] In the present work, detailed analyses of inter- and intramolecular pendant conversions and MWD with conversion have been carried out. Moreover, the effects of (*i*) dilution of the organic phase with toluene, and (*ii*) high concentration of a hydrophobe (tetradecane) have been investigated to expose the mechanisms at play that set the heterogeneous and homogeneous systems apart.

Experimental and Methodology

Materials

Styrene (S) was purified by distillation under reduced pressure in a nitrogen atmosphere. Divinylbenzene (DVB) (32% *p*-DVB, 68% *m*-DVB; Nippon Steel Chemical; purity 99%) was washed with 1 N NaOH and distilled water to remove inhibitors. Benzoyl peroxide (BPO) was purified by recrystallization using chloroform/methanol. TEMPO (Aldrich) and special-grade toluene, tetradecane and methanol were used as received.

Preparation of Polystyrene-TEMPO (PS-T) Macroinitiator

S (13.5 g), BPO (0.371 g; 0.103 mol L^{-1}) and TEMPO (0.285 g; 0.122 mol L^{-1}) were charged in a glass tube, degassed with several N$_2$ cycles, sealed off under vacuum and heated at 125 °C for 4 h in an oil bath. The polymer was recovered by precipitation in excess methanol, and subsequently purified by reprecipitation four times using toluene/methanol and dried in a high vacuum oven. Conversion = 18.2%, M_n = 2650, M_w/M_n = 1.14.

Polymerization Procedures

Miniemulsion polymerizations (5.0 wt.-% solids content based on 100% monomer conversion): A solution of S (0.7405 g; 99 mol-% rel. to total monomer), DVB (9.5 mg; 1 mol-% rel. to total monomer) and PS-T macroinitiator (44 mg; 20 mmol L-monomer^{-1}) was mixed with an aqueous solution of dodecyl benzenesulfonic acid sodium salt (DBS; 32 mg; 4 wt.-% rel. to total monomer). The recipe for the miniemulsion polymerization containing tetradecane was the same as above, except that tetradecane (0.325 g; 30 wt.-% of organic phase) was added to the organic phase.

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Miniemulsion polymerization (20 wt.-% solids) containing toluene: A solution of S (0.2962 g; 99 mol-% rel. to total monomer), DVB (3.8 mg; 1 mol-% rel. to total monomer), toluene (2.7 g; 90 wt.% of organic phase) and PS-T (17.6 mg; 20 mmol L-monomer^{-1}) was mixed with the same aqueous solution as above.   The molar ratio of monomer to macroinitiator was the same in all polymerizations.

Emulsification was carried out using either: (*i*) ultrasonication (Ultrasonic Homogenizer, Nissei, US-600T) for 12 min at 0 °C, or (*ii*) NISSEI ABM-2 homogenizer at 1000 rpm for 2 min followed by 2000 rpm for an additional 2 min.   The resulting emulsions were transferred to glass ampules (each ampule contained approximately 4 mL), degassed using several N_2/vacuum cycles and sealed off under vacuum, and the reactions were carried out at 125 °C shaking the ampules horizontally at a rate of 100 cycles/min.   The homogeneous polymerizations were also performed in glass ampules (ca. 1.5 g monomer per ampule).

Measurements

Particle size distributions were measured using dynamic light scattering (DLS-7000, Otsuka Electronics, Osaka, Japan) at the light scattering angle of 90° at room temperature after dilution of the emulsion to 10 ppm using water saturated with S.   Number- (d_n) and weight-average (d_w) particle diameters were obtained using the Marquadt analysis routine.

S and DVB 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.

MWDs were measured by gel permeation chromatography (GPC) with two S/DVB gel columns (TOSOH Corporation, TSKgel GMH$_{HR}$-H, 7.8 mm i.d x 30 cm) using THF as eluent at 40°C at a flow rate of 1.0 mL/min employing refractive index (TOSOH RI-8020/21) and ultraviolet

detectors (TOYO SODA UV-8II). The columns were calibrated with six standard PS samples $(1.05 \times 10^3 - 5.48 \times 10^6, M_w/M_n = 1.01 - 1.15)$.

^{1}H NMR spectra were recorded on a Bruker DPX250 MHz spectrometer (Karlsruhe, Germany) with deuteriochloroform and hexamethyldisiloxane as solvent and internal standard, respectively. The polymer concentration was approximately 10 wt.-%. The polymer from the bulk system was isolated by precipitation in methanol, whereas the miniemulsion polymer was collected by centrifugation and drying followed by reprecipitation using toluene/methanol to ensure complete removal of residual monomer. Pendant conversions were estimated by ^{1}H NMR as described previously.[32]

Intermolecular Pendant Conversion

Pendant unsaturations may undergo addition reactions with propagating radicals in different ways; (*i*) intramolecular cyclization, (*ii*) intramolecular crosslinking, and (*iii*) intermolecular crosslinking.[33] Only intermolecular crosslinking results in an increase in MW. It is therefore possible to gain information about the extent of intermolecular crosslinking by analysis of the number-average MW (M_n). In a conventional radical polymerization, the primary chains are initiated and terminated on the time scale of seconds, and it is complicated to correlate the conversion with the primary chain length, mainly due to conversion-dependence of the termination rate coefficient, and the MWD of the primary chains is broad. However, in a controlled/living radical polymerization, M_n of the primary chains increases linearly with conversion. The extent of intermolecular crosslinking can be estimated by comparing the theoretical number-average MW ($M_{n,th}$) based on an ideal controlled/living mechanism in the absence of intermolecular crosslinking with the experimentally observed M_n ($M_{n,exp}$).

