

# Synthesis of Polybutadiene Nanoparticles via Emulsion Polymerization: Effect of Reaction Temperature on the Polymer Microstructure, Particle Size and Reaction Kinetics

Mahdi Abdollahi<sup>1,2,\*</sup>, Mohammad Reza Yousefi<sup>2</sup>, Parisa Alamdari<sup>1</sup>, Heidar Ranjbar<sup>3</sup>, Fardin Seyyed Najafi<sup>3</sup>, Fatemeh Rekabdar<sup>2</sup>

1. Polymer Engineering Department, Faculty of Chemical Engineering, Tarbiat Modares University, P.O.BOX:14115-143, Tehran, Iran

2. Division of Polymer Science and Technology, Research Institute of Petroleum Industry, P.O. Box: 14665-1998, Tehran, Iran

3. Reseach and Development Center, Tabriz Petrochemical Company, Tabriz, Iran

## ARTICLE INFO

### Article history:

Received: August 20, 2013

Accepted: December 9, 2013

### Keywords:

Emulsion polymerization,  
Polybutadiene nanoparticles,  
Polymerization kinetics,  
Reaction temperature,  
Polymer microstructure

\* Corresponding author:

Email:

[abdollahim@modares.ac.ir](mailto:abdollahim@modares.ac.ir)

Tel: +98 21 82884959

Fax: +98 21 82884931

## ABSTRACT

Polybutadiene nanoparticles were synthesized via batch emulsion polymerization of butadiene in the presence of potassium persulfate, disproportionate rosinate potassium cation and t-dodecyl mercaptane as initiator, emulsifier and chain transfer agent, respectively. Polymerization reaction was performed at different temperatures (60, 70 and 80 °C). Conversion was measured at various time intervals by gravimetry method. Particle size and its distribution of the polybutadiene latex were measured by dynamic light scattering (DLS) and SEM analyses. Polymer microstructure was investigated by FT-IR spectroscopy. By increasing the polymerization temperature, average diameter of the polybutadiene nanoparticles decreased from 104 nm (at final conversion of 80.6%) at 60 °C to 88.7 nm (at final conversion of 98.0%) at 80 °C. Dominant microstructure, i.e. 1,4-trans isomer content, in the synthesized polymers was calculated to be about 60%. Results showed that by increasing the reaction temperature, size of the particles decreased while the number of the polymer particles and polymerization rate increased.

## 1. Introduction

The first attempts to develop emulsion polymerization of main diene monomers such as butadiene were undertaken to reduce dependence on natural resources, i.e. natural rubber. The initial publications on emulsion polymerization of butadiene back to shortly after World War II. Much of the fundamental knowledge about the subject, for the first time, was briefly published by the Synthetic Rubber Program [1]. A few years later, a series of articles were published by Morton et al. [2-5] about the cross-linking behavior of polybutadiene and the use of several initiator systems in the emulsion polymerization of butadiene.

Persulfate-mercaptan initiator system was extensively investigated by Kolthoff et al. [6-8] during 1991-1995. They studied persulfate decomposition reactions and the effect of its concentration on the polymerization trend by using various analytical methods for the determination of the persulfate [6] and mercaptan [7] concentration. Bhankuni [9] proved that in the persulfate-mercaptan emulsion polymerization of butadiene, the kinetics of reaction is affected by the nature of the emulsifier. Moreover, network formation within the latex particles has no influence on the saturation monomer solubility in the particles. The radiation-induced emulsion polymerization of butadiene was reported in 1974 [10]. Polymerization was found to be much faster in the presence of n-dodecylmercaptan. Consistent results about the effect of almost all relevant chemical and physical factors on emulsion polymerization of butadiene were obtained by Weerts and coworkers [11-17]. These investigations led to the following conclusions: 1) Average polymerization rate per particle isn't influenced by the nature and the concentration of emulsifier and/or initiator rather it is significantly influenced by the particle size. 2) Bimolecular termination within the particles is not a rate-determining reaction, and radical exit from the particles is significant. Low initiator efficiency limits radical entry into the particles. Therefore, it was concluded that emulsion polymerization of butadiene is a typical of Smith-Ewart case I system ( $\bar{n} \ll 0.5$ ,  $\bar{n}$ : average number of growing radicals per particle). 3) The so-called "promoting effect" of mercaptans in emulsion polymerizations of butadiene is related to impurities present in the emulsifier. Well-defined seeded emulsion polymerizations were performed by Verdurmen et al. [18-21] on the monodisperse seed latexes prepared by emulsifier-free emulsion polymerization in order to solve the problem of relatively low emulsion polymerization rate of butadiene. They measured the value of the propagation rate coefficient, studied the effect of the persulfate concentration on the polymerization rate and investigated the effect of tert-dodecyl mercaptan (TDM) as a chain transfer agent. It was shown that colloiddally highly stable latexes up to high final solid contents (up to 60%), with relatively small particle diameters (below 300 nm) are produced by the emulsifier-free emulsion polymerization process. The efficient in-situ production of surface active oligomers and low polymerization rate in the particles were introduced as the main explanations for this observation. Also, it was proved that this polymerization process behaves like Smith-Ewart case I and II systems.

Chemical structure of polybutadiene consists of three major microstructures: 1,4-cis, 1,4-trans and 1,2 vinyl. High cis-polybutadiene has a high elasticity, whereas the so-called high vinyl is a plastic crystal. Emulsion polymers of butadiene contain all three types of these microstructures although

1,4-trans is the predominant microstructure (~ 60%). Amount of each microstructure in the produced polymer depends on various parameters such as initiator type, surfactant type and content and polymerization temperature. Temperature dependence of microstructure in emulsion polymerization of polybutadiene was studied [22]. It was proved that the content of unreacted vinyl groups is not considerably influenced by the polymerization temperature. However, while 1,4-trans decreases, 1,4-cis content increases with increasing polymerization temperature. Indeed, the cis-trans ratio is lower by lowering the polymerization temperature. The polybutadiene produced at low temperatures contains high amounts of 1,4-trans configuration and this structurally more ordered polymer has improved physical properties. On the other hand, polybutadiene, which is produced at higher temperatures contains random sequence of 1,2-vinyl, 1,4-trans and 1,4-cis configurations. Such random sequence is the main reason for weak physical properties of the produced polybutadiene. Therefore, polybutadiene elastomers are generally synthesized at lower temperatures. Emulsion polymerization is the most usual method for the production of acrylonitrile-butadiene-styrene (ABS) engineering terpolymer. For this purpose, polybutadiene latex (PBL) is synthesized via emulsion polymerization method, then styrene and acrylonitrile monomers are added to the latex and make it swelled. The swelling amount of polybutadiene nanoparticles and terpolymer morphology are affected by the content of gel formed during polymerization which itself is controlled by different parameters such as polymerization temperature.

