Research Article

Polyisoprene Nanoparticles Prepared by Polymerization in Microemulsion

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Batch polymerization of isoprene was carried out at 25°C in a normal microemulsion stabilized with sodium dodecyl sulfate and initiated with the redox couple *tert*-butyl hydroperoxide/tetraethylene-pentamine. Characterization by transmission electronic microscopy showed that polyisoprene nanoparticles with number-average diameter close to 20 nm were obtained. The low molecular weights obtained, as determined by gel permeation chromatography, were probably due to chain scission as inferred from the oxidative ambient at which polymerization was carried out. Microstructure calculated from infrared spectroscopy data indicates that the obtained polyisoprene contains around 80% total 1,4 units, which is in accordance with its glass transition temperature (−60.8°C) determined by differential scanning calorimetry.

1. Introduction

An improvement in the toughness of glassy polymers can be achieved by dispersion of rubber particles into the polymer matrix [1–3]. According to the literature, rubber particles with diameters between 1 and 2 μm give the best results in the preparation of high-impact polystyrene (HIPS) [4, 5]. Nevertheless, it has been reported that smaller rubber particles combined with large ones (diameter > 1 μm) lead to a greater increase in the HIPS toughness [6]. Polyisoprene (PI) is a polymer used for preparing micrometric rubber particles, which in turn are used for successfully increasing the glassy polymers toughness [7, 8].

On this basis, it has been thought that it would be interesting to evaluate the effect of PI nanoparticles for improving the toughness of some glassy polymers. However, the reports on synthesis of PI nanoparticles are very scarce. Only two reports were found describing the synthesis of PI nanoparticles [9, 10]. Cheong et al. polymerized isoprene in emulsions with low polymer content stabilized with different surfactants, using thermal and redox initiation systems and a very small concentration of *tert*-dodecyl mercaptan

(*t*-DM) in order to enhance the entry efficiency of radicals into micelles and particles [9]. They obtained PI particles with diameters in the range of 35 nm –100 nm. Furthermore, when polymerizations were carried out at 25°C using redox systems, polymer gel content was zero in most cases. It is noticeable that polymerization times were very long ($\approx$40 h) and that micrographs were not included in this report. On the other hand, Lorenz et al. [10] obtained PI particles between 80 and 200 nm when polymerizing isoprene at 72°C overnight in miniemulsions stabilized with various surfactants and only using thermal initiators. Surprisingly, as far as we know, microemulsion polymerization has not been used for synthesizing PI nanoparticles, in spite of the extensive use of this technique in research since 1980 for preparing polymeric nanoparticles with diameters < 50 nm [11, 12].

We report here a study on the synthesis of PI nanoparticles with average diameters close to 20 nm by polymerization at 25°C in a normal microemulsion stabilized with sodium dodecyl sulfate (SDS). The system *tert*-butyl hydroperoxide (*t*-BHP) and tetraethylene-pentamine (TEPA) was used as redox couple initiator.

2. Materials and Methods

2.1. Materials. SDS (98.5%), *t*-BHP (99.5%), TEPA (>99%) and *t*-DM (99%), all from Aldrich were used as received. Isoprene (Aldrich) was distilled under reduced pressure and stored at 4°C. Water was of tridistilled deionized grade.

2.2. Phase Diagram Determination. Microemulsion region at 25°C was determined by titration with isoprene of SDS/water mixtures at the following weight ratios: 2.5/97.5, 5/95, 10/90, and 15/85. Titration was stopped when the appearance of the mixture changed from transparent or translucent to opalescent, obtaining a first approximation to the boundary between the microemulsion region and the two phase region. Then, samples with isoprene content slightly higher and lower than the visually determined phase boundary were prepared by weighing each component and allowing each sample to reach equilibrium in a water bath at 25°C in order to determine the phase boundary more accurately. The normal microemulsion region corresponds to transparent or translucent samples that do not exhibit birefringence when observed through cross polarizers.

