

Emulsifier-Free Emulsion Polymerization of *N*-Butyl Methacrylate

PIERRE BATAILLE,¹ MARJAN ALMASSI,¹ MITSUO INOUE²

¹ CRASP, Département de Génie Chimique, École Polytechnique de Montréal, C.P. 6079, Succ. Centre-Ville, Montréal, H3C 3A7, Canada

² PAPRICAN, 570, St. Jean Blvd., Pointe-Claire, H9R 3J9, Canada

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ABSTRACT: A cationic polymer of *n*-butyl methacrylate was prepared in an emulsifier-free system. Using, as a base, a 30% solid content, the variables studied were the monomer and initiator concentrations, the agitation, and the temperature. The molecular weight, the zeta potential, and the particle size were determined. The results are compared with earlier work done on similar systems. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1711–1719, 1998

Key words: butyl methacrylate; cationic polymer; emulsifier-free polymerization; agitation; activation energy

INTRODUCTION

Physical and mechanical properties of paper can be improved by various additives.^{1–6} Polymers were incorporated to paper to enhance the interfiber bonding, improve the water resistance, or to modify the fiber surface. The latex particles are deposited on the suspended fibers and remained attached during the sheet forming process. In order to facilitate the latex deposition, latex particles, bearing positive charge, are preferable because of their attraction to the negatively charged fibers.⁷

Cationic latices produced by synthesizing emulsifier-free cationic latices may improve not only the tensile strength but also the sizing properties of the paper. Another important property for this type of latex is its low polydispersity and smaller size compared with one obtained by conventional emulsion polymerization. The particle size significantly af-

fects end-use performance of paper. Finer particles can cover a greater surface area of the pulp fiber; thus, a lower amount of latex is necessary. Another important factor in choosing the polymer as a reinforcing material is to have a proper glass transition temperature (T_g). Latices with T_g closer to room temperature are preferred because of easier film-forming tendencies and lower brittleness. The cationic latices, due to their nature, are resistant to bacteria growth; thus, they can be stored for very long times.

N-butyl methacrylate (BMA) has been used as the monomer in an emulsifier-free emulsion polymerization. It was selected because BMA has a glass transition temperature near room temperature. Furthermore, in the last few years, the research done in this area was with a solid content of no higher than 10%. The purpose of the present work is to explore the polymerization conditions in order to obtain a 30% solid content and to optimize the reaction in terms of initiator concentration, agitation speed, and reaction temperature.

2,2-azobisisobutyramidine dihydrochloride, abbreviated as $\text{ABAH}_2^+2\text{Cl}^-$, was chosen as initiator. This is a water-soluble initiator decomposing to

Correspondence to: P. Bataille.

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two positively charged radicals, which will start the polymerization in the aqueous phase.⁸ These positive charges carried on the initiator will provide the stabilization of the polymer particle. The decomposition rate of this initiator is affected by temperature. In this work, the reaction rate was determined at four temperatures of 60, 70, 75, and 80°C, and the overall activation energy of the reaction for this system was determined.

To investigate the effect of mixing conditions on the rate of polymerization and particle size, four different speeds of 300, 400, 500, and 600 rpm have been chosen. The experimental results were analyzed with a theory recently proposed⁹⁻¹¹ for the emulsifier-free emulsion polymerization.

MATERIALS AND METHODS

Materials

Distilled water and hydrochloric acid were used for pH controls in all of the polymerization reactions.

N-butyl methacrylate, (the monomer), was obtained from Omega Chemical Company (Quebec, Canada) as 99% pure and with a density of 0.889 g/cm³. In order to eliminate the inhibitor, the monomer was washed three times with 5*M* sodium hydroxide solution at a volume ratio of 5 : 1, monomer-to-caustic, respectively. The washed monomer was chilled to -4°C to freeze out the residual caustic soda. The frozen caustic was then filtered out, and the monomer was stored at 4°C in a dark bottle until required. The purified monomer was used within one month.

The initiator used was 2,2-azobisisobutyramidine dihydrochloride, supplied by Wako Chemicals Company, (Richmond, Virginia) as V-50. It was kept at 4°C and was used without further purification.

Formulation

The formulation used throughout this study is given in Table I. The polymerization reactions were carried out in a 1-L round-bottomed flask with a four-necked flanged top. A total reactant mass of 350 g was normally used. A typical preparation is as follows.