Batch emulsion polymerization of butadiene is long in time. Therefore, finding appropriate strategies to improve the initiator efficiency in the particle nucleation and to increase  $\bar{n}$  and consequently increase the polymerization rate has found high industrial importance. In the previous work, we studied the effect of initiator and emulsifier concentrations on the reaction kinetics and latex's particle size [23]. In the continuum of the previous study, the effect of temperature on the kinetics of batch emulsion polymerization of butadiene has been studied in the present work. To our knowledge, there is no report on the effect of the reaction temperature on the particle nucleation and growth processes, i.e. on the average number of the particles per unit volume of the continuous phase ( $N_p$ ) and growing chains per particle ( $\bar{n}$ ), respectively. For this purpose, the PBL with solid content of 30% was produced through batch emulsion polymerization. Polymerization reaction was performed at different temperatures (60, 70 and 80 °C) in a Buchi reactor equipped with mechanical stirrer (300 rpm) in order to determine temperature dependence of the polybutadiene particle size and its distribution (particle nucleation and growth processes). Moreover, the effect of polymerization temperature on the polybutadiene microstructure and the amount of gel formed during the polymerization were evaluated.

## 2. Research Method

### 2.1. Materials and instrumentations

Butadiene gas as monomer and disproportionate potassium rosinate (DPR) as anionic emulsifier were supplied from Tabriz Petrochemical Company (TPC). The emulsifier is the mixture of abietic acid derivatives including dehydroabietic acid, dihydroabietic acid and tetrahydroabietic acid. Abietic acid

content of the emulsifier is less than 2wt%. Potassium persulfate initiator, potassium carbonate and potassium hydroxide electrolytes, laboratory grade, were used without further purification. Tert-dodecyl mercaptan was supplied from TPC and used as chain transfer agent. Hydroquinone (Merck) was used as inhibitor in the conversion measurement. Deionized water was used in all of the polymerizations.

Fourier transform infrared (FTIR) (Model IF505, Bruker) analysis was performed to characterize the final product. Dynamic light scattering (DLS) (Model Zetasizer Nano Series, Malvern) technique was used to measure average particle size and particle size distribution (PSD) of the produced latex. Scanning electron microscopy (SEM) (Model Stereoscan 360, Cambridge Instrument Co.) was applied to determine the particle size.

## 2.2. Synthesis of PBL

Batch emulsion polymerizations were carried out in a stainless steel/glass Buchi reactor (model bmd 300, volume 1dm<sup>3</sup>) equipped with an anchor shape mechanical stirrer, which was set at 300 rpm. The maximum operating pressure was 20 bar [23, 24]. The required amounts of initiator and emulsifier were dissolved in a part of the needed water for each experiment and the resulting mixture was added to the reactor. The reactor was charged with all the ingredients, except for Bu (Table 1). In order to exit oxygen from the reactor, a stream of nitrogen was passed over the reaction mixture (initiator, emulsifier, chain transfer agent and etc.) for 30 minutes. After evacuation, the degasification process was performed for another 15 minutes and the inert gas in the headspace was then evacuated, the reactor was completely sealed and the weighted amount of butadiene was injected into the reactor [23, 24]. The reactor was heated to the specific temperature with silicon oil circulation. The pressure never exceeded a certain amount (for example, 6.5 bar at 70°C) in the reactor during the polymerization. Polymerization reactions were performed at 60 (PBL1), 70 (PBL2) and 80°C (PBL3).

Table 1. Batch emulsion polymerization recipe of butadiene with 30% final solid content

Components	Amount(phm) <sup>a</sup>
Monomer	100.00
Emulsifier (DPR)	9.72
Potassium karbonate	0.80
Potassium hydroxide	1.70
Potassium persulfate (KPS)	0.80
t-dodecyl mercaptane (TDM)	0.35
Distilled water	230.00

<sup>a</sup> parts per hundred monomer

Total solid content of latex at any reaction time (TSC(t)) was measured gravimetrically according to ASTM D1417(method B). Samples of about, 10 g were withdrawn from the bottom of reactor in a closed vial. After weighing, each sample was quenched immediately by the addition of 1 ml of 1% (w/v) hydroquinone solution in water. Then, samples were dried at 60 °C under reduced pressure condition until the weight of dried samples become constant. Total solid content at any time t (TSC(t)) was calculated by dividing the weight of dried

sample ( $m_2$ ) to that of initial sample ( $m_1$ ). It should be noted that the weight of dried samples was corrected by considering the amount of hydroquinone added to each sample (0.01 g).

### 2.3. Determination of conversion

Overall mass conversion ( $X_{ov}(t)$ ) was calculated according to the following equation (Eq. (1)) for each sample.

$$X_{ov}(t) = \frac{TSC(t) - TSC(initial)}{TSC(final) - TSC(initial)} \quad (1)$$

in which,  $TSC(t)$  is the total solid content at time  $t$ ,  $TSC(initial)$  is the total solid content at the start of the polymerization and  $TSC(final)$  is the total solid content at the complete conversion of the butadiene.

### 2.4. Determination of particle size and particle size distribution

Particle size and its distribution was measured by dynamic light scattering (using a He-Ne laser as light source with wavelength of 632.8 nm under scattering angle of  $90^\circ$  with effective detection capability from 20 to 2000 nm) which is a relatively fast technique for determining such parameters. The average z-diameter is measured and number average, weight average and volume average diameters are calculated from this amount. Moreover, polydispersity index which is a criterion of particle size distribution can be determined by this technique. Polydispersity index is defined as the standard deviation of the particle size distribution divided by the average particle size. The measurements of particle size were done using high-performance particle sizer (Zetasizer Nano S) with DLS (Dynamic Light Scattering) and NIBSTM (Non-invasive Back Scatter) technology from Malvern Instruments (Malvern, UK). It measures the scattering information close to  $180^\circ$  (backscatter detection) using patented NIBS™ (Non Invasive Back Scattering) technology to increase detection sensitivity and reduce multiple scattering (minimum at  $180^\circ$  hence, higher concentration can be measured). The effect of dust particles was greatly reduced. DLS measurements were performed at  $25^\circ\text{C}$  in a square glass cuvette with a round aperture at a fixed angle of  $90^\circ$ .