2.3. Polymerization. The polymerization was carried out at 25°C in a 200 mL jacketed glass reactor equipped with a reflux condenser and inlets for argon, monomer feed, mechanical agitation (450 rpm) and sampling. A 45°-pitched down flow four-bladed impeller was used. The procedure was as follows: 9.64 g of SDS, 86.78 g of water, 0.035 g of *t*-BHP and 0.0053 g of *t*-DM were charged into the reactor. This solution was heated to 25°C and bubbled with argon for 1 h. Thereafter, 3.5 g of previously degasified isoprene were added and one minute later, 0.035 g of TEPA, were also added to the solution for starting the reaction, which was allowed to proceed for 24 h. During the reaction, samples were withdrawn at given times to determine conversion (gravimetrically) and particle size. Samples from final latex were collected for characterization.

2.4. Characterization. Particle size of samples taken during polymerization was measured at 25°C in a Malvern Zetasizer Nano S90 quasielastic light scattering (QLS) apparatus equipped with an Argon laser ($\lambda = 633$ nm). To measure the monomer-free average particle size, latex samples were diluted with water up to 200 times to remove nonreacted monomer. This diameter is the intensity-weighted average diameter (D_z). Particle number density (N_p) at time t was calculated dividing the polymer concentration in the reaction mixture by the particle weight in accordance with the following:

$$N_P = \frac{6C_o(X/100)}{\pi \rho_p D_z^3}, \tag{1}$$

where C_o is the monomer initial concentration, ρ_p the polymer density (0.91 g/mL) [13] and X and D_z the conversion and the average diameter at time t, respectively.

Particle size of a sample from final latex was measured in a JEOL 1200 eXII transmission electronic microscope.
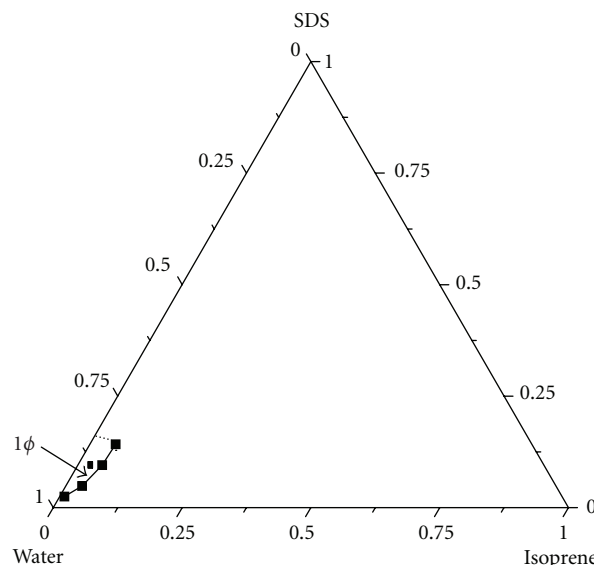

Figure 1: Partial phase diagram at 25°C of SDS/water/isoprene showing the normal microemulsion region (1ϕ). Composition of the microemulsion where polymerization was carried out is shown by (■).

Previous to this measurement, polymer in the latex sample was crosslinked using a UV lamp (10 W, $\lambda = 280$–315 nm) for 6 h. Then a drop of latex diluted up to 20 times was deposited on a copper grid, which was subsequently stained with osmium tetroxide. Polymer molecular weight distribution in the final latex was measured in a Hewlett-Packard-110 Gel Permeation Chromatograph (GPC) equipped with a refractive index detector. HPLC-grade tetrahydrofurane (THF) was used as mobile phase. The GPC was calibrated using 12 narrow polystyrene standards (Polyscience) with molecular weights ranging 162–6.3×10^6 g/mol. Molecular weights (M) were calculated with the viscosimetric equation for PI in THF, $[\eta] = 1.77 \times 10^{-4} M^{0.735}$ [14]. Glass transition temperature (T_g) determination was carried out in a modulated differential scanning calorimeter (DSC) TA Instruments 2920. Measurement was performed at a heating rate of 10°C/min in the range -120°C to -10°C, under a nitrogen flow of 50 mL/min. After the first heating scan, samples were quenched and a second scan was carried out at equal heating rate (10°C /min). The glass transition temperature was evaluated from the second scan by analyzing the reversible heat flow signal using the criteria of half-height. Infrared spectroscopy was carried out in an FT-Infrared Spectrophotometer Termo Nicolet/Mangro-550. For this, the dried polymer sample was grinded with potassium bromide powder and subsequently pressed to form a disk, which was analyzed in the apparatus.

