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**Nitroxide-Mediated Radical Polymerization in Miniemulsion:
Bimolecular Termination in Monomer-Free Model Systems**

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ABSTRACT: Bimolecular termination in nitroxide-mediated radical polymerization in miniemulsion has been investigated by heating a polystyrene-2,2,6,6-tetramethylpiperidiny-1-oxyl (TEMPO) macroinitiator, and its 4-hydroxy-TEMPO analogue, in an aqueous toluene dispersion using sodium dodecylbenzenesulfonate as surfactant at 125 °C. The level of bimolecular termination by combination, evaluated from the high molecular weight shoulder, was higher in miniemulsion than solution, and increased with decreasing particle size. Quantitative analysis revealed that these results cannot be rationalized solely by nitroxide partitioning to the aqueous phase. The results are explained by an “interface effect”, whereby nitroxide is adsorbed at or located at the aqueous-organic interface.

Keywords: colloids; controlled/living radical polymerization; interfaces; kinetics (polym.); miniemulsion

INTRODUCTION

Controlled/living radical polymerization (CLRP) makes it possible to prepare polymers of predefined molecular weights (MW), narrow molecular weight distributions (MWD) and various complex architectures.^{1,2} The most well-established of these methods are nitroxide-mediated radical polymerization (NMP),^{3,4} atom transfer radical polymerization (ATRP),^{5,6} and reversible addition fragmentation chain transfer (RAFT) polymerization.⁷ Recent years have seen significant developments in the adaptation of CLRP to aqueous heterogeneous systems due to their importance from an industrial perspective.⁸⁻²¹

Heterogeneous polymerizations (*e.g.* emulsion, miniemulsion) are associated with several phenomena that are absent in their homogeneous counterparts, such as phase transfer

events (exit/entry), partitioning of reactants between the continuous and the particle phases, and compartmentalization effects.²² In order to further develop and improve CLRP in heterogeneous systems, it is essential to quantitatively understand how such factors influence CLRP. For example, when implementing ATRP in miniemulsion, a sufficiently hydrophobic ligand is required to minimize partitioning effects and for control of the polymerization to be maintained.^{8,23} However, the ideal scenario is to exploit these features to improve current homogeneous CLRP systems. For example, our recent theoretical work on compartmentalization effects in NMP^{20,24} and ATRP²⁵ in dispersed systems suggests that it may be possible to improve both control and livingness (at the expense of a lower polymerization rate) by employing sufficiently small particles under appropriate conditions.

“Monomer-free” ATRP systems (atom transfer radical coupling (ATRC)) have previously been examined under homogeneous conditions as novel synthetic routes to telechelic polymers.²⁶⁻³⁰ These systems comprise polymeric dormant species (alkyl halides) that upon reversible activation undergo some extent of bimolecular termination. From a synthetic viewpoint, one tries to optimize the yield of polymer obtained by termination by using conditions different from normal ATRP, *e.g.* by addition of Cu(0) (which reduces Cu(II) to Cu(I) and thus increases the macroradical concentration). There are, as far as we are aware, to date no reports on the corresponding monomer-free “NMP” systems. This is not surprising from a synthetic point of view, because in NMP there is no simple way of decreasing the deactivation rate (or increasing the activation rate) and thereby maximizing the termination rate.

The present study aims at increasing the level of understanding of the effects of heterogeneity on NMP by making use of a monomer-free system. Unlike the above ATRC studies, the current objective is not to maximize termination, but instead to use conditions similar to a normal NMP system. The specific focus has been the extent of bimolecular termination in the 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) mediated polymerization of

styrene in aqueous miniemulsion at 125 °C. In the monomer-free system employed, a polystyrene-TEMPO macroinitiator undergoes reversible thermal dissociation in the absence of monomer. Subsequent examination of the resulting MWD provides information about the extent of bimolecular termination in a way that is not accessible in a polymerizing system.

EXPERIMENTAL

Materials

Styrene (S) was purified by distillation under reduced pressure in a nitrogen atmosphere. Benzoyl peroxide (BPO) was purified by recrystallization using chloroform/methanol. TEMPO and 4-hydroxy-TEMPO (Aldrich), sodium dodecylbenzenesulfonate (SDBS), toluene, methanol and *n*-tetradecane (TD) (Nacalai Tesque Inc.) were used as received.

Preparation of Macroinitiator

Polystyrene-TEMPO (PS-TEMPO): S (13.5 g), BPO (371 mg; 0.103 mol L⁻¹) and TEMPO (285 mg; 0.122 mol L⁻¹) were charged in a glass tube, degassed with several N₂ 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. S conversion = 18%, $M_n = 2350$, $M_w/M_n = 1.14$. The recipe for polystyrene-(4-hydroxy-TEMPO) (PS-(OH-TEMPO)) was the same as above, except that (314 mg; 0.122 mol L⁻¹) was used instead of TEMPO. S conversion = 17 %, $M_n = 2050$, $M_w/M_n = 1.11$.

Monomer-Free Experiments

Solution: A solution of PS-TEMPO (20 mg; 2.5 mM) in toluene (3 g) was degassed with N₂, sealed off under vacuum and held at 125 °C for various times. The same experiment was also carried out in the presence of 30 wt% TD (relative to total mass of toluene and TD: 3 g), as well as in the presence of 0.5 wt% SDBS (relative to toluene, in the absence of TD).

Miniemulsion: A solution of PS-TEMPO (20 mg; 2.5 mM) in toluene (3 g) was mixed with a solution of water (12 g) and SDBS (0.15 g; 5 wt% rel. to total organic phase). Experiments containing TD were carried out as above, except that the organic solution comprised toluene and various amounts of TD (total mass of toluene and TD: 3 g). The resulting mixtures were emulsified using two different techniques: (i) ultrasonication (Ultrasonic Homogenizer, Nissei, US-600T) for 12 min at 0 °C, or (ii) using a NISSEI ABM-2 homogenizer at 2000 rpm for 2 min followed by 3500 rpm for an additional 4 min. The resulting emulsions were transferred to glass ampules, degassed with N₂ and sealed off under vacuum, and the reactions were carried out at 125 °C shaking the ampules (each ampule contained approx. 4 mL) horizontally at a rate of 100 cycles/min. The recipes for solution and miniemulsion reactions containing PS-(OH-TEMPO) were the same as above, except that PS-(OH-TEMPO) (18 mg; 2.5 mM) was used instead of PS-TEMPO.

Partitioning Experiments

A solution of toluene (10 g) and TEMPO (0.098 mg; 0.055 mmol L⁻¹ rel. to toluene) was mixed with water (40 g), transferred to a glass ampoule, sealed off and shaken horizontally at 100 cycles/min for 10 h at room temperature. The ampoule was subsequently left to stand at room temperature until complete phase separation had occurred (approx. 1 h). The organic phase was sampled for electron paramagnetic resonance (EPR) spectroscopy analysis using a pipette.

Measurements

Droplet 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 reactions (the diameters increased somewhat with reaction time).

MWs 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 PS samples (1.05×10^3 – 5.48×10^6). Prior to application of eq 1 for estimation of the extent of termination by coupling, the MWD of the original macroinitiator was shifted so that the MW of the peak coincided with that of the polymer after reaction. This was done in order to decouple the effect of depropagation (which has no significant effect on the shape of the MWD, but affects M_n) from that of termination.

The TEMPO content in the organic phase in the partitioning experiments was measured by EPR spectroscopy employing a JEOL (Japan) JES-T300 spectrometer using 5 mm o.d. quartz tubes at room temperature. EPR parameters: Center field: 3350 G; Sweep width: 100 G; Microwave power: 0.5 mW; Modulation amplitude: 5 G.