### 2.5. Determination of the gel content

In order to determine the gel content, aluminum sulfate was added to precipitate the polymerized product. The precipitated polybutadiene was separated from water phase and washed repeatedly by distilled water and methanol until the residual impurities were removed. Samples were then dried at  $50^\circ\text{C}$  under reduced pressure until the weight of dried samples became constant. Dried polybutadiene ( $W_1$ , 0.5 g) was added to pure toluene (50 ml) and stirred at ambient temperature and dark conditions for 48 hours. The resulted mixture which contained both dissolved polybutadiene and non-dissolved polybutadiene gel in toluene was centrifuged at 10000 rpm for 5 minutes. In this way, dissolved polybutadiene was separated from the polybutadiene gel. 25 ml of solution phase was dried at  $60^\circ\text{C}$  under reduced pressure condition until the weight of dried samples became constant ( $W_2$ ). Finally, gel content was calculated from equation (2).

$$Gel \text{ content} (\%) = \frac{W_1 - (2 \times W_2)}{W_1} \times 100 \quad (2)$$

## 2.6. Determination of polybutadiene microstructure by FTIR spectroscopy

According to ISO standard 12965 [25], the elastomeric polybutadiene was dispersed in dichloromethane (or chloroform) solvent and the solution was carefully poured on a KBr plate and dried before being analyzed by FT-IR. Indeed, 0.1 g of dried polybutadiene, which was extracted with azeotropic mixture of toluene-ethanol (according to ISO standard 1407) was introduced in a test-tube containing 20 ml of dichloromethane (or chloroform) and was mixed using a mechanical vibrator for 6 hours until the mixture became clear. A few drops of the resulted mixture were poured on a KBr plate. The solvent was then evaporated at ambient temperature for 30 minutes and finally a thin uniform film was formed. The FTIR spectra of samples were recorded at the wave number of 600-2000  $\text{cm}^{-1}$ . Adsorption at 965 ( $A_{965}$ ), 909 ( $A_{909}$ ) and 728 ( $A_{728}$ )  $\text{cm}^{-1}$  were, respectively, assigned to trans, vinyl and cis configurations. These measured adsorptions were normalized by the following equations:

$$\% A_{965} = \frac{A_{965}}{A_{965} + A_{909} + A_{728}} \times 100 \quad (3)$$

$$\% A_{909} = \frac{A_{909}}{A_{965} + A_{909} + A_{728}} \times 100 \quad (4)$$

$$\% A_{728} = \frac{A_{728}}{A_{965} + A_{909} + A_{728}} \times 100 \quad (5)$$

The different isomer contents ( $C_{cis}$ ,  $C_{trans}$  and  $C_{vinyl}$  ( $\text{g.dm}^3$ )) were calculated by equations (6)-(8) below:

$$c_{cis} = 1.7896 \times \% A_{728} - 0.0253 \times \% A_{965} - 0.0085 \times \% A_{909} \quad (6)$$

$$c_{trans} = 0.3971 \times \% A_{965} - 0.0502 \times \% A_{728} - 0.0142 \times \% A_{909} \quad (7)$$

$$c_{vinyl} = 0.2954 \times \% A_{909} - 0.0075 \times \% A_{728} - 0.0065 \times \% A_{965} \quad (8)$$

At last, the polybutadiene microstructure was calculated by equations (9)-(11):

$$\% cis = \frac{c_{cis}}{c_{cis} + c_{trans} + c_{vinyl}} \times 100 \quad (9)$$

$$\% trans = \frac{c_{trans}}{c_{cis} + c_{trans} + c_{vinyl}} \times 100 \quad (10)$$

$$\% vinyl = \frac{c_{vinyl}}{c_{cis} + c_{trans} + c_{vinyl}} \times 100 \quad (11)$$

## 3. Results and Analysis

Batch emulsion polymerization of butadiene was performed in a 1-L Buchi reactor. The effects of polymerization temperature on the average particle size, particle size distribution, polymer microstructure, final gel content and

polymerization kinetics were investigated in the present study. The detailed polymerization procedure was presented in the previous section and also in Table 1. The polymerization reactions were conducted at 60, 70 and 80 °C and polymerization times varied from 7 to 16 hours depending on the polymerization temperature. The inner reactor pressure as an indication of the polymerization progress was followed with the reaction time. The pressure versus time plot of PBL2 experiment (polymerization performed at 70°C), as an example, has been illustrated in Figure 1. The pressure remained constant while there existed butadiene as a separate phase (In intervals I and II of emulsion polymerization, up to about 60% conversion). In the interval III of emulsion polymerization (above 60% conversion) where there is no monomer droplets, latex particles are in equilibrium with the monomers dissolved in the water phase, which in turn are in equilibrium with the monomers existing in the gas phase. Therefore, in the last interval of emulsion polymerization, by increasing conversion, the pressure strongly decreases (Figure 1).

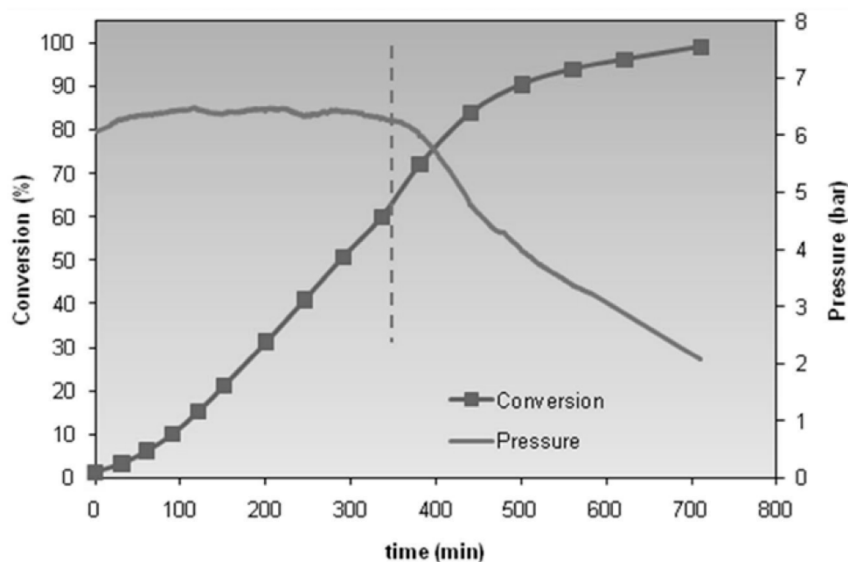


Figure 1. Monomer conversion and inner reactor pressure versus time plot for batch emulsion polymerization of butadiene at 70°C (PBL2)

