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Study on emulsion copolymerization of styrene and *n*-butyl acrylate

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SUMMARY

The emulsion copolymerization of styrene and n-butyl acrylate has been investigated. Copolymers were obtained at 70ºC in the presence of sodium lauryl sulfate, an anionic micelle generator and ammonium persulfate as initiator. The ideal time of reaction, the effect of the amount of initiator, temperature and comonomer composition were also studied. The copolymers have been characterized through gel permeation chromatography (GPC) and Fourier transform infrared spectroscopy (FTIR).

INTRODUCTION

Emulsion copolymerization is a process very important to produce copolymers with varied compositions for a wide range of aplications (1). It is well known that the copolymer properties are determined by their molecular weight distributions and nature, relative quantities and arrangement of the monomeric units along the polymer chains. However, all these parameters are dependent on the type of copolymerization process (1-4). Several studies have been made on the mechanism and kinetics of emulsion copolymerizations. However few papers have been published about the emulsion copolymerization of styrene and n-butyl acrylate. The emulsion copolymerization of styrene and n-butyl acrylate requires special attention because of the nature of its components. It is known that the water solubility of monomers influences the final characteristics of the product. The water solubility at 70ºC of butyl acrylate is approximately four times the solubility of styrene that is considered the ideal monomer for emulsion polymerization (5-6).

The purpose of this paper is to present a study of the emulsion copolymerization of styrene and n-butyl acrylate. The ideal time of reaction, temperature,initiator concentration and comonomer composition were studied.

EXPERIMENTAL PROCEDURES

Materials

The monomers, styrene (STY) and n-butyl acrylate (BuA), from Rohm and Haas, commercial products were vacuum distilled

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after the removal of inhibitor and then stored at -5ºC under nitrogen. Reagent grade ammonium persulfate (AP), sodium hydrogen fosfate (SHF), lauryl sodium sulfate (LSS), toluene, acetone, isopropanol, methanol, hydrochloric acid and ethyl alcohol were used without further purification. Water, distilled and deaerated by purging with N_2 freed from O_2, was employed for the preparation of the polymerization recipes and all standard solutions.

Polymerization

Polymerizations were carried out in 1 liter, glass reactor, equipped with a mechanical stirrer, a termocouple, a temperature indicator and an inert gas inlet. The system was heated by circulating silicon oil through the cylinder-jacket of the reactor.

The reactor was initially loaded with distilled water and deaerated, at constant agitation speed (250 rpm), with N_2 freed from O_2, for a 15 min period. The emulsifier was added, and the stirring speed and nitrogen flow were reduced to avoid foam formation. The temperature was slowly raised to 70 ± 0.2ºC. A deaerated water solution containing the electrolyte and the purified monomers, BuA and STY were then added. A deaerated water solution of initiator was added at the beginning of each polymerization run. In all cases the reaction was carried out under a nitrogen atmosphere. Samples were colected and the reaction was stopped by the addition of hydroquinone.

The global conversion was determined by gravimetric analysis. The copolymers were coagulated by adding to the latex, drop by drop and with agitation, isopropanol. After filtration the copolymers were dried in an air circulation oven at 120ºC for 12 h.

To study the effect of the monomer composition, the copolymers were dried in a vacuum oven at 50ºC for 24 h. The copolymers were purified by dissolution in acetone (samples 1,2 and 3) or toluene (samples 4,5 and 6) and precipitation in methanol (1:10), separated by decantation and dried in the conditions described above.

Characterization of the Copolymers

The molecular weight of the copolymers was determined by gel permeation chromatography, GPC (Waters, Model 150-C ALC/GPC). The copolymers were eluted with 1,2,4-trichlorobenzene (lichrosolv) through columns of ultrastyragel with pore sizes of 10^6, 10^5, 10^4 and 10^3 Å at 135ºC. The copolymers were characterized by Fourier transform infrared spectroscopy, FTIR (Perkin Elmer, Model 1750). The samples 1,2 and 3 were solubilized in acetone and 4,5 and 6 were solubilized in toluene. The solution concentration for all samples was 1.5% w/v. On a NaCl crystal was put 0.1 ml of each solution. The solvent was evaporated and for each sample were made 50 scans in the range of 4000-500 cm^{-1}.