The average number of primary chains per polymer molecule is given by $M_{n,exp}/M_{n,th}$. The average number of intermolecular crosslinks (number of intermolecularly reacted pendants) per

polymer molecule, and the average number of intermolecularly reacted pendant unsaturations per primary chain ($n_{p,inter}$), are subsequently given by Equation (1) and (2):

Number of intermolecular crosslinks per molecule $= (M_{n,exp} / M_{n,th}) - 1$ (1)

$$n_{p,inter} = [(M_{n,exp} / M_{n,th}) - 1] / (M_{n,exp} / M_{n,th}) = 1 - (M_{n,th} / M_{n,exp})$$ (2)

where $0 \le n_{p,inter} < 1$. The value of $M_{n,th}$ of primary chains is calculated according to Equation (3) by assuming that no pendant unsaturations react:

$$M_{n,th} = M_{n(PS\text{-}T)} + \frac{\alpha_S [S]_0 M_S + \alpha_{DVB} [DVB]_0 M_{DVB}}{[PS-T]_0}$$ (3)

where α denotes fractional conversion, and $[S]_0$, $[DVB]_0$ and $[PS\text{-}T]_0$ are the initial concentrations of styrene, divinylbenzene and macroinitiator, respectively. The intermolecular pendant conversion ($\alpha_{p,inter}$) is given by:

$$\alpha_{p,inter} = \frac{n_{p,inter}}{n_{DVB}}$$ (4)

where n_{DVB} is the number of DVB units (with reacted or unreacted pendant unsaturation) per primary chain (based on $M_{n,th}$). The value of n_{DVB} is related to $M_{n,th}$ via Equation (5) and (6):

$$n_{DVB} / (n_S + n_{DVB}) = F_{DVB}$$ (5)

$$n_S M_S + n_{DVB} M_{DVB} = M_{n,th} - M_{n(PS\text{-}T)}$$ (6)

where F_{DVB} is the mol fraction of DVB in the polymer, n_S is the number of S units per primary chain (based on $M_{n,th}$), M denotes molar masses, and $M_{n(PS-T)}$ is the MW of the macroinitiator. Solving for n_{DVB} gives Equation (7):

$$n_{DVB} = \frac{M_{n,th} - M_{n(PS-T)}}{M_{DVB} + M_S(1 - F_{DVB})/F_{DVB}} \tag{7}$$

Equation (2), (4) and (7) give the expression for $\alpha_{p,inter}$:

$$\alpha_{p,inter} = \left(1 - \frac{M_{n,th}}{M_{n,exp}}\right)\left(\frac{M_{DVB} + M_S(1 - F_{DVB})/F_{DVB}}{M_{n,th} - M_{n(PS-T)}}\right) \tag{8}$$

Conversion of pendant unsaturations via intramolecular cyclization and intramolecular crosslinking is denoted $\alpha_{p,intra}$, and it follows that:

$$\alpha_{p,tot} = \alpha_{p,inter} + \alpha_{p,intra} \tag{9}$$

The pendant conversion estimated by ^{1}H-NMR corresponds to $\alpha_{p,tot}$, because no distinction is made with regards to the reaction mode by which pendant unsaturations are lost,[32] and it is thus possible to estimate $\alpha_{p,intra}$ from Equation (8) and (9).

Results and Discussion

Polymerization Rates

First-order plots for S/DVB copolymerizations initiated by PS-T in 90 wt.-% toluene relative to the organic phase at 125 °C in solution and miniemulsion (emulsification by ultrasonication; $d_n \approx 280$ nm) show that R_p was higher in miniemulsion than in solution (Figure 1a). Moreover, the miniemulsion and solution polymerizations with toluene were much slower than the corresponding polymerizations without toluene,[32] the main reason being the reduced rate of thermal initiation of S as a result of dilution. In TEMPO-based nitroxide-mediated polymerization (NMP) of S at 125 °C in bulk/solution, the concentration of propagating radicals is determined by the rates of bimolecular termination and thermal initiation ($R_{i,th}$),[2] where $R_{i,th}$ is proportional to $[S]^3$.[34] Dilution by a factor of 10 thus results in a reduction in $R_{i,th}$ by a factor of 10^3, which translates to a reduction in R_p by a factor of 32 based on the effect on $R_{i,th}$ only (R_p is proportional to $(R_{i,th}/k_t)^{0.5}$).[2] Experimentally, dilution by 90% toluene led to decreases in R_p by factors 23 for solution and 16 for miniemulsion (comparing with the miniemulsion in the absence of toluene with $d_n = 585$ nm). Copolymerizations of S/DVB initiated by PS-T were also carried out in 30 wt.-% tetradecane at 125 °C in solution and miniemulsion (emulsification by ultrasonication; $d_n \approx 125$ nm; Figure 1b). The addition of tetradecane resulted in reductions in R_p of factors of 1.5 and 3.6 for solution and miniemulsion, respectively, to be compared with the calculated 1.71 based on the expected decrease in $R_{i,th}$. Thus, in all cases, the reductions in R_p due to dilution were relatively similar to expectation based on the resulting decreases in $R_{i,th}$.

"Compartmentalization" refers to the effects of the separation of the reaction system into discrete units in a dispersed system.[19,35] Compartmentalization effects can be subdivided into: (*i*) "Segregation effects" (radical species in different particles are unable to react with one another, leading to an overall reduction in reaction rate between these two species); (*ii*) "Confined space

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effects" (the reaction rate between two radical species located in the same particle increases with decreasing particle size for sufficiently small particles[19,35,36]). Recent extensive analyses of NMP in dispersed systems based on modified Smith-Ewart equations accounting for compartmentalization of both propagating radicals and nitroxide[35] (previous theoretical work by Charleux has omitted compartmentalization effects on the nitroxide, giving different results[37]) as well as thermal initiation show that compartmentalization effects are only significant in the S/TEMPO system at 125 °C if $d < 100$ nm. For $d = 53$ nm (the miniemulsion system without toluene), compartmentalization effects are expected to result in a reduction in R_p of approx. 10% (due to the confined space effect on the deactivation reaction).[35] However, in the present study (miniemulsions without toluene and tetradecane, $d_n = 53$ and 585 nm, respectively, and bulk in Fig. 1b), R_p increased with decreasing particle size. It is clear that further research is needed to fully understand the polymerization rates in these systems.

Molecular Weight Distributions

Figure 2 shows MWDs at different conversions for the radical copolymerization of S/DVB initiated by PS-T in bulk and miniemulsion (these MWs are linear PS equivalents and are thus underestimated due to branching/crosslinking). In the cases of bulk and the miniemulsion with d_n = 585 nm, the MWDs shifted to higher MWs with higher conversion and a high MW shoulder gradually appeared. This trend is harder to discern for the miniemulsion with $d_n = 53$ nm, which had a very broad MWD even at low conversion. The differences are highlighted in Figure 3a, which shows an overlay of MWDs of the three systems at close to 30% conversion. The evolution of the MWDs is strongly affected by not only the aqeouuos heterogeneous nature of the system, but also by the particle size, and the results thus clearly show that the individual polymer particles cannot simply be considered "micro-reactors" within which the polymerization proceeds as in the

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corresponding bulk system. The MWDs in the miniemulsion with the smaller particle size (Figure. 2b) exhibited two pronounced peaks at approximately $10^{4.15}$ and $10^{5.75}$ g mol^{-1} at 39 and 49% S conversions, and there was very little change in MW of the highest MW peak as the conversion increased from 39 to 49%.