The average particle size and its distribution were studied by SEM technique. Film formation on the SEM holder during drying of dilute latex due to low glass transition temperature (lower than 0°C) of polybutadiene particles caused low quality SEM images. In order to overcome this problem, latex samples were more diluted and subjected to stiffening treatment via bromination. A small droplet of the resulted latex was poured on the holder and dried by freeze-drying technique. SEM micrograph of polybutadiene particles is presented in Figure 2. The average diameter of particles was measured; however, some latex particles got deformed during the film formation. The particle size distribution was found to be broad and average diameter of polybutadiene particles varied from 30 to 300 nm although said value was fixed at 100 nm for most of the particles. Aggregation of small particles led to the formation of the non-spherical large particles. Particle size data obtained directly from SEM measurements were in good agreement with those obtained by DLS measurements (see next section).

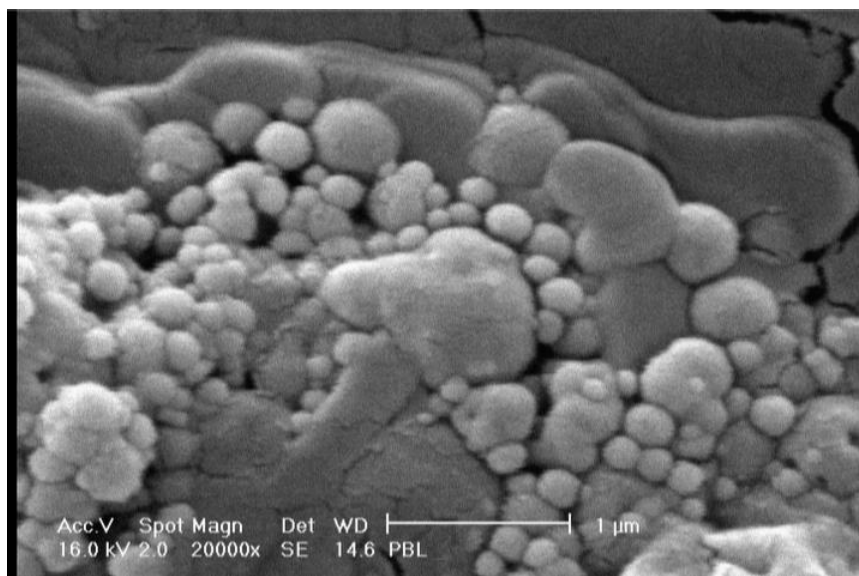


Figure 2. SEM image of polybutadiene nanoparticles synthesized at 70°C (PBL 2, Table 1)

### 3.1. Polybutadiene structure and microstructure characterization

Microstructure of the produced polymer was determined using FT-IR technique. FT-IR spectra of synthesized polybutadiene at various temperatures have been illustrated in Figure 3. The addition of butadiene monomers into a growing polymer chain occurs as either 1,4-cis, 1,4-trans or 1,2-vinyl. The mono-substituted double bond (pendant vinyl group) which is formed during 1,2-addition appears at 910 and 990  $\text{cm}^{-1}$  in FTIR spectra of 1,2-butadiene. However, the 1,2 di-substituted double bond formed during 1,4-addition appear at 720 and 970  $\text{cm}^{-1}$  in FTIR spectra of 1,4-cis and 1,4-trans, respectively, polybutadiene. (Figure 3)

Therefore, from the FTIR spectra of synthesized polybutadiene (Figure 3) it could be found that the produced polymer was highly trans in microstructure. The results of microstructure studies have been compared for the synthesized and commercial PBLs in Table 2. FTIR and NMR analysis of polybutadiene produced in an emulsion polymerization demonstrated that about 60% of monomer addition to the propagating chains occurs through 1,4-trans addition while the proportion of 1,4-cis and 1,2-vinyl addition are almost the same and about 20% [26]. Moreover, the 1,4-cis and 1,4-trans isomers increase and decrease, with increasing polymerization temperature, respectively. However, the 1,2-vinyl content isn't influenced by reaction temperature [27]. The results of isomer content calculations and how it is affected by temperature have been presented in Table 2. These results are consistent with those reported previously. Indeed, the proportion of 1,4-cis, 1,4-trans and 1,2-vinyl isomers, respectively, increased, decreased and was not influenced by temperature. The gel content increased from 69.2% at 60°C to 85.6% at 80°C. The temperature increase in the range of 60 to 80°C didn't considerably change the isomer proportions. Therefore, the temperature increase in this range (60 to 80°C) could provide an appropriate strategy to reduce polymerization time if the polymerization rate increased in this temperature range.



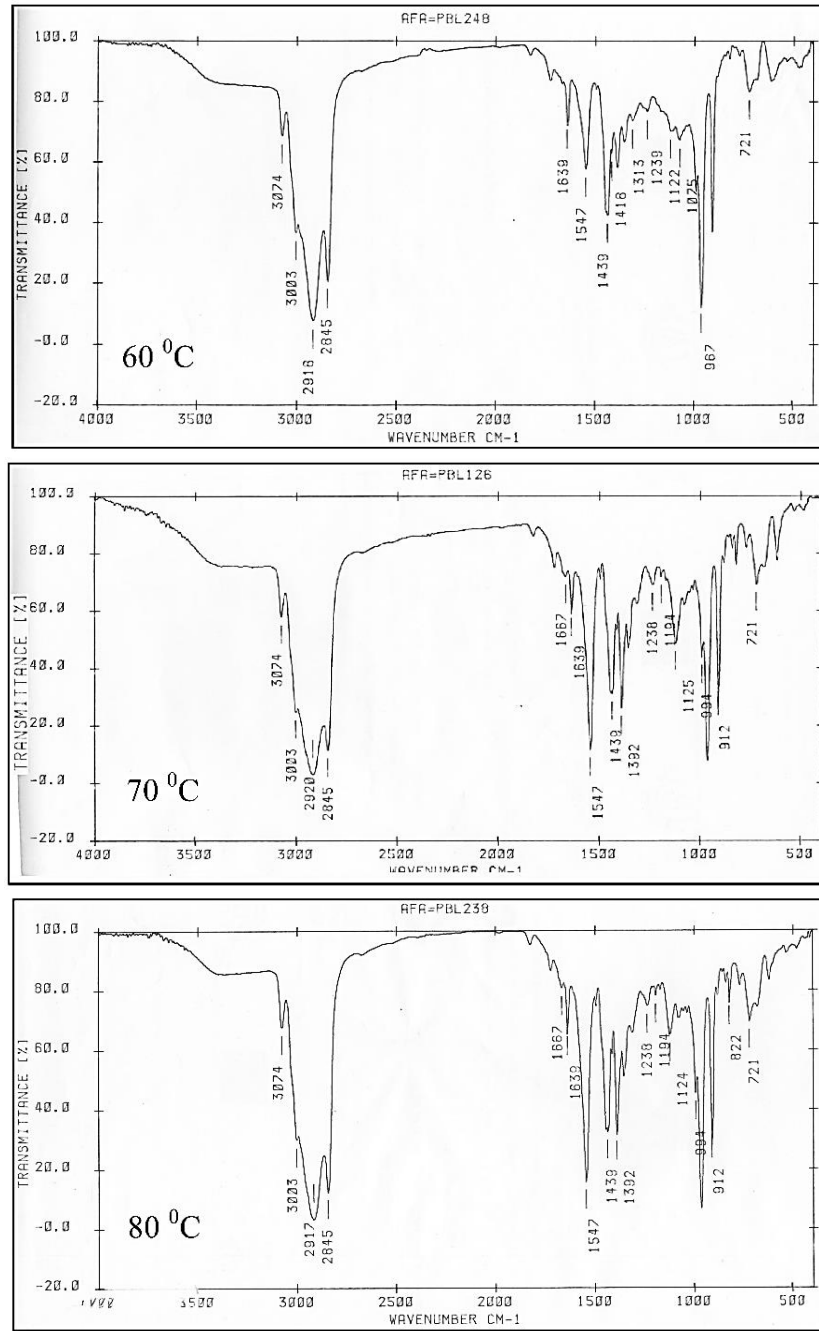


Figure 3. FTIR spectra of synthesized polybutadiene at various temperatures (70°C-PBL1, 80°C-PBL2, 90°C-PBL3)

Table 2. Specifications of commercial and synthesized polybutadienes

Property	Commercial <sup>a</sup>	PBL1	PBL2	PBL3
Reaction temperature (°C)	50	60	70	80
Total solid content (%)	41.2	32.9	32.9	32.9
Conversion (%)	-	100	100	100
Gel content (%)	86.6	69.2	79.2	85.6
Average particle diameter (nm)	94.7	104	89.3	88.7
Particle size polydispersity index (PDI)	0.34	0.106	0.167	0.141
1,4-trans content (%)	60.5	65.8	58.8	57.0
1,4-cis content (%)	25.9	21.4	28.4	31.8
1,2-vinyl content (%)	13.6	12.8	12.8	11.2

<sup>a</sup> synthesized via emulsion polymerization at 50°C, CNPC Daqing Chemical Ltd. PetroChina [26]

### 3.2. Effect of reaction temperature on average particle size and its distribution

In all butadiene emulsion polymerizations colloidal highly stable latexes up to 30% final solid contents were produced. DLS analysis indicated relatively broad particle size distribution. Figure 4 illustrates particle size and its distribution analysis via DLS technique for PBL produced at 70°C (PBL2) and 99% conversion. The average diameter of latex nanoparticles was 89.3 nm, particle size distribution varied from 35 to 350 nm and polydispersity index was 0.167 which indicated broad particle size distribution.

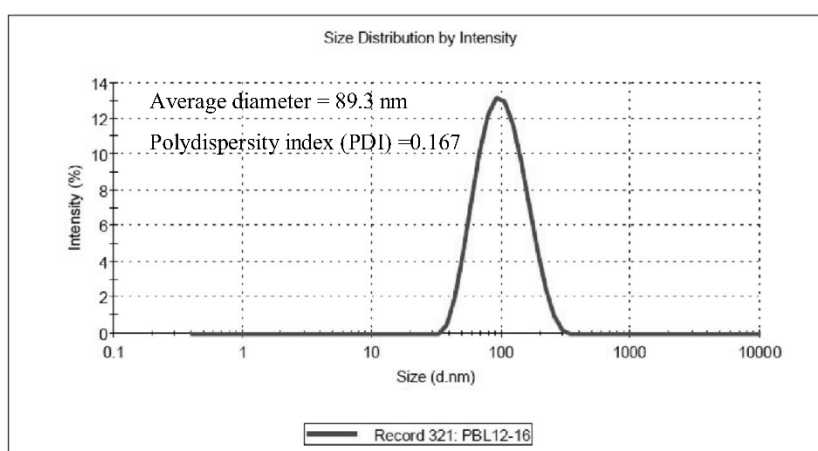


Figure 4. Particle size and its distribution analysis of polybutadiene synthesized at 70°C with 99% conversion via DLS

The average particle size ( $d_p$ ) and polydispersity index ( $PDI$ ) of the particle size distribution obtained from DLS technique have been presented in Table 3. At the same conversions, particle size decreased with increasing temperature. For example, by increasing the polymerization temperature, average diameter of polybutadiene nanoparticles decreased from 104 nm (at final conversion of 80.6%) at 60 °C to 88.7 nm (at final conversion of 98.0%) at 80°C. Table 3 demonstrates that independence of polymerization temperature the particle size distribution was broad and average diameter of nanoparticles was less than 104 nm.