225 mL of distilled water was added to the flask. A Teflon stirrer of half-moon shape was connected to a stainless steel shaft fitted with a Teflon guide and added to the central outlet of the

Table I Polymerization Conditions

Material	Condition
<i>n</i> -Butyl methacrylate	105 g
Distilled water	245 g
Concentrated hydrochloric acid	20 drops
Initiator	2.5-4 g, as indicated
Temperature	70°C, or as indicated
Speed	As indicated

flask cover. The shaft was connected to a digital motor, which indicated the agitator speed. Care was taken to ensure that the stirrer was at uniform distance from the bottom of the flask in each experiment. The water-cooled reflux condenser was added to the second outlet of the flask. A J-type thermocouple, connected to a computer, was placed in the third outlet in order to record the temperature inside the reactor. The flask was immersed in a thermostat water bath, and a thermometer was placed in the water bath (70 ± 0.5°C). A nitrogen gas blanket was maintained over the reacting medium throughout the reaction. The flow rate was maintained at a low level to minimize monomer evaporation. To prevent the back diffusion of oxygen into the system, the condenser was connected to the atmosphere via a beaker filled with water. After stirring for 10 minutes under nitrogen atmosphere, 105 g of butyl methacrylate was added to the vessel. The system was then left for 20 min to attain temperature equilibrium. The initiator was dissolved in 10 mL of water, and the weighting glass was washed down with another 10 mL of distilled water. A reaction time of 90 to 120 min was found to be adequate, although this depended on the experimental conditions. Samples were taken at different time intervals for each reaction. At the end of the reaction time, the vessel was removed from the thermostat bath and allowed to stand for a few minutes; the product was then stored in polyethylene bottles.

Sampling

A small amount of latex was removed from the reactor at given polymerization time intervals and stored in covered test tubes. The polymerization was stopped with hydroquinone. The samples were left standing for 24 h. The unreacted monomer separated out from the top layer and removed, as it may dissolve the polymer, thereby affecting the particle size and the charge density of polymer particles.

Yield

The polymer conversion was followed gravimetrically at different time intervals during the reaction.

Zeta (ζ) Potential

The zeta potential was determined from electrophoretic mobility measured using a MK-II Rank Brothers Microelectrophoresis instrument. Measurements were done in a rectangular cell at 25°C. The zeta potentials were calculated using Smoluchowski equation.

Particle Size

A laser light-scattering goniometer from Brookhaven Instruments Corporation was used to determine the particle size of the latices. Dust-free distilled water was used for dilution latex samples for measurement. The sampling were places in a paraffin bath at 25°C. The laser light was sent through two narrow adjustable windows to the sample, and the scattered beams were collected, identified, and counted by a laser detector (type TFL) adjusted on 90° from the main beam. The signals obtained from the detector were sent to a primary computer to measure and calculate particle size. The data were sent to a BI-203AT Digital Corrolator, where they were compared and correlated and then saved in a second computer.

Molecular Weights and Molecular Weight Distribution

The molecular weight and the molecular weight distributions of the polymer were determined by passing the samples through two gel permeation chromatography (GPC) columns in series, from Waters Associates Inc. (Milford, MA). The first column was an ultrastryragel-type, which has a linear pore size with an effective molecular weight of 2000 to more than 10,000,000. The second column was also an ultrastryragel-type with a pore size of 500 Å and an effective fractionation of molecular weight of 100 to 10,000.

Glass Transition Temperature

The glass transition temperature of the latex was determined via a Dielectric Analyzer, DEA 2970. The polymer was predried in an aluminum foil dish and was kept in a vacuum desiccator until placed in the two parallel plates of DEA appara-

tus. A minimum spacing of 0.5 mm was chosen between the two parallel plates, along with a ram maximum force of 250.00 N. 10 different frequencies were chosen between 0.1 and 3000 Hz for temperature of -40 to 75°C and a speed of 1°C/min. These temperature and frequency intervals let the polymer chains become rubber-like, and the movements can be verified; thus, the polymer glass transition is determined.

RESULTS AND DISCUSSION

As expected, the polymerization rate was affected by the monomer and initiator concentrations and agitation rate, as well as by the temperature. The sudden change in reaction temperature associated with the stability of latex suspension was also noticed. In order to follow the reaction temperature, a thermocouple was placed inside the reaction medium.

Polymerization Rate

It was found that the polymerization rate was affected strongly by the monomer and initiator concentration and agitation, as well as by reaction temperature. Our objective of having a 30% solid content, as compared to the usual 10% solid content, further amplify the problem of coagulation.

