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# Emulsion Polymers

Selected papers presented at the
217th American Chemical Society National Meeting
Polymeric Materials Science and Engineering Division

*held in Anaheim, California, USA*
*March 21-25, 1999*

*Symposium Editors*

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# Preface

A symposium entitled "Emulsion Polymers" was held at the 217th American Chemical Society National Meeting in Anaheim, CA on March 21–25, 1999 in the Polymeric Materials Science and Engineering Division. Thirty-one oral presentations and thirteen poster presentations were given. Topic areas presented included novel concepts in emulsion and miniemulsion homo- and copolymerization, the role of polymeric stabilizers in emulsion polymerization, particle morphology and film formation and applications of latex systems. The papers within this volume cover a broad range of topics representative of the symposium. Emulsion polymers have been an industrially important product area for over 50 years. Currently, it is estimated that about 5 billion (dry) pounds of latex polymers are produced in the U.S. and about 10 billion dry pounds are produced worldwide at a total worldwide market value of up to about $10 billion U.S. To put that total volume in perspective, approximately 1 liter of emulsion polymer is produced for each person on earth. End uses for this diverse slate of products include architectural coatings, paper, adhesives, construction materials, textiles, non-wovens, carpet, drug-delivery systems, diagnostics and others. Monomer types include acrylics, styrenics and vinyl acetate-based systems. Much of this market advance has been made in replacing solvent-borne polymers for these varied applications; in this manner, the emulsion polymerization market can be viewed as one of the first large-scale environmentally friendly polymer applications. However, it is clear from the shear volume of research that continues in this area from both academic and industrial organizations that this is not yet a mature technology. New applications are continually being sought and found, and novel methods and compositions are commonly found in both the open and patent literature. This symposium volume is a snapshot of some of the current research topics in the area.

We would like to acknowledge the financial support for the symposium from *ACS Corporation Associates Grant for Industrial Programming* and *Air Products Polymers, L.P.* We also would like to acknowledge the diligent and efficient support of *Mrs. Kathryn Plotts* of The Emulsion Polymers Institute, Lehigh University.

Mohamed S. El-Aasser

Carrington D. Smith

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**Anaheim, California, 1999**

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# Nitroxide–Mediated Living Free Radical Miniemulsion Polymerization of Styrene

T. Prodpran, V. L. Dimonie, E. D. Sudol and M. S. El-Aasser*

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SUMMARY: Living free-radical bulk polymerization using a stable free r
initiator system based on nitroxide stable radicals such as TEMPO (2,2
tetramethyl-1-piperidynyloxy) has permitted the synthesis of polymers
molecular weight distributions only slightly broader than those obtained via ar
polymerization (PDI < 1.3). Most recently we were able to successfully appl
living free-radical polymerization in a miniemulsion polymerization proces
prepare stable latexes with 20% solids and having relatively narrow mol
weight distributions (1.14 – 1.6). Styrene miniemulsions were prepared usi
anionic surfactant Dowfax 8390 with hexadecane as costabilizer. The miniem
polymerizations were carried out at 125°C in pressure bottles using be
peroxide (BPO) and TEMPO. The kinetics of the living free radical miniem
polymerization were followed as a function of the [TEMPO]/[BPO] ratio in or
develop a mechanistic understanding of the nucleation and growth processes i
disperse system. The development of particle number and the total numb
polymer chains (through the molecular weight analysis) during the cour
polymerizations in the presence and absence of TEMPO are used to deve
comprehensive picture of the process.

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## Introduction

Most advanced polymeric materials with special and superior properties have cont
molecular and supramolecular structures such as controlled and narrow molecular w
distributions, specific chain architecture and in many cases desired chain end groups.
chemo- and stereoselectivity of polymer chains is generally achieved by using
polymerization processes either by anionic or cationic initiation. Free radical polymeriz
has been severely limited for such applications because broad molecular weight distribu
are inherent due to irreversible termination of growing chains by bimolecular termir
between two radicals. Much interest has been devoted to "living" polymerizations, a
growth process without reactions that lead to "dead" polymers, namely, transf
termination by coupling or disproportionation. In such systems polymer chains
spontaneously resume their growth whenever fresh monomer is supplied to the sy

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leading to novel polymer architectures as well as block, star or comb polymers. Unfortunately, the extreme purity conditions necessary for ionic polymerizations strongly limit the application of such processes on a large scale.

Recently, the rapid development of "pseudo-living" free radical polymerization has opened new avenues for the synthesis of specialty polymers[1]. The concept of reversible termination of a growing chain to form a dormant species P-X that can be reactivated as a polymer radical, $P^{\bullet}$, was applied to produce "living" polymers through free radical initiation. Several "living" free radical polymerization processes based on the common concept of alternating the activation and deactivation steps, including stable free radical polymerization (SFRP) using stable nitroxyl radicals[2-4], atom transfer radical polymerization (ATRP) mediated by transition metal complexes[5,6], and reversible addition-fragmentation chain transfer (RAFT) using dithioester derivatives[7], were developed.

The SFRP method is one of the most investigated types of living free radical polymerization. The main advantage of using a nitroxide stable radical, such as TEMPO (2,2,6,6,-tetramethyl-1-piperidynyloxy), is that they do not initiate polymerization by addition to double bonds but they react selectively with growing carbon-centered radicals to form reversibly covalent species at nearly diffusion controlled rates. This reversible capping reaction dramatically reduces the concentration of radical chain ends in the polymerization, and therefore the termination reactions, leading to a significant degree of "living" character. This approach, until recently, was successfully applied only in bulk polymerizations to form homopolymers[2,8,9] and block copolymers[10], in suspension copolymerization[11], and in one case, the aqueous solution polymerization of sodium styrene sulfonate[12]. The first few attempts to extend the application of SFRP to the preparation of submicron latex particles by conventional emulsion polymerization were made without success. Bon et al.[13] were able to apply the SFRP process only in a seeded emulsion polymerization by using preformed monodisperse latex particles. Marestin et. al[14] reported very little success in preparing stable polystyrene latexes using various nitroxide derivatives, resulting in latexes with a maximum 5% solids content and low conversions. Recently, we were able to demonstrate the feasibility of applying the living free radical polymerization in a miniemulsion polymerization process to prepare stable (coagulum-free) polystyrene latexes with 20% solids contents and high conversions, exceeding 90%, and having relatively narrow molecular weight distributions (PDI = 1.14 - 1.6)[15,16].

The application of the miniemulsion polymerization technique, where the monomer is homogenized to yield small droplets (0.05 to 0.5 μm in diameter) that are made stable against diffusional degradation through the use of a surfactant plus costabilizer system (e.g., an anionic surfactant + cetyl alcohol or hexadecane)[17,18] helped to eliminate the problems which lead to catastrophic coagulum formation and low conversions in conventional emulsion polymerizations. Most recently, another group has been able to reproduce our findings[19].

## Experimental

Styrene monomer (Aldrich) was cleaned before use by passing it over activated alumina to remove the inhibitor. Benzoyl peroxide (BPO) oil-soluble initiator (Aldrich), 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) (Aldrich), camphorsulfonic acid (CSA), a rate accelerant (Aldrich), and hexadecane (Aldrich) were used as received. DOWFAX 8390 surfactant (Dow Chemical Co.), a highly anionic surface active agent consisting of a disulfonated alkyl diphenyl oxide sodium salt, and hexadecane costabilizer were used in the preparation of the styrene miniemulsions. The recipe listed in Table 1 is based on a typical bulk styrene polymerization system reported in the literature[8,11,20] using BPO and TEMPO.

The miniemulsions were made by first preparing two solutions: BPO, TEMPO, CSA and hexadecane in styrene monomer and DOWFAX 8390 in DI water, mixing these under mild agitation for 5 min, then sonifying the mixture for 10 min at 50% duty cycle and power level 8, using a Branson Sonifier. Miniemulsion polymerizations were carried out in high pressure polymerization bottles in an oil bath at a controlled temperature of 125°C. During a polymerization, the reaction mixture was stirred with a magnetic bar at about 380 rpm. Samples taken periodically via syringe throughout the course of the polymerization were characterized for conversion, molecular weight and molecular weight distribution, as well as particle size and particle size distribution. Monomer conversion was determined by gravimetric analysis. Molecular weight distributions were determined by gel permeation chromatography (GPC, Millipore Waters). Capillary hydrodynamic fractionation (CHDF 1100, Matec Applied Sciences) was used to determine the particle size distribution. The number of particles ($N_p$) was then determined as a function of conversion from the volume average diameter ($D_v$).

Various polymerizations, in the presence and absence of BPO and/or TEMPO, were performed as control experiments. For comparison, a bulk styrene polymerization was also performed using benzoyl peroxide (BPO) initiator in the presence of TEMPO and CSA at the same concentrations as used in the miniemulsion polymerizations.

Table 1. Recipe for the miniemulsion polymerization of styrene in the presence of TEMPO at 125°C.

| Ingredient | Weight (g) | Concentration |
|---|---|---|
| *Oil Phase:* | | |
| Styrene | 15.6 | |
| BPO | 0.0433 | 0.0104 M[a)] |
| TEMPO | 0.0347 | 0.013 M[a,b)] |
| CSA | 0.0520 | 0.013 M[a,c)] |
| Hexadecane | 0.8814 or 1.4690 | 60 or 100 mM[d)] |
| *Water Phase:* | | |
| Deionized water | 65 | |
| DOWFAX-8390 | 0.6240 or 1.0400 | 15 or 25 mM[d)] |

[a)] based on styrene; [b)];$[TEMPO]_o/[BPO]_o=1.25$; [c)] $[CSA]_o/[TEMPO]_o=1.0$
[d)] based on water; [Hexadecane]:[DOWFAX] = 4:1; Total solids ~19%

## Results and Discussion

### *Effect of the presence of BPO and/or TEMPO and Autothermal Polymerization*

Four different miniemulsion polymerizations were initially conducted at 125°C using 25 mM DOWFAX as surfactant: 1) with both TEMPO and BPO (the basic reaction recipe); and three control experiments 2) thermal polymerization of styrene in the absence of both BPO and TEMPO; 3) polymerization in the absence of BPO but with TEMPO; and 4) polymerization with BPO but without TEMPO. The conversion was measured gravimetrically as a function of time for samples withdrawn during the polymerizations.

As seen in Figure 1 from the conversion-time curves, the presence of TEMPO affects the rate of polymerization. In the presence of TEMPO, the polymerization rate is slower being controlled by the equilibrium between active and dormant species, $P_n^*$ and $P_n$-T. In the

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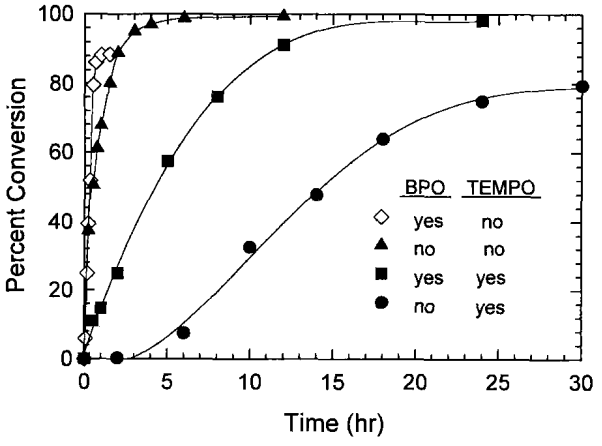


Fig. 1: Conversion-time curves for miniemulsion polymerizations of styrene performed under different conditions at 125°C.

reaction where TEMPO was used without any added initiator, an induction period is observed. During this period, spontaneous thermal initiation must generate an amount of radicals comparable to the initial TEMPO concentration before the polymerization starts. This result is similar to what was observed in bulk polymerizations reported in previous publications[21,22]. When BPO initiator was added in a comparable amount to that of TEMPO, the polymerization started without an induction period and reached a conversion of ~90% in about 12 hrs of polymerization. In the absence of TEMPO, the reactions at 125°C were fast even in the absence of initiator (i.e., pure autothermal polymerization), indicating that considerable thermal initiation took place. It has been reported that at temperatures above 100°C, styrene can polymerize by a third-order self-initiation via formation of an unstable Diels-Alder intermediate, which is further aromatized with another styrene molecule, generating radicals[23]. In conclusion, the rate of polymerization is controlled by the presence of TEMPO. This phenomenon has been reported previously for bulk systems where the polymerization rate is accelerated by the disappearance of TEMPO and this was included in the rate expression ($d[M]/dt \propto [M]/[TEMPO]$)[24].

The evolution of the number-average molecular weight and polydispersity index (PDI = $M_w/M_n$) as a function of conversion for these four systems is shown in Figures 2 and 3, respectively. Significant differences can be observed between the cases where TEMPO was present or absent. When TEMPO was used, the molecular weight showed a nearly linear

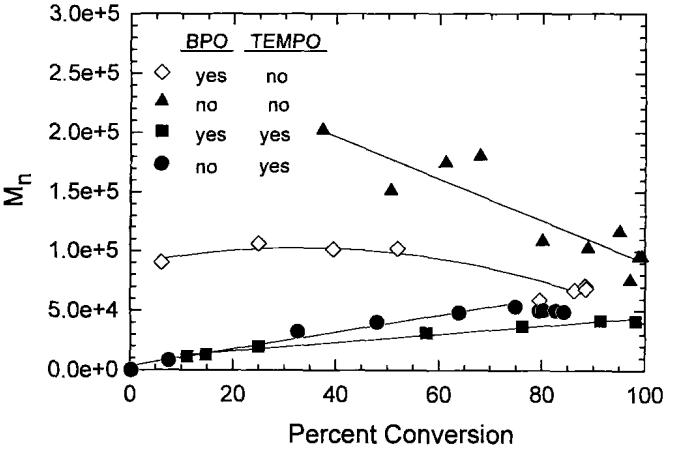


Fig. 2: The evolution of the number-average molecular weight as a function of conversion in miniemulsion polymerizations of styrene as reported in Figure 1.

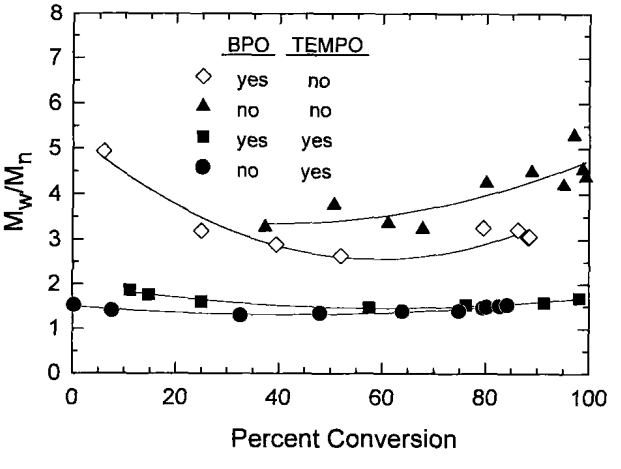


Fig. 3: The evolution of molecular weight polydispersity index as a function of conversion in miniemulsion polymerizations of styrene as reported in Figure 1.

increase with conversion, indicating the expected characteristic of a living system, and also the PDI's were relatively constant and low, in the range of 1.4 to 1.7. In contrast, in the absence of TEMPO higher molecular weight polymers were formed at the beginning of the reactions and then tended to decrease as polymerization proceeded. Moreover, the PDI's were high at about 2.5 to 5 and increased after 50% conversion, showing the typical behavior of traditional free radical polymerizations which is dramatically different from the behavior observed in the case of TEMPO mediated polymerizations where the molecular weight

evolves in a linear fashion with increasing conversion. This linear relationship is characteristic of living polymerizations and has been detailed previously by Georges et al.[11] for nitroxide-mediated bulk free radical polymerization. Nevertheless, even in the presence of TEMPO, a slight increase in the PDI was observed especially in the later stages of the polymerizations. A possible explanation for this is that at longer reaction times autothermal polymerization of styrene becomes a significant process, which leads to uncontrollable molecular weights and the increase in PDI.

The total number of polymer chains calculated from the experimentally measured molecular weights ($M_n$) show a continuous increase with conversion, which is a consequence of the slow continuous thermal generation of new radicals. The theoretical total number of chains based on the concentration of TEMPO in the recipe is $1.35 \times 10^{20}$ and is shown in Figure 4 by the dotted line. In the presence of TEMPO, the total number of polymer chains at the beginning of a reaction was always lower than the theoretical one and increased much slower in the case of pure thermal polymerization compared to that initiated with BPO. In non-TEMPO mediated polymerizations, the number of chains was much smaller due to unrestricted termination reactions by recombination of the free radicals, which resulted in higher polydispersities and a lower degree of control over the molecular weight.

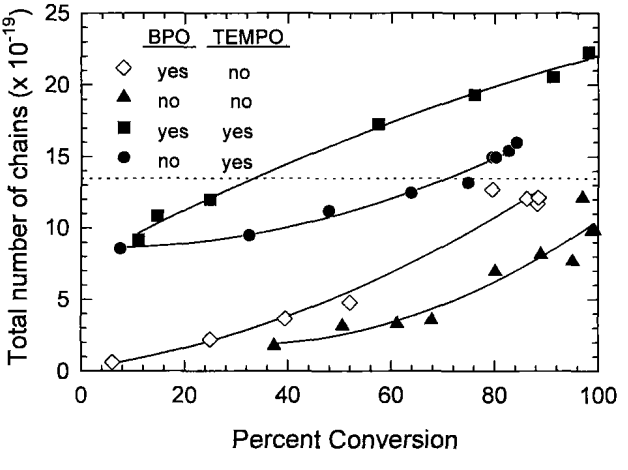


Fig. 4: Evolution of the total number of polymer chains as a function of conversion for the systems reported in Figure 1. Dotted line represents the theoretical total number of chains based on TEMPO in the recipe ($1.35 \times 10^{20}$).

The particle size data presented in Table 2 show that the presence of TEMPO resulted in larger latex particles. The evolution of the number of particles with conversion showed an increase in all experiments, which could be partly attributed to the thermal initiation. In the presence of TEMPO, the number of newly created particles was much lower due to the diminished contribution from the thermal initiation and homogeneous nucleation in the continuous phase (see Figure 5).

Table 2. Final Latex Particle Size, Particle Size Polydispersity and Number of Particles of Polystyrene Latexes Prepared under Different Reaction Conditions as Measured via CHDF.

| Conditions | $D_w$ (nm) | $D_n$ (nm) | $D_v$ (nm) | PDI ($D_w/D_n$) | $N_p$ ($dm^{-3}$) |
|---|---|---|---|---|---|
| With TEMPO & BPO | 191.3 | 121.1 | 143.7 | 1.58 | $14.2 \times 10^{16}$ |
| No BPO with TEMPO | 344.4 | 188.3 | 237.6 | 1.83 | $2.7 \times 10^{16}$ |
| No TEMPO with BPO | 84.1 | 75.3 | 78.9 | 1.12 | $77.5 \times 10^{16}$ |
| Without TEMPO & BPO | 99.6 | 90.2 | 93.8 | 1.10 | $51.8 \times 10^{16}$ |

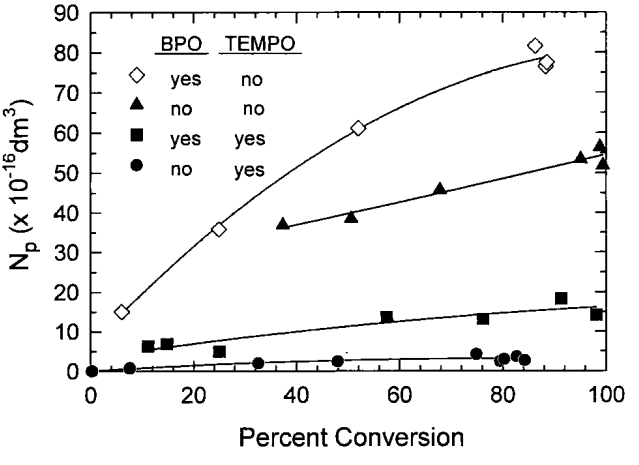


Fig. 5: Evolution of the number of particles as a function of conversion for the systems reported in Figure 1.

***Miniemulsion versus Bulk Living Free Radical Polymerization***

In order to have a direct comparison, the bulk styrene polymerization in the presence of TEMPO and under the same conditions used in the basic recipe for miniemulsion

polymerizations was performed. The rate of polymerization in bulk was found to be faster than that in miniemulsion; in bulk, 90% conversion was reached in 2.5 hrs compared to 12 hrs in miniemulsion (see Figure 6). This result should be attributed to the segregation of the monomer in discrete droplets and the diffusion of active species to the aqueous phase. As seen in Figure 7, for both processes, the experimental molecular weights obtained were close to the

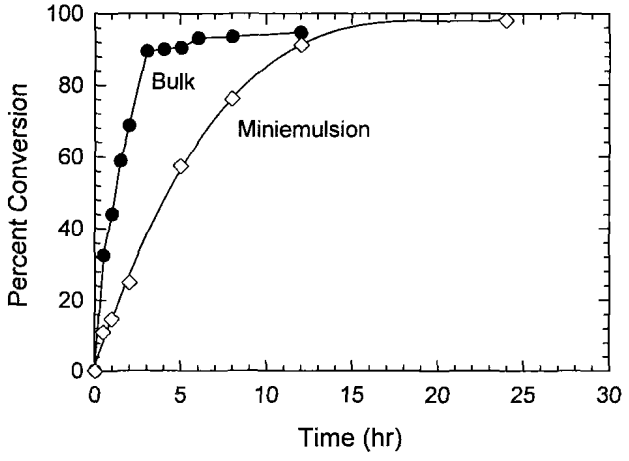


Fig. 6: Conversion-time behavior for the living free-radical polymerization of styrene in bulk and miniemulsion in the presence of TEMPO and BPO as initiator at 125°C; $[BPO]_0 = 0.0104$ M based on styrene, $[TEMPO]_0/[BPO]_0 = 1.25$.