3. Results and Discussion

Partial phase diagram for the system isoprene/water/SDS at 25°C is shown in Figure 1. Samples within the one-phase region (1ϕ) are transparent and very fluid, which suggests
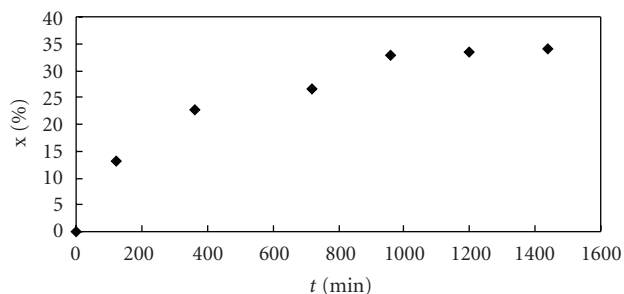
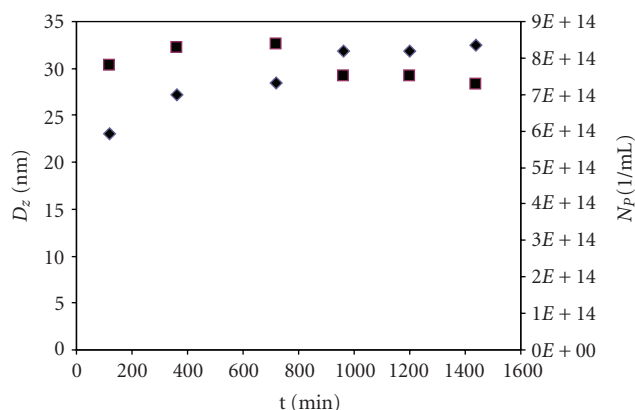FIGURE 2: Evolution of monomer conversion in the polymerization of isoprene in a normal microemulsion at 25°C.

FIGURE 3: Evolution of the average particle diameter measured by QLS, D_z, (♦) and the particle number density, N_p, (■) in the polymerization of isoprene in a normal microemulsion at 25°C.

that this region is a normal microemulsion one. To carry out the polymerization, a composition inside the microemulsion region was chosen. The square in Figure 1 indicates this composition.

Evolution of monomer conversion (X) versus polymerization time is shown in Figure 2. As can be seen in this figure, polymerization proceeds very slowly and the final conversion is relatively low. Cheong et al. [9] indicate that low yields in emulsion polymerization of isoprene were possible due to its low propagation rate constant (k_p). These authors argue that low k_p of isoprene would lead to a low propagation rate inside the latex particles as well as to a long aqueous-phase lifetime before particle entry, and hence low entry efficiency, due to termination of isoprene oligomers in the aqueous phase. For increasing the final conversion in emulsion polymerization of isoprene, Cheong et al. added t-DM to the reaction mixture [9]. It is believed that mercaptan enhances entry efficiency in particles through chain transfer from a sulfate (when a persulfate is used as initiator) or oligomeric isoprene radical to the thiol, which may enter micelles/particles directly and/or form an entering species after fewer propagation steps in comparison with those required for oligomeric isoprene radicals [15]. In our case, in spite of using t-DM, final conversion after 24 h reaction was about 35%. This result could be due to the

low concentrations of initiator (6.6 mM) and transfer agent (0.3 mM) used.

