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Network Formation in Nitroxide-Mediated Radical Copolymerization of Styrene and Divinylbenzene in Miniemulsion: Effect of Macroinitiator Hydrophilicity

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Abstract

Nitroxide-mediated crosslinking radical copolymerizations of styrene and divinylbenzene have been carried out in aqueous miniemulsion with Dowfax-8390 as surfactant at 125 °C employing TEMPO-based macroinitiators of various hydrophilicity (random copolymers comprising styrene and methyl acrylate). The pendant conversion (*i.e.* the degree of crosslinking) increased with increasing macroinitiator hydrophilicity and with decreasing particle size. It is proposed that a concentration gradient is generated within the particle such that the macroinitiator concentration tends to be higher near the oil-water interface than in the particle interior. The macroinitiators are surface active and are thus preferentially adsorbed at/located near the oil-water interface. This in turn leads to an increase in the ratio [pendant unsaturation]/[monomer] in the vicinity of propagating radicals, which are generated from the macroinitiators, and thus an increase in pendant conversion. This effect is enhanced by an increase in macroinitiator hydrophilicity and a decrease in particle size. The present approach offers novel means of controlling network formation in dispersed systems.

1. Introduction

Controlled/living radical polymerization (CLRP) enables preparation of polymer of low polydispersity, pre-determined molecular weight (MW) and various more complex polymer architectures [1]. Significant progress has recently been made with regards to making CLRP compatible with industrially relevant aqueous dispersed (heterogeneous) systems, and aqueous heterogeneous controlled/living CLRP is now possible for various systems [2-8]. Polymerization in dispersed systems (*e.g.*, emulsion and miniemulsion) is often characterized by intrinsic features such as phase transfer events, reactants partitioning, interface effects and compartmentalization [2, 3].

Recent years have seen a rapidly increasing number of papers describing CLRP of crosslinking systems [9-15]. CLRP yields polymer networks that are much more homogeneous than what can be synthesized by conventional, non-living radical polymerization. The much shorter primary chains in CLRP result in less intramolecular crosslinking, and consequently the formation of local domains of very high crosslink density, microgels, is minimized. This results in the formation of gels with higher swelling capability and different mechanical properties [10, 12, 16].

Crosslinking CLRP in dispersed systems results in the formation of crosslinked polymer particles (nanogels) [17-21], which may find a range of applications, for example in drug delivery [20, 21]. We have previously investigated the nitroxide mediated polymerization (NMP) of styrene (S) and divinylbenzene (DVB) using 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) in aqueous miniemulsion at 125 °C, focusing on the development of the polymer network and molecular weight distributions (MWDs) [22-24]. It was revealed that the apparent pendant reactivity increased upon addition of 30 wt% of the hydrophobe tetradecane, and a pronounced high molecular weight shoulder appeared. The interface between the particle (organic phase) and the aqueous phase appears to play an important role with regards to the crosslinking process [23]. 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 polystyrene (PS) or hexadecane [25]. This is the basis of the self-assembling of phase separated polymer (SaPSeP) method for hollow polymer particle synthesis [26, 27].

In the present contribution, this interface effect is further examined by employing TEMPO-based macroinitiators (P(S-*r*-MA)-TEMPO) comprising various proportions of S and methyl acrylate (MA). It is shown that the crosslinking process, assessed by examination of pendant conversions and MWDs, can to some extent be controlled via the macroinitiator hydrophilicity.

2. Experimental

2.1. Materials

S and MA were purified by distillation under reduced pressure in a nitrogen atmosphere. 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), DOWFAX 8390 (disulfonated alkyl diphenyloxide sodium salt; Dow Chemical, USA, 35.7% aqueous solution), PS (degree of polymerization (DP) = 2000; Wako Pure Chemical Industries, Ltd., Japan), special-grade tetradecane (TD), tetrahydrofuran (THF), N,N-dimethylformamide (DMF), toluene and methanol were used as received (all from Nacalai Tesque Inc., Kyoto, Japan).