Table 3. Kinetics of batch emulsion polymerization of butadiene (particle nucleation and growth) at various temperatures

Parameter	PBL1	PBL2	PBL3
Temperature( $^{\circ}C$ )	60	70	80
$X_{ov}(kg/kg)^a$	0.806	0.990	0.980
$M/W(kg/kg)$	0.435	0.435	0.435
$P/W(kg/kg)$	0.350	0.430	0.426
$d_p(nm)$	104	89.3	88.7
$PDI$	0.106	0.167	0.141
$N_p(dm^{-3})$	$6.68 \times 10^{17}$	$13.0 \times 10^{17}$	$13.1 \times 10^{17}$
$dX_{ov}/dt(\min^{-1})$	$0.966 \times 10^{-3}$	$2.05 \times 10^{-3}$	$2.45 \times 10^{-3}$
$C_{M,0}(mol.dm^{-3})$	8.038	8.038	8.038
$R_p(mol.dm^{-3}.sec^{-1})$	$1.29 \times 10^{-4}$	$2.75 \times 10^{-4}$	$3.29 \times 10^{-4}$
$R_p/N_p(mol.sec^{-1})$	$1.94 \times 10^{-22}$	$2.12 \times 10^{-22}$	$2.51 \times 10^{-22}$
$\bar{n}$	0.095	0.080	0.056

<sup>a</sup> reported conversion is belong to the sample analyzed by DLS

In free radical polymerization, initiator decomposition rate is a function of temperature [28]. In general, by increasing the emulsion polymerization temperature the initiator decomposition rate increases and this causes more nucleated particles and an increase in the number of oligo-radicals entered to the particles. Hence, the polymerization rate will increase if the number of particles increases.

### 3.3. Effect of polymerization temperature on polymerization kinetics

In batch emulsion polymerization the overall polymerization rate per continuous phase volume unit is calculated from equation 12:

$$R_p(t) = C_{M,0} \frac{d\theta(t)}{dt} \cong C_{M,0} \frac{dX_{ov}(t)}{dt} \quad (12)$$

in which,  $C_{M,0}$  and  $X_{ov}(t)$  are initial monomer concentration per water phase volume unit and the overall weight conversion. In the above equation, overall conversion is a molar one ( $\theta(t)$ ) which is the same as the weight conversion in the present study since only butadiene existed as the monomer. The polymerization rate was calculated from the slope of the conversion versus time plots in the conversion range between 10-60% (interval II of the emulsion polymerization of butadiene).

The number of particles per continuous phase volume unit ( $N_p$ ) and  $\bar{n}$  were calculated from equations (13) and (14), respectively [24].

$$N_p = \frac{6 \frac{M}{W} X_{ov}}{\frac{\rho_p}{\rho_w} \cdot \pi \cdot d_p^3} \quad (13)$$

$$R_p = \frac{\bar{k}_p \cdot \bar{n} \cdot N_p \cdot C_M}{N_{Av}} \quad (14)$$

where  $M/W$ ,  $\rho_p$  and  $\rho_w$  indicate to the ratio of monomer to water weight, average density of polymer (0.89 g.cm<sup>-3</sup> for polybutadiene) and density of water (1.0 g.cm<sup>-3</sup> at the ambient temperature), respectively. Moreover,  $d_p$  is the average diameter of particles,  $\bar{k}_p$  is average propagation rate coefficient in particle phase,  $\bar{n}$  is the average number of propagating radicals per particle,  $C_M$  is the overall monomer concentration in the particles (5.5 M),  $N_p$  is the number of latex particles per continues phase volume unit and  $N_{Av}$  is the Avogadro's number [24]. The propagation rate coefficient of butadiene was reported to be 165, 289 and 190, respectively, at 60, 70 and 80°C [29, 30].

The nucleation which occurs in interval I of emulsion polymerization was defined by Harkins as a period in which latex particles are formed [31]. Also, in order to explain performed emulsion polymerization it was suggested that the micellar seeding (entrance of oligomeric radicals into surfactant micelles) is the predominant mechanism of seeding. Quantitative study of Harkin's model conducted by Smith and Ewarts paved the way to understand the kinetics of emulsion polymerization [32]. The number of particles ( $N_p$ ) formed in interval I of emulsion polymerization was formulated by  $N_p \propto [I]^{0.4}[S]^{0.6}$  in which  $[I]$  and  $[S]$  were the initiator and surfactant concentrations, respectively. However, this model isn't sufficient to describe the polymerization kinetics of a wide range of monomers especially those which are considerably soluble in water phase and also for butadiene.

The kinetics of emulsion polymerization of butadiene is very similar to those of high water soluble monomers such as vinyl acetate and various acrylates. In the emulsion polymerization of these monomers, the polymerization rate is constant while the number of the particles decreases. Moreover, radical desorption occurs in such systems and polymerization obeys Smith-Ewart case I ( $\bar{n} \ll 0.5$ ) kinetics and thereby polymerization time is very long. Therefore, finding appropriate strategies to improve the initiator efficiency in particle nucleation and to increase  $\bar{n}$  and consequently increase the polymerization rate has found high industrial importance.

The effect of polymerization temperature on the monomer conversion is shown in Figure 5. The plots of conversion versus time were S-shape similar to the most of emulsion polymerization systems. As expected, the polymerization rate during Interval I increased by increasing reaction temperature. The increased polymerization rate was attributed to either increased propagation rate coefficient or increased particle nucleation as a consequence of more radical concentration generated from initiator decomposition in the water phase.

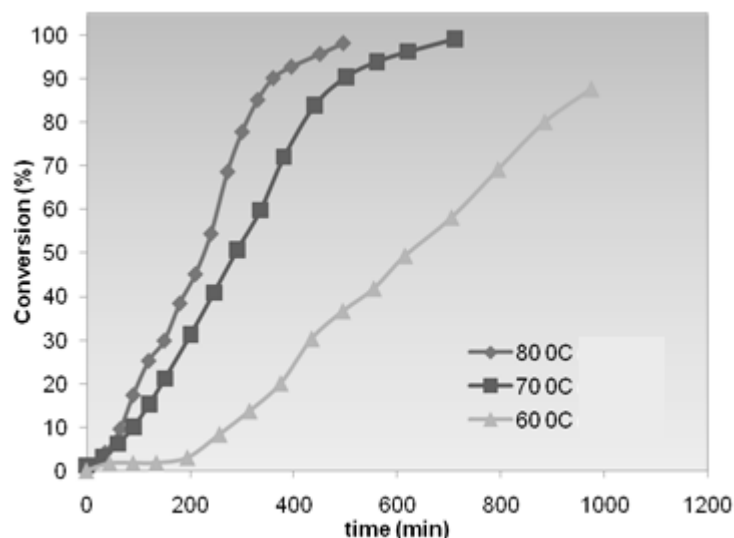


Figure 5. Effect of temperature on conversion versus time plots for batch emulsion polymerization of butadiene

The higher polymerization rate at elevated temperature for low water soluble monomers was attributed to the enhancement of initiator decomposition rate and the propagation rate coefficient. From Figure 5 and Table 3, it can be inferred that by increasing the temperature from 60 to 80°C the polymerization rate and the number of polymer particles in continuous phase volume unit considerably increased; however, the polymerization rate per particle slightly decreased. So, it can be concluded that an increase in temperature caused an increase in initiator efficiency to nuclei particles but the enhancement of initiator efficiency in particle propagation was not significant. As the number of particles increased, the average diameter of particles decreased and it caused a decrease in oligo-radical trapping efficiency of the particles. Moreover, the radical desorption from particles might increase and the number of propagating radicals per particle slightly decreased [24]. As mentioned before, the temperature increase in the range of 60 to 80°C didn't considerably change the isomer proportions. Consequently, polymerization rate enhancement through enhancing polymerization temperature will be an effective strategy for reaction time reduction if particle size variation is not important. Polymerization temperature mainly affects the number of nucleated particles and then particle size varies with temperature as a result.