RESULTS AND DISCUSSION

Prelimirary reactions were made to select the reaction conditions to be used during all experimental work. The conditions for the preliminary study were based on data of literature (2,5,7). From this study were selected the temperature and time of copolymerization.

The temperature is a very important factor in the emulsion polymerization because it affects the ordinary parameters of any polymerization reaction and in this case also the latex morphology.

To select the copolymerization temperature four experiments at 60, 65, 70 and 85ºC were carried out. Figure 1 shows the effect of the temperature on the conversion in the emulsion copolymerization of STY and BuA. It was observed a limiting conversion around 40% at 60ºC, 75% at 65ºC, 84% at 70ºC and 90% at 85ºC.

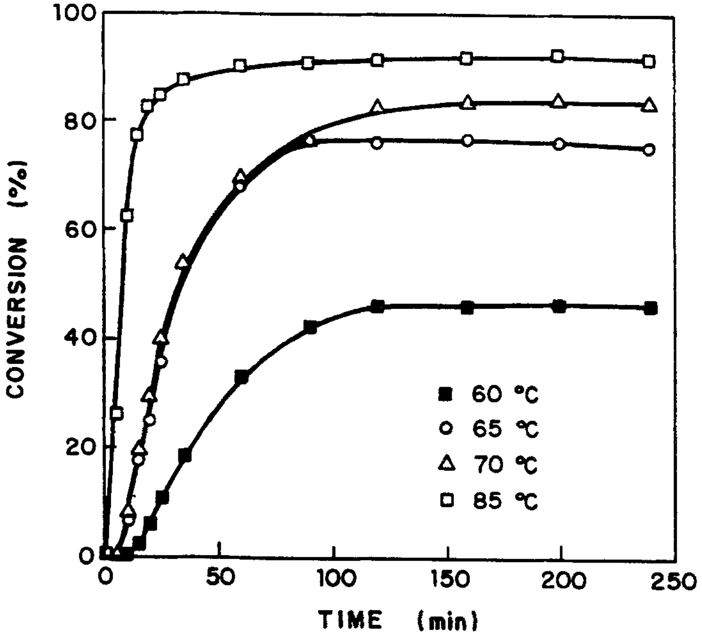

Figure 1: Conversion **versus** time for STY-BuA copolymerization Effect of polymerization temperature BuA=3.9x10^{-1}mol, STY=4.8x10^{-1}mol, LSS=2.6x10^{-1}mol, AP=3.9x10^{-4}mol, SHF=6.3x10^{-4}mol, water=750g

As expected at 60ºC, was observed a higher induction period than at higher temperatures. For posterior studies the temperature of 70ºC was selected.

The conversion curve **vs** time (Figure 2) for the copolymerization shows that in the first 150 min, the reaction has attained the maximum conversion (approximately 85%). This value of limiting conversion is common for copolymerizations with high proportion of BuA (5).

From Figure 2, was chosen the ideal time of copolymerization, that is, the time in which the conversion has attained a "plateau". In the reaction conditions employed in this study that time was 150 min.