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 $\pm 0.2\text{ mN/m}$.

Simulations

The system of differential equations was solved by numerical integration (Backward Euler integration algorithm) using the software VisSim (version 6.0A11, Visual Solutions Inc.).

RESULTS AND DISCUSSION

Bimolecular Termination in Miniemulsion and Solution

NMP is based on the reversible deactivation of propagating radicals ($P\cdot$) by nitroxide ($T\cdot$) according to Scheme 1, where k_d , k_{da} , k_p and k_t are the rate coefficients for activation, deactivation, propagation and termination, respectively, and PT is a polymeric alkoxyamine. When PT is heated in solution in the absence of monomer, the extent of termination can be monitored by examination of the MWD when some fraction (or all) of the termination events occur by combination (disproportionation does not alter the MW), resulting in a high MW shoulder.²⁸

Fig. 1 shows MWDs of the initial PS-TEMPO macroinitiator and the polymer at various reaction times at 125 °C in solution and miniemulsions with $d_n \approx 900$ nm (homogenization using approach (ii) in Experimental) and 320 nm (homogenization using approach (i) in Experimental). In solution and the miniemulsion with $d_n \approx 900$ nm (Figs. 1a and 1b), no significant change in the high MW region was observed. However, in the miniemulsion with $d_n \approx 320$ nm (Fig. 1c), a pronounced high MW shoulder emerged with time due to bimolecular termination.

Fig. 2 shows MWDs of the initial PS-(OH-TEMPO) macroinitiator and the polymer at various reaction times at 125 °C in solution (Fig. 2a) and miniemulsions with $d_n \approx 900$ nm (Fig. 2b) and 340 nm (Fig. 2c). In solution, no discernible change in the MWD occurred (as for PS-TEMPO). However, as indicated by the size of the high MW shoulders, termination in miniemulsion was more extensive for PS-(OH-TEMPO) than PS-TEMPO for both particle sizes. In the case of PS-(OH-TEMPO), a significant high MW shoulder was detected also for $d_n \approx 900$ nm, whereas no shoulder appeared for PS-TEMPO for the same droplet size.

From the above results it is evident that both the heterogeneous nature of the miniemulsion system and the droplet size exert significant influence on the process depicted in Scheme 1.

The extent of bimolecular termination by coupling (x_c) is given by eq 1.²⁷

$$x_c = 2 \left(1 - \frac{M_{n,0}}{M_n} \right) \quad (1)$$

where M_n and $M_{n,0}$ are the number-average MWs at times t and 0, respectively. Fig. 3 shows x_c plotted vs. time for PS-TEMPO ($d_n \approx 320$ nm), PS-(OH-TEMPO) ($d_n \approx 340$ nm) and PS-(OH-TEMPO) ($d_n \approx 900$ nm). The value of x_c is approximately 2-3 times higher for PS-(OH-TEMPO) than PS-TEMPO for similar droplet sizes. A decrease in droplet diameter from 900 to 340 nm for PS-(OH-TEMPO) resulted in x_c increasing markedly.

Nitroxide Partitioning

The styrene-water partitioning coefficients for TEMPO and OH-TEMPO at 135 °C ($[\text{nitroxide}]_s/[\text{nitroxide}]_{aq}$) are 98.8 and 2.2, respectively.^{31,32} Theoretical work has indicated that nitroxide phase equilibrium is reached very rapidly under typical miniemulsion NMP conditions ($< 10^{-4}$ s).¹⁵ At phase equilibrium, there is no effect of particle size on the nitroxide concentration in the organic phase (although the time to reach phase equilibrium increases with increasing particle size).³¹ Consequently, the effect of nitroxide partitioning on the extent of termination is not expected to be influenced by droplet size, suggesting that nitroxide partitioning alone cannot explain the present results (Figs. 1 and 2).

In order to further confirm the above theoretical argument, simulations were carried out based on a homogeneous system using the generally accepted mechanism² with equations added to account for nitroxide partitioning:³³

$$\frac{d[\text{PT}]}{dt} = k_c[\text{P}\bullet][\text{T}\bullet]_{\text{org}} - k_d[\text{PT}] \quad (2)$$

$$\frac{d[\text{P}\bullet]}{dt} = k_d[\text{PT}] - k_c[\text{P}\bullet][\text{T}\bullet]_{\text{org}} - 2k_t[\text{P}\bullet]^2 \quad (3)$$

$$\frac{d[\text{T}\bullet]_{\text{org}}}{dt} = k_d[\text{PT}] - k_c[\text{P}\bullet][\text{T}\bullet]_{\text{org}} + k_2[\text{T}\bullet]_{\text{aq}} - k_1[\text{T}\bullet]_{\text{org}} \quad (4)$$

where k_c ($7.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ^{34,35}) is the rate coefficient for combination of a propagating radical and nitroxide (deactivation), k_d ($1.6 \times 10^{-3} \text{ s}^{-1}$ ³⁴) is the rate coefficient for thermal dissociation of alkoxyamine (activation), and k_t is the rate coefficients for bimolecular termination, and the subscripts org and aq denote organic and aqueous phase, respectively. The alkoxyamines corresponding to the ethylbenzene radical and TEMPO and OH-TEMPO have very similar k_d (differing by < 20%).³⁶ It was assumed that the values of k_d and k_{da} were the same for TEMPO and OH-TEMPO. The value of k_t at 125 °C was calculated using the Arrhenius parameters reported by Buback et al.³⁷ Chain-length dependent termination³⁸ may cause k_t in the current system (which comprises relatively short chains of degree of polymerization of approximately 20) to be slightly higher than that measured by Buback et al. Although the MW of the polymer in Buback's study is not known, k_t in the current study was estimated to be approximately twice that reported by Buback using the reported chain-length dependence of k_t for S³⁹; $k_t = 3.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ was used. Termination was assumed to occur by combination only. The phase transfer rate coefficients k_1 and k_2 are defined according to:



The partitioning was modeled by assigning values to k_1 and k_2 so that the system was always at phase equilibrium ($k_1, k_2 > 10^3 \text{ s}^{-1}$).³¹ The partition coefficient (Γ) is given by:

$$\Gamma = \frac{[\text{T}\cdot]_{\text{org}}}{[\text{T}\cdot]_{\text{aq}}} = \frac{k_2}{k_1} \quad (7)$$

Simulations were performed based on eqs 2 – 6 using the experimentally obtained partitioning coefficients for TEMPO ($\Gamma = 98.8$ ^{31,32}) and OH-TEMPO ($\Gamma = 2.2$ ^{31,32}) for a solids content of 20% (i.e. same as in the present experiments).

The simulated fraction of chains having undergone bimolecular termination by coupling ($x_c = 1 - ([\text{PT}]/[\text{PT}]_0)$) is plotted vs. time in Fig. 4 for PS-TEMPO and PS-(OH-TEMPO). A simulation was also carried out for PS-TEMPO in the absence of partitioning ($\Gamma = \infty$). Two important deductions can be made from the simulations: (i) Partitioning of TEMPO to the aqueous phase cannot explain the experimental result (Fig. 1) of more termination in miniemulsion than in solution. The difference in x_c due to TEMPO partitioning obtained by simulations is close to negligible, i.e. much less than the experimentally observed difference. (ii) The difference in x_c between TEMPO and OH-TEMPO is approximately a factor 2, which is relatively similar to the difference observed experimentally. It is thus likely that the difference in x_c observed experimentally between TEMPO and OH-TEMPO was mainly caused by the higher level of partitioning to the aqueous phase of OH-TEMPO.