The average particle diameter measured by QLS (D_z) and the particle number density (N_p) versus polymerization time are depicted in Figure 3. Particle size increases sharply at the beginning of the polymerization; after that it increases slowly and stabilizes at 34-34 nm during the last third of the polymerization. It is noteworthy that monomer conversion also stabilizes about 35% in the same period of the polymerization. This evolution of particle size could be explained as follows. While, most of the isoprene polymerization conducted in our study proceeds slowly, there is a fast polymerization period occurring at the beginning of the reaction. In this period (0–400 min), the relatively high monomer availability in the micelles favors the simultaneous nucleation and growing of the particles, which is reflected in the relatively fast increase in the monomer conversion (Figure 2) and in the sharp increase in D_z and N_p (Figure 3). Then, between 400 and 1000 min, the polymerization becomes slower, probably because the drop in the monomer concentration in the system starts to become important. At the end of this period, between 800 and 1000 min, the N_p curve in Figure 3 shows a decrease whereas the growth rate of the particle size appears to increase. After that, in the last part of the polymerization, the particle size shows a very small increase, while N_p decreases slightly. It is believed that the observed decrease in N_p from approximately 27% in conversion is due to interparticle coalescence. This phenomenon can be explained taking into account the very low glass transition temperature (T_g) of polyisoprene, typically much lower than room temperature [16]. Because of this, particles are very soft at the temperature at which polymerization was carried out, which would lead to an increase in the fraction of the interparticle collisions resulting in coalescence.

Figure 4 shows a micrograph of a sample taken at the end of polymerization along the histogram of particle size made from measuring more than 250 particles. From this figure it is evident that spherical nanoparticles of polyisoprene can be obtained by microemulsion polymerization. Particle size data in the histogram allowed us to calculate a value of 27.0 nm for weight-average diameter (Dw) and of 22.2 nm for number-average diameter (Dn). Polydispersity calculated as Dw/Dn show a value of 1.2, which indicates a relatively broad particle size distribution. Average particle size obtained here is in accordance with typical values obtained in microemulsion polymerization. However, such broad particle size distribution as that obtained in our study is not common in this type of polymerization, in spite of the particle nucleation through the whole polymerization, as a consequence of the high content of surfactant in the parent microemulsions [11, 12]. It is believed that this broad particle size distribution could be explained on the basis of the interparticle coalescence. It is a well-known fact that in a particle population the coalescence between larger particles contributes to the widening of the particle size distribution.

The result of GPC analysis for a sample taken at the end of polymerization is shown in Figure 5. Weight-average
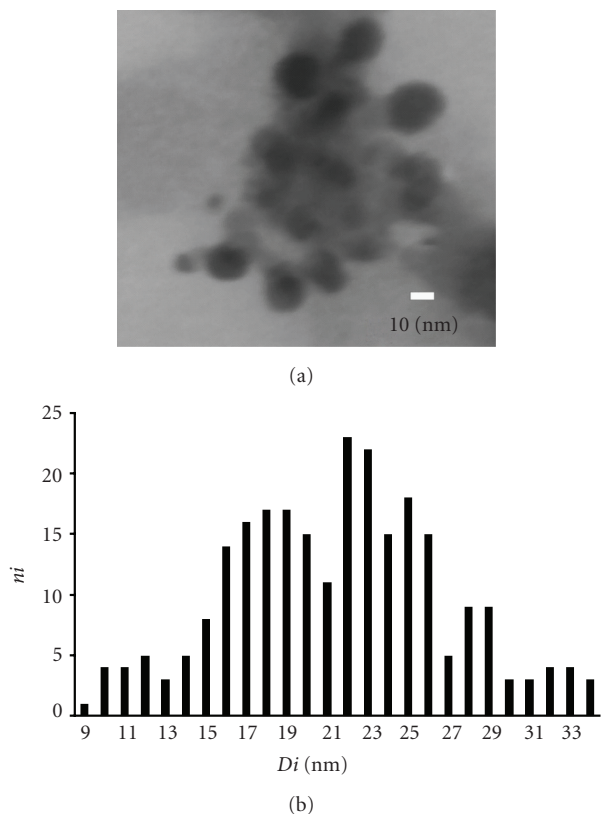
(a)

(b)

FIGURE 4: TEM micrography (a) and the particle diameter histogram (b) of final latex sample prepared by polymerization of isoprene in a normal microemulsion at 25°C.
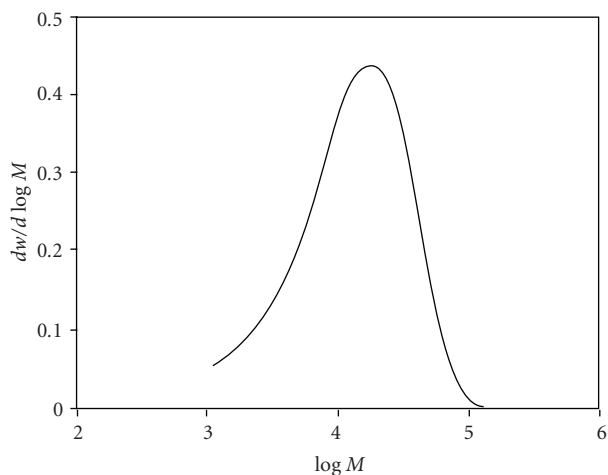