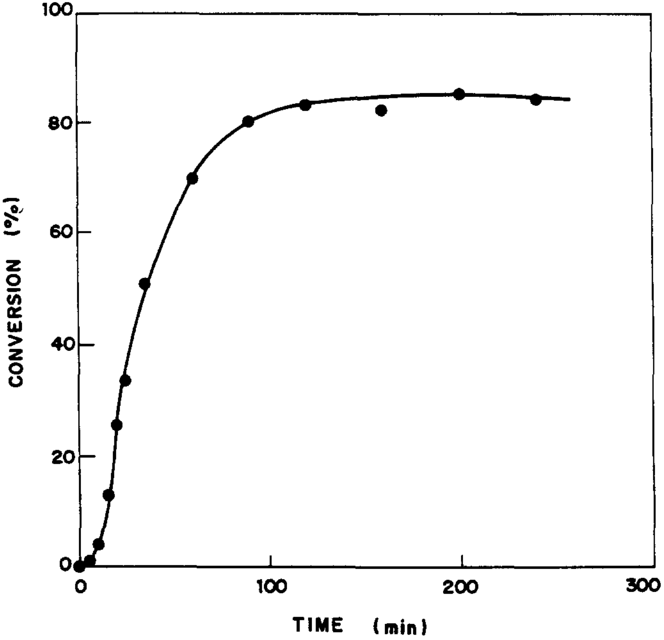

Figure 2: Conversion **versus** time for STY-BuA copolymerization at 70ºC
BuA=$3.9x10^{-1}$mol, STY=$4.8x10^{-1}$mol, LSS=$2.6x10^{-1}$mol, AP=$3.9x10^{-4}$mol, SHF=$6.3x10^{-4}$mol, water=750g

It is known that the initiator concentration is a very important variable in the emulsion copolymerization of STY with BuA. This parameter affects the overall reaction rate, the molecular weight of the copolymer and consequently its viscoelastics properties (1). The rate of copolymerization and the limiting conversion increase as the initiator content increases (2,5,8,9). In this study, four different initiator concentrations were used (1.8, 2.9, 5.2 and $6.4x10^{-4}$M) with the other reaction parameters kept constant. The curves of overall conversion **vs** time (Figure 3), show that the rate of copolymerization and the limiting conversion increased as the initiator concentration increased.

At a concentration of ammonium persulfate of $1.8x10^{-4}$M, the lowest value of limiting conversion (approximately 34%) was obtaneid, and the highest induction period for the reaction of copolymerization was observed.

The study of the variation of comonomer composition was performed in the same way as described for the other parameters. The reaction overall conversion was determined and the polymers were characterized by infrared spectroscopy and gel permeation chromatography. From Figure 4, can be seen that, in the same synthesis conditions, the rate of polymerization was higher for BuA than for STY. The conversion curves **vs** time for the copolymerizations are between the curves of the respective

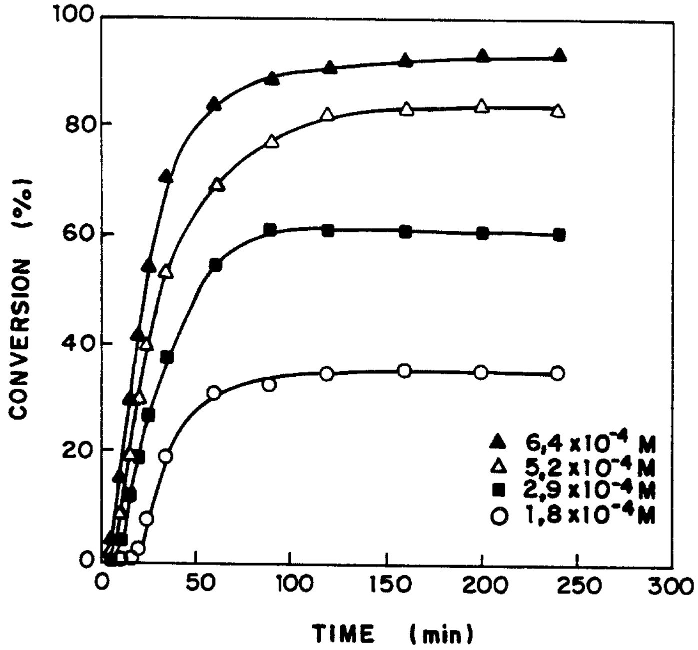

Figure 3: Conversion **versus** time for STY-BuA copolymerization
Effect of initiator
BuA=3.9x10^{-1}mol, STY=4.8x10^{-1}mol, LSS=2.6x10^{-1}mol,
SHF=6.3x10^{-1}mol, water=750g, T=70ºC

homopolymerizations. It was observed the lowest limiting conversion and the highest induction period for the homopolymerization of BuA. It is known that, the reactivity ratio of STY is higher than the reactivity ratio of BuA, consequently the acrylic radical adds more readily to STY than styril radical to BuA. In the presence of a small amount of BuA, the terminal units are therefore largely STY and the penultimate units being either STY or BuA. Considering BuA being a penultimate unit of the macroradical, there is a possibility of this unit in offering steric repulsion reduces the termination rate leading consequently to a higher rate of polymerization. Thus for compositions with high proportion of BuA, the terminal units containing this monomer will be predominant, resulting on a increase of the copolymerization rate. These results show that, the reactivities of radicals play a more important role in determining the magnitude of the propagation rate constant than the reacitivities of the monomers (10).