Tobita et al. have shown experimentally[29,38] and theoretically[29,39] that bimodal MWDs are formed in conventional (not CLRP) crosslinking radical emulsion polymerization of vinyl/divinyl monomers (particle diameter ≈ 100 nm) over wide conversion ranges if the amount of crosslinker is sufficiently low in relation to the primary chain length.   This was attributed to so called "limited space effects", the central idea of which is that a macromolecule cannot experience an infinite increase in MW in a compartmentalized system (*i.e.* if the particles are small enough) because of limited access to other macromolecules.   The present system (controlled/living crosslinking radical polymerization in miniemulsion) is intrinsically very different from the systems studied by Tobita et al.[29] (conventional crosslinking radical emulsion polymerization), and direct comparison is therefore difficult.   However, the MWDs in the miniemulsion with the smaller particle size (Fig. 2b) are similar to those in Tobita's work, and efforts are currently underway to clarify whether "limited space effects" are playing a role also in the present work.

The relative rate of consumption of DVB, an important parameter affecting the polymer network formation, can be discussed quantitatively within the framework of the terminal copolymerization model based on Equation (10):[32]

$$\ln \frac{[\text{DVB}]_0}{[\text{DVB}]} = \frac{k_{\text{SDVB}}}{k_{\text{SS}}} \ln \frac{[\text{S}]_0}{[\text{S}]} \qquad (10)$$

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.   In our previous communication,[32] it was shown by plotting $\ln[\text{DVB}]_0/[\text{DVB}]$ vs. $\ln[\text{S}]_0/[\text{S}]$ that the values of $k_{\text{SDVB}}/k_{\text{SS}}$ (the slope) were 2.53, 1.45 and 1.91 for bulk,

miniemulsion (d_n = 53 nm) and miniemulsion (d_n = 585 nm), respectively, *i.e.* the rate of consumption of DVB relative to that of S was lower in miniemulsion than in bulk. Figure 4 shows results for the systems with 90 wt.-% toluene and 30 wt.-% tetradecane. The relative rate of DVB consumption was lower in both miniemulsions (k_{SDVB}/k_{SS} = 2.14) than in the solution polymerizations (k_{SDVB}/k_{SS} = 2.57), and no marked differences were detected between the toluene and tetradecane polymerizations in solution or miniemulsion. The origin of the lower apparent DVB reactivity in miniemulsion is at present not clear, and is currently under investigation in our laboratory.

When comparing the MWDs, (Figure 2, 3, 7, 8) it must thus be considered that the number of potential crosslinks is lower in miniemulsion than in the homogeneous systems (bulk/solution). The difference is very significant; the mol fraction of DVB incorporated in the polymer network was approximately 43% lower in miniemulsion (d_n = 53 nm) than in bulk in the S conversion range 0 – 50%. Thus, if the only difference between the polymerizations in bulk and miniemulsion were the relative rates of incorporation of DVB, the MWD in the homogeneous systems would be anticipated to be much broader due to reaction of pendant unsaturations. This was clearly not the case.

Inter- vs. Intramolecular Crosslinking

Figure 5 shows $\alpha_{p,tot}$ and $\alpha_{p,inter}$ (estimated from Equation (8)) plotted vs. S conversion for the bulk and miniemulsion polymerizations. The MW measurements used in Equation (8) are linear PS equivalents and the term $M_{n,exp}$ is therefore underestimated, and these must thus be considered minimum values of $\alpha_{p,inter}$. However, the analysis is still meaningful as a semi-quantitative means of comparing the nature of the crosslinked/branched networks of the different systems, in particular at low conversion where the error would be expected to be less significant. A similar approach was

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recently employed by Wang and Zhu, also based on linear PS standards, to estimate the number of branching points per molecule in bulk ATRP of methyl methacrylate/ethylene glycol dimethacrylate using relatively low mol fractions of crosslinker.[15]

The $\alpha_{p,tot}$ values are much lower in both miniemulsions than in bulk, with the miniemulsion with the largest particles exhibiting the lowest values.[32]   The levels of inter- and intramolecular crosslinking are comparable in the miniemulsion with the smallest particles, and this is also the case in bulk.   It is difficult to draw any conclusions with regards to $\alpha_{p,inter}$ and $\alpha_{p,intra}$ for the miniemulsion with the largest particles due to scatter, although it is evident that both quantities are much lower than for the other two systems.   Reduced pendant reactivity in emulsion polymerization (not miniemulsion) compared to in bulk has been reported for the conventional system (not CLRP) methyl methacrylate/ethylene glycol dimethacrylate,[31,41] but the proposed explanation[31] cannot be applied to the current controlled/living miniemulsion system.

The concentration of intermolecular crosslinks at the gel-point based on the Flory-Stockmeyer (FS) theory is given by:[11,42]

$$[\text{intermolecular crosslinks}]_{FS} = \left(\frac{M_{n,0}}{2M_{w,0}} \right) [PS - T]_0 \tag{11}$$

where $[PS - T]_0$ is the concentration of primary chains (which is equal to the initial macroinitiator concentration assuming the number of chains initiated by S thermal initiation is insignificant) and $M_{w,0}/M_{n,0}$ is the polydispersity of the primary chains at the gel-point (taken as 1.25, which is a typical value for the S/TEMPO system).   The polymer corresponding to all data points in Figure 5 was completely soluble in THF (clear solutions).   According to Equation (11) (with $[PS - T]_0 =$ 0.02 M), gelation should occur at [intermolecular crosslinks]$_{FS}$ = 8.0 mM.   The experimental values for the total concentration of crosslinks ([crosslinks]$_{tot,exp}$) were calculated according to Equation (12):

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$$[\text{crosslinks}]_{\text{ot,exp}} = [\text{DVB}]_0 \, \alpha_{\text{DVB}} \, \alpha_{\text{p,tot}} \qquad\qquad (12)$$

The values of $[\text{crosslinks}]_{\text{tot,exp}}$, are: 27 mM ($d_n$ = 53 nm; α_S = 54.2%); 4.1 mM (d_n = 585 nm; α_S = 47.4%); 21 mM (bulk; α_S = 44.2%).   For the miniemulsion with the largest particle size, $[\text{crosslinks}]_{\text{tot,exp}}$ < $[\text{intermolecular crosslinks}]_{\text{FS}}$, consistent with gelation not being observed. However, in the case of the miniemulsion with the smallest particles and the bulk system, $[\text{crosslinks}]_{\text{tot,exp}}$ > $[\text{intermolecular crosslinks}]_{\text{FS}}$.   Gelation not being observed for these systems is consistent with $\alpha_{\text{p,inter}}$ < $\alpha_{\text{p,tot}}$ (Figure 5), *i.e.* there is significant intramolecular pendant reactions occurring causing gelation to occur later than if all pendant reactions resulted in intermolecular crosslinks.   This implies that approximately 2/3 of the crosslinks are intramolecular crosslinks at these conversions, which is in agreement with the experimental data on $\alpha_{\text{p,inter}}$ and $\alpha_{\text{p,tot}}$ within experimental error.