#### 4. Conclusion

Polybutadiene nanoparticles were synthesized via batch emulsion polymerization of butadiene in the presence of KPS, DPR and TDM as the initiator, emulsifier and chain transfer agent, respectively. The effects of the polymerization temperature on the average particle size, polymer microstructure, gel content and reaction kinetics were studied. By increasing the polymerization temperature, average diameter of polybutadiene nanoparticles decreased from 104 nm (at final conversion of 80.6%) at 60 °C to 88.7 nm (at final conversion of 98.0%) at 80 °C. A decrease in the average diameter of nanoparticles by increasing the reaction temperature was attributed to the increase in the number

of nucleated particles. Polymer microstructure and gel content of the final polymer were affected by the reaction temperature; however, this effect was not significant. Results showed that by increasing the reaction temperature, size of the particles decreased while number of the polymer particles and the polymerization rate increased.  $R_p/N_p$  or equivalently  $\bar{n}$  was observed not to be significantly dependent on the reaction temperature. However,  $R_p/N_p$  or  $\bar{n}$  decreased slightly by increasing the reaction temperature. Such behavior was attributed to low efficiency of oligo-radical entrance in the polymer particles or possibility of the radical exit from polymer particles. Consequently, polymerization rate enhancement through enhancing polymerization temperature in the mentioned range will be an effective strategy for reaction time reduction with no significant effects on polymer microstructure where changes in the particle size are not important.

## References

- [1] F. Bovey, I. Kolthoff, A. Medalia, and E. Meehan, *Emulsion Polymerization*. New York: Interscience Pub. Inc, 1955.
- [2] M. Morton and P. P. Salatiello, "Cross-linking reaction in butadiene polymerization," *Journal of Polymer Science*, vol. 6, pp. 225-237, 1951.
- [3] M. Morton, P. P. Salatiello, and H. Landfield, "Absolute propagation rates in emulsion polymerization. II. Butadiene in hydroperoxide-polyamine systems," *Journal of Polymer Science*, vol. 8, pp. 215-224, 1952.
- [4] M. Morton, P. P. Salatiello, and H. Landfield, "Absolute propagation rates in emulsion polymerization I. Butadiene in mutual system," *Journal of Polymer Science*, vol. 8, pp. 111-121, 1952.
- [5] M. Morton, P. P. Salatiello, and H. Landfield, "Polymerization Rates in Emulsion Systems," *Industrial & Engineering Chemistry*, vol. 44, pp. 739-742, 1952.
- [6] I. M. Kolthoff and I. K. Miller, "The Chemistry of Persulfate. I. The Kinetics and Mechanism of the Decomposition of the Persulfate Ion in Aqueous Medium<sup>1</sup>," *Journal of the American Chemical Society*, vol. 73, pp. 3055-3059, 1951.
- [7] I. M. Kolthoff and I. K. Miller, "The Chemistry of Persulfate. II. The Reaction of Persulfate with Mercaptans Solubilized in Solutions of Saturated Fatty Acid Soaps<sup>1</sup>," *Journal of the American Chemical Society*, vol. 73, pp. 5118-5122, 1951.
- [8] I. M. Kolthoff, P. R. O'Connor, and J. L. Hansen, "Mechanism of emulsion polymerization of styrene with persulfate as activator in the absence and presence of mercaptan and a retarder," *Journal of Polymer Science*, vol. 15, pp. 459-473, 1955.
- [9] R. S. Bhakuni, "Kinetics of the persulfate-mercaptan emulsion polymerization of butadiene," University of Akron, 1964.
- [10] K. Ishigure, T. O'Neill, E. P. Stahel, and V. Stannett, "The Radiation-Induced Polymerization and Copolymerization of Butadiene in Emulsion," *Journal of Macromolecular Science: Part A - Chemistry*, vol. 8, pp. 353-372, 1974.
- [11] P. A. Weerts, "Emulsion polymerization of butadiene: a kinetic study," Technische Universiteit Eindhoven, Eindhoven, 1990.
- [12] P. Weerts, J. Van Der Loos, and A. German, "Initiation phenomena in the emulsion polymerization of butadiene and isoprene," *Polym. Commun.*, vol. 29, pp. 278-279, 1988.
- [13] P. A. Weerts, J. L. M. van der Loos, and A. L. German, "Emulsion polymerization of butadiene, 1. The effects of initiator and emulsifier concentration," *Die Makromolekulare Chemie*, vol. 190, pp. 777-788, 1989.