Effect of Droplet Size

Miniemulsions containing PS-TEMPO were prepared using different amounts of TD in order to vary the droplet size (homogenization using approach (i) in Experimental). An increase in the TD content led to a decrease in droplet size; 30 wt% TD resulted in $d_n \approx 95 \text{ nm}$, to be compared with $d_n \approx 320 \text{ nm}$ in the absence of TD. The interfacial tensions between the

aqueous phase and the toluene phase in the presence of TEMPO and TD are listed in Table 1. The presence of 30 wt% TD in the toluene phase resulted in a decrease in the interfacial tension from 34.6 to 32.1 mN/m. The smaller droplets obtained in the presence of TD is probably a combined effect of TD acting as a hydrophobe, i.e. reducing the extent of Oswald ripening,⁴⁰ as well as the effect of TD on the interfacial tension (lower interfacial tension allows formation of smaller droplets).

Fig. 5 shows MWDs at various reaction times at 125 °C for solution (with 30 wt% TD; Fig. 5a) and miniemulsion with $d_n \approx 95$ nm (with 30 wt% TD; Fig. 5b). The presence of TD had no effect on the MWD obtained in solution (i.e. no high MW shoulder; Fig. 5a), but the extent of bimolecular termination was much more significant in the miniemulsion with $d_n \approx 95$ nm (Fig. 5b) compared to that with $d_n \approx 320$ nm (Fig. 1c).

Fig. 6 shows the MWDs obtained after heating toluene/TD (of different ratios) miniemulsions of PS-TEMPO (2.5 mM) for 27 h, revealing how the high MW shoulder increased markedly with decreasing d_n (i.e. increasing TD content).

It is conceivable that the amount of TD in the toluene phase may alter the TEMPO partition coefficient between the toluene phase and the aqueous phase. Separate partitioning experiments were conducted, whereby TEMPO was allowed to reach phase equilibrium between the organic and aqueous phases in the systems toluene/water and (toluene and TD)/water (30 wt% TD). The amount of TEMPO in the organic phase was measured directly by EPR, revealing that the presence of TD had no significant effect on the TEMPO partitioning.

Examination of the low MW side of the MWDs (Figs. 1, 2, 4, 5) reveals that there was a slight shift to lower MWs with increasing reaction time. The origin of this shift is not clear at present, but it is speculated that it may be related to depropagation of propagating radicals. Another complication is alkoxyamine decomposition, which generates ω -unsaturated polymer and hydroxylamine.^{36,41} Based on the reported Arrhenius parameters for the decomposition

reaction of PS-TEMPO, as much as 37% of the alkoxyamine would decompose in 27 h at 125 °C.⁴¹ The MW of the high MW shoulder was somewhat higher than expected from bimolecular termination only. A possible explanation, although speculative at this stage, is that a propagating radical adds onto the polymer unsaturated end group, and coupling of the thus generated radical (possibly preceded by deactivation-activation with TEMPO) with another propagating radical generates a three armed star.

Compartmentalization

Compartmentalization (segregation effects and confined space effects) can significantly influence both deactivation and bimolecular termination in NMP in dispersed systems.^{20,24} Simulations employing modified Smith-Ewart equations, accounting for compartmentalization effects on both propagating radicals and nitroxide, have shown that for S/TEMPO/125 °C, $d < 120$ nm is required for compartmentalization effects to become important.^{20,24} The main effect of compartmentalization in the present system would be an increase in the deactivation rate as a result of the confined space effect and a decrease in termination rate due to the segregation effect.^{22,42} Therefore, the effect of compartmentalization on the miniemulsion with $d_n \approx 95$ nm (Fig. 5b) would be a decrease in termination (compared to the corresponding homogeneous system), i.e. opposite to what was observed experimentally. This suggests that another factor(s) exerts stronger influence on the reaction system than compartmentalization.

Effect of SDBS

Cunningham et al.⁴³ 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. However, the PS-TEMPO experiment in the present study with the largest droplets ($d_n \approx 900$ nm; Fig. 1b) resulted in no apparent high MW shoulder despite the

presence of 5 wt% SDBS (rel. to total organic phase) (an additional source of radicals would consume TEMPO, and thus lead to more bimolecular termination). An experiment was also carried out in solution (same as in Fig. 1a) in the presence of SDBS (0.5 wt% rel. to toluene), and the result was the same as in the absence of SDBS, i.e. no high MW shoulder was observed. The above suggests that there was no significant participation of SDBS in radical generation in the present study.

Interface Effect

It is proposed that an interface effect is operative in the present miniemulsion systems, whereby some fraction of the nitroxide is preferentially located near or is adsorbed at the interface of the droplet/aqueous medium.

The effect of TEMPO on the interfacial tensions of toluene/water and (toluene/TD)/water are listed in Table 1, revealing how the presence of TEMPO and OH-TEMPO results in significant reductions in interfacial tension. Similar results have been reported for TEMPO and 4-oxo-TEMPO in the system dodecane/water.⁴⁴ The reduction in interfacial tension observed on addition of nitroxide is consistent with some fraction of the nitroxide being located at the organic/aqueous interface. This is further supported by EPR⁴⁵⁻⁴⁷ and optical absorption spectroscopy⁴⁸ data indicating that the nitroxide group (NO•) of various nitroxides tends to be located at the interface in colloid particles^{45,46} and micelles.⁴⁵⁻⁴⁸ In the present study, some fraction of the nitroxide being located at the interface would result in a lower effective nitroxide concentration in the toluene droplet, and consequently a reduced rate of deactivation, which in turn leads to increased termination (manifested as a high MW shoulder in the MWD). Such an interface effect would increase in significance with decreasing particle size due to the accompanying increase in interfacial area/droplet volume, thus qualitatively explaining the increase in termination with decreasing particle size (Figs. 1, 2 and 6).

We recently reported that the polymerization rate increased and the control decreased with decreasing particle size in the TEMPO-mediated radical polymerization of S in aqueous miniemulsion at 125 °C (using SDBS as stabilizer), consistent with the rate of deactivation being reduced to some extent due to an interface effect involving TEMPO.²¹

CONCLUSIONS

Monomer-free model systems comprising an aqueous dispersion of a toluene/TD solution of a PS-TEMPO or PS-(OH-TEMPO) macroinitiator using SDBS as surfactant at 125 °C have been employed to investigate the extent of bimolecular termination in nitroxide-mediated radical polymerization in aqueous miniemulsion. The extent of termination, as evidenced by a high MW shoulder due to bimolecular termination by coupling, was more significant in miniemulsion than solution. Furthermore, the level of bimolecular termination increased with decreasing particle size (95 – 900 nm). Simulations indicated that the results could not be explained by nitroxide partitioning to the aqueous phase.

The results are consistent with a reduced deactivation rate (i.e. propagating radical coupling reversibly with nitroxide) due to a previously proposed interface effect,²¹ according to which some fraction of the nitroxide is located near or is adsorbed at the interface of the droplet/aqueous medium. This is further supported by the presence of TEMPO or OH-TEMPO in the organic phase of the systems toluene/water and (toluene/TD)/water resulting in a reduction in the interfacial tension.

The present results are consistent with our previous work on TEMPO-mediated radical polymerization of S in aqueous miniemulsion at 125 °C, where it was shown that the polymerization rate increased and the control decreased with decreasing particle size.²¹ The results have implications with regards to optimization of NMP in aqueous dispersed systems,

in particular with regards to utilizing the particle size as an additional experimental parameter to achieve a suitable balance between the polymerization rate and the level of control.