The polymerizations containing 90% toluene resulted in very extensive intramolecular crosslinking in both solution and miniemulsion.   It is well-known that dilution favours intramolecular relative to intermolecular crosslinking.[33,41]   The $\alpha_{\text{p,inter}}$ values were very low, significantly less than 10% in most cases, and relatively similar in solution and in miniemulsion (Figure 6).   However, the MWDs in solution (35% conv.) and miniemulsion (32% conv.; Figure 3b) clearly show that intermolecular crosslinking was much more significant in the miniemulsion system, which exhibited a very distinct high MW peak that was absent in solution. The individual data points corresponding to these MWDs are $\alpha_{\text{p,inter}}$ = 0.054 (miniemulsion) and $\alpha_{\text{p,inter}}$ = 0 (solution), illustrating how a relatively small change in $\alpha_{\text{p,inter}}$ has a very significant effect on the MWD.

Effect of Interface

It is conceivable that the interface between the aqueous and the organic phase exerts some influence on the polymerization process. A concentration gradient affecting the ratio [monomer]/[pendant unsaturation] would influence the MWD, because it would change the rate of monomer addition relative to the rate of consumption of pendant unsaturations. It is also credible that the reduced mobility of polymeric species located near the interface[43] or adsorbed at the interface may affect pendant reactivity. Polydivinylbenzene (PDVB) is known to migrate to the interface of toluene droplets in an aqueous emulsion, the driving force being lowering of the interfacial tension, and this process is accelerated by the presence of linear PS or hexadecane. This is the basis of the so called SaPSeP method (developed by one of the authors of the present paper) for preparation of hollow polymer particles (microcapsules).[44-46] Other methods based on similar principles have also been reported.[47,48] The role of the hydrophobic non-solvent is to promote migration of PDVB to the interface, and it is thus essential that the non-solvent does not adsorb at the interface preferentially over PDVB. For this reason, SaPSeP does not work if PS is replaced by the more hydrophilic PMMA.[45] El-Aasser et al.[23] speculated that the gelation behavior during copolymerization of *n*-butyl methacrylate and a diacrylate macromonomer (with an aliphatic main chain) was influenced by concentration gradients within the particles arising due to the different hydrophobicities of the two monomers.

Based on the above considerations, it was postulated that a similar mechanism may influence the apparent pendant reactivities and MWDs in the present work. If so, it would be anticipated that the effect would be enhanced on addition of a hydrophobe, and therefore polymerizations were carried out in bulk and miniemulsion in the presence of 30 wt.-% of tetradecane.

A very pronounced high MW peak (MW = $10^5 – 10^6$) appeared in the miniemulsion MWD, and this peak was absent in solution (Figure 7 and 8). The MWDs obtained in bulk in the presence and absence of tetradecane were very similar (Figure 8a), thus ruling out any significant solvent

effect on the MWD.   There were much more significant differences in the MWDs obtained in bulk (solution) and miniemulsion in the presence of tetradecane (Figure 8) than in the absence.

Figure 9 shows $\alpha_{p,tot}$ plotted vs. S conversion for the miniemulsion and solution polymerizations with and without 30 wt.-% tetradecane.   The total pendant conversion was much higher in miniemulsion in the presence of tetradecane than in the absence; it increased from 10 – 30% to between 50 – 80% in the conversion range 10 – 40%, whereas the effect was the opposite in solution.   The fact that the presence of tetradecane had a very minor effect on the MWD in the homogeneous system, but a very significant effect in miniemulsion, is considered to be consistent with the interface between the organic phase and the aqueous phase having an effect on the development of the polymer structure.   It is speculated that the interface may affect the reactions of pendant unsaturations in two opposite ways; (*i*) it may enhance the rate of pendant reactions relative to propagation as a result of a concentration effect, whereby the ratio [pendant unsaturation]/[monomer] is increased in the shell region; (*ii*) the apparent pendant reactivity may be lowered as a result of low mobility of pendant containing polymeric segments located near the interface and/or being adsorbed at the interface.   The work presented here constitutes a first step towards understanding these effects, which are not only of academic interest, but may also offer novel means of controlling crosslinking in radical polymerization processes.

Conclusions

Controlled/living radical crosslinking copolymerization of S/DVB initiated by a PS-TEMPO macroinitiator in aqueous miniemulsion at 125 °C has been investigated, focusing on pendant reactivities and polymer network development.

The development of the crosslinked network in miniemulsion is completely different from that in bulk as evidenced by different apparent pendant reactivities and MWDs. The apparent pendant reactivities and the crosslink densities are markedly lower in miniemulsion than in bulk. Moreover, the miniemulsion particle size strongly influences the polymerization behavior. The relative rate of DVB consumption is lower in miniemulsion than in bulk/solution, most likely due to DVB partitioning between the organic and the aqueous phase, and consequently the number of potential crosslinks is lower in miniemulsion. If this were the main difference between miniemulsion and bulk/solution, the MWD would be broader in bulk/solution, which was not observed.

The interface between particle and aqueous phase may play an important role with regards to polymer network development in the current miniemulsion systems. The fact that addition of a hydrophobe (30 wt.-% tetradecane) to the miniemulsion had a strong effect on both the apparent pendant reactivity and the MWD is taken as experimental support (but not proof) of this explanation, because a hydrophobe promotes migration of PDVB to the interface of toluene droplets in an aqueous emulsion.[45,46] The MWDs obtained in bulk in the presence and absence of tetradecane were very similar. Two possible effects are envisaged; (*i*) enhancement of the pendant reaction rate due to a concentration effect whereby [pendant unsaturation]/[monomer] is increased in the shell region; (*ii*) the apparent pendant reactivity may be lowered as a result of low mobility of polymeric segments near the interface and/or being adsorbed at the interface.