- [14] P. A. Weerts, J. L. M. van der Loos, and A. L. German, "Emulsion polymerization of butadiene, 2. Polymerizations with sodium dodecyl sulfate," *Die Makromolekulare Chemie*, vol. 191, pp. 2615-2630, 1990.
- [15] P. A. Weerts, J. L. M. Van der Loos, and A. L. German, "Emulsion polymerization of butadiene, 3. Kinetic effects of stirring conditions and monomer/water ratio," *Die Makromolekulare Chemie*, vol. 192, pp. 1993-2008, 1991.
- [16] P. A. Weerts, J. L. M. van der Loos, and A. L. German, "Emulsion polymerization of butadiene, 4. Effect of thiols," *Die Makromolekulare Chemie*, vol. 192, pp. 2009-2019, 1991.
- [17] P. A. Weerts, A. L. German, and R. G. Gilbert, "Kinetic aspects of the emulsion polymerization of butadiene," *Macromolecules*, vol. 24, pp. 1622-1628, 1991.
- [18] E. M. Verdurmen, J. M. Geurts, and A. L. German, "Particle growth in butadiene emulsion polymerization, 1. The use of Fremy salt as aqueous radical scavenger," *Macromolecular Chemistry and Physics*, vol. 195, pp. 621-633, 1994.
- [19] E. M. Verdurmen, A. L. German, E. D. Sudol, and R. G. Gilbert, "Particle growth in butadiene emulsion polymerization, 2. Gamma radiolysis," *Macromolecular Chemistry and Physics*, vol. 195, pp. 635-640, 1994.
- [20] E. M. Verdurmen, J. M. Geurts, and A. L. German, "Particle growth in butadiene emulsion polymerization, 3. Radical adsorption and desorption rate coefficients," *Macromolecular Chemistry and Physics*, vol. 195, pp. 641-645, 1994.
- [21] E. M. Verdurmen, J. M. Versteegen, and A. L. German, "Particle growth in butadiene emulsion polymerization, 4. The promoting effect of mercaptans," *Macromolecular Chemistry and Physics*, vol. 195, pp. 647-659, 1994.
- [22] R. R. Hampton, "Infrared Analysis of Low Temperature Polymers," *Analytical Chemistry*, vol. 21, pp. 923-926, 1949.
- [23] M. Abdollahi and M. Sharifpour, "Effect of carboxylic acid monomer and butadiene on particle growth in the emulsifier-free emulsion copolymerization of styrene-butadiene-carboxylic acid monomer," *Polymer*, vol. 48, pp. 2035-2045, 2007.
- [24] B. Standard, "Butadiene rubber: Determination of microstructure by infra-red spectrometry," ed, 2000.
- [25] Y. Liu, Y. Huang, C. Zhang, J. Hou, and X. Zhang, "Vulcanization of polybutadiene latex induced by  $^{60}\text{Co}$   $\gamma$  radiation," *Radiation Physics and Chemistry*, vol. 77, pp. 806-810, 2008.
- [26] J. L. Binder, "Microstructures of Polybutadienes and Butadiene-Styrene Copolymers," *Industrial & Engineering Chemistry*, vol. 46, pp. 1727-1730, 1954.
- [27] G. Odian, *Principles of Polymerization*: Wiley, 2007.
- [28] S. Deibert, F. Bandermann, J. Schweer, and J. Sarnecki, "Propagation rate coefficient of free-radical polymerization of 1,3-butadiene," *Die Makromolekulare Chemie, Rapid Communications*, vol. 13, pp. 351-355, 1992.
- [29] F. Bandermann, C. Günther, and J. Schweer, "Towards the propagation rate coefficient for the free-radical polymerization of 1,3-butadiene," *Macromolecular Chemistry and Physics*, vol. 197, pp. 1055-1069, 1996.
- [30] W. D. Harkins, "A General Theory of the Mechanism of Emulsion Polymerization1," *Journal of the American Chemical Society*, vol. 69, pp. 1428-1444, 1947.
- [31] W. V. Smith and R. H. Ewart, "Kinetics of Emulsion Polymerization," *The Journal of Chemical Physics*, vol. 16, pp. 592-599, 1948.

## سنتر نانوذرات پلی بوتادین به روش پلیمریزاسیون امولسیون: تاثیر دمای واکنش بر ریزساختار پلیمر، اندازه ذرات و سینتیک واکنش

مهدی عبداللهی<sup>۱\*</sup>، محمد رضا یوسفی<sup>۲</sup>، پریسا علمداری<sup>۱</sup>، حیدر رنجبر<sup>۲</sup>،  
فریدین سید نجفی<sup>۲</sup>، فاطمه رکابدار<sup>۲</sup>

۱. گروه مهندسی پلیمر، دانشکده مهندسی شیمی، دانشگاه تربیت مدرس، صندوق پستی: ۱۴۳-۱۴۱۱۵، تهران، ایران

۲. پژوهشکده علوم و تکنولوژی پلیمر، پژوهشگاه صنعت نفت، صندوق پستی ۱۹۹۸-۱۴۶۶۵، تهران، ایران

۳. مرکز پژوهش و فناوری، شرکت پتروشیمی تبریز، تبریز، ایران

### مشخصات مقاله

#### تاریخچه مقاله:

دریافت: ۲۹ مردادماه ۱۳۹۲  
پذیرش نهایی: ۱۸ آذرماه ۱۳۹۲

#### کلمات کلیدی:

پلیمریزاسیون امولسیون،  
نانوذرات پلی بوتادین،  
سینتیک پلیمریزاسیون،  
دمای واکنش،  
ریزساختار پلیمر

\* عهده دار مکاتبات:

رایانامه: [abdollahim@modares.ac.ir](mailto:abdollahim@modares.ac.ir)

تلفن: +۹۸ ۲۱ ۸۲۸۸۴۹۵۹

دورنما: +۹۸ ۲۱ ۸۲۸۸۴۹۳۱

### چکیده

نانوذرات پلی بوتادین به روش پلیمریزاسیون امولسیونی ناپیوسته بوتادین در راکتور بوچی مجهز به همزن مکانیکی (۳۰۰ دور بر دقیقه) در حضور آغازگر پتاسیم پرسولفات، امولسیفایر رزین تسهیم نامتناسب شده و عامل انتقال زنجیر ترشیو- دودسیل مرکاپتان در دماهای ۶۰، ۷۰ و ۸۰ درجه سانتیگراد سنتز شدند. تبدیل واکنش در فاصله‌های زمانی مختلف به روش وزن‌سنجی تعیین شد. میانگین و توزیع اندازه ذرات لاتکس پلی بوتادین توسط پراکندگی نور دینامیک و میکروسکوپی الکترونی پویایی اندازه‌گیری شد. ریزساختار پلیمرها توسط طیف‌سنجی FT-IR بررسی شد. با افزایش دما، قطر متوسط نانوذرات از ۱۰۴ نانومتر (در تبدیل نهایی ۸۰/۶ درصد) در دمای ۶۰ درجه سانتیگراد به ۸۸/۷ نانومتر (در تبدیل نهایی ۹۸/۰ درصد) در دمای ۸۰ درجه سانتیگراد کاهش یافت. ریزساختار غالب در پلیمرهای سنتزی، ایزومر ۱،۴-ترانس با مقداری در حدود ۶۰ درصد بود. نتایج نشان داد که با افزایش دما، اندازه ذرات کاهش اما تعداد ذرات و سرعت پلیمریزاسیون افزایش می‌یابد.