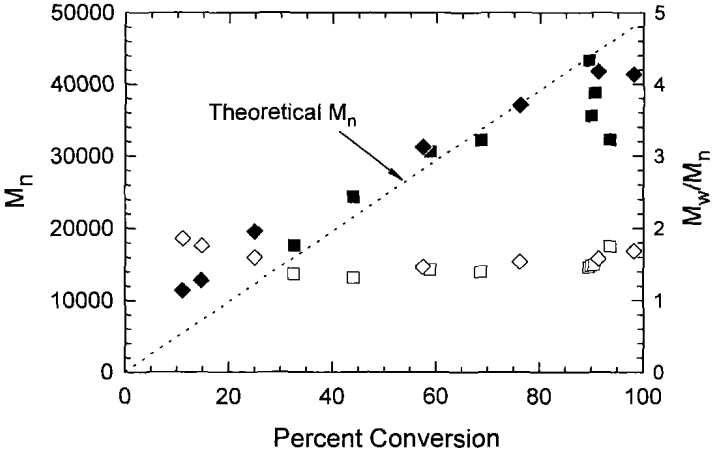


Fig. 7: Effect of TEMPO on the evolution of the number average molecular weight (closed symbols) and polydispersity (open symbols) for bulk (■) and miniemulsion (◆) polymerizations of styrene using BPO at 125°C; $[BPO]_0 = 0.0104$ M based on styrene.

theoretical one, indicating that the reaction was controlled by a living mechanism. The slightly higher PDI found for the miniemulsion (1.6 – 1.7) at low conversions may result from the increased partitioning of the styrene monomer into the aqueous phase at the high reaction temperature, which could support the growth of new polymer chains by thermal initiation. However, while the number of polymer chains in the miniemulsion increased throughout the reaction, the PDI still remained low and almost constant until high conversions. The steeper decrease in the molecular weight (higher number of polymer chains) and the increase in the PDI in the later stages of the bulk polymerization reflect a limitation of the living mechanism, where it is more difficult to have reversible dormant species in the high viscosity of the reaction mixture.

***Effect of the TEMPO concentration***

Based on the recipe in Table 1, polymerizations at three concentrations of TEMPO ([TEMPO]/[BPO] ratios of 1.25, 1.35 and 3.0) were run at a constant BPO concentration of 0.0104 M based on styrene. The conversion-time results are plotted in Figure 8. The rate of polymerization, as well as the maximum conversion, decreased with increasing TEMPO concentration, as expected. At the highest TEMPO concentration the maximum conversion was still greater than 80%. In all cases the molecular weight ($M_n$) increased linearly with conversion as shown in Figure 9. The highest level of TEMPO ([TEMPO]/[BPO]=3.0) lead to the lowest molecular weight. In agreement with the literature results observed in bulk

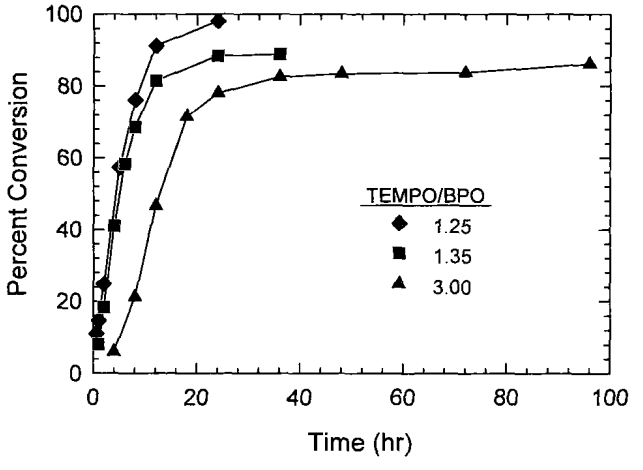


Fig. 8: Effect of the amount of TEMPO on the conversion-time behavior of miniemulsion polymerizations of styrene using BPO as initiator at 125°C; $[BPO]_o$=0.0104M based on styrene.

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