The results presented reveal very significant differences in polymer network formation between bulk/solution and aqueous miniemulsion for the controlled/living radical crosslinking copolymerization of S/DVB initiated by a polymeric PS-TEMPO macroinitiator. This work provides some clues as to what the origin(s) of these differences are in terms of kinetics and mechanism. These systems are at present not well understood, and more research is clearly needed. The results offer novel means of controlling polymer network formation, and moreover, suggest that it may be possible to prepare linear polymer and lightly branched/crosslinked polymer not easily accessible in homogeneous systems, *e.g.* linear polymer of well-defined MW and narrow MWD with pendant unsaturations, useful for crosslinking in a separate reaction.

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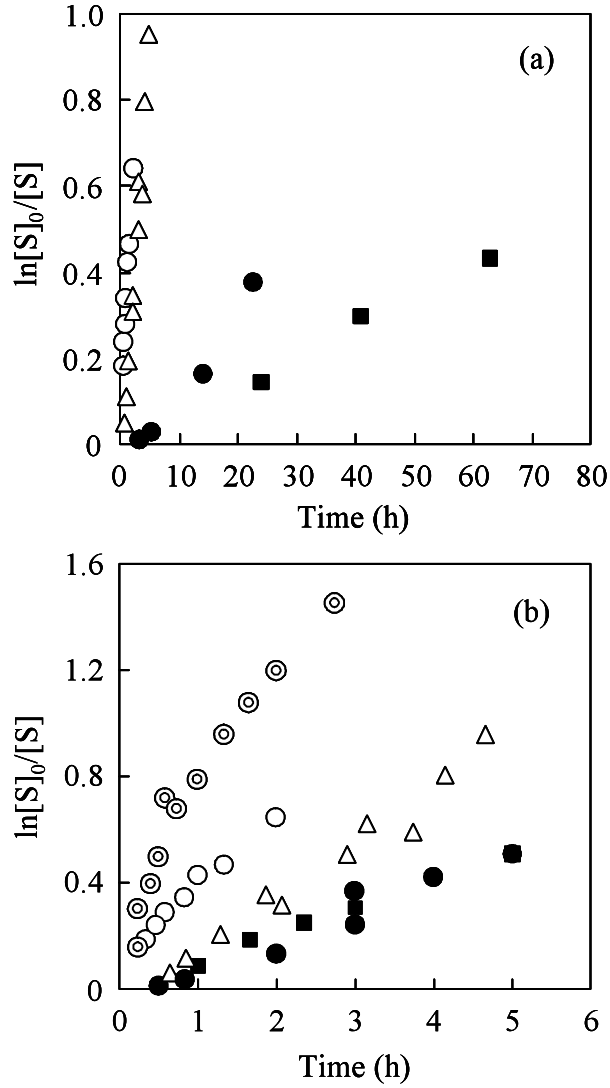[48]   P. J. Dowding, R. Atkin, B. Vincent, P. Bouillot, *Langmuir* **2004**, *20*, 11374.

Figure 1. First-order plots based on S concentration for TEMPO-mediated radical copolymerization of S (1) and DVB (2) ($f_1^0 = 0.99$, $f_2^0 = 0.01$) with $[\text{PS-T}]_0 = 20$ mM (●, ■) and 23 mM (◎, ○, △) at 125 °C. (a) Solution (■) and miniemulsion with $d_n \approx 280$ nm (●) with 90 wt.-% toluene and bulk (△) and miniemulsion with $d_n = 585$ nm (○) without toluene. (b) Solution (■) and miniemulsion with $d_n \approx 125$ nm (●) with 30 wt.-% tetradecane, and bulk (△) and miniemulsions with $d_n = 53$ nm (◎) and 585 nm (○) without tetradecane.
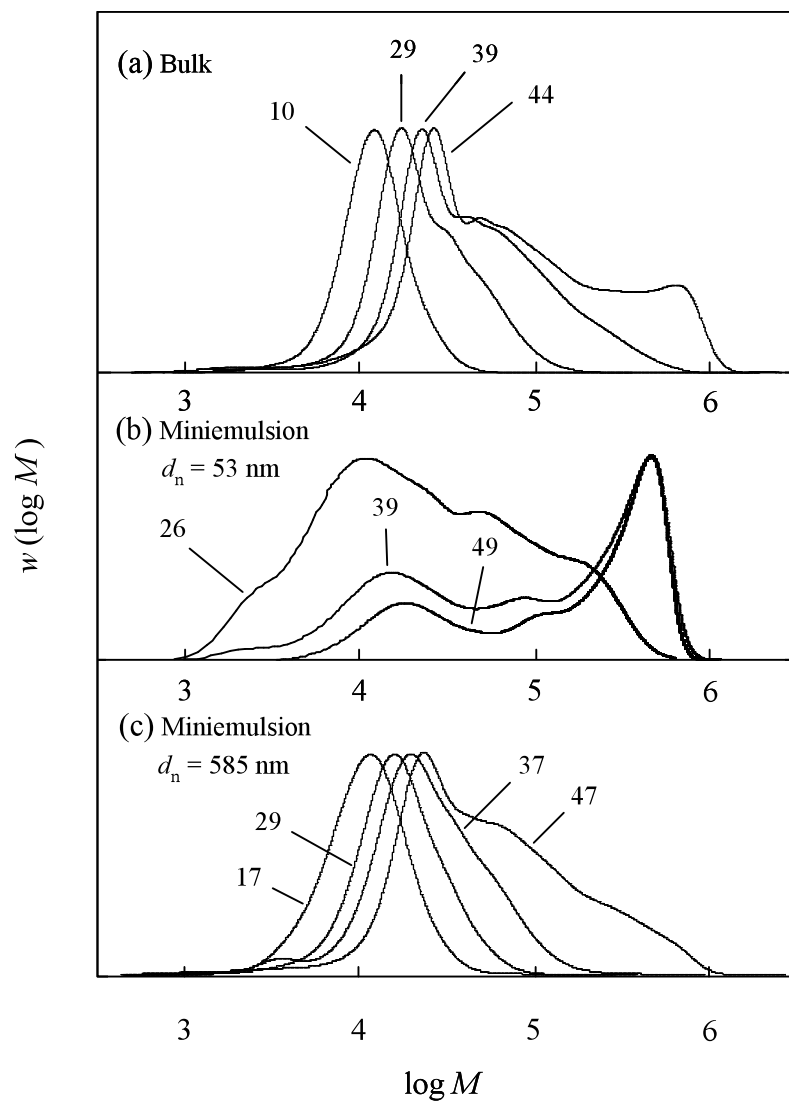
Figure 2.   Molecular weight distributions (normalized to peak height) at different S conversions (%) as indicated for TEMPO-mediated radical copolymerization of S (1) and DVB (2) ($f_1^0 = 0.99$, $f_2^0 = 0.01$) with [PS-T]$_0$ = 23 mM at 125 °C in (a) bulk and (b, c) miniemulsion (all without tetradecane).
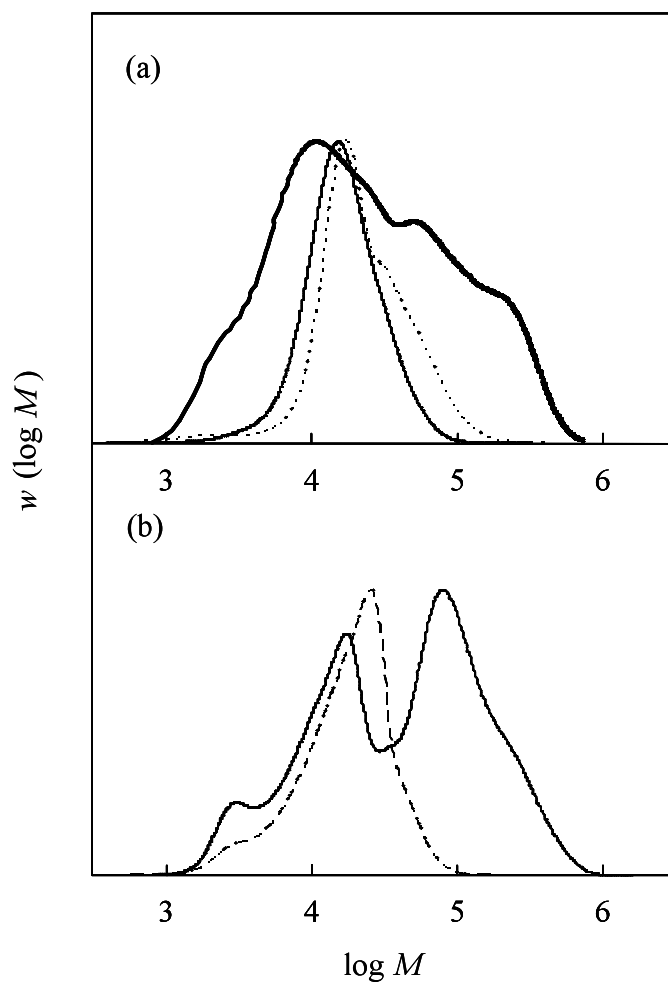
Figure 3. Molecular weight distributions for TEMPO-mediated radical copolymerization of S (1) and DVB (2) ($f_1^0 = 0.99$, $f_2^0 = 0.01$) at 125 °C in bulk and miniemulsion at similar S conversions. (a) Bulk (dotted line; 29% S conversion), and miniemulsions with $d_n = 53$ nm (thick line; 26% S conversion) and $d_n = 585$ nm (thin line; 29% S conversion) without tetradecane. [PS-T]$_0 = 23$ mM. (b) Solution (broken line; 35% S conversion) and miniemulsion with $d_n \approx 280$ nm (thin line; 32% S conversion) with 90 wt.-% toluene. [PS-T]$_0 = 20$ mM.
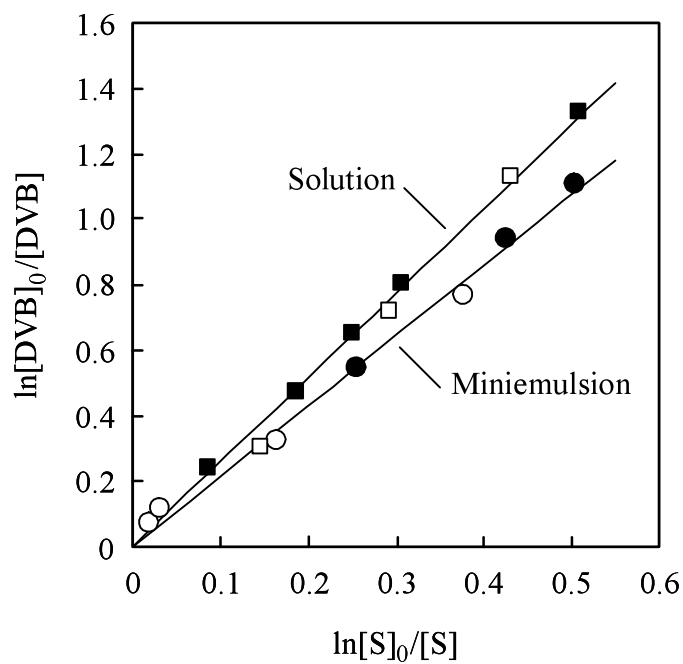
Figure 4. Relative rates of S and DVB consumption expressed as $\ln[\text{DVB}]_0/[\text{DVB}]$ vs. $\ln[\text{S}]_0/[\text{S}]$

for TEMPO-mediated radical copolymerizations of S (1) and DVB (2) ($f_1^0 = 0.99, f_2^0 = 0.01$) with

$[\text{PS-T}]_0 = 20$ mM at 125 °C in the presences of toluene and tetradecane; solution (□) and

miniemulsion with $d_n \approx 280$ nm (○) with 90 wt.-% toluene; solution (■) and miniemulsion with d_n
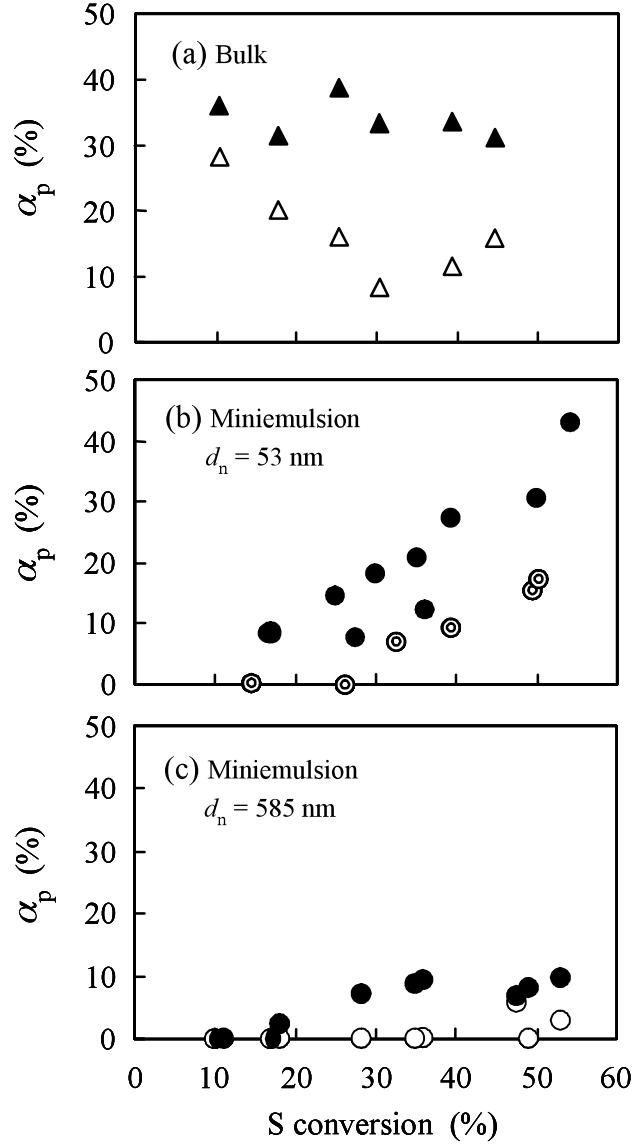
≈ 125 nm (●) with 30 wt.-% tetradecane.

Figure 5. Total (filled symbols) and intermolecular (open symbols) pendant conversions (α_p) obtained from Equation (7) and (8) for TEMPO-mediated radical copolymerization of S (1) and DVB (2) ($f_1^0 = 0.99, f_2^0 = 0.01$) with [PS-T]$_0$ = 23 mM at 125 °C in (a) bulk and miniemulsions with (b) d_n = 53 nm and (c) d_n = 585 nm.
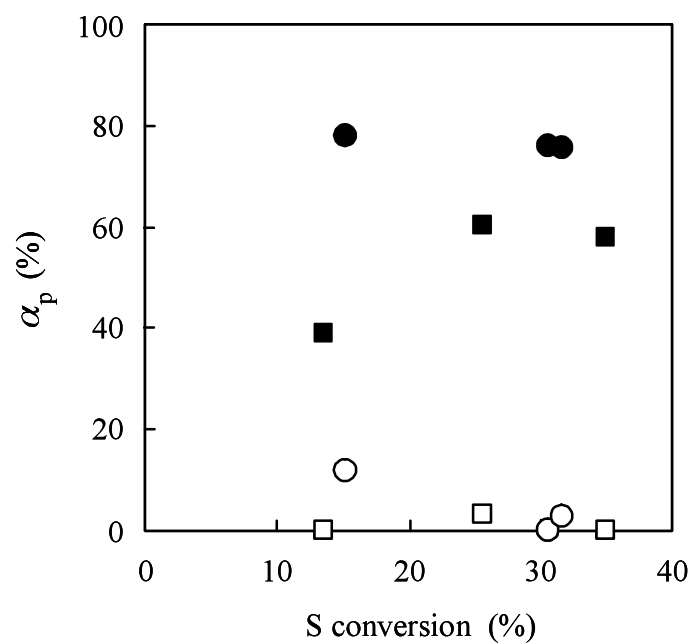
Figure 6. Total (filled symbols) and intermolecular (open symbols) pendant conversions (α_p) for TEMPO-mediated radical copolymerization of S (1) and DVB (2) ($f_1^0 = 0.99$, $f_2^0 = 0.01$) with [PS-T]$_0$ = 20 mM at 125 °C in solution (■,□) and miniemulsion (●,○) ($d_n \approx$ 280 nm) with 90 wt.-% toluene.
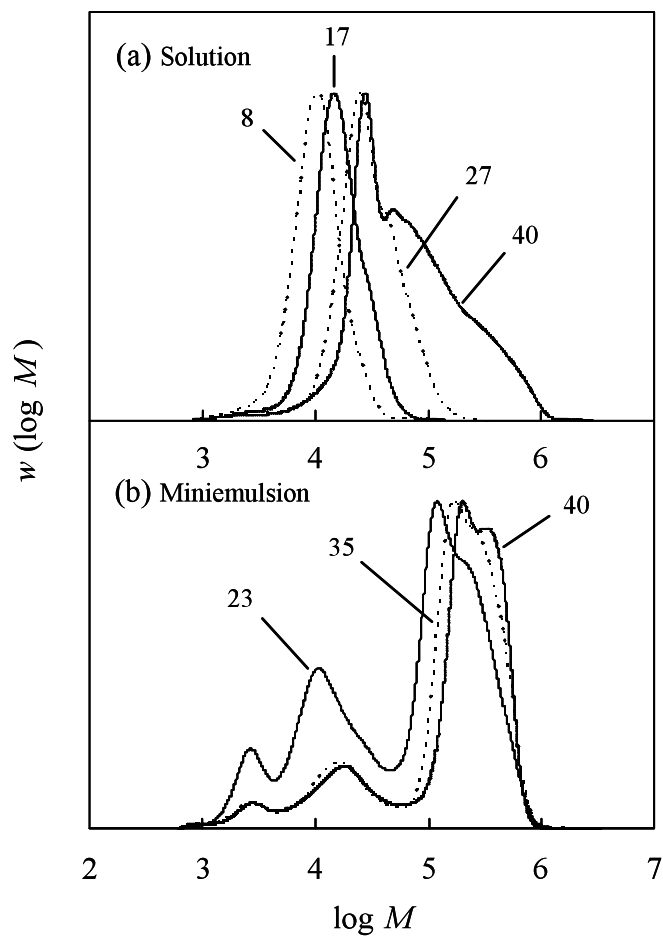
Figure 7. Molecular weight distributions (normalized to peak height) at S conversions (%) as indicated for TEMPO-mediated radical copolymerization of S (1) and DVB (2) ($f_1^0 = 0.99$, $f_2^0 = 0.01$) with [PS-T]$_0$ = 20 mM at 125 °C (a) solution and (b) miniemulsion ($d_n \approx 125$ nm) with 30 wt.-% tetradecane.
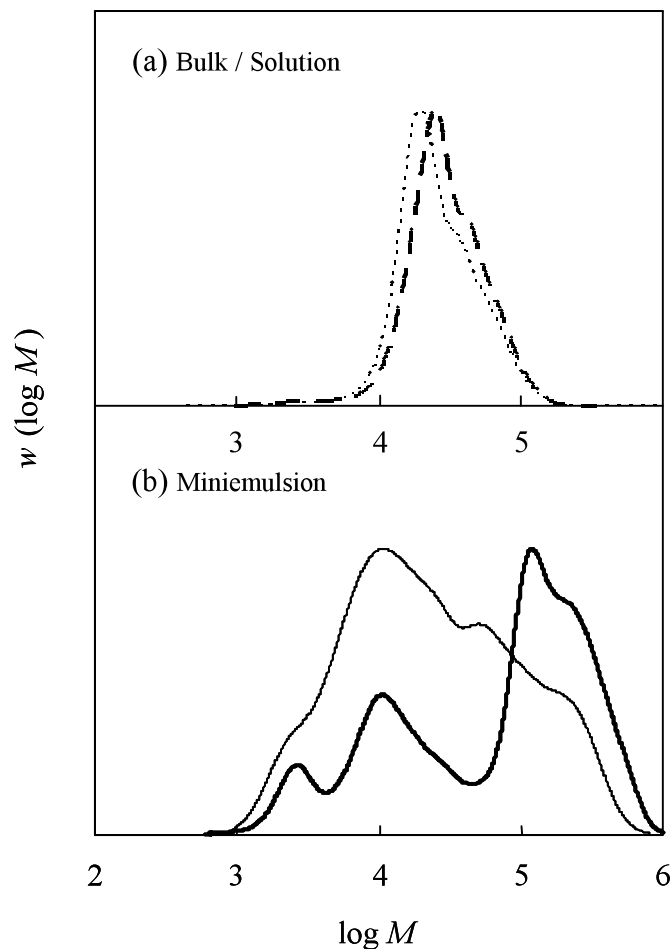
Figure 8. Molecular weight distributions (normalized to peak height) for TEMPO-mediated radical copolymerization of S (1) and DVB (2) ($f_1^0 = 0.99$, $f_2^0 = 0.01$) at 125 °C. (a) Bulk without tetradecane (dotted line; 27% S conversion) and solution with 30 wt.-% tetradecane (broken thick line; 27% S conversion). (b) Miniemulsion with (thick line; 23% S conversion) and without (thin line; 26% S conversion) 30 wt.-% tetradecane. [PS-T]$_0$ = 20 mM (with tetradecane), 23 mM (without tetradecane).
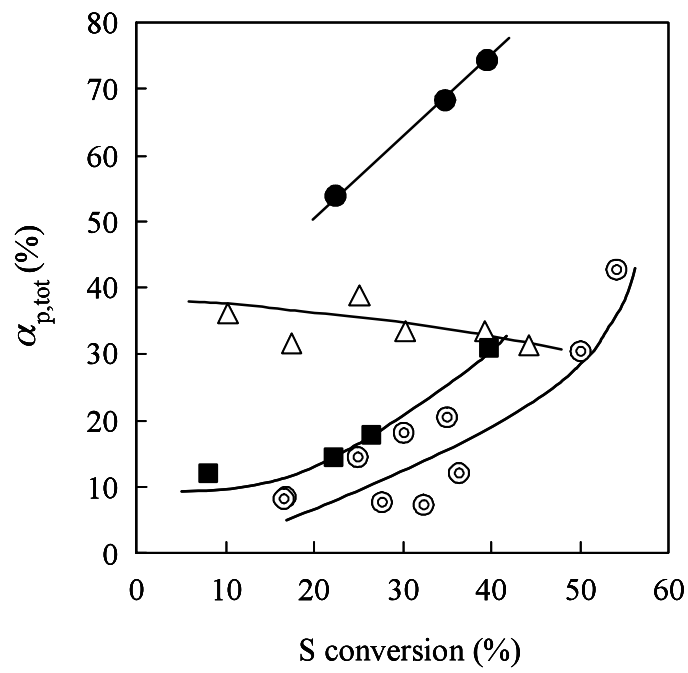
Figure 9. Total pendant conversions ($\alpha_{p,tot}$) for TEMPO-mediated radical copolymerization of S