2.2. Preparation of P(S-r-MA)-TEMPO macroinitiator

TEMPO-mediated copolymerizations of S and MA were carried out to prepare macroinitiators (P(S-*r*-MA)-TEMPO) comprising 13 and 32 mol% MA. 32 mol% MA: S (9.97 g; 96 mmol), MA (3.53 g; 41 mmol), BPO (0.371 g; 1.53 mmol) and TEMPO (0.285 g; 1.83 mmol) were charged in a glass tube, degassed with several N_2 cycles, sealed off under vacuum and heated at 125 °C for 4.5 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. S conversion = 20%, MA conversion = 22 %, M_n = 2700 g/mol, M_w/M_n = 1.16. 13 mol% MA: Prepared in the same way using S (9.16 g; 88 mmol), MA (0.891 g; 10.4 mmol), BPO (0.274 g; 1.13 mmol) and TEMPO (0.212 g; 1.36 mmol); S conversion = 17%, MA conversion = 27% (4 h), M_n = 2600 g/mol, M_w/M_n = 1.13. The PS-TEMPO macroinitiator was prepared as described previously[23] (M_n = 2650, M_w/M_n = 1.14).

2.3. Polymerization procedures

Miniemulsions (5 wt% solids): A solution of S (0.7405 g; 99 mol% rel. to total monomer), DVB (9.5 mg; 1 mol% rel. to total monomer), TD (26.5 mg), linear PS (0.75 mg) and P(S-*r*-MA)-TEMPO macroinitiator (45 mg; 20 mM) was mixed with an aqueous solution of DOWFAX 8390 (60 mg; 8 wt% rel. to monomer). TD and high MW PS (DP = 2000) were added to increase the stability of the emulsion. Emulsification was carried out using an ultrasonicator (Ultrasonic Homogenizer, Nissei, US-600T) for 12 min at 0 °C (giving $d_n < 90$ nm) or a mixer (NISSEI ABM-2 homogenizer) at 1000 rpm for 2 min followed by 2000 rpm for an additional 2 min (giving $d_n > 1000$ nm) to generate monomer droplets of different sizes. 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 polymerizations were carried out at 125 °C shaking the ampules horizontally at a rate of 110 cycles/min. The bulk polymerizations were also performed in glass ampules (ca. 1.5 g polymerization mixture per ampule) at 125 °C.

2.4. Measurements

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 (given in Figure captions) were obtained using the Marquadt analysis routine. The values given are average values over the course of the polymerizations.

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.

Molecular weight distributions (MWDs) 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. x 30 cm) using tetrahydrofuran (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 polystyrene samples (1.05×10^3 – 5.48×10^6 g/mol).

Interfacial tensions were measured by the pendant drop method using a Drop Master 500 (Kyowa Interface Science Co. Ltd.) instrument at room temperature. The accuracy of the measured interfacial tensions is of the order ±0.2 mN/m.

^{1}H NMR spectra were recorded on a Bruker (Avance-500) 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 oven 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 [22, 23].

3. Results and discussion

3.1. Interfacial tensions

TEMPO-based macroinitiators (P(S-*r*-MA)-TEMPO) comprising 0, 13 and 32 mol% MA with M_n = 2600-2700 g/mol were synthesized. It was anticipated that incorporation of MA would impart some degree of interfacial activity on the macroinitiators. The interfacial tensions between S and water, with the S-phase containing 1 wt% macroinitiator, are displayed in Table 1. The macroinitiators containing MA were indeed interfacially active as evidenced by the interfacial tension decreasing with increasing MA content. An increase in the mol% MA from 0 to 32% resulted in a reduction in interfacial tension from 35.7 to 30.8 mN/m. The PS-TEMPO macroinitiator exhibited no interfacial activity (Table 1), *i.e.* addition of PS-TEMPO to the S-phase did not lead to a significant change in interfacial tension.

3.2. Rates of polymerization

Fig. 1 shows conversion vs. time data for TEMPO-mediated radical copolymerizations of S and DVB in miniemulsion with DOWFAX 8390 and in bulk at 125 °C using P(S-*r*-MA)-TEMPO macroinitiators (0, 13 and 32 mol% MA; M_n = 2600-2700 g/mol). Using the macroinitiator with 32 mol% MA, the polymerization rates (R_p) were higher in the miniemulsion with particle diameter $d_n \approx 85$ nm than $d_n \approx 1000$ nm and the bulk system, *i.e.* R_p increased with decreasing particle size.

This trend is similar to what has been observed and discussed in detail previously for PS-TEMPO [22]. In short, R_p is higher for smaller particles as a combined result of the interface effect on the free TEMPO and enhanced rates of spontaneous initiation. The interface effect on free TEMPO refers to how interfacial activity of free TEMPO causes some fraction of the nitroxide to reside at/near the oil/water interface, thus giving rise to a reduction in the deactivation rate [6, 28-30]. The rate of spontaneous generation of radicals in aqueous dispersed systems of styrene has been shown to be greater than in bulk styrene [30-33]. Both of these effects are enhanced as the total facial area of the system increases.