The induction period depends on the concentration of initiator as well as on the nature of the monomer. The induction period appears to be related to the water solubility of the monomer. For more soluble monomers, the polymerization takes place to some extent in the aqueous phase before it proceeds in the micellar phase. As the rate in solution is

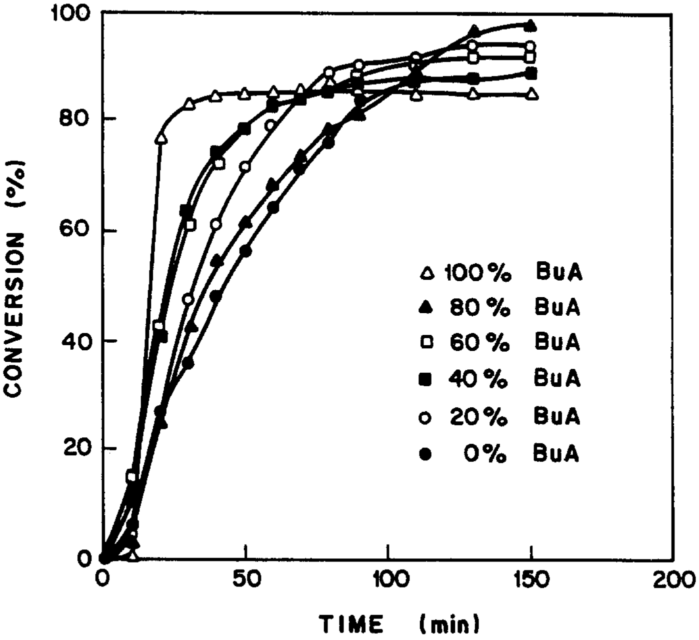

Figure 4: Conversion **versus** time for STY-BuA copolymerization Effect of monomer composition AP=3.9x10^{-4}mol, LSS=1.7x10^{-2}mol, water=700g, T=70ºC

lower than the rate of emulsion polymerization, the induction period in that case will be higher (10).

Guillot (11) et al., studied the emulsifier free emulsion copolymerization of STY with BuA and they concluded that the effect of monomer composition variation was analogous to the effect of the same copolymerization in the presence of sodium sulfate dodecyl. The authors verified a great increase in the rate of polymerization for pure BuA. They also observed that the values of limiting conversion decreased with the increase of the amount of BuA in the feed. Acoording to the authors, the copolymerization rate increase for the system with high proportion in BuA, could be provoked by an increase of the average number of radicals ($\bar{n}$) per particle, resulting from gel effect or from a floculation of small particles leading to the oclusion of oligoradicals. This rate increase would correspond to a large decrease of the termination rate constant, as it is assumed in bulk conditions.

During this study, was observed the occurrence of a large gel effect for the homopolymerization of BuA. In the begining of the reaction (10 min), was observed a sudden raise of the temperature from 70ºC to 84ºC, returning and stabilizing at 70ºC after 20 min.

CONCLUSIONS

The ideal temperature for emulsion copolymerization of STY with BuA was 70ºC. In this temperature, the time necessary to attain the maximum conversion was 150 min.

The variation of monomer composition affected the overall rate of copolymerization. The rate of polymerization was higher for the system with 100% of BuA and much more smaller for the system with 100% STY. The conversion curves **vs** time for the copolymers were between those of the homopolymers. In the system with 100% of BuA, was observed a larger gel effect in the begining of the reaction, indicated by a sudden increase of the temperature medium.

It was obtained polymers with ultrahigh molecular weight ($>10^6$) due to the absence of a transfer agent. Hence, it was not possible to determine the real values of molecular weight, because they were out of the calibration curve of the GPC apparatus.

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