FIGURE 5: Molecular weight distribution of polyisoprene obtained at the end of the polymerization in a normal microemulsion at 25°C.
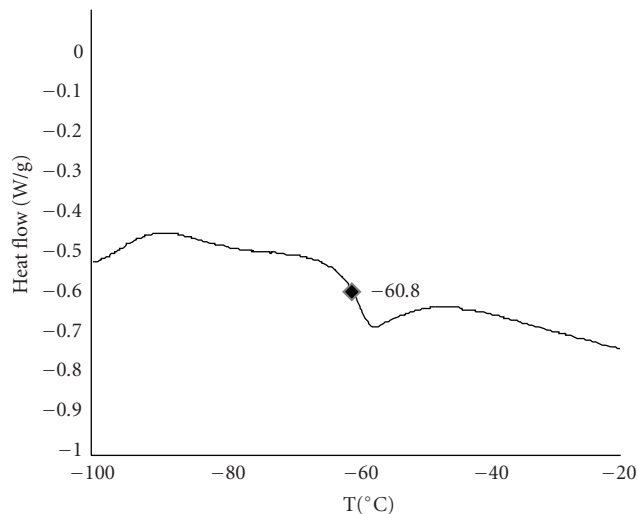

FIGURE 6: Thermogram obtained by DSC of a final sample of polyisoprene prepared by polymerization in a normal microemulsion at 25°C.

molecular weight values obtained in this polymerization, it is believed that the dominant mechanism would be one that would promote the formation of short chains, such as chain scission, which occurs during the polymerization by oxidative degradation, as has been seen in polydienes exposed to oxygen [17, 18] or in polyisoprene in the presence of hydroperoxides [9], as in our case. The absence of a shoulder in the high molecular weight region would indicate a negligible contribution of crosslinking reactions. This could be ascribed to the relatively low temperature at which polymerization was carried out and the relatively low final conversion, considering that crosslinking reaction becomes important in the last stages of the polymerizations where high final conversions (>90%) are attained [9]. Another possible mechanism of polymer chain termination is that resulting from the interparticle coalescence. When this phenomenon occurs between two particles containing polymer growing chains, the probability of bimolecular termination increases as the polymer particle size decreases. The average diameter of polymer particles obtained in our study suggests that bimolecular termination cannot be discarded as a contributing mechanism to the final population of polymer chains. Nevertheless, according to Figure 3, the interparticle coalescence becomes important from 800–1000 min in reaction time (or 27%–32% in conversion) that is, near the end of the reaction (see Figure 2). This indicates that the contribution of the polymer chains resulting from bimolecular termination to the final population of polymer chains would be very small.

Polyisoprene obtained at the end of the polymerization shows a T_g of −60.8°C (see Figure 6). The effect of both microstructure and molecular weight on T_g of polyisoprene has been reported in a number of studies [17–23]. According to Cowie [19] and Kow et al. [21], T_g becomes molecular weight independent above Mn ≈ 9-10 × 10³ g/mol. As the polyisoprene obtained in

molecular weight (Mw) and number-average molecular weight (Mn) were determined from molecular weight distribution (MWD) data as $20.4 × 10^3$ and $10.1 × 10^3$ g/mol, respectively. Figure 5 shows a monomodal MWD, which suggests that the final size of polymer chains is determined by only one main dominant mechanism. Based on the low
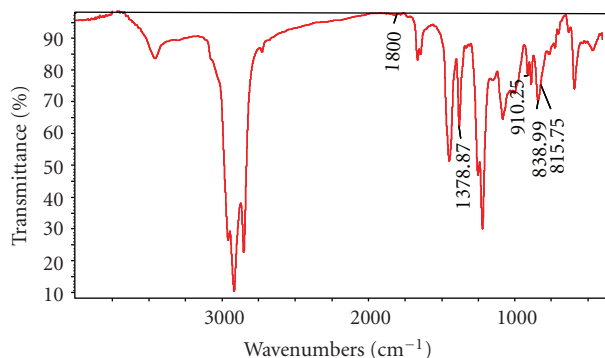
FIGURE 7: FT-IR spectra of polyisoprene obtained at the end of the polymerization in a normal microemulsion at 25°C.

our study has a Mn $= 10.1 \times 10^3$ g/mol it is believed that T_g was mainly determined by its microstructure. About the T_g-microstructure relationship, Widmaier and Meyer [20] determined T_g values for a series of polyisoprene samples obtained by anionic polymerization with different microstructures. They found T_g values in the range −71 to −36°C for 3,4 units content ranging from 9 to 49%, with a direct dependence T_g-3,4 content. The increase of T_g with 3,4 units content was explained by Widmaier and Meyer adducing that the steric hindrance resulting from the side-chain vinyl groups lead to stiffening of polymer chains. May be due to its obviousness because of the absence of 1,2 units in the samples of polyisoprene, they did not mention the inverse dependence between T_g and total 1,4 units content. Kow et al. [21] also reported an inverse dependence between T_g and total 1,4 content. So, according to the findings reported by Widmaier and Meyer, a polyisoprene with a T_g value of −60.8°C, as in our case, should be expected to have around 80% of total 1,4 units.

According to the literature [24, 25] it is possible to know the microstructure of polyisoprene from FT-IR spectroscopy. Tsurugi et al. [24] developed a method for calculating the cis-1,4 content in a polyisoprene based on its FT-IR spectra. This method uses the following:

$$
\begin{aligned}
D_{839} &= \log\left(\frac{I_{815}}{I_{839}}\right), \\
D_{1379} &= \log\left(\frac{I_{1379}}{I_{1800}}\right),
\end{aligned}
\tag{2}
$$

where I indicates the transmittances at the corresponding wave lengths. The ratio D_{839}/D_{1379} is directly proportional to the cis-1,4 content in a correlation chart included in the report of Tsurugi et al. [24]. Figure 7 shows the FT-IR spectra of the polyisoprene obtained at the end of the polymerization. Substitution of the corresponding transmittance values in (2) and using the chart in reference [23] allowed us to obtain a value of 30% cis-1,4 content in the polyisoprene prepared in this work. In order to determine the complete microstructure we calculated the areas under the peaks at 839 cm^{-1} for cis-1,4 units, 890 cm^{-1} for 3,4 units and 910 cm^{-1} for 1,2 units, using the software of our

spectrometer. After that, the calculated areas were affected by a factor for rendering the contribution of the area under the peak corresponding to cis-1,4 units in 30%. In this way, the 3,4 units content was 8.2% and that of 1,2, was 8.4%. The difference with 100%, that is, 53.4%, corresponds to the trans-1,4 content. The dominance of the trans-1,4 units agrees with that of polyisoprene synthesized in emulsion polymerization by other groups [9, 25]. Furthermore, the total content of 1,4 units ($\approx$83%) calculated by Tsurugi's method is in accordance with our previous estimation of about 80% based in the T_g value of the polyisoprene synthesized in this study.

4. Conclusions

Batch polymerization of isoprene carried out in a normal microemulsion proceeded very slowly and the final conversion was relatively low. This behavior was ascribed to the low concentrations of initiator and/or the transfer agent originally added to enhance the micelle/particle radicals entry. Nanoparticles obtained showed a number-average diameter close to 20 nm and a relatively broad particle size distribution. It is believed that the latter is promoted by particle coalescence. Low molecular weight and monomodal molecular weight distribution of obtained polyisoprene suggest that the final size of polymer chains was determined by only one main dominant mechanism, which promotes the formation of short chains, such as chain scission. Microstructure determined by Tsurugi's method shows that the polyisoprene synthesized in this study contains around 80% 1,4 units, which matches with its T_g value (−60.8°C).

Acknowledgments

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