The value of R_p was not significantly affected by the MA content for small particles (Fig. 1), *i.e.* independent of the macroinitiator hydrophilicity. In TEMPO-based NMP of S at 125 °C in homogeneous systems, [P•] (R_p is proportional to [P•]) is determined by the rates of bimolecular termination and thermal initiation of S ($R_{i,th}$); R_p is proportional to $(R_{i,th}/k_t)^{0.5}$ [34]. The activation rate coefficient (k_{act}) for a MA-terminated TEMPO alkoxyamine adduct would be lower than that of the corresponding S-terminated adduct [34]. The P(S-*r*-MA)-TEMPO macroinitiators would comprise a mixture of species with –S-TEMPO or –MA-TEMPO alkoxyamine moieties at the chain ends. However, this effect does not appear to be significant as expected based on the fact that R_p is dictated by $(R_{i,th}/k_t)^{0.5}$. Moreover, the effect of MA on k_{act} would disappear once MA-TEMPO terminated macroinitiators have undergone one activation-deactivation cycle, allowing S and/or DVB monomer addition.

Compartmentalization can have a significant effect on NMP in dispersed systems if the particles are sufficiently small [35-38]. According to theory [35, 36], based on an ideal system in the absence of fluctuation effects [37], compartmentalization for S/TEMPO/125 °C is important for $d_n < 70$ nm for $[\text{PS-TEMPO}]_0 = 20$ mM, the effect of which would be a reduction in R_p due to the confined space effect [35] on deactivation. In the present study, R_p increased with decreasing particle size, suggesting that the interface effect on free TEMPO [6, 28-30] and enhanced spontaneous radical generation [30, 33] are dominant factors.

3.3. Pendant conversion

Fig. 2 shows the pendant conversions (the instantaneous conversion of pendant unsaturations originating from DVB units) vs. S conversion corresponding to the data in Fig. 1. The pendant conversions were estimated based on the content of pendant vinyl groups as determined by ^{1}H NMR as described in our previous work [22, 23]. For miniemulsions with similar particle size ($d_n \approx$ 85 nm), the pendant conversion increased with increasing hydrophilicity of the macroinitiator, *i.e.* as the MA mol% was increased from 0 to 32%. Moreover, the pendant conversion increased markedly with decreasing particle size ($d_n \approx 85$ vs. 1000 nm) for the macroinitiator containing 32 mol% MA. For particles with $d_n \approx 1000$ nm, the pendant conversions were approximately the same as in bulk.

These results can be explained by an interface effect [23, 39] whereby some fraction of polymer (macroinitiator) accumulates near the oil-water interface as a result of interfacial activity, creating a concentration gradient within the particles. This in turn results in an increase in the rate of reaction of propagating radicals with pendant unsaturations relative to monomer due to an increase in the ratio [pendant unsaturations]/[monomer] near the oil/water interface. The interface effect would increase in significance with decreasing particle size because the total interfacial area of the system increases. The effect of increasing macroinitiator hydrophilicity is similar to that of the addition of the hydrophobe tetradecane, which promotes migration of P(S-*r*-DVB)-TEMPO to the interface [23, 39].

3.4. Molecular weight distributions

Fig. 3 shows the MWDs at different S conversions corresponding to the data in Fig. 1 for the macroinitiator comprising 32 mol% MA (these MWs are linear PS equivalents and are thus underestimated due to branching/crosslinking). In the case of bulk and miniemulsion with $d_n \approx$ 1000 nm, the MWDs shifted to higher MWs with increasing conversions and a high MW shoulder gradually appeared. The low MW peaks correspond to primary chains that have not yet undergone pendant reaction, whereas the high MW shoulder constitutes branched chains. The miniemulsion system with $d_n \approx 85$ nm, however, yielded a very broad MWD even at low conversion (15%), and there was very little change in highest MW peak with increasing conversions. The differences are highlighted in Fig. 4a, which shows an overlay of the MWDs at close to 35% conversion. The effect of macroinitiator hydrophilicity on the MWD is clarified in the overlay in Fig. 4b, which shows the MWDs at approximately 15% conversion employing the PS-TEMPO ($d_n \approx 65$ nm) and the P(S-*r*-MA)-TEMPO macroinitiator with 30 mol% MA ($d_n \approx 85$ nm). A very prominent high MW component is present for P(S-*r*-MA)-TEMPO, in sharp contrast with the situation when using PS-TEMPO, consistent with the higher pendant conversion (Fig. 2) in the case of P(S-*r*-MA)-TEMPO. These results are consistent with the interface between the organic phase and the aqueous phase having an effect on the development of the polymer structure, as outlined in the section on pendant conversions).