Effect of Monomer Concentration

In Figure 1, the effect of monomer concentration is shown. As the monomer concentration is increased, the reaction rate decreases. If one takes into account the relatively higher concentration of monomer, a higher value for n^* , the critical chain length for the formation of particle number, will result. This will give fewer but larger particles. This will also decrease the total surface of the particle and the diffusion of the monomer inside the particle. The charge density of these particles may not be large enough so that these particles may coagulate more readily and the probability of flocculation increases.

Effect of Initiator Concentration

As shown in Figure 2, the polymerization rate increased with increasing initiator concentration. This is due to the greater amount of free radicals in the system, resulting in smaller oligomers with higher critical micelle concentration (CMC).

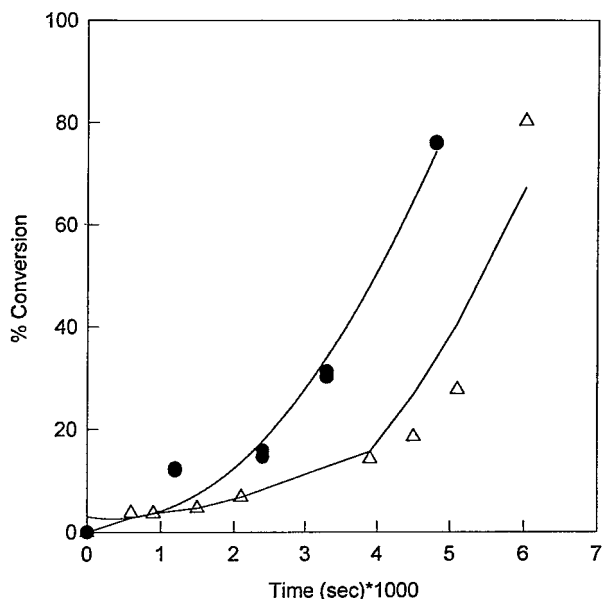


Figure 1 Rate of polymerization for different monomer concentrations at 70°C, 400 rpm, and $[I] = 3.41$ g: (●) 0.21 g of monomer per g of the total material added to the reactor; (△) 0.30 g of monomer per g of the total material added to the reactor.

Therefore, the number of particles will increase, thus increasing the chance of diffusion of the monomer in the particles and, as a consequence, increasing the polymerization rate.

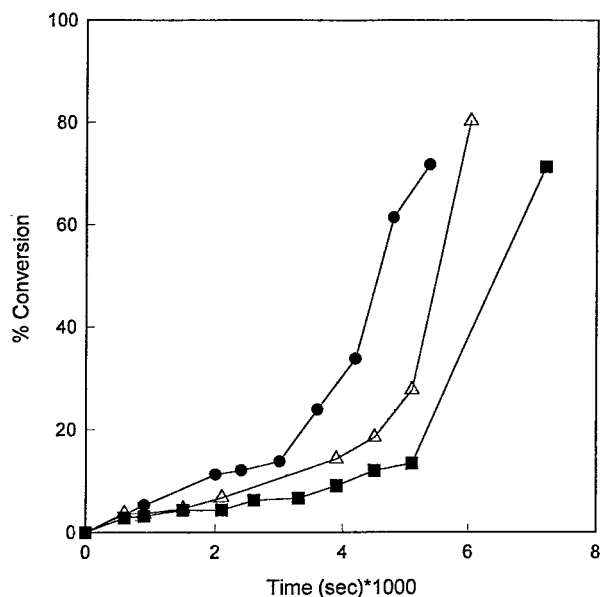


Figure 2 Effect of the amount of initiator on the polymerization rate at 70°C and 400 rpm: (■) 3.00 g, (△) 3.41 g, and (●) 3.70 g.

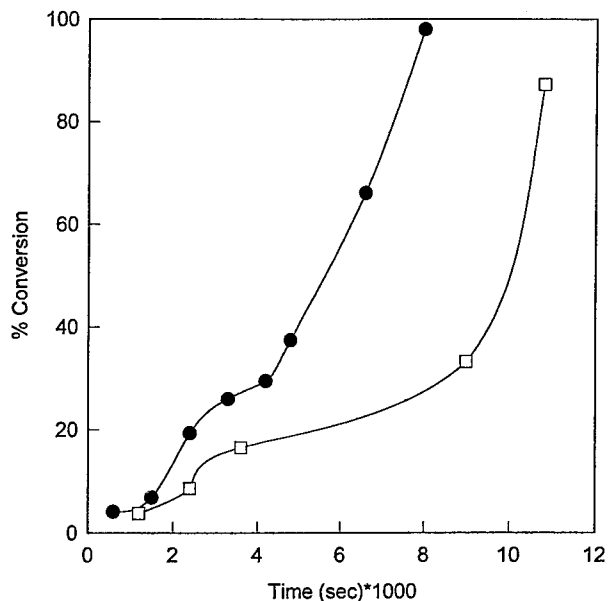


Figure 3 Effect of agitation on the rate of polymerization at 70°C and $[I] = 3.0$ g: (●) 400 rpm and (□) 500 rpm.