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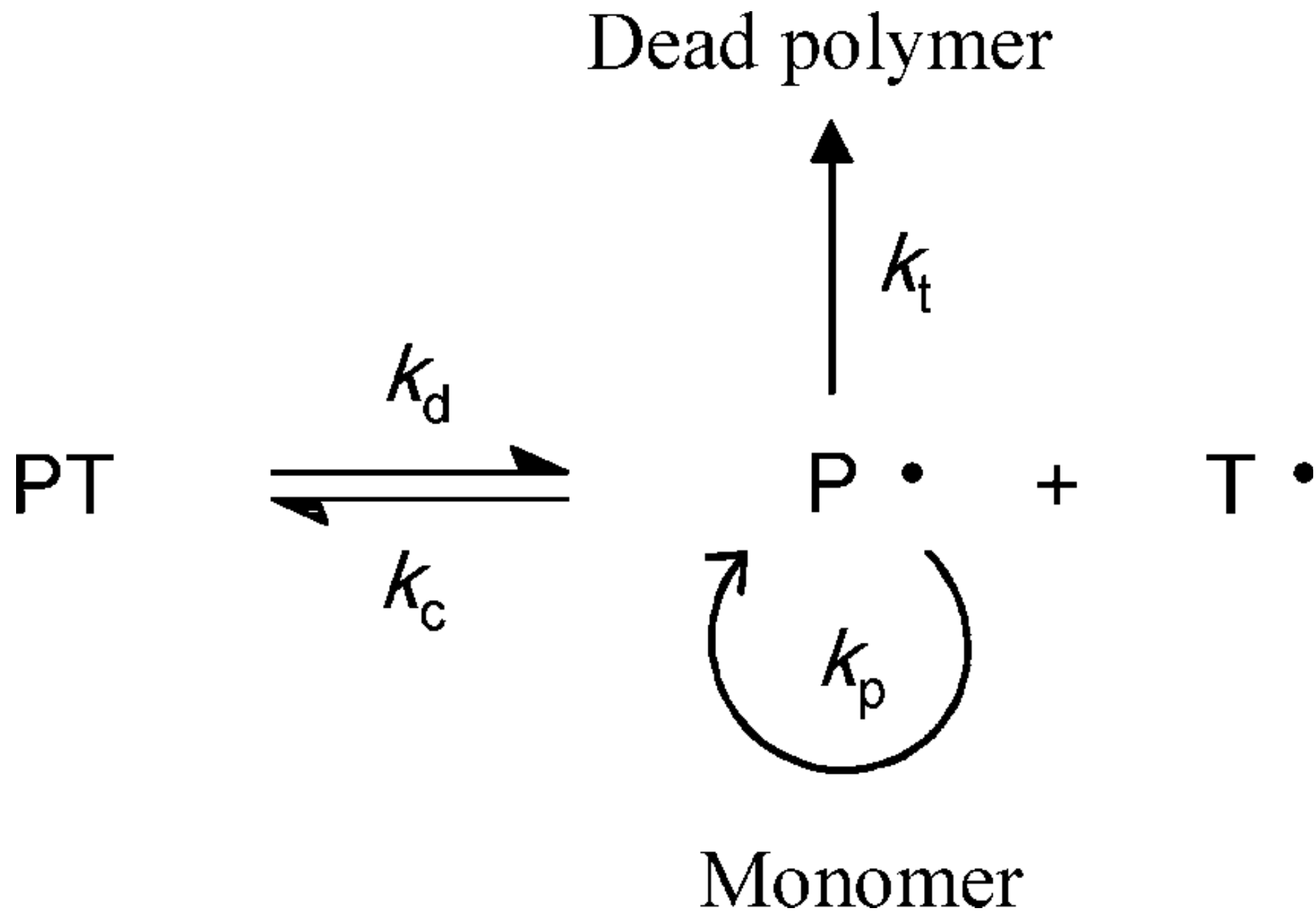
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REFERENCES

1. Matyjaszewski, K. In *Advances in Controlled/Living Radical Polymerization*; American Chemical Society: Washington, DC, 2003.
2. Goto, A.; Fukuda, T. *Prog. Polym. Sci.* 2004, 29, 329-385.
3. Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* 1993, 26, 2987-2988.
4. Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* 2001, 101, 3661-3688.
5. Matyjaszewski, K.; Xia, J. In *Handbook of Radical Polymerization*; Matyjaszewski, K.; Davis, T. P., Ed.; Wiley-Interscience: New York, 2002; Chapter 11, p 523.
6. Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* 2001, 101, 3689-3745.
7. Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem.* 2006, 59, 669-692.
8. Qiu, J.; Charleux, B.; Matyjaszewski, K. *Prog. Polym. Sci.* 2001, 26, 2083-2134.
9. Cunningham, M. F. *Prog. Polym. Sci.* 2002, 27, 1039-1067.
10. Okubo, M.; Minami, H.; Zhou, J. *Colloid Polym. Sci.* 2004, 282, 747-752.
11. Kagawa, Y.; Minami, H.; Okubo, M.; Zhou, J. *Polymer* 2005, 46, 1045-1049.
12. Zetterlund, P. B.; Alam, M. N.; Minami, H.; Okubo, M. *Macromol. Rapid Commun.* 2005, 26, 955-960.
13. Alam, M. N.; Zetterlund, P. B.; Okubo, M. *Macromol. Chem. Phys.* 2006, 207, 1732-1741.
14. Save, M.; Guilleaume, Y.; Gilbert, R. G. *Aust. J. Chem.* 2006, 59, 693-711.
15. Li, M.; Matyjaszewski, K. *J. Polym. Sci., Part A: Polym. Chem* 2003, 41, 3606-3614.
16. Ferguson, C. J.; Hughes, R. J.; Nguyen, D.; Pham, B. T. T.; Gilbert, R. G.; Serelis, A. K.; Such, C. H.; Hawket, B. S. *Macromolecules* 2005, 38, 2191-2204.
17. Nicolas, J.; Charleux, B.; Guerret, O.; Magnet, S. *Macromolecules* 2005, 38, 9963-9973.

18. Prescott, S. W.; Ballard, M. J.; Rizzardo, E.; Gilbert, R. G. *Aust. J. Chem.* 2002, 55, 415-424.
19. Cunningham, M. F.; Ng, D. C. T.; Milton, S. G.; Keoshkerian, B. J. *Polym. Sci.; Part A: Polym. Chem.* 2006, 44, 232-242.
20. Zetterlund, P. B.; Okubo, M. *Macromolecules* 2006, 39, 8959-8967.
21. Nakamura, T.; Zetterlund, P. B.; Okubo, M. *Macromol. Rapid Commun.* 2006, 27, 2014-2018.
22. Gilbert, R. G. In *Emulsion Polymerization: A Mechanistic Approach*; Academic Press: London, 1995.
23. Kagawa, Y.; Zetterlund, P. B.; Minami, H.; Okubo, M. *Macromolecules*, in press.
24. Zetterlund, P. B.; Okubo, M. *Macromol. Theory Simul.* 2007, 16, 221-226.
25. Kagawa, Y.; Zetterlund, P. B.; Minami, H.; Okubo, M. *Macromol. Theory Simul.* 2006, 15, 608-613.
26. Yurteri, S.; Cianga, I.; Yagci, Y. *Macromol. Chem. Phys.* 2003, 204, 1771-1783.
27. Sarbu, T.; Lin, K. Y.; Ell, J.; Siegwart, D. J.; Spanswick, J.; Matyjaszewski, K. *Macromolecules* 2004, 37, 3120-3127.
28. Yoshikawa, C.; Goto, A.; Fukuda, T. *e-Polymers* 2002, 013.
29. Nagelsdiek, R.; Keul, H.; Hocker, H. *e-Polymers* 2005, 049.
30. Sarbu, T.; Lin, K.-Y.; Spanswick, J.; Gil, R. R.; Siegwart, D. J.; Matyjaszewski, K. *Macromolecules* 2004, 37, 9694-9700.
31. Ma, J. W.; Cunningham, M. F.; McAuley, K. B.; Keoshkerian, B.; Georges, M. K. *Macromol. Theory Simul.* 2002, 11, 953-960.
32. Ma, J. W.; Cunningham, M. F.; McAuley, K. B.; Keoshkerian, B.; Georges, M. K. J. *Polym. Sci.; Part A: Polym. Chem.* 2001, 39, 1081-1089.
33. Zetterlund, P. B.; Okubo, M. *Macromol. Theory Simul.* 2005, 14, 415-420.

34. Goto, A.; Terauchi, T.; Fukuda, T.; Miyamoto, T. *Macromol. Rapid Commun.* 1997, 18, 673-681.
35. Fukuda, T.; Terauchi, T.; Goto, A.; Ohno, K.; Tsujii, Y.; Miyamoto, T.; Kobatake, S.; Yamada, B. *Macromolecules* 1996, 29, 6393.
36. Goto, A.; Kwak, Y.; Yoshikawa, C.; Tsujii, Y.; Sugiura, Y.; Fukuda, T. *Macromolecules* 2002, 35, 3520-3525.
37. Buback, M.; Kowollik, C.; Kurz, C.; Wahl, A. *Macromol. Chem. Phys.* 2000, 201, 464-469.
38. Buback, M.; Egorov, M.; Gilbert, R. G.; Kaminsky, V.; Olaj, O. F.; Russell, G. T.; Vana, P.; Zifferer, G. *Macromol. Chem. Phys.* 2002, 203, 2570-2582.
39. Olaj, O. F.; Vana, P. *Macromol. Rapid Commun.* 1998, 19, 433.
40. Taylor, P. *Adv. Colloid Interface Sci.* 1998, 75, 107-163.
41. Ohno, K.; Tsujii, Y.; Fukuda, T. *Macromolecules* 1997, 30, 2503-2506.
42. Charleux, B. *Macromolecules* 2000, 33, 5358-5365.
43. Lin, M.; Hsu, J. C. C.; Cunningham, M. F. *J. Polym. Sci., Part A: Polym. Chem.* 2006, 44, 5974-5986.
44. Pyter, R. A.; Ramachandran, C.; Mukerjee, P. *J. Phys. Chem.* 1982, 86, 3206-3210.
45. Baglioni, P.; Cocciaro, R.; Dei, L. *J. Phys. Chem.* 1987, 91, 4020-4023.
46. Zhou, J.; Chen, S.; Duan, H.; Jiang, M.; Zhang, Y. *Langmuir* 2001, 17, 5685-5687.
47. Weber, S.; Wolff, T.; Bunau, G. v. *J. Colloid Interface Sci.* 1996, 184, 163-169.
48. Ramachandran, C.; Pyter, R. A.; Mukerjee, P. *J. Phys. Chem.* 1982, 86, 3198-3205.



Scheme 1

Table 1. Interfacial Tension Measured by the Pendant Drop Method

	Interfacial Tension (mN/m)
Toluene/water	34.6
Toluene (0.5 wt % TEMPO)/water	32.8
Toluene (0.5 wt % OH-TEMPO)/water	31.0
Toluene (30 wt % TD)/water	32.1
Toluene (30 wt % TD, 0.5 wt % TEMPO)/water	30.5

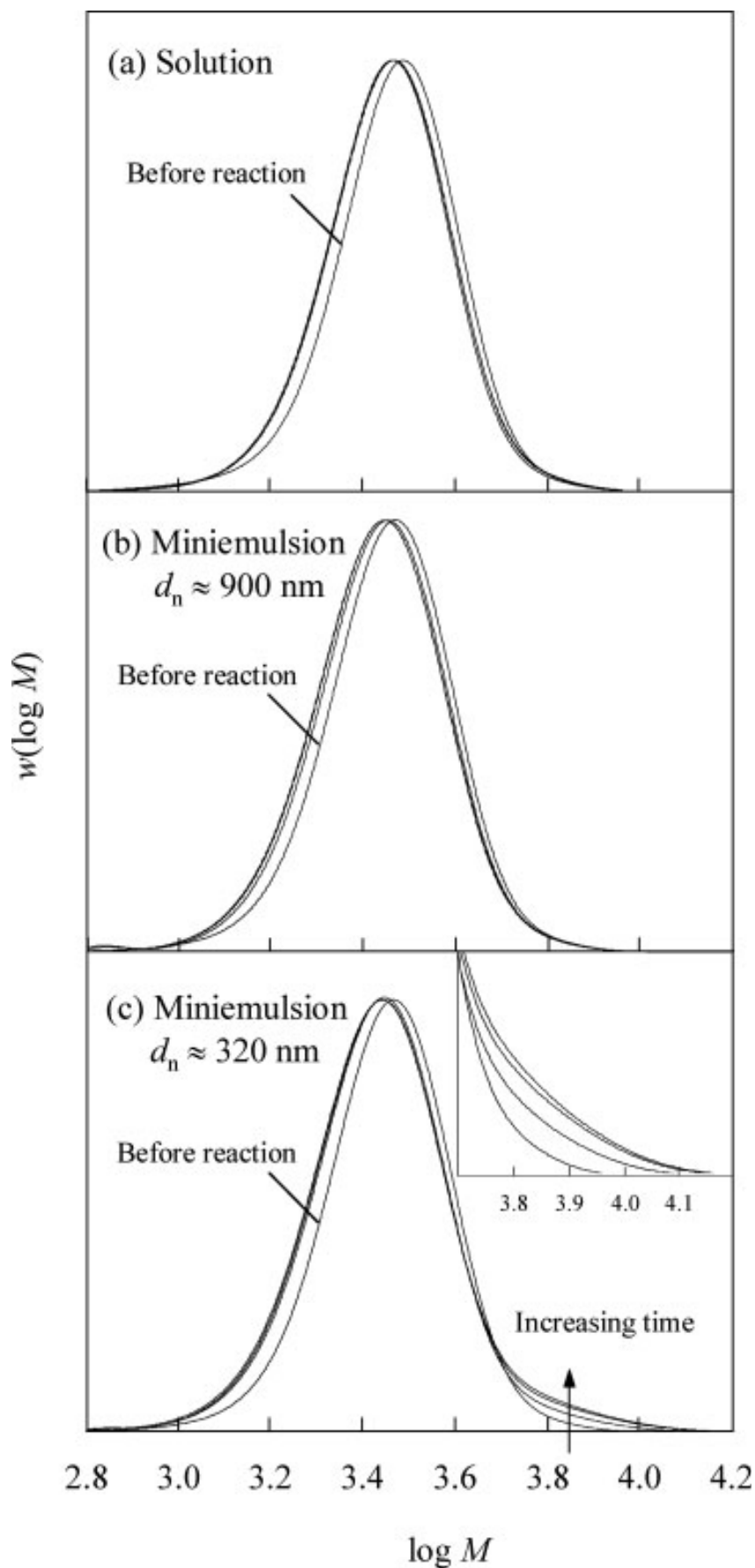


Figure 1. GPC MWDs [$w(\log M)$ vs $\log M$] normalized to peak height after heating a solution/miniemulsion of PS-TEMPO ($M_n = 2350$, $M_w/M_n = 1.14$) in toluene ($[\text{PS-TEMPO}]_0 = 2.5$ mM in the organic phase) at 125 °C for 0, 9, 27, and 45 h: (a) solution, (b) miniemulsion with $d_n \approx 900$ nm and $d_w \approx 960$ nm, and (c) miniemulsion with $d_n \approx 320$ nm and $d_w \approx 340$. The miniemulsions were 20 wt % toluene and 5 wt % SDBS (with respect to the organic phase).

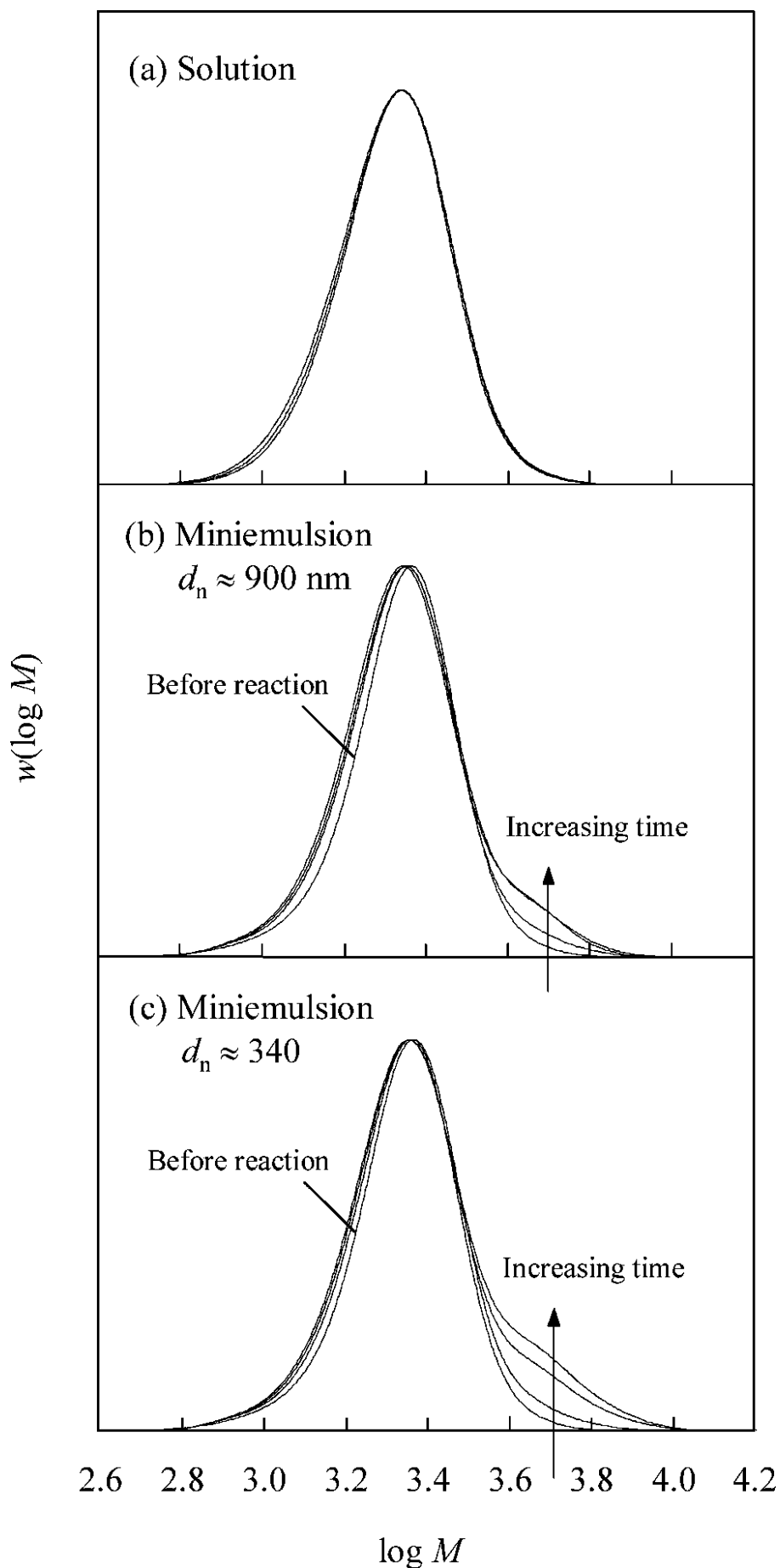


Figure 2. GPC MWDs [$w(\log M)$ vs $\log M$] normalized to peak height after heating a miniemulsion of PS-(OH-TEMPO) ($M_n = 2050$, $M_w/M_n = 1.11$) in toluene ($[\text{PS}-(\text{OH-TEMPO})]_0 = 2.5$ mM in the organic phase) at 125 °C for 9, 27, and 45 h: (a) solution, (b) miniemulsion with $d_n \approx 900$ nm and $d_w \approx 960$ nm, and (c) miniemulsion with $d_n \approx 340$ nm and $d_w \approx 360$ nm.

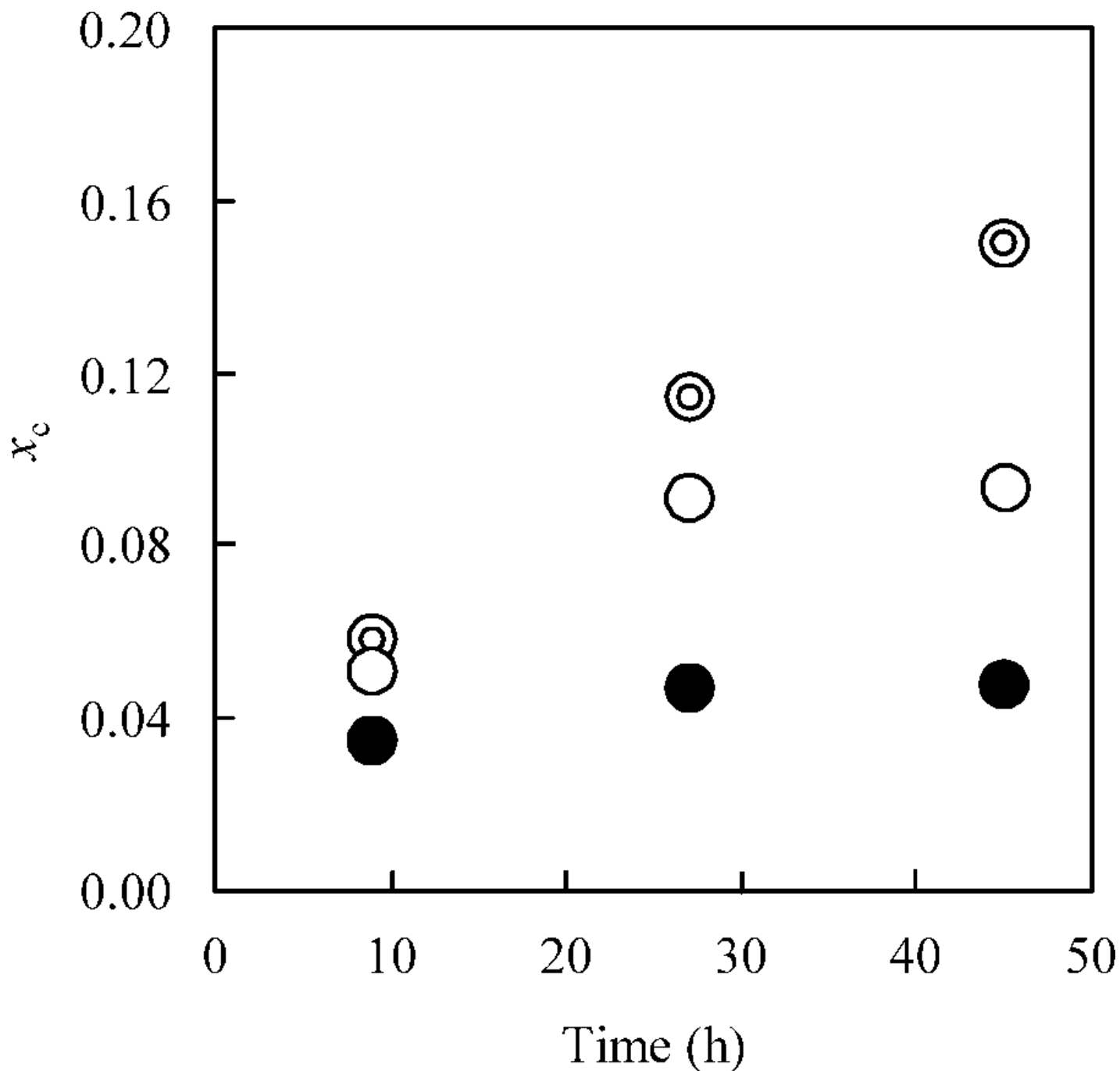


Figure 3. Plot of x_c versus time during heating (125 °C) of a miniemulsion (surfactant: SDBS) consisting of a polymeric alkoxyamine (2.5 mM in the organic phase) and toluene in the absence of monomer: (○) PS-(OH-TEMPO) ($d_n \approx 900$ nm), (⊙) PS-(OH-TEMPO) ($d_n \approx 340$ nm), and (●) PS-TEMPO ($d_n \approx 320$ nm).

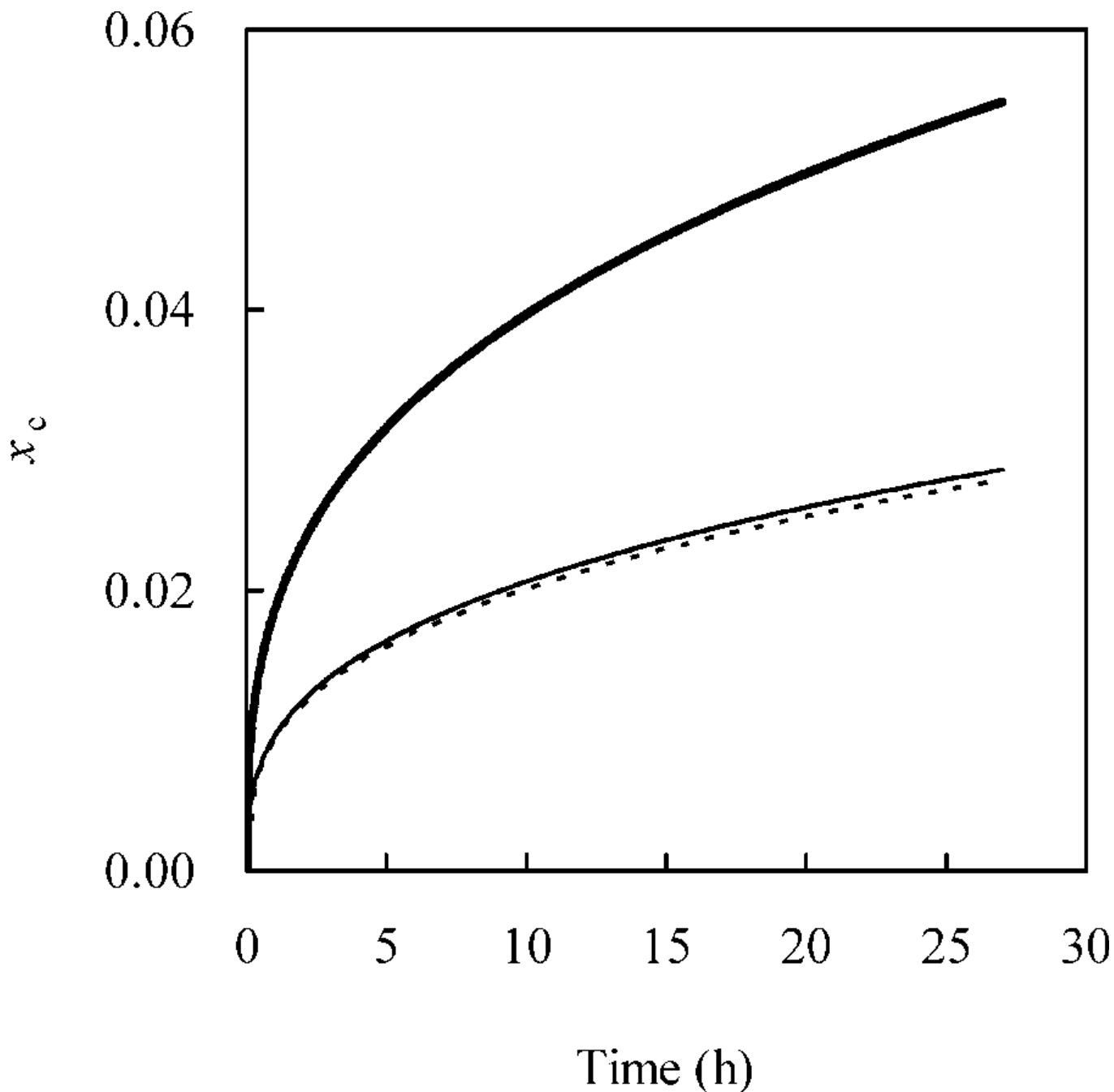


Figure 4. Simulated values of x_c (eqs 2–6) versus time during heating (125 °C) of polymeric alkoxyamines (2.5 mM in the organic phase) in a dispersed system (solid content = 20%) in the absence of monomer. The thick line represents PS-(OH-TEMPO) (nitroxide partitioning included in the model), the thin line represents PS-TEMPO (nitroxide partitioning included in the model), and the dotted line represents PS-TEMPO and PS-(OH-TEMPO) (no partitioning included in the model).