4. Conclusions

Miniemulsion polymerizations of S and DVB in aqueous miniemulsion with Dowfax-8390 as surfactant at 125 °C with particle diameters in the range 65-1000 nm were carried out employing TEMPO-based macroinitiators of various hydrophilicity comprising S and MA. The results have shown that the pendant conversion in aqueous miniemulsion is strongly influenced by both the particle size and the macroinitiator hydrophilicity.

The P(S-*r*-MA)-TEMPO macroinitiators employed are interfacially active and are thus to some extent preferentially adsorbed at/located near the oil-water interface. This in turn leads to an increase in the ratio [pendant unsaturation]/[monomer] in the vicinity of propagating radicals, which are generated from the macroinitiators, and thus an increase in pendant conversion at any given overall monomer conversion. Moreover, the pendant conversion increased markedly with decreasing particle size, which is a result of the interface effect increasing in significance as the total interfacial area of the system is increased.

The present results illustrate how characteristic features of dispersed systems can be exploited to control network formation in crosslinking CLRP in a way not possible in the corresponding homogeneous (bulk/solution) system.

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Table 1. Interfacial tension (*γ*) measured by the pendant drop method

Interfacial tensions	γ (mN/m)
S/water	35.9
S/PS-TEMPO (0 % MA)/water	35.7
S/P(S-*r*-MA)-TEMPO (13 % MA)/water	31.2
S/P(S-*r*-MA)-TEMPO (32 % MA)/water	30.8

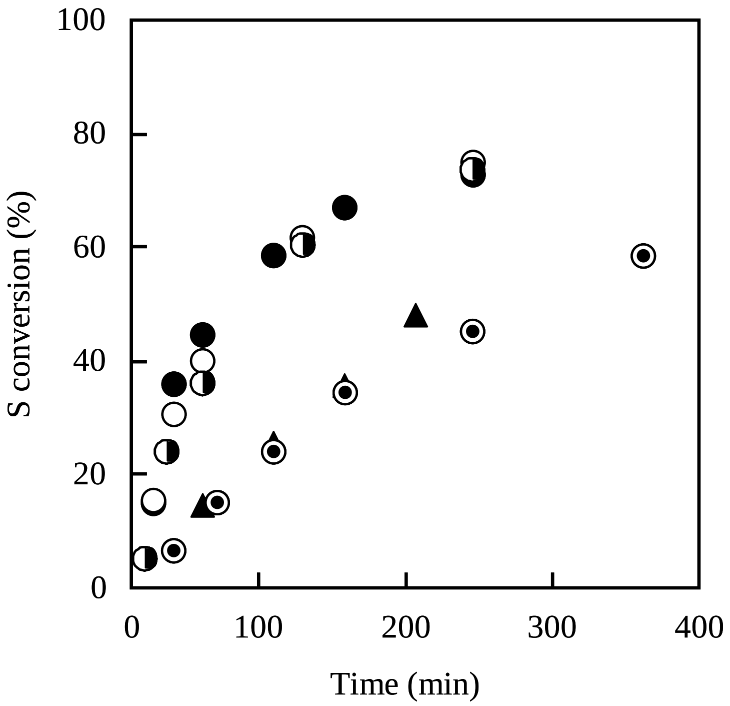

Fig. 1. Conversion-time plots based on S for TEMPO-mediated copolymerization of S and DVB (1 mol%) at 125 °C using DOWFAX 8390 as surfactant under various conditions ([macroinitiator]$_0$ = 20 mM): Miniemulsion with P(S-*r*-MA)-TEMPO containing 32 mol% MA (●; $d_n \approx 85$ nm; $d_w \approx 111$ nm; ⦿; $d_n \approx 1000$ nm; $d_w \approx 1075$ nm), 13 mol% MA (◑; $d_n \approx 87$ nm; $d_w \approx 107$ nm), PS-TEMPO (0 mol% MA) (○; $d_n \approx 65$ nm; $d_w \approx 79$ nm) and bulk (▲; P(S-*r*-MA)-TEMPO with 32 mol% MA).