Effect of Agitation

Agitation has a great influence on the dispersion of the insoluble monomer in the continuous phase. As the particles produced during these reactions are larger than 500 nm, shearing will have an effect on the particles, and it will be greater with higher agitation speeds. The shear rate in these

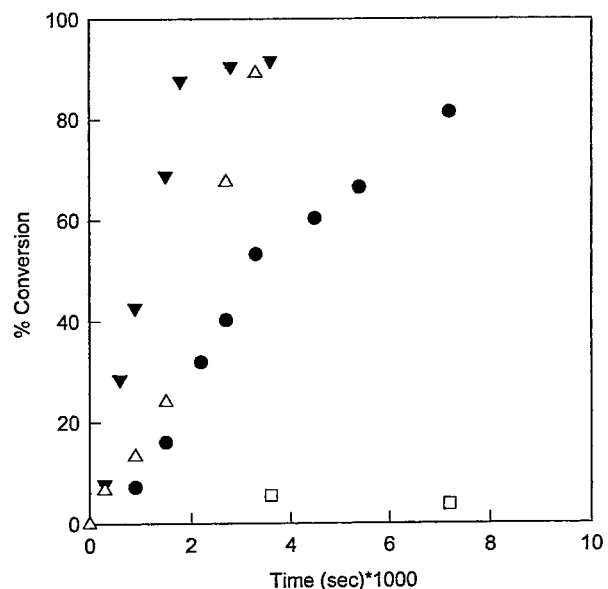


Figure 4 Effect of temperature on the rate of polymerization at 400 rpm with $[I] = 3.41$ g: (□) 60°C, (●) 70°C, (△) 75°C, and (▼) 80°C.

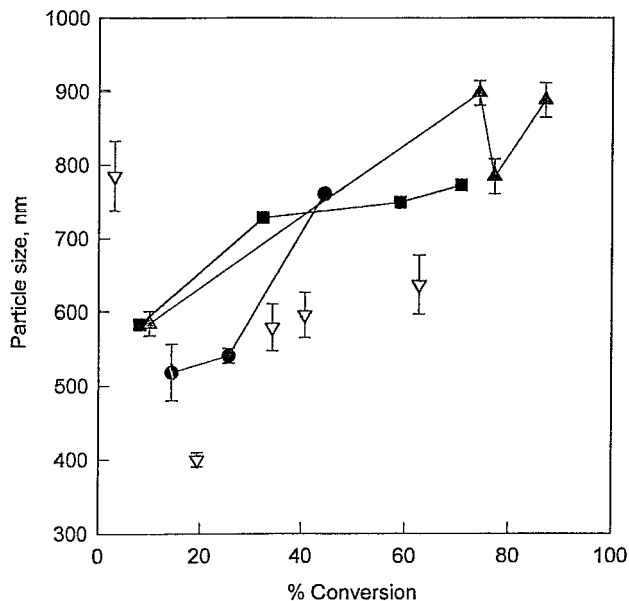


Figure 5 Variation of particle size with conversion for different amount of initiator at 600 rpm and 70°C: (●) 3.5 g, (△) 3.7 g, (□) 3.8 g, and (▼) 4.0 g.

systems is estimated to be between 66 to 100 s⁻¹. As mentioned by Nomura et al.,¹² the stirring effect is not negligible as long as the concentration of emulsifier is lower than CMC. In this case, in the polymerization system, their concentration is lower than CMC in stage 1. The initial oligomers formed will have longer chain lengths and, thus, lower CMC. The precursor particles will form rapidly. By increasing the speed, as suggested by Song and Poehlein, the radical capture by micelles will increase.¹¹ The produced oligomers will tend to adsorb onto the surface of the premier mature particles by increasing the agitation speed.¹² Therefore, the rate of micelle formation will decrease as the speed increases. This will cause a decrease in the final number of particles that decrease the coagulation at very high speeds during the reaction. At very high conversions, by increasing the particle size at which the shear rate can

Table II Zeta Potential at Different Amounts of Initiator

Zeta Potential (mV)	Amounts of Initiator (g)
15	3.5
87	3.7
91	3.8
90	4.0

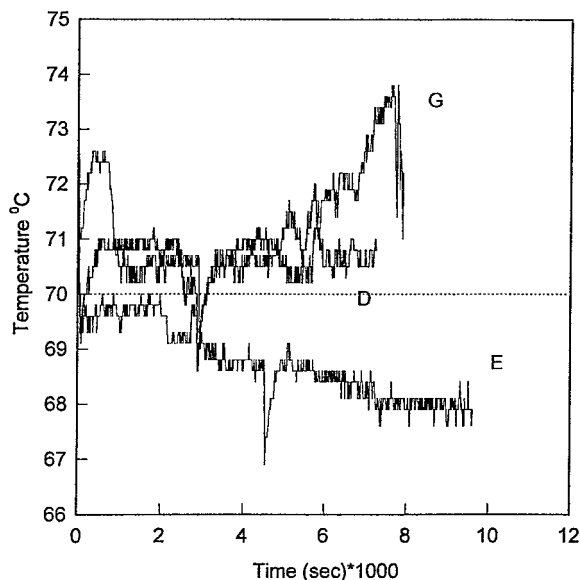


Figure 6 Recorded temperature with different amounts of initiator at 400 rpm and 70°C: exp. E, 2.7 g; exp. D, 3.0 g; exp. G, 3.7 g.

have its own effect on these particles, the coagulation of these large particles will take place. This may decrease the conversion at higher agitation,¹²⁻¹⁴ as shown in Figure 3.

Effect of Temperature

As to be expected, the polymerization rate increased with increasing the temperature, as

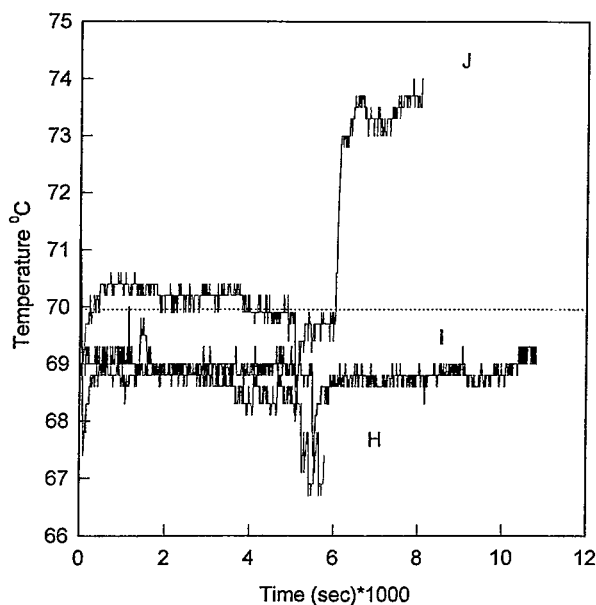


Figure 7 Recorded temperature with different amounts initiator of at 500 rpm and 70°C: exp. H, 3.0 g; exp. I, 3.4 g; exp. J, 3.8 g.

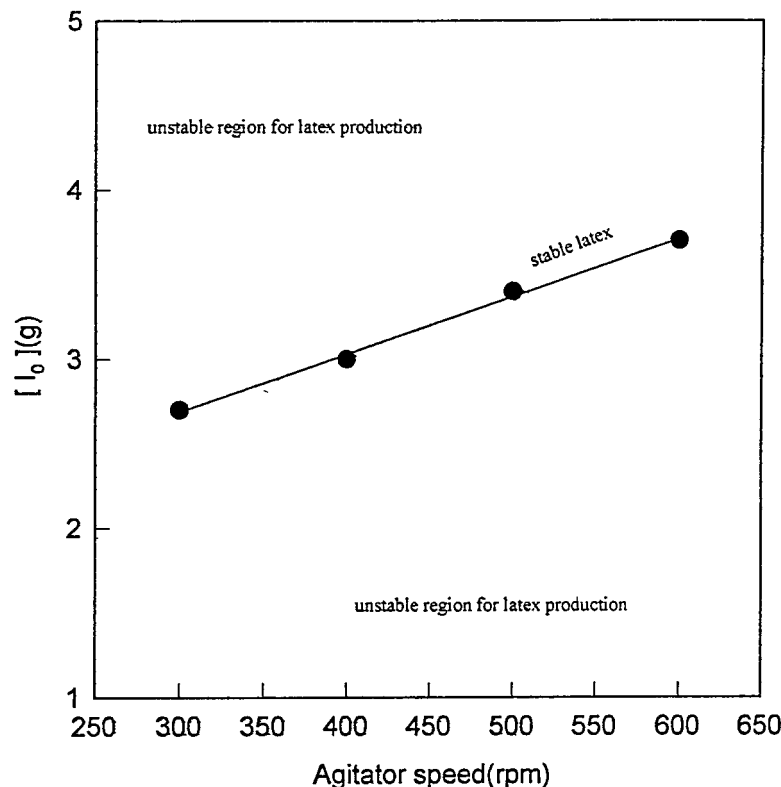


Figure 8 Initiator concentration versus agitation speed.

shown in Figure 4. Studies⁸ have shown that the half-life of the initiator radicals formed is 300 min at 60°C and 38 min at 70°C. Furthermore, the increase in temperature may increase the diffusion rate of monomer, as well as that of the polymeric radical.

Particle Size

For emulsion polymerization, the particle size usually increases with conversion. We have the same phenomena with this emulsion surfactant-free system except that, in this case, the level of initiator has a definite effect (see Fig. 5). As we go from 3.5 to 3.7 g of initiator, there is a general increase in particle size with conversion. If the initiator concentration is increased further, the particle size decreases, suggesting that we have a critical level at which an optimum particle size is attained.

At lower levels of this critical concentration, in the early stage of the reaction, long oligomer chains are produced. Having a low CMC, it is reached quickly, and the micelles will be formed rapidly. As the oligomer chains are relatively long, they will have great difficulty in maintaining

their stability as more and more monomer penetrate inside the micelle. Coagulation will occur, and an increase in the particle size takes place.

At concentrations of initiator higher than the critical concentration, the particle size will decrease. The higher amount of initiation will promote a greater amount of shorter surfactant oligomers. This will increase the CMC. The steric hindrance of the oligomers, which prevented them from diffusing through the particle surface, will decrease. The particles will retain their stability through oligomer diffusion rather than by mature particles coagulation.

Zeta (ζ) Potential

Table II shows the zeta potential at 70% conversion for different amounts of initiator. This is interesting, as it indicates that by a proper design of the experiment, one can obtain particles that have a better chance of survival in the process as the ones having the greatest zeta potential have the greatest stability.

Reaction Temperature

Probably one of the most interesting aspect of the experimental results is the variation of tempera-

