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Suspension Polymerization of Styrene with Tricalcium Phosphate as Stabilizer

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Abstract : Suspension polymerizations of styrene were conducted in the aqueous phase with tricalcium phosphate (TCP) as a stabilizer and α, α'-azobis(isobutyronitrile) (AIBN) as an initiator. Various amounts of initiator and stabilizer were selected and the reaction was carried out at a selected temperature between 60 to 80°C. It was found that the combination of 5 wt% stabilizer and 2.427×10^{-3} mol/L of costabilizer is the minimum amount for suspension polymerization reaction to produce particles in the aqueous phase. Particles were found to be polydisperse in diameter, regardless of reaction conditions. Glass transitions were observed to be around 95°C, nearly independent of reaction temperature and initiator. Homogenizer was found to be essential in forming particles in the proximity of tens of micrometers in diameter in suspension polymerization with TCP as stabilizer.

Introduction

Spherical polymeric particles find a wide variety of applications in areas, such as standards for particle separation, column packing materials, paintings, cosmetics, drug delivery vehicles, toners and electrophotographic image display. Controlling particle size and its uniformity in these polymerization reactions have been of major interest. It is particularly challenging to produce particles with narrow dispersity in diameter and molecular weight.

There are several ways of forming micron-sized particles by polymerization reaction. Among these, emulsion polymerization is the most widely studied reaction technique with regard to its mechanism and particle size.[1-6] As emulsion polymerization usually produces submicron-sized particles, seeded emulsion polymerization technique is employed to increase particle size.[7-10] Dispersion

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polymerization is a technique which is often used to produce monodisperse particles in diameter.[11-15] In this method, a nonpolar organic medium such as hydrocarbon is usually selected as a reaction medium.[16] Recently, monodisperse particles were successfully synthesized in polar media, such as alcohols, mixtures of alcohols and water and ether.[17,18] There was a report by Shen *et al.*[19,20] that monodisperse particles were prepared using poly (vinyl pyrrolidone) as stabilizer in an alcohol. Takahashi *et al.*[21] have investigated the effect of solvents in dispersion polymerization using a mixture of good and poor solvents, and found that dispersity could be adjusted by controlling the ratio between the two kinds of solvents. Particles produced by these dispersion polymerization reactions rarely exceed 5 μm in diameter. In terms of application to industrial scale, however, suspension polymerization is most popular since it uses water as reaction medium. It is well known that suspension polymerization usually produces polydisperse particle distributions, especially with water-insoluble stabilizers, such as tricalcium phosphate,[22] magnesium hydroxide,[23,24] and other inorganic chemicals. Beads prepared by suspension polymerization with these stabilizers usually exhibit diameters ranging from 50 μm to a few millimeters.

As we focus our attention on polymeric composite particles with their diameters ranging from 5 to 15 micrometers, we have recently selected to prepare these particles by suspension polymerization. Tricalcium phosphate (TCP) was selected as stabilizer, as it is often used in industry for polymerization of acrylonitrile. A high-speed homogenizer was adopted to minimize particle size in addition to a typical suspension polymerization method. Styrene was chosen as a monomer and its reacti-vity was studied.

Experimental Details

Materials. The styrene monomer, 2,2'-azobis-isobutyronitrile (AIBN, initiator), tricalcium phosphate (TCP) and sodium lauryl sulfate (SLS) are Junsei Chemical products. The water used for polymerization was distilled water prepared in our lab. Methanol is analytical reagent grade from Mallinckrodt Co., and nitrogen was purchased from Sugi Industries Gas Co.

Polymerization. Prior to polymerization, phenolic inhibitors added to the styrene monomer was removed by washing three times with 10% sodium hydroxide solution and then three times with water or deactivated by bubbling nitrogen through the mixture.

Polymerization was carried out in a 1-liter kettle reactor with internal stirring. The reactor was 10.7 cm wide and 16 cm high. A four-blade stirrer was placed at 1/5 height from the bottom to the top of the reactor, where each blade was 3.5 cm in length. The reactor was immersed in a thermostated water bath to maintain a constant temperature. A water-cooled condenser, which was connected to the atmosphere via a wash-bottle containing water, was fixed to the reactor to prevent back-diffusion of oxygen into the reacting system. Nitrogen was bubbled through a thin teflon tube into the reactor.

Usually, the ratio between monomer and water was 1 to 3 by volume. Typically, 200 mL of the styrene monomer and 600 mL of water were used. A specified amount of initiator dissolved in monomer was added to the reacting system with stabilizer and was subjected to high-speed mixing with a Fisher Powergen 700D homogenizer. Then, the mixture was placed into the reactor and nitrogen was bubbled through to exclude oxygen from the reacting system. The stirring speed was

Table I. Various Reaction Conditions with Different Amounts of Initiator and Stabilizer at Different Temperatures

Reaction	1	2	3	4	5	6	7
Monomer(mL)	200	200	200	200	200	200	200
Initiator(g)	0.4	0.8	1.6	0.8	0.8	0.8	0.8
Distilled Water (mL)	600	600	600	600	600	600	600
Stabilizer(g)	10	10	10	6	14	10	10
Temperature(°C)	70	70	70	70	70	60	80

maintained at 600 rpm with a digital controller. The reaction was sustained for several hours, depending on temperature, initiator and stabilizer concentration. At selected intervals, aliquots were removed from the reactor and conversion and bead size were determined. When the reaction was over, most solid beads sedimented at the bottom of reactor. They were isolated, washed with water and methanol, to remove unreacted initiator and monomer. Beads were then dried in a vacuum oven at 40°C.

Characterization

Gel Permeation Chromatography (GPC). The molecular weight of polystyrene beads was determined by gel permeation chromatography (Waters, Model 6000-A) using calibration curves with PS standards.

Differential Scanning Calorimetry (DSC). Glass transition temperatures (T_g) were determined with a differential scanning calorimeter (DSC-4, Perkin-Elmer) which was repeatedly calibrated with indium standards for maximum accuracy. Samples were heated to 200°C for 2.5 minutes and quenched to room temperature. After 3 minutes, samples were slowly heated to 200°C at 10°C/min. T_g was identified at the midpoint of the endothermic displacement between linear baselines.

Results

The effect of polymerization temperature is shown in Figure 1. When reaction was carried out at 60°C, conversion reached only 40% after 8 hours of reaction, and did not form particles. Reaction at 70 and 80°C showed 85 and 86% conversion, respectively. When these two reactions were done, however, there was a large amount of materials floating on the surface. Increase in reaction temperature led to decrease in molecular weight as seen in Table II.

Conversion of PS beads with various amounts of stabilizer was plotted against reaction time (Figure 2). Although the initial reaction rate of reaction was nearly the same among the three reactions, the reaction with 3 wt% stabilizer stopped at 30%

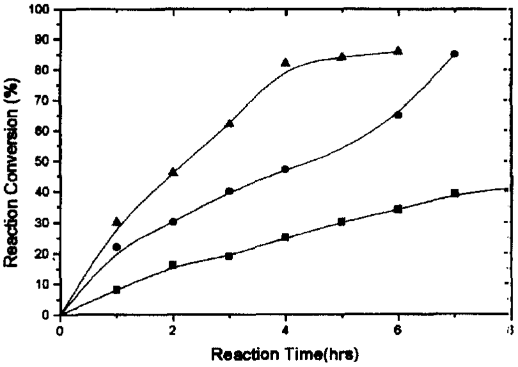

Figure 1. Conversion of polystyrene in suspension polymerization with 5 wt% TCP as stabilizer and 0.4 wt% initiator at various reaction temperatures: ■ : Reaction 6, ● : Reaction 2, ▲ : Reaction 7.

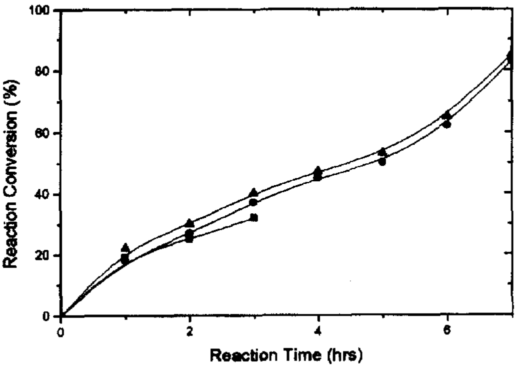

Figure 2. Effect of the amount of stabilizer in suspension polymerization of styrene with 0.4 wt% initiator at 70°C:■ : Reaction 4, ● : Reaction 2, ▲ : Reaction 5.

Table II. Change in Molecular Weight, Polydispersity Index and Conversion Depending on Various Reaction Conditions Specified in Table I

Reaction	1	2	3	4	5	6	7
M_n (g/mole)	130,000	90,100	54,600	-	82,700	-	68,600
M_w (g/mole)	597,600	283,000	137,900	-	212,072	-	211,644
PDI	4.6	3.14	2.53	-	2.56	-	3.08
Conversion(%)	64%	85%	87%	32%	83%	41%	86%

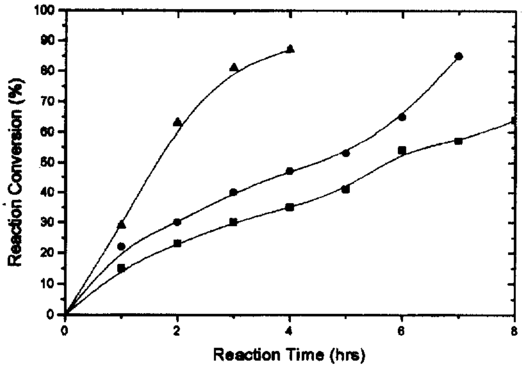

Figure 3. Effect of the amount of initiator in suspension polymerization of sytrene with 5 wt% TCP as stabilizer at 70 °C: ■ : Reaction 1, ● : Reaction 2, ▲ : Reaction 3.

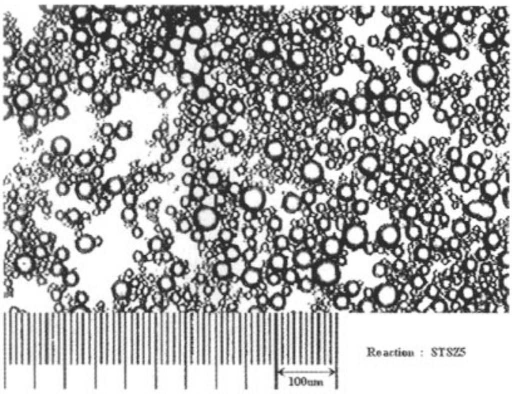

Figure 4. Optical microscopic photograph of synthesized polystyrene particles by suspension polymerization with 5 wt% TCP as stabilizer and 0.4 wt% AIBN as initiator at 70 °C.

conversion and reactants agglomerated. Molecular weight measurements exhibited a slight decrease in both number and weight average molecular weights with increased amount of stabilizer.

Reaction rate is found to be sensitive to initiator concentration as illustrated in Figure 3. Three initiator concentrations of 0.2, 0.4 and 0.8 wt% were selected and tried. When 0.2 wt% initiator was used, reaction reached 65% conversion after 8 hours. Conversion reached nearly 90% after 4 and 7 hours of reaction with 0.8 and 0.4 wt% initiator, respectively. Increase in initiator concentration contributed to decrease in both number and weight average molecular weights and their ratio. Glass transition temperatures did not show any difference, and found to be around 95 °C, regardless of initiator concentration.

Polymeric particles prepared in suspension polymerization with 5 wt% TCP as stabilizer exhibited polydispersity in size of polystyrene beads (Reaction 2) as illustrated in Figure 4. Particle diameter ranges from a few micrometers to 40 μm. Increased amount of stabilizer decreased particle diameter ranging from a few to 30 μm.

Discussion

Suspension polymerization is usually conducted in the aqueous phase with a water-soluble stabilizer such as polyvinyl alcohol or cellulose to obtain submicron particles. As we attempt to produce micron-sized particles, we selected a heterogeneous stabilizer of TCP in order to form particles in the aqueous phase. TCP is an inorganic and hydrophilic material, often used in industry. We, however, found that a small amount of sodium lautyl sulfate (SLS) must be added as costabilizer for reaction to take place and produce stabilized particles. It was observed that 2.427 × 10^{-3} mol/L of SLS was the minimum concentration of costabilizer necessary to form particles. As higher costabilizer concentration tends to produce micelles,[25] we have used the minimum concentration of 2.427 × 10^{-3} mol/L of SLS throughout reactions.[26] Once reaction was over, particles ranging from a few micrometers to 50 micrometers formed (Figures 4 and 5) and sedimented at the bottom of

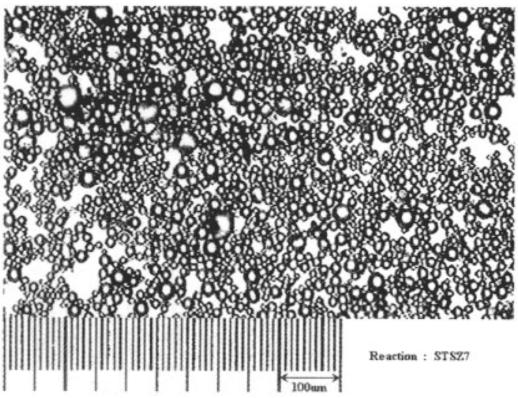

Figure 5. Optical microscopic photograph of synthesized polystyrene particles by suspension polymerization with 7 wt% TCP as stabilizer and 0.4 wt% AIBN as initiator at 70 °C.

the reactor. Beads were isolated and washed with water and methanol to remove unreacted monomer, and then with an 0.1 N-HCl solution to dissolve out TCP and retrieve beads.

Particles in suspension polymerization reaction with a water-insoluble stabilizer, such as TCP, appears to be unstable, as reaction agents often agglomerate in the midst of reaction. In order to ameliorate this problem, we employed a homogenizer to form preparticles, prior to polymerization reaction. These preparticles, once formed, were found to maintain their size till the end of reaction. We used 10 minutes of stirring at 5,000 rpm with the homogenizer. It was observed that the size of preparticles, though, do not seem to be affected by stirring time and speed, as they maintained their early size throughout reaction. Preparticles of monomer containing initiator may be surrounded by TCP particles in the course of mixing with the homogenizer and stable particles formed. We also used a small amount of sodium lauryl sulfate as costabilizer in order to reduce surface tension and thus enhance compatibility between monomer preparticles and water. When costabilizer was not added, reaction was unstable and particles agglomerated. None of the reaction conversion showed completion. When reaction was over, a portion of products always floated on the surface of suspension, which means a conversion lower than completion.

Reaction was carried at a selected temperature from 60 to 80 °C. Figure 1 shows conversion vs. reaction time for suspension polymerization of styrene with TCP as stabilizer at varying reaction temperatures. As seen in this Figure, reaction conversions at different temperatures show a large increase with increasing reaction temperature. When reaction was carried out at 60 °C, conversion reached 41% after 8 hours of reaction. With increasing reaction temperature, reaction showed faster kinetics and showed final conversion to be 85% after 7 hours of reaction and 86% after 6 hours of reaction at 70 and 80 °C, respectively. Since increased reaction temperature enhances production of more initiator radicals, reaction proceeds faster at higher reaction temperatures. Particles formed at the three reaction temperatures exhibit various beads in diameter. Suspension polymerization is known to produce polydisperse beads, as particle size is dependent on the size of monomer droplets. In this reaction, TCP particles were found to be varying in size, which in combination with varying monomer droplets, is speculated to contribute to this phenomenon (Figures 4 and 5). Molecular weight measurements by GPC with polystyrene standards exhibit 90,100 g/mol at the reaction temperature of 70 °C and 68,600 g /mol at 80 °C (Table II). It is common that molecular weight decreases with increasing reaction temperature, as more radicals form due to higher reaction temperature.

When reaction was conducted with varying amounts of TCP stabilizer, it was found that polymerization reaction rate was nearly independent of its concentration (Figure 2). When 3 wt% TCP relative to monomer was used, reaction did not proceed and the entire reactants agglomerated in the middle of reaction. 5 wt% TCP saw the reaction reach a higher conversion and particles formed (Figure 4). When 7 wt% of TCP was used, reaction did not show any difference from 5 wt% TCP, but particle size decreased (Figure 5). It is conceivable that more stabilizer helped form more particles, