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# Microemulsion polymerization of 1,3-butadiene

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**Abstract** One-phase microemulsion regions at 25 and 60 °C and the polymerization at 60 °C in o/w microemulsion formed by 1,3-butadiene, water, and a mixture of the surfactants, dodecyltrimethylammonium bromide, and didodecyldimethylamonium bromide (3/1 w/w), are reported. The polybutadienes obtained here have similar characteristics to those of their homologous obtained by emulsion polymerization, with the only difference that the average particle size of the former (25–30 nm) was smaller by an order of magnitude. The obtained polymer had high average molecular weights, but the gel content at high conversion is lower than the value for a conventional emulsion polymerization. The DSC measurements showed that the polymer has a single glass transition temperature at −72.5 ± 1.5 °C.

**Keywords** Microemulsion polymerization · 1,3 Butadiene · Nanoparticles

## Introduction

Similar to emulsion polymerization, microemulsion polymerization is a process that yields high-molecular weight polymer latexes with fast reaction rates [1–4]. Nevertheless, microemulsion polymerization allows the synthesis of particles in the

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nanometer range in a routinely fashion, in contrast to emulsion polymerization [2]. In addition, microemulsion polymerization exhibits different kinetics than that of emulsion process; moreover, the microemulsion-made polymers often have different characteristics than those made by emulsion polymerization [5–12]. Up to date, all reports on microemulsion homo- and copolymerization have been related to liquid monomers at normal atmospheric conditions [4, 13, 14].

The majority of the reports of industrial interest on rubbers are related to polybutadiene and its copolymers, such as butadiene rubber (BRs), styrene/butadiene (SBRs), acrylonitrile/butadiene/styrene (ABS), methyl methacrylate/butadiene/styrene (MBS), and so on [15]. Most of these polymers have been synthesized by the so-called living radical (anionic or cationic) polymerization [4, 15, 16] and/or in conventional free radical emulsion polymerization [15, 17–20]. For materials application, polymer latex with high *trans* fractions and low crosslinking degrees are desired [18]. However, to our knowledge, there are no reports on microemulsion polymerization of butadiene. For this reason, we have focused this work on the microemulsion polymerization of 1,3-butadiene and compared the results with the reports of conventional emulsion polymerization. First, the one-phase microemulsion regions at 25 and 60 °C were located and then, the reaction was performed at 60 °C. Particles smaller than 30 nm, which are an order of magnitude smaller than those reported by emulsion polymerization, with molecular weights around $10^7$ Dalton, and moderate gel content were obtained. Final gel content is lower than those typically reported in emulsion polymerization of this monomer [18].

## Experimental section

### Materials

1, 3-Butadiene with a purity >99.5% from Aldrich was used. This monomer is inhibited with *tert*-butylcatechol, which was removed passing it through a packed column containing an alumina mixture ($Al_2O_3$ mesh 100) and molecular mesh 13×, both products with purities of 99.5% from Aldrich. Didodecyldimethylammonium bromide (DDAB) (98% pure from Eastman Kodak) and dodecyltrimethylammonium bromide (DTAB) (99%+ from Tokyo Kasei) were used without further purification. Potassium persulfate (KPS), 99.9% pure, was from Aldrich. The inhibitor of the reaction was either hydroquinone (HQ) or hydrated dimethyldithiocarbamic acid sodium salt (ADDSH), both with a purity >98% from Aldrich. *N*-phenyl-2-naphtylamine (NF2N), with a purity >97% from Aldrich, was used as antioxidant. Double distilled water with a conductivity <6 μS/cm from Selectrom México was used. Reactive-grade toluene and methanol were both from Merck. HLPC-tetrahydrofurane (THF) was from Aldrich.

### Phase diagrams

To obtain the phase diagrams, different glass cells equipped with high vacuum accessories from Ace-Glass, were constructed. These cells allow safe operation at high pressures and to support thermal shocks. The 7-mL cells were connected to a high vacuum line and operated with a turbo-molecular pump (Balzer), which can achieve pressures as low as $10^{-7}$ mBar.

For determining the one-phase microemulsion regions, mixtures of DTAB/DDAB (3/1 w/w) in water with various compositions were made by weighing the components; then these solutions were transferred to the glass cells and shaken until homogenization. Then each cell is connected to the high-vacuum line designed to allow the addition of inhibited 1, 3-butadiene. Once the desired weight of monomer is added, the cell under vacuum is closed (or sealed), separated from the system and placed inside a thermo-stabilized bath at 25 or 60 °C during 24 h to reach equilibrium. Samples appearing homogeneous transparent or bluish to the naked eye, and that did not exhibit static or streaming birefringence, when observed though cross polarizers, were considered microemulsions.

## Microemulsion polymerization

The one-phase microemulsion composition chosen for polymerization was 9 wt% 1,3-butadiene, 15 wt% DTAB-DDAB-mixture (3/1 w/w), and 76 wt% water. Polymerization was carried out at 60 °C using KPS ($w_{\mathrm{KPS}}/w_{\mathrm{monomer}} = 0.01$) in a 100-mL glass reactor with capability for high vacuum from Ace-Glass. The procedure was the following: first, the surfactants/initiator/water solution was loaded in the reactor, which was then connected to the vacuum line to remove the dissolved oxygen by five consecutive freeze–vacuum ($10^{-5}$ bar)–thaw cycles. Once the oxygen was removed, inhibitor-free 1,3-butadiene was added to the frozen aqueous solution to produce the composition specified above. Next, the reactor was introduced in a thermo-stated water bath at 60 °C and the polymerization reactions started. Samples were withdrawn at given times and put into frozen glass vials. Two different procedures were used to stop the polymerization reaction: (a) by adding 1.25 g of a 0.05 M hydroquinone solution per gram of latex and (b) by adding 1.25 g of a 0.05 M solution of ADDSH and then 0.5 g of 0.05 M solution of NF2N per 5 g of latex. The sample was divided in two portions: one for determination of conversion by gravimetric analysis, and the other for latex and polymer characterization.

## Characterization

For conversion determination, excess methanol was added to each withdrawn sample to precipitate the polymer, which was recovered by filtration and washed with abundant water to remove the excess surfactant. Then, the samples were dialyzed at 40 °C for 3 days to remove the remaining adsorbed surfactant. Finally, the wet polymer was set into Petri boxes and dried in a vacuum-oven at 40 °C until constant weight.

For characterization, except for particle size, the soluble polymer-fraction was used. The gel content, which is a relative measure of network formation, was measured by extracting the soluble polymer-fraction with toluene, drying the insoluble polymer and weighing it.

Particle size was measured with a Malvern 4700 quasielastic light scattering (QLS) apparatus equipped with an Argon laser ($\lambda = 488$ nm). Measurements were performed at 25 °C and at an angle of 90°. Intensity correlation data were analyzed by the method of cumulants to provide the average decay rate, $<\Gamma^2>$ ($=q^2D$), where $q$ [$=(4\pi n/\lambda)\sin(\theta/2)$] is the scattering vector, $n$ the index of refraction, and $D$ the diffusion coefficient. The measured diffusion coefficients were represented in terms of apparent diameters ($D_z$) by means of Stokes law assuming that the solvent has the viscosity of water. Lattices were diluted up to 100 times (which is enough to eliminate particle–particle interaction) to determine the actual isolated particle size, and filtered through 0.2 μm Millipore filters before QLS measurements to remove dust particles.

Molecular weights of the soluble fraction were determined with a Perkin-Elmer LC 30 RI gel permeation chromatograph (GPC) equipped with a Dawn S multi-angle light scattering detector using THF as the mobile phase.

The 1,4-*cis*, 1,4-*trans*, and 1,2-(or vinyl) stereo-isomers contents of the soluble fraction, and its chemical composition were determined in a FTIR-SZDA spectrophotometer from Nicolet, using the method developed by Binder [21].

The glass transition temperature ($T_g$) was measured with a DSC-4 scanning differential calorimeter (DSC) from Perkin-Elmer; the measurements were done in the temperature interval from −200 to 150 °C, with a 10 °C/min heating rate.

## Results and discussion

Figure 1 depicts the pseudo-ternary phase diagrams at 25 and 60 °C, where the one-phase microemulsion regions appear at the water-rich side. The o/w microemulsions located in this region are transparent, slightly bluish and fluid, except at surfactant concentrations greater than 25 wt%, where samples are highly viscous. From this figure, it is clear that the one-phase microemulsion region increases as the temperature is increased from 25 to 60 °C.

Figure 2 shows a typical conversion-versus-time curve for the microemulsion polymerization carried out at 60 °C in the glass reactor. High conversions (94 ± 4.0%) were obtained in a relatively short time (120 min). The reaction is faster than the conventional emulsion polymerization of the same monomer [13, 14, 17]. Weerts [17] reported that in the emulsion polymerizations of 1,3-butadiene at 62 °C, the time to reach 60% conversion depended on the surfactant employed: 5.85 h when Dresinate 214 was used and 8.2 h when SDS was used (to reach 100% conversion, 72 h were required using Dresinate 214).

The gel or crosslinked polymer content, considered a quality control parameter in the manufacture of synthetic rubber-type (BR) polymers [17], is presented in Table 1 at different conversions for samples in which HQ was used as a reaction inhibitor, and in those where polymerization was short-stopped and protected with ADDSH immediately and then NF2N was added as an antioxidant to avoid further attack by free radicals and to prevent over-branching and gel formation. The reported gel problem in conventional emulsion polymerization is related to the reaction temperature as well as the high-molecular weights and the long reaction

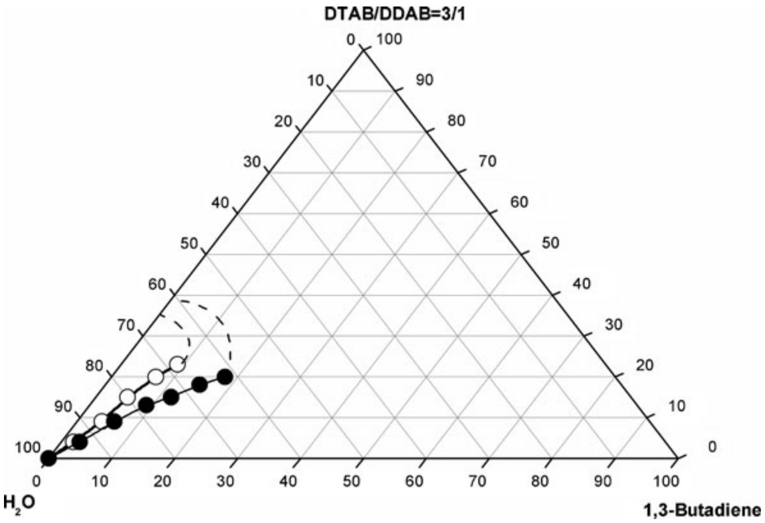

**Fig. 1** Phase diagrams at 25 (*open circles*) and 60 °C (*closed circles*)

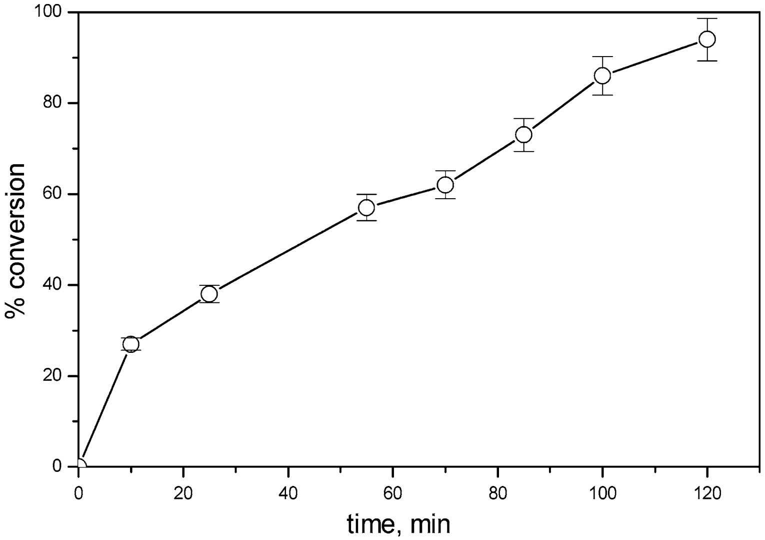

**Fig. 2** Conversion as a function of time for the microemulsion polymerization of 1,3-butadiene. *Error bars* indicate the reproducibility obtained in three different runs

times [15]. The values of gel fraction of the polymer obtained in this work (72 wt% at ~95% conversion when HQ is used as inhibitor and 61.2 wt% at ~92% conversion when using ADSH/NF2N) are smaller than that typically obtained in conventional emulsion polymerization (>90% gel content at high conversions) [18]. When HQ is used as an inhibitor the gel content increases as conversion increases, whereas when the combination of ADDSH/NF2N is used, gel content remains

**Table 1** Gel fraction as a function of conversion

| % Conversion | % Gel fraction | |
|---|---|---|
| | HQ | ADSH/NF2N |
| 30.0 | – | 51.8 |
| 33.9 | – | 62.0 |
| 40.9 | – | 60.9 |
| 47.1 | 60.4 | – |
| 52.5 | – | 59.6 |
| 53.3 | 65.4 | – |
| 58.0 | 66.0 | – |
| 67.7 | – | 59.6 |
| 69.2 | 66.5 | – |
| 84.4 | 67.4 | – |
| 91.8 | – | 61.2 |
| 94.0 | 72.2 | – |

constant with increasing conversion. This result indicates that the ADDSH/NF2N pair stopped the reaction and hence the amount of gel that is present in this case is only due to the crosslinking taking place during reaction and not to post-reaction polymerization.

Particle size of the latex remains approximately constant with conversion and the average size is below 30 nm (Fig. 3). This very small particle size, which is common in microemulsion polymerization [2], would be almost impossible to obtain by conventional emulsion polymerization of this monomer. The composition

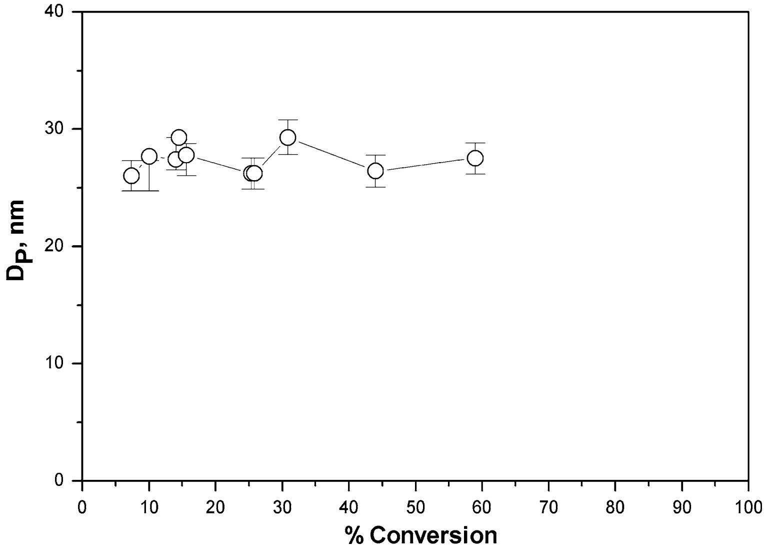

**Fig. 3** Evolution of particle size as a function of conversion

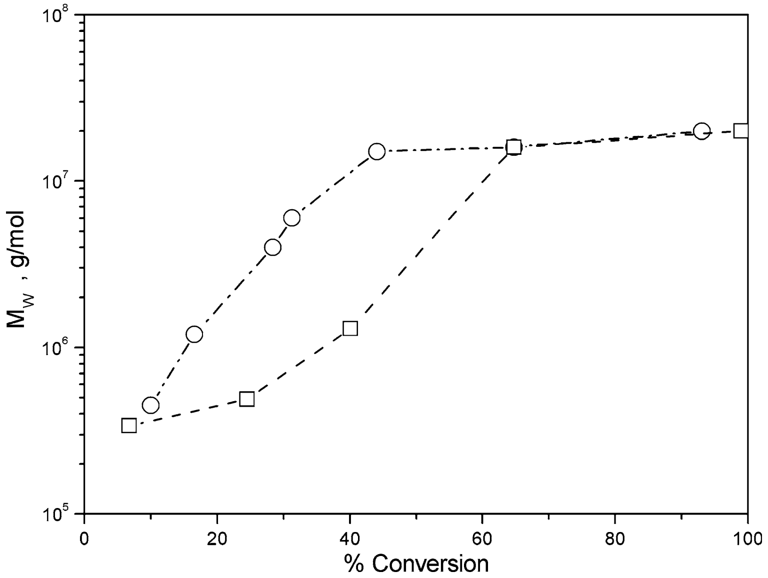

**Fig. 4** Evolution of weight-average molecular weight as a function of conversion when (*open circle*) HQ or (*open square*) ADDSH/NF2N are used to stop the polymerization reaction

of the microemulsion-made BR remains constant, within experimental error, at about 27 ± 2.0% for 1,4-*cis*, 55 ± 2.0% for 1,4-*trans* and 18 ± 1.0% for vinyl (1,2-) isomers, at all conversions analyzed. In comparison, the typical composition of an emulsion-made BR at similar temperatures ($T = 62$ °C) is 23% 1,4-*cis*, 58% 1,4-*trans*, and 19% vinyl (1,2-) [17, 19]. The glass transition temperature ($T_g$) for the microemulsion-made BR is −72.0 ± 1.0 °C. For an emulsion-made BR with vinyl content about 15–20%, the $T_g$ is around −80 °C [19].

Figure 4 depicts the weight-average molecular weights ($M_w$) of the polybutadiene soluble fraction versus conversion. As conversion increases, the probability that the second double bond reacts increases, giving as a result a higher molecular weight of the soluble fraction and more gel content. $M_w$ increases with conversion to high-molecular weights of the order of $10^7$ g/mol; at high conversions, this trend is observed even when a combination of short-stopper (ADDSH) and antioxidant (NF2N) was added to the microemulsion-made BR. However, better control of the molecular weights (less crosslinking) is achieved at low and intermediate conversions when the antioxidant plus NF2N were used together indicating that the pair is more effective to stop reactions than HQ.

## Conclusions

This study shows the feasibility of producing synthetic BR-rubber by microemulsion polymerization. The physicochemical characterization of the latex and the polymer yield by this process are similar to those obtained by conventional emulsion polymerization, although time to achieve high conversions is much shorter in the microemulsion process. The particle size of the polybutadiene particles synthesized by microemulsion polymerization is below 30 nm, which is an order of magnitude smaller than those obtained by the conventional emulsion polymerization process. However, microemulsion polymerization produced high-molecular weight ($>10^7$ g/mol) polybutadiene with moderate gel content at the end of the reaction, reaching values around 72% at high conversions for polymerizations that were deactivated with HQ. When using a combination of antioxidant-stopper, the gel content is constant above 30% at a conversion of about 61%.

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