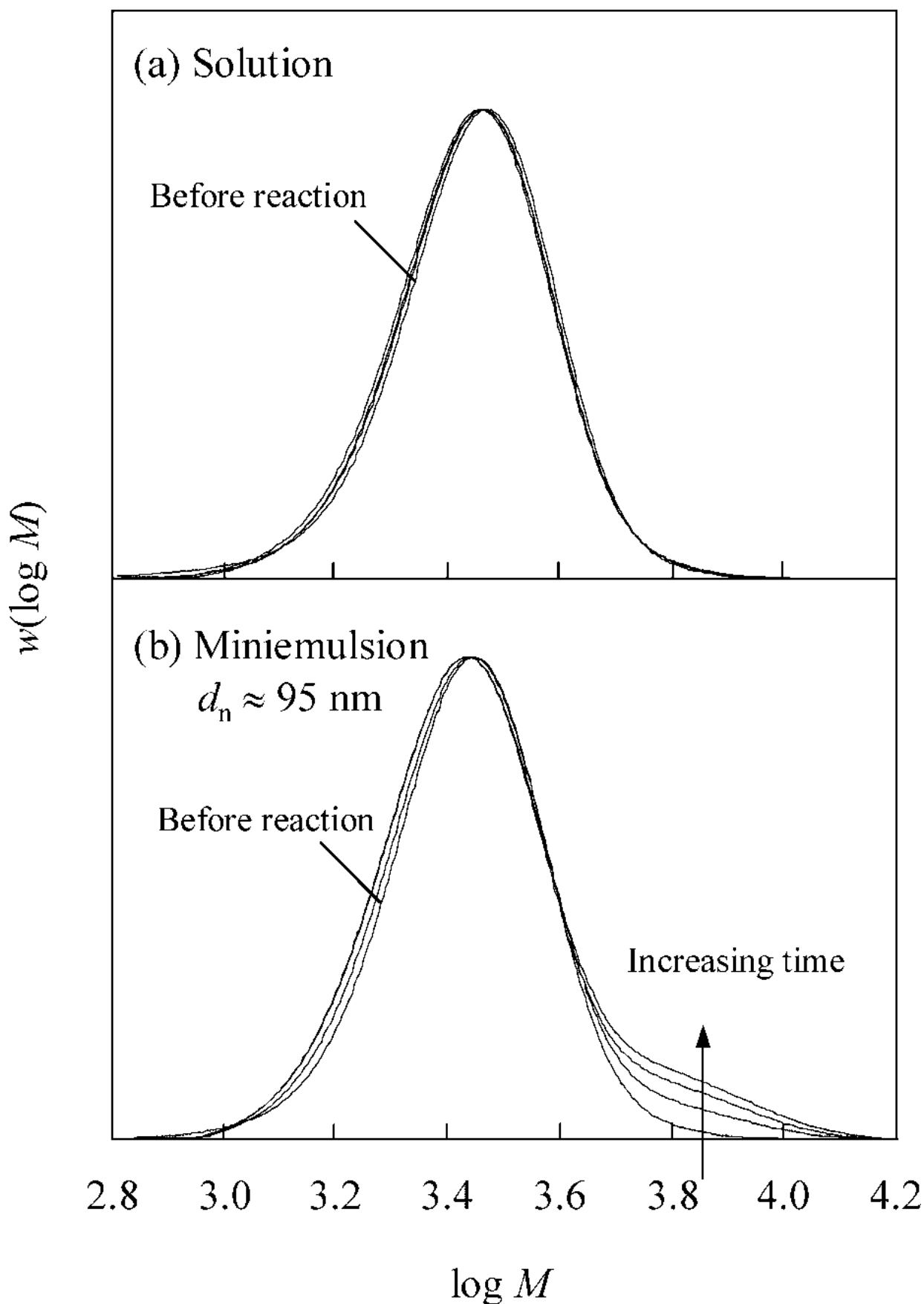


Figure 5. GPC MWDs [$w(\log M)$ vs $\log M$] normalized to peak height after heating a solution/miniemulsion of PS-TEMPO ($M_n = 2350$, $M_w/M_n = 1.14$, $[\text{PS-TEMPO}]_0 = 2.5$ mM in the organic phase, toluene/30 wt % TD) at 125 °C for 0, 9, 27, and 45 h: (a) solution and (b) miniemulsion with $d_n \approx 95$ nm and $d_w \approx 120$ nm.

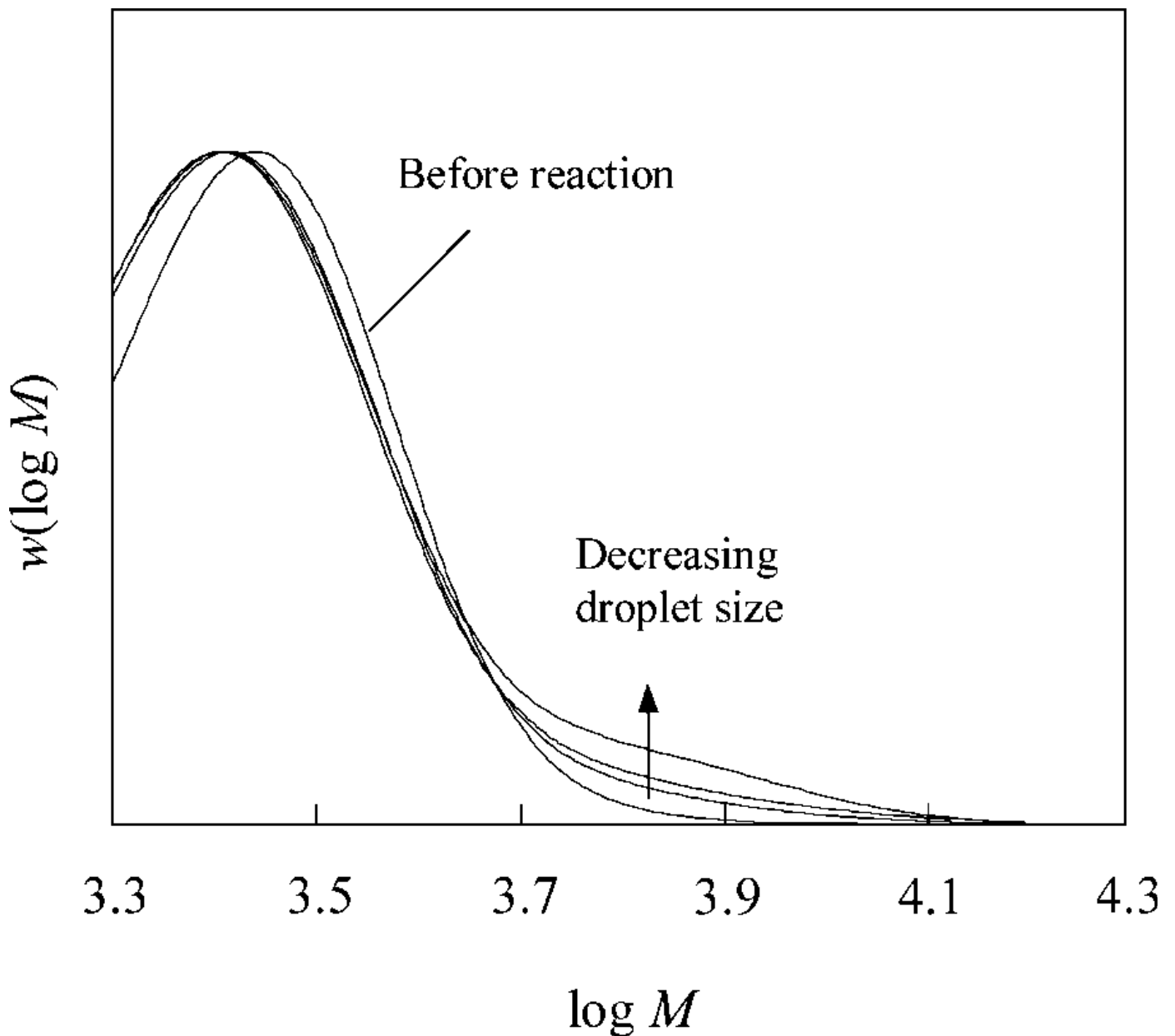


Figure 6. GPC MWDs [$w(\log M)$ vs $\log M$] normalized to peak height after heating miniemulsions of PS-TEMPO ($M_n = 2350$, $M_w/M_n = 1.14$, $[\text{PS-TEMPO}]_0 = 2.5$ mM in the organic phase) comprising different amounts of toluene/TD at 125 °C for 27 h: $d_n \approx 320$ nm and $d_w \approx 340$ (without TD in the organic phase), $d_n \approx 140$ nm and $d_w \approx 160$ (10 wt % TD in the organic phase), and $d_n \approx 95$ nm and $d_w \approx 120$ (30 wt % TD in the organic phase).