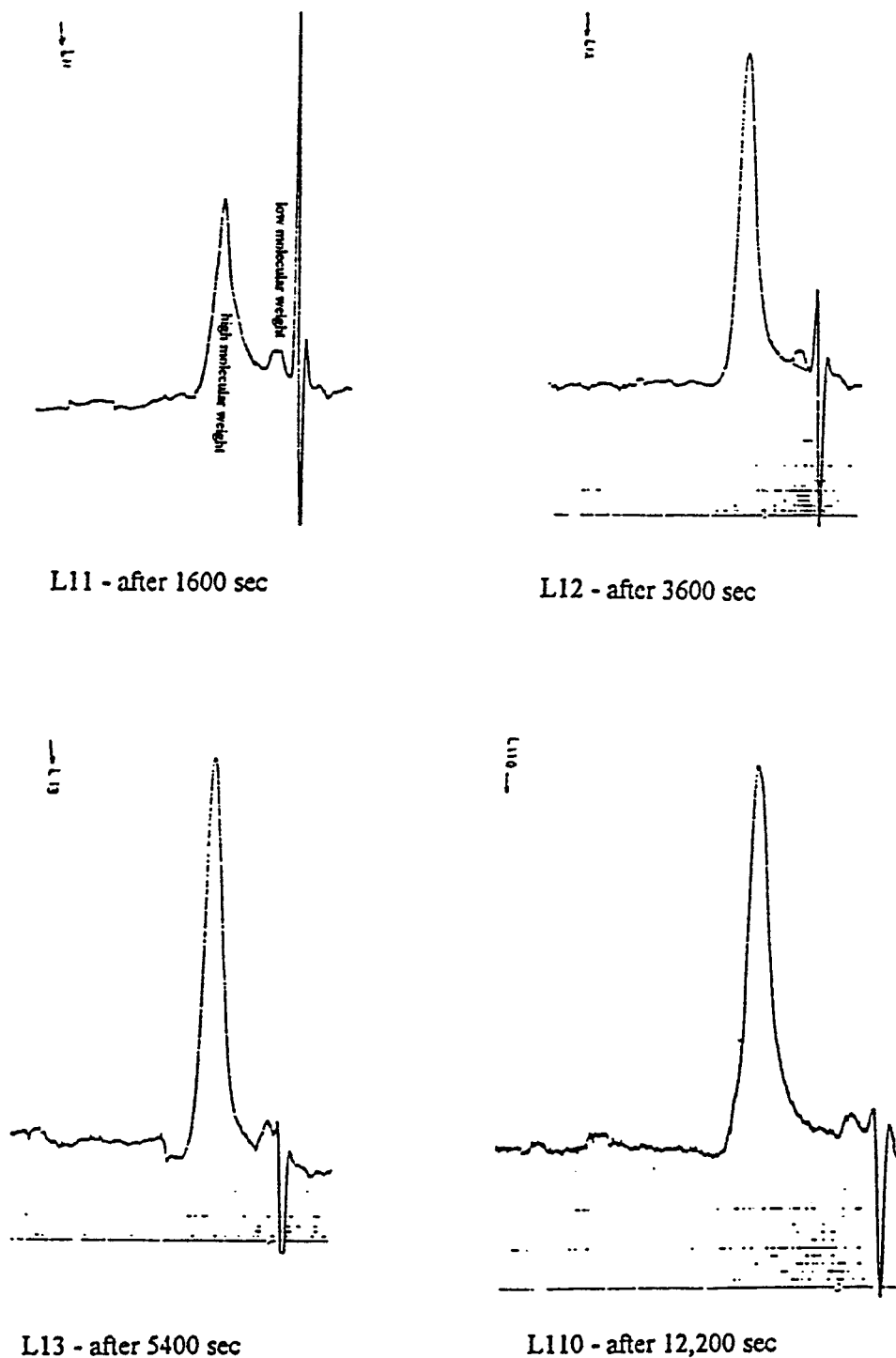


Figure 9 Typical GPC curves for agitation at 600 rpm and 3.8 g of initiator.

ture during the polymerization and its relation to coagulation.

In Figure 6, we have recorded the temperature inside the reaction medium with time and with the level of initiator. In Figure 7, we have the

same phenomena but at a different agitation speed of 500 rpm. In both cases, we have either a sudden rise in the temperature, a sudden drop, or a flat temperature record. Usually, this sudden rise or drop is associated with coagulation. Figure

8 shows the critical initiator concentration and agitation conditions at which stable BMA latex can be produced. For each agitation speed, a specific concentration of initiator is required to have a steady reaction rate.

The following consideration might help in order to elucidate this phenomena. The activation energy of this reaction was found to be 9.37 kcal/mol. This was obtained from the reaction rate at a different temperature and by applying Arrhenius equation. This value is much lower than the activation energies reported for this monomer in other systems.^{15,16} Furthermore, this exothermic or endothermic aspect of these reaction may be attributed to the way the reaction terminates. As shown by workers,¹⁷ the activation energy of termination is different when the reaction terminates by disproportionation rather than by combination. This might affect the overall energy of the reaction at the end of the reaction. Due to agglomeration problems, it was difficult for us to obtain samples for molecular weight analysis.

MECHANISM OF EMULSIFIER-FREE EMULSION POLYMERIZATION

Several particle nucleation mechanisms have been proposed for the emulsifier-free systems. Fitch¹⁸ has suggested a homogeneous nucleation mechanism by which growing oligomeric free radicals precipitate from the aqueous phase when they reach a critical chain length n^* to form a primary particle. Coagulation of terminated free radical was proposed by Ugelstad and Hansen.¹⁹ Micellar type nucleation takes place as growing free radicals attain a size and a concentration at which they become surface active and undergo micellization.^{20,21}

Munro et al.²² suggested that none of the three mechanisms alone can predict nucleation for all the monomers. As with emulsifier containing polymerization, the solubility of monomer in water has a great influence on the mechanism.^{23,24}

Song and Poehlein,⁹⁻¹¹ in a series of articles, have suggested a two-stage model of particles formation. Stage 1 is characterized by the generation of a large number of micelle-like oligomeric particles. These oligomeric particles lose their stability and begin to undergo particle coagulation at the end of stage 1 due to the decrease of the surface charge density. Stage 2 begins with a decrease in particle number due to coagulation. An equilib-

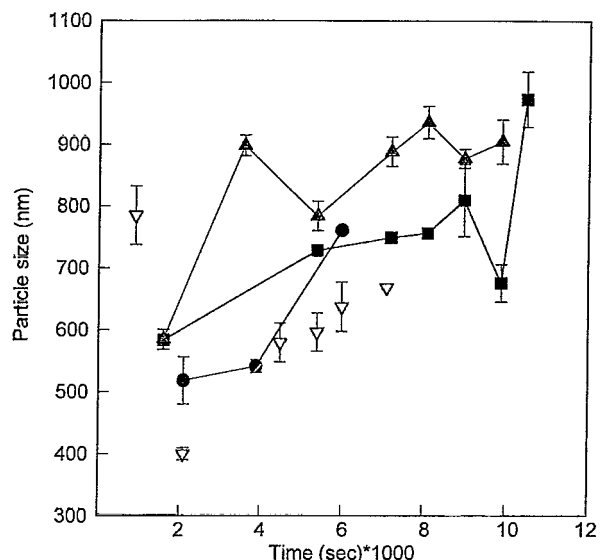


Figure 10 Effect of the amount of initiator on the particle size for agitation at 600 rpm and 70°C: (●) 3.5 g, (△) 3.7 g, (□) 3.8 g, and (▼) 4.0 g.

rium will be established between particle nucleation and particle coagulation.

From the experimental results obtained, the mechanism of the polymerization and of the particle formation is similar to the one proposed by workers using styrene^{10,11} as a monomer in an emulsifier-free aqueous polymerization. This should not be of a great surprise as both BMA and styrene has the same low solubility in water. One of the key points of this theory, as discussed previously, is the formation of the critical chain length n^* of growing radicals. This will change with the monomer or the initiator concentration; this, in turn, will affect the CMC of the growing oligomers.

This was considered as stage 1. After this initial stage, the particle number continues to increase, and particles grow through polymerization. The mechanism of radical capture by particles will eventually become much more significant than aqueous phase termination. This is considered as stage 2.¹⁰

In Figure 9, it can be seen that at early stages of the polymerization, low-molecular-weight oligomers are made and remain throughout the reaction. This formation of low-molecular-weight polymers, of less than 1000, was also observed by other workers^{13,18} using styrene. The particle size analysis (see Fig. 10) show that there is a rapid growth in the particle size of the polymer at stage 2 of the reaction where, as indicated earlier, the polymerization continues

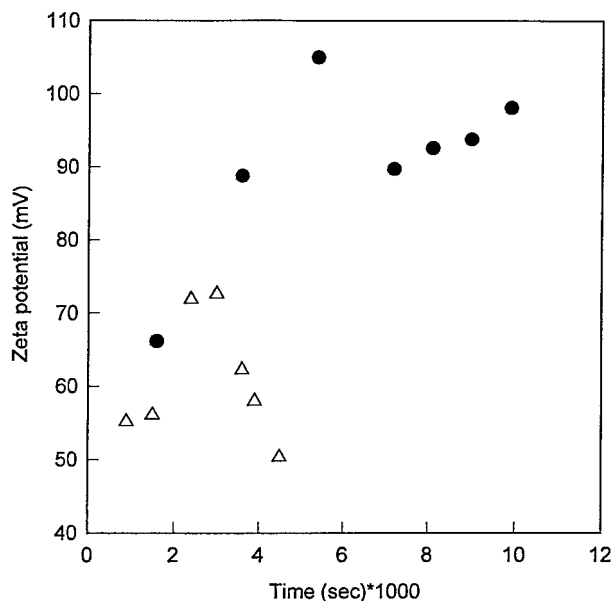


Figure 11 Effect of agitation on the zeta potential at 70°C with 3.8 g of initiator: (▼) 500 rpm and (●) 600 rpm.

inside the micellized particles. Furthermore, the rapid increase of the zeta potential in the first half hour of reaction (Fig. 11), which is the particle formation stage, indicates that the particle formation takes place by micellization nucleation. This cannot be observed in the homogeneous nucleation of particles.^{10,11}

CONCLUSION

A high solid content (30%) of an emulsifier-free *n*-butyl methacrylate was obtained. Due to the high concentration of monomer present, a delicate balance must be struck between the initiator and monomer concentration, as well as agitation. For each agitation speed, the optimum concentration of initiator was found in order to obtain a stable latex. The glass transition temperature of the polymer is 36°C and is on the low side of a desired value as a sizing agent, but it may be considered for certain applications. The overall activation energy for this polymerization was found to be 9.37 kcal/mol. The polymerization mechanism of BMA was found to follow the same mechanism suggested by Song and Poehlein for styrene.

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