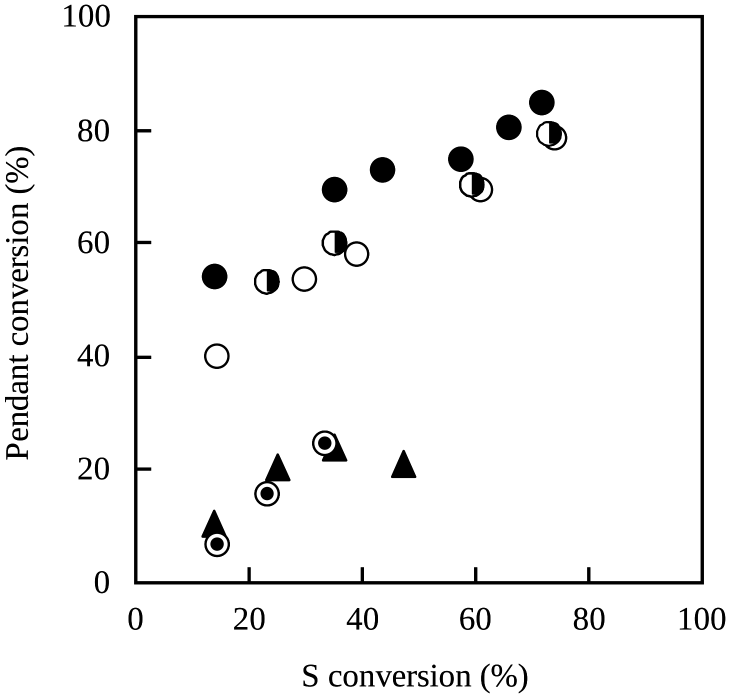

Fig. 2. Pendant conversions plots for TEMPO-mediated radical copolymerization of S and DVB (1 mol%) at 125 °C ([P(S-*r*-MA)-TEMPO]$_0$ = 20 mM) using DOWFAX 8390 as surfactant under various conditions: Miniemulsion with P(S-*r*-MA)-TEMPO containing 32 mol% MA (●; $d_n \approx 85$ nm; $d_w \approx 111$ nm; ⦿; $d_n \approx 1000$ nm; $d_w \approx 1075$ nm), 13 mol% MA (◑ ; $d_n \approx 87$ nm; $d_w \approx 107$ nm), PS-TEMPO (0 mol% MA) (○; $d_n \approx 65$ nm; $d_w \approx 79$ nm) and bulk (▲; P(S-*r*-MA)-TEMPO with 32 mol% MA).

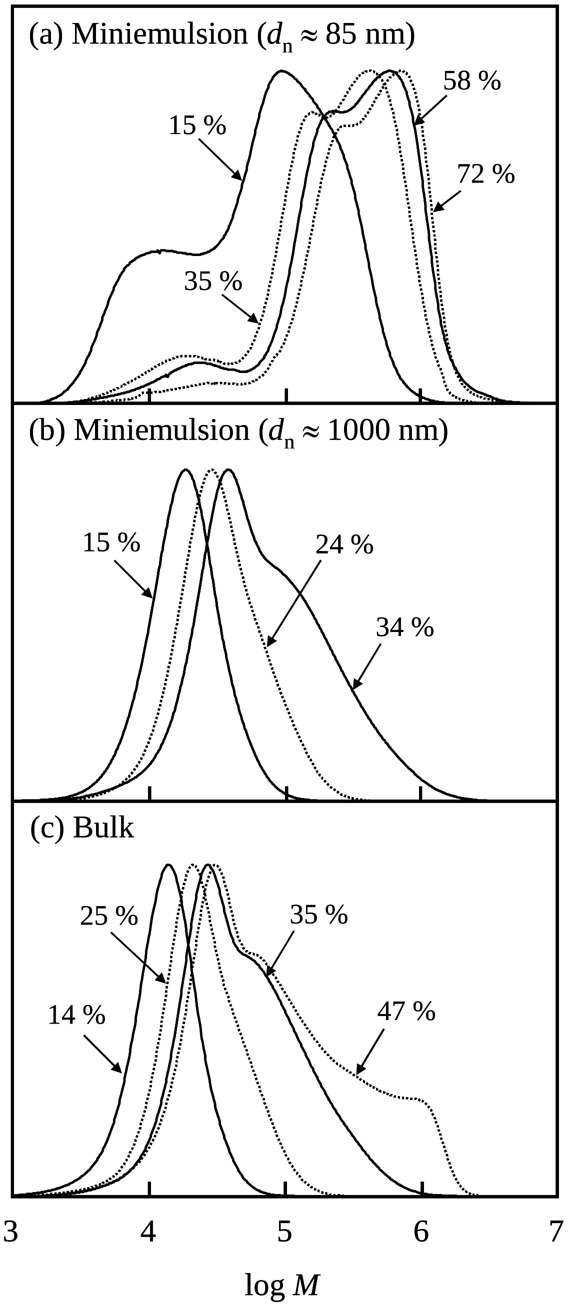

Fig. 3. Molecular weight distributions normalized to peak height for TEMPO-mediated copolymerization of S and DVB (1 mol%) using DOWFAX 8390 as surfactant at 125 °C ([P(S-*r*-MA)- TEMPO]$_0$ = 20 mM; 32 mol% MA macroinitiator) in (a) miniemulsion (d_n ≈ 85 nm; d_w ≈ 111 nm) (b) miniemulsion (d_n ≈ 1000 nm; d_w ≈ 1075 nm) and (c) bulk.

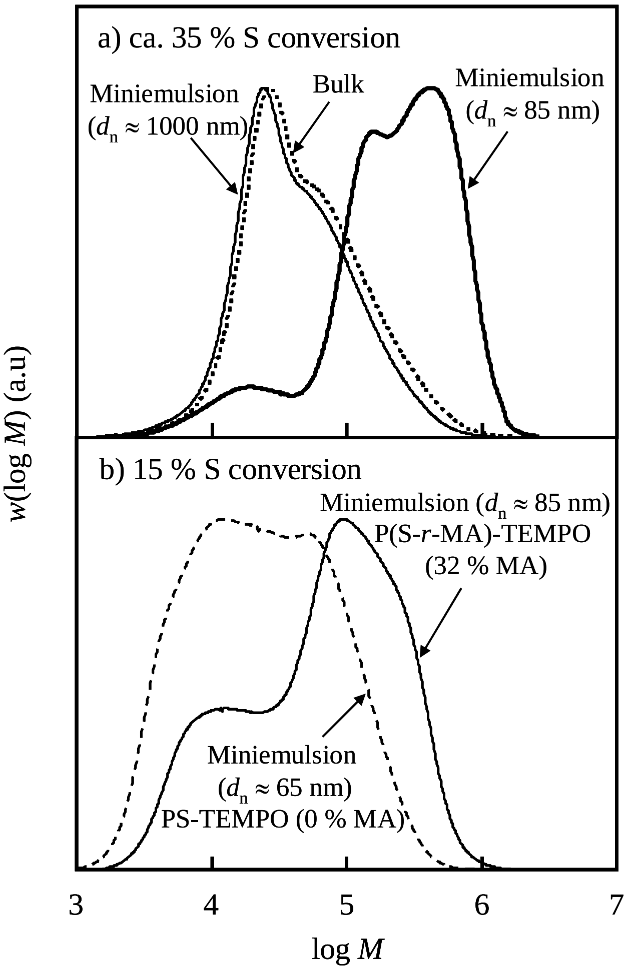

Fig. 4. Molecular weight distributions for TEMPO-mediated copolymerization of S and DVB (1 mol%) at 125 °C using $[\text{macroinitiator}]_0$ = 20 mM in bulk and miniemulsion at similar S conversions. (a) P(S-*r*-MA)-TEMPO (32 mol% MA) in miniemulsion with $d_n \approx$ 85 nm; $d_w \approx$ 111 nm (thick line; 35% S conversion) and $d_n \approx$ 1000 nm; $d_w \approx$ 1075 nm (thin line; 34% S conversion), and bulk (dotted line; 35% S conversion). (b) Miniemulsion: P(S-*r*-MA)-TEMPO (32 mol% MA) with $d_n \approx$ 85 nm; $d_w \approx$ 111 nm (full line; 15% S conversion) and PS-TEMPO (0 mol% MA), $d_n \approx$ 65 nm; $d_w \approx$ 79 nm (broken line; 15% S conversion).