(1) and DVB (2) ($f_1^0 = 0.99$, $f_2^0 = 0.01$) with $[PS-T]_0 = 20$ mM ($\bullet$, $\blacksquare$) and 23 mM ($\circledcirc$, $\triangle$) at 125 °C

in bulk without tetradecane ($\triangle$) and solution with 30 wt.-% tetradecane ($\blacksquare$), and miniemulsions

with ($\bullet$; $d_n = 125$ nm) and without ($\circledcirc$; $d_n = 53$ nm) 30 wt.-% tetradecane.
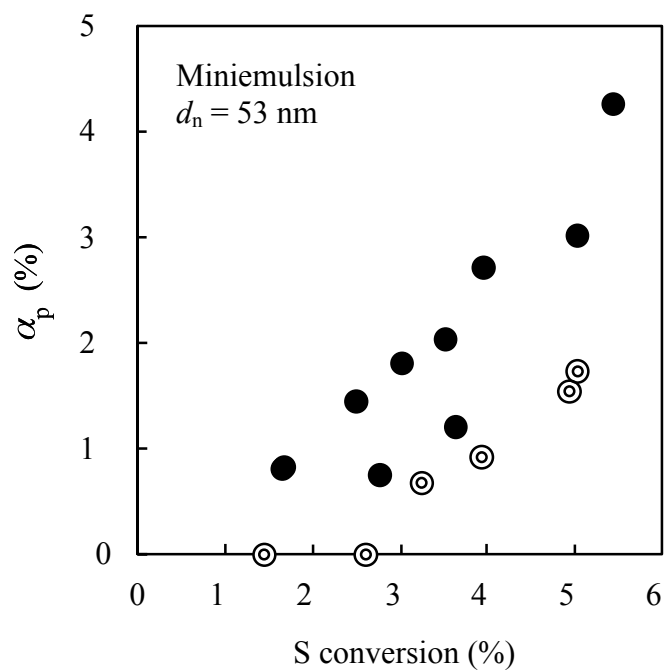
Figure.   Total (filled symbols) and intermolecular (open symbols) pendant conversions (α_p) obtained from Equation (7) and (8) for TEMPO-mediated radical copolymerization of S (1) and DVB (2) ($f_1^0 = 0.99, f_2^0 = 0.01$) with [PS-T]$_0$ = 23 mM at 125 °C in miniemulsion with d_n = 53 nm.