

# Miniemulsion and Conventional Emulsion Copolymerization of Styrene and Butadiene: Effect of Process on Gel Content

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**ABSTRACT:** The properties of styrene/butadiene copolymers obtained by conventional emulsion and miniemulsion polymerizations were studied. Thin layer chromatography with flame ionization detection was used to determine the gel fraction of the copolymer in the latex particles as a function of conversion. It was found that the gel formation began at a higher conversion in the miniemulsion polymerization when compared with that in the conventional process. Also, a lower glass transition tem-

perature was noted at the lowest conversion sampled (~25%), implying a higher initial butadiene monomer concentration within the nucleated miniemulsion monomer droplets when compared with particles formed conventionally. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4616–4622, 2006

**Key words:** miniemulsion copolymerization; microstructure; gel fraction; TLC/FID analysis

## INTRODUCTION

Styrene/butadiene copolymers are generally synthesized using conventional emulsion polymerization methods. The microstructure of copolymers can be affected by factors such as the polymerization system, reaction conditions, and monomer characteristics (solubility, reactivity ratios, monomer/water and comonomer ratio). The microstructure of poly(styrene-*co*-butadiene) (SBR) copolymers has been studied using IR,<sup>1,2</sup> NMR,<sup>3</sup> and other techniques.<sup>4</sup> It was found that, for the conventional emulsion polymerization of SBR, the initiator, surfactant, and chain transfer agent have little or no effect on the microstructure of the resulting emulsion polymers. The main influence was the polymerization temperature. Although the composition of the copolymers was not affected by temperatures between 30 and 70°C, below 0°C, a minimum in the styrene content in the copolymer composition was reported.<sup>5–7</sup> Such a minimum would seem inconsistent with copolymerization theory, but was ascribed to the differences in the solubilities of the two monomers in the polymer particles.

A miniemulsion polymerization differs from a conventional emulsion polymerization in terms of the

nucleation mechanism, as well as the monomer concentration in the nucleated particles.<sup>8</sup> In the miniemulsion system, nucleation occurs mainly in the small and relatively stable monomer droplets, instead of in monomer-swollen micelles or by homogeneous nucleation as in the case of conventional emulsion polymerization. In the miniemulsion, the monomer droplets are larger in size and relatively rich in monomer when compared with the newly nucleated particles in a conventional emulsion polymerization. Therefore, it is suggested that the microstructure could differ from the conventional emulsion polymerization particularly early in the polymerization. Previous work showed that the copolymer compositions varied between the conventional emulsion and miniemulsion copolymerizations of vinyl acetate and butyl acrylate,<sup>9</sup> which indicates that the monomer behavior (partitioning, reactivity ratios) within the nucleation sites can affect the microstructure of the copolymers. In this work, a further study on the microstructure using a combined thin layer chromatography with flame ionization detection method (TLC/FID), <sup>1</sup>H-NMR, and differential scanning calorimetry (DSC) is performed to obtain a better understanding of the effect of the polymerization process on the microstructure of the resulting styrene/butadiene copolymers. A model recipe based on a styrene/butadiene weight ratio of 70/30 was chosen based on the composition of industrial recipes used to prepare latexes for compounding of rubber.<sup>10</sup>

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## EXPERIMENTAL

### Materials

The chemicals used in this work include styrene (Sigma–Aldrich, St. Louis, MO), butadiene (Air Products and Chemicals, Allentown, PA), hexadecane (HD; Fisher Scientific, Springfield, NJ), sodium lauryl sulfate (SLS, Fisher Scientific), and potassium persulfate (KPS, Sigma–Aldrich). The styrene monomer was treated by passing it through an inhibitor-removal column (Sigma–Aldrich) before use. The butadiene monomer was first cleaned by passing it through two successive columns to remove moisture (Drierite, Fisher Scientific) and inhibitor (Ascarite II, Thomas Scientific, Swedesboro, NJ). It was condensed using a bath comprising a mixture of liquid nitrogen and isopropanol and then charged into a 300-mL stainless steel cylinder. All other chemicals were used as received. Deionized water was used in all polymerizations. A commercial sample of poly(styrene-*co*-butadiene) (SBR; Polysar, Sarnia, Ontario, Canada) was obtained for comparison by NMR analysis.

### Miniemulsion preparation

Styrene miniemulsions with HD as costabilizer were prepared in the following way. The surfactant (SLS) was dissolved in the deionized water, and the monomer was mixed with the HD. The latter was then added to the aqueous solution, and the resulting mixture was homogenized by first sonifying for 60 s at 50% duty, power seven (Branson sonifier Model 450, Ultrasonics Corp., Danbury, CT) to create a crude emulsion that was subsequently passed through the Microfluidizer (Model 110T, Microfluidics Corp.) 10 times with a pump inlet pressure set point of 80 psig. After homogenization all of the styrene miniemulsions appeared homogeneous and opaque. The styrene/butadiene miniemulsions were then created by adding the butadiene monomer to the styrene miniemulsions with mixing (400 rpm, pitched blade impeller with baffle) and under pressure, allowing 20 min for the butadiene to be absorbed by the styrene miniemulsion droplets. This was accomplished in the 1 L MP10 reactor of the RC1 reaction calorimeter (Mettler-Toledo, Columbia, MD) as described here.

### Polymerization methods

The basic recipes used in this study are presented in Table I. Each polymerization was carried out at 70°C using the RC1. For a conventional emulsion copolymerization, the aqueous surfactant solution was first charged into the MP10 reactor, followed by the styrene monomer. The reactor was purged with nitrogen for about 10 min, and then, the pressure cylinder containing the butadiene monomer was connected to the reac-

tor via quick disconnect fittings. Before charging the butadiene monomer, leak checks were performed using a soap solution. Then, the temperature of the reactor was decreased to about 15°C, and the butadiene monomer was charged into the reactor.

After the addition of butadiene monomer, the system was slowly heated to the reaction temperature and then held there for about 40 min while the calorimeter was calibrated. An aqueous initiator solution (KPS) was then injected to begin the polymerization.

The procedure for the miniemulsion polymerizations was similar to the preceding except for the preparative modifications as described earlier.

### Characterization

Samples were periodically withdrawn from the reactor for conversion, composition, gel fraction, and  $T_g$  determination. Owing to the elevated pressure in the reactor, sampling was performed using a pressure-protected syringe. After being withdrawn from the reactor, the samples were short-stopped immediately with a 1% aqueous hydroquinone solution and placed in an ice bath.

The characteristics of the SBR latexes were determined using several different techniques. The unreacted styrene monomer was measured via gas chromatography (GC, HP Model 5890A, Avondale, PA) using dioxane as the internal standard. The butadiene composition in the copolymer was calculated by subtracting the reacted styrene fraction from the overall conversion, which was measured gravimetrically. The glass transition temperature ( $T_g$ ) was measured by DSC (TA Instruments, New Castle, DE); the heating rate was 10°C/min. The gel formed in the copolymer particles was measured by a combined thin layer chromatography (TLC) and flame ionization detection (FID) (Iatroscan TH-10, Iatron Laboratories, Tokyo, Japan). The compositions of styrene/butadiene copolymers were analyzed using high-resolution  $^1\text{H-NMR}$  (AM-500, Bruker Instruments, Billerica, MA).

TABLE I  
Basic Recipes for the Emulsion and Miniemulsion Copolymerization of 70 : 30 Weight Ratio Styrene and Butadiene

Ingredient	Amount	Weight (g)
Deionized water	80 parts	480
Sodium lauryl sulfate	10 mM <sup>a</sup>	1.3834
Hexadecane	0 or 30 mM <sup>b</sup>	0 or 3.260
Potassium persulfate	5 mM <sup>a</sup>	0.8630
Sodium bicarbonate	5 mM <sup>a</sup>	0.2685
Styrene/butadiene (70/30)	20 parts	120.0

<sup>a</sup> Based on the aqueous phase.

<sup>b</sup> 30 mM based on aqueous phase (2.7 wt % based on monomer) for miniemulsion polymerizations.

## RESULTS AND DISCUSSION

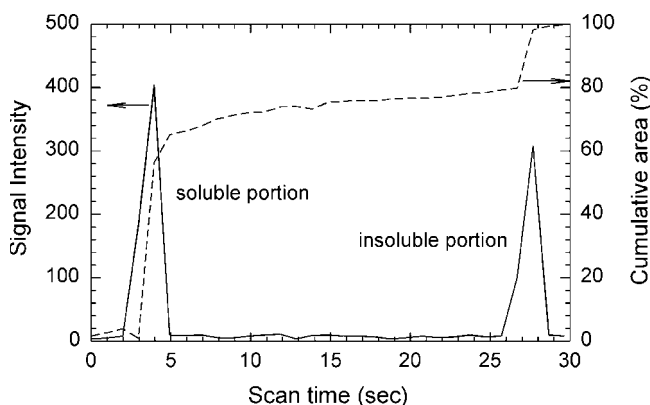
### Determination of gel formation

In the copolymerization of styrene and butadiene, a gel or crosslinked structure will normally form in the latter stages of the reaction in the absence of any chain transfer agent. This is a consequence of the two carbon-carbon double bonds in butadiene; one of them can react to form polymer chains, while the other can continue to react to form branches or crosslinks (gel formation) if the ratio of the crosslinking rate coefficient to the propagation rate coefficient increases, or if the ratio of monomer-to-polymer in the particles decreases below a critical point.

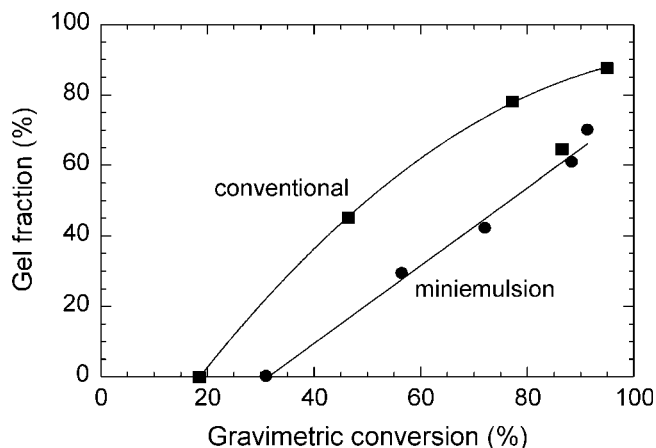
Generally, the so-called gel or microgel is a material having a structure with highly branched or crosslinked polymer chains, which does not dissolve in a solvent as similar linear polymer chains do.<sup>11,12</sup> The size of the microgel varies with the polymerization system and the reaction conditions, and also changes with the final form of the polymer. In a latex, the microgel exists within the individual particles, and its size must be equal to or smaller than the particle size. If a polymer film is used in determining the gel content, the microgels could coalesce themselves, and a macrogel would be formed because of the molecular interdiffusion of polymer chains during film formation. This temporary macrogel structure can be disrupted by using some methods like ultrasonic scission.<sup>13</sup>

Obviously, it is important to find an effective means of determining the gel fraction in latexes as it develops during the polymerization. Currently, there are several techniques available for the determination of the microgel fraction.<sup>12-21</sup> In our work, a combined TLC/FID method<sup>22</sup> is used to study the characteristics of the microgels developed during the polymerization.

Compared with the other methods, the TLC/FID method has some advantages. First, the sample can be prepared directly from the latex, with no need to cast a



**Figure 1** Typical TLC/FID curves of the signal intensity and cumulative value for a latex polymer sample with both soluble and insoluble components.



**Figure 2** Gel fraction as a function of conversion for the conventional emulsion and miniemulsion copolymerizations of 70:30 weight ratio styrene and butadiene;  $T_r = 70^\circ\text{C}$ ,  $[\text{KPS}] = 5 \text{ mM}$ ,  $\text{SLS} = 10 \text{ mM}$  or  $\text{SLS}/\text{HD} = 10/30$  (mM/mM).

film. Second, the time required to measure the gel fraction is shorter than some standard methods; and third, a relatively small amount of sample is needed.

### TLC/FID separation technique

The Iatroscan TH-10 TLC/FID analyzer was used for quantitative chromatographic separation of the styrene/butadiene copolymers. The separations were carried out on the TLC chromarods in the normal manner by solvent development.

The following procedure was applied. First, the latex samples were directly mixed and dispersed in a suitable solvent, in this case tetrahydrofuran (THF). With the aid of a microsyringe, a small portion of this polymer dispersion (or solution if there is no gel) containing about  $4 \mu\text{g}$  of polymer was then placed on a TLC rod, 1 cm from the end, and then placed in a closed tank containing the developing solvent (toluene). The solvent front was allowed to travel to about 9 cm before the rods were removed and placed in a warm oven ( $50^\circ\text{C}$ ) for 1 min to evaporate the toluene, after which the developing procedure was repeated three more times. After the final cycle, the rods were kept in the oven for 10 min before analysis was accomplished using the automated Iatroscan FID unit. Output from the unit includes the sample peaks and the cumulative curve.

If a sample contains both soluble and insoluble components, a TLC/FID curve is obtained as shown in the example of Figure 1. The linear polymer chains are dissolved in the solvent and developed to the solvent front level (first peak), while the crosslinked or highly branched, insoluble portion is not dissolved and remains at the original starting point where the sample is initially spotted on the rod (second peak). In this way, the soluble and insoluble portions can be sepa-

**TABLE II**  
**Glass Transition Temperatures ( $T_g$ ) for Conventional Emulsion and Miniemulsion Styrene/Butadiene Copolymers (70 : 30 weight ratio) as a Function of Conversion**

Conventional emulsion copolymerization		Miniemulsion copolymerization	
Fractional conversion	$T_g$ (°C)	Fractional conversion	$T_g$ (°C)
0.277	-1.0	0.252	-13.0
0.542	0.4	0.582	0.1
0.761	1.8	0.688	1.7
0.862	2.0	0.811	1.7
0.911	2.2	0.912	3.1
0.970	2.1	0.979	2.0

rated. The relative amounts of the soluble and insoluble fractions can be estimated from the cumulative curve. In this study, a calibration curve using the method described by Kauffman<sup>23</sup> was used to analyze the gel fraction in the lattices.

### Gel fraction analysis

To study the development of gel fraction during the conventional emulsion and miniemulsion polymerizations, latex samples were taken as a function of time and conversion throughout the course of the polymerizations. The relationship between the gel content and fractional conversion for the two polymerization methods is shown in Figure 2. First, it is seen that there was no measurable gel at early conversions and the formation of gel in the copolymer prepared by conventional emulsion polymerization occurred earlier (~20% conversion) apparently than in the miniemulsion polymer (~30% conversion). Second, the increase in the gel fraction for the two reactions are roughly parallel each other with the miniemulsion requiring ~15–25% higher conversions to achieve the same gel fractions as in the conventional emulsion polymers. These results indicate that the miniemulsion copolymerization does indeed delay gel formation to a higher conversion. The original hypothesis is that this could be attributed to the higher monomer/polymer ratio within the polymer particles

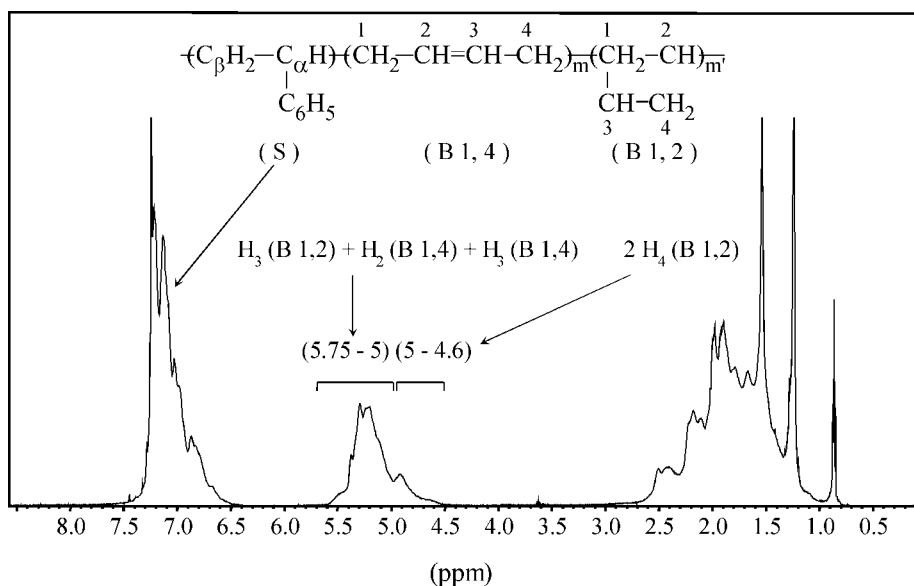
in the early stages of the polymerization brought about by the presence of the HD costabilizer. It should be noted that this effect is enhanced at low conversions, since the particles nucleated by the conventional process are small (on the order of 10 nm) and have a relatively low monomer/polymer ratio initially, reportedly as low as 1/1, increasing and then leveling off as the particle size increases. There is another possible contribution based on differences in molecular weight development. Although no measurements were made of molecular weight ostensibly because of the gel formation, there could be a contribution. On the basis of our experience with similar comparisons (miniemulsion versus conventional), we can say that the molecular weight could be higher in the conventional system for the following reasons. The particle diameter in the conventional latex ( $D_v = 89$  nm) is about half the diameter of the miniemulsion latex ( $D_v = 171$  nm). This has two effects. First, the polymerization is faster for the conventional reaction, and thus, fewer radicals are produced in the time scale of the reaction. And second, the smaller size or greater number of particles also means that fewer radicals enter a given particle. Both of these lead to *higher* molecular weights, which could indeed contribute to an earlier gel formation. Without further work, however, the relative contributions of these two mechanisms to the gel formation are not known. Nonetheless, these results verify the initial supposition that polymerization in miniemulsion droplets could delay the formation of gel in the styrene/butadiene copolymers prepared in the form of latex particles.

### Glass transition temperature

Differences in the copolymer composition could also result from the differing thermodynamics of the two polymerization processes, which could in turn cause a variation in other properties such as the glass transition temperature ( $T_g$ ).  $T_g$ 's were measured using DSC. The results for the conventional emulsion and miniemulsion copolymerizations of styrene and butadiene are presented in Table II as a function of conversion. It is seen that there is a substantial difference in the  $T_g$ 's only

**TABLE III**  
**Mole Fraction of Butadiene in Copolymer for Conventional Emulsion and Miniemulsion Copolymerizations of 70 : 30 Weight Ratio (54.7/45.3 Mole Ratio) Styrene and Butadiene as a Function of Conversion (X)**

Conventional			Miniemulsion		
X (%)	Butadiene mole fraction	1,2-Butadiene (%)	X (%)	Butadiene mole fraction	1,2-Butadiene (%)
27.7	0.561	18.8	25.2	0.589	20
54.2	0.532	17.9	36	0.572	20.1
76.1	0.502	20	46.2	0.547	19.5
91.1	0.476	19.5	58.2	0.532	19.4
97	0.463	19.8	68.9	0.51	19.1
–	–	–	81.14	0.506	18.9

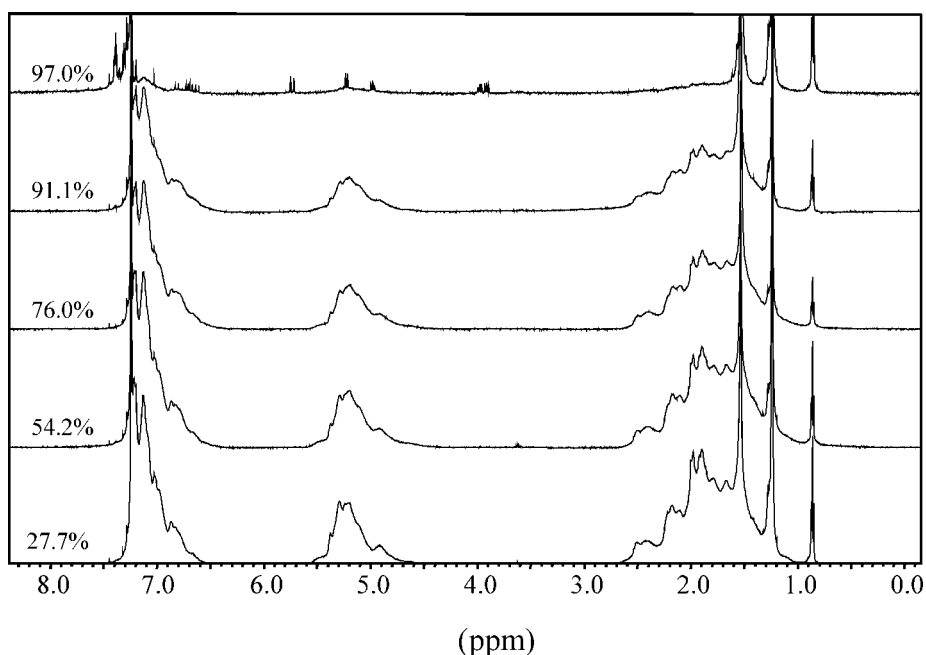


**Figure 3**  $^1\text{H-NMR}$  spectrum of commercial styrene/butadiene copolymer showing relevant peak assignments.

at the lowest conversions ( $\sim 25\%$ ). However, by the next measurement points ( $\sim 55\%$ ), the  $T_g$ 's have basically converged and are essentially the same thereafter. More data at lower conversions are needed for a clearer look at this phenomenon. Similar results were reported previously. For example, Kitzmiller<sup>24</sup> found that the miniemulsion copolymer prepared from vinyl acetate (VAc) and vinyl 2-ethylhexanoate (V2EH) had a lower  $T_g$  than that of the copolymer prepared by conventional emulsion copolymerization. Delgado et al.<sup>9</sup> also found that in the miniemulsion copolymerization of VAc and *n*-

butyl acrylate (BuA), the copolymer in the early stages of a reaction contained less VAc monomeric units than those in the conventional emulsion copolymerization. They suggested that the relative monomer concentrations in the polymerization loci differed between the conventional emulsion and miniemulsion copolymerization. They further showed this by carrying out thermodynamic simulations via a mathematical model.<sup>25</sup>

The reason for these differences is considered to lie in the differing thermodynamics brought about by the presence of the HD in the droplets and particles in the



**Figure 4**  $^1\text{H-NMR}$  spectra of copolymers prepared via conventional emulsion polymerization of 70 : 30 weight ratio styrene/butadiene as a function of conversion.

mini-emulsion polymerization. This affects the distribution of the comonomers. For the copolymer to be richer in butadiene units in the mini-emulsion particles, a shift in the concentration of the butadiene to values higher (relative to styrene) than in the corresponding particles in the conventional emulsion polymerization must occur. A copolymer richer in butadiene in the early stages of the reaction results in a lower  $T_g$  material ( $T_g$  polybutadiene =  $-86^\circ\text{C}$  by emulsion polymerization at  $50^\circ\text{C}^{12}$ ).

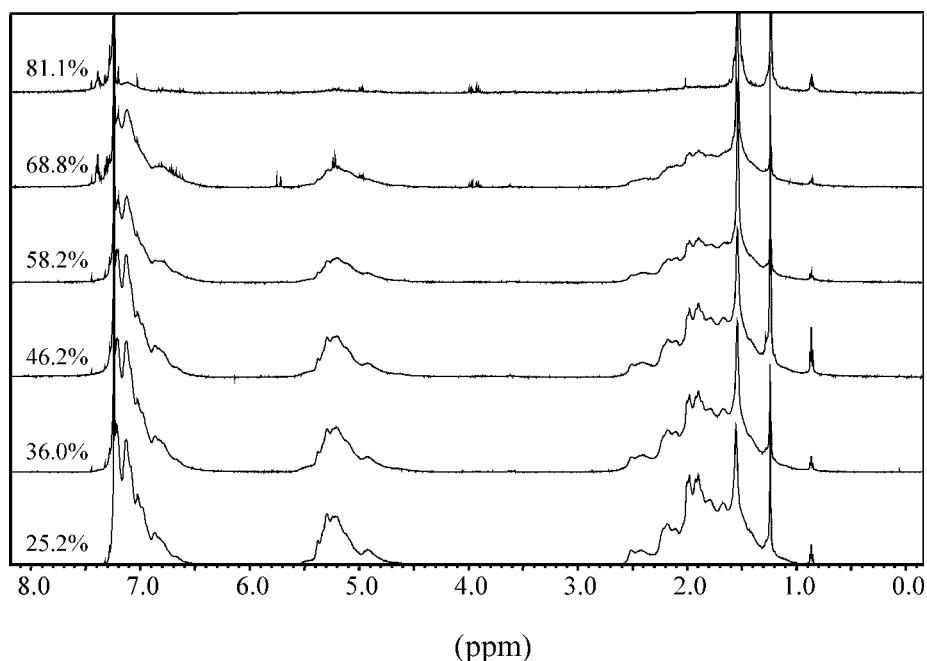
### Copolymer composition

For the two copolymerization systems, the microstructures of the resulting copolymers should differ, since different relative monomer concentrations within the nucleated particles would result in different copolymer compositions. Since the reactivity ratio of butadiene ( $r_{\text{Butadiene}} = 1.39$ ) is larger than that of styrene ( $r_{\text{Styrene}} = 0.78$ ), it would be expected that more butadiene units would be incorporated into the copolymer chains early in the reactions. On the basis of the preceding  $T_g$  results, the initial copolymer compositions are expected to differ between the mini-emulsion and conventional polymers. Combining gravimetric and GC measurements, the copolymer composition was determined for samples taken during the experiments. The results are presented in Table III. A small but statistically significant (error estimated to be less than  $\pm 0.01$ ) difference in the butadiene content in the copolymers can be noted at the lowest conversion ( $\sim 25\%$ ) with the mini-emulsion having the higher butadiene content.

A more detailed analysis of the microstructures of the copolymers produced via the two polymerization methods was done using  $^1\text{H-NMR}$  spectroscopy. The spectra of the samples were compared with the commercial sample of SBR (Polysar<sup>26</sup>). A spectrum showing the peak assignments is presented in Figure 3. As indicated in the figure, the 6.7–7.3 ppm range corresponds only to styrene, while the 4.6–5 ppm range is only related to the 1,2-butadiene structure. In addition, the 5–5.75 ppm range represents the combined effect of the 1,2 and 1,4 structures of the butadiene. The area ratios as obtained by integration of the peaks over these ranges were used to obtain the relative amount of 1,2-butadiene in the polymers.

The latex samples taken at different times during the conventional emulsion and mini-emulsion copolymerizations were dried in a vacuum oven and added to deuterated chloroform ( $\text{CDCl}_3$ ) dissolving the linear polymer and swelling the microgels. The  $^1\text{H-NMR}$  spectra were recorded as shown in Figures 4 and 5. The results of the analyses are also presented in Table III. It was found that the relative amount of the 1,2-butadiene structural units in the copolymer was almost constant with conversion; these values only varied from 17.9% to 20.1% over the whole conversion range. These results are close to those found in the literature with 17.3% 1,2-butadiene for polybutadiene and 19.8% 1,2-butadiene for SBR prepared at a  $70^\circ\text{C}$ .<sup>3</sup>

It is seen from the above results that the mini-emulsion copolymer had a slightly higher initial butadiene content in the copolymer chains compared with the conventional emulsion system, which, as stated previ-



**Figure 5**  $^1\text{H-NMR}$  spectra of copolymers prepared via miniemulsion polymerization of 70 : 30 weight ratio styrene/butadiene as a function of conversion.

ously, is related to the higher relative butadiene concentration in the reaction sites. All of these results indicate that the differing polymerization mechanisms of the conventional emulsion and miniemulsion copolymerizations affect the composition of the resulting copolymers, leading to differences in the mechanical properties of the latex polymers.

### SUMMARY

Differences between the miniemulsion and conventional emulsion copolymerizations of styrene and butadiene in terms of the nucleation mechanism, and absolute and relative monomer concentrations within the nucleated particles leads to some differences in copolymer composition and the resulting physical and mechanical properties. It was found that the miniemulsion copolymer has a lower gel fraction compared with the conventional emulsion at the same conversion, which means that gel formation can be delayed by applying the miniemulsion technique. This is attributed to the different monomer concentrations in the growing particles early in the reactions. In addition, the relative concentration of the butadiene to styrene is apparently higher in the resulting miniemulsion particles as reflected in the early  $T_g$ 's and the measured copolymer composition. No distinction in the polymer microstructure could be made by NMR analysis with a 1,2-butadiene content of ~20% being formed in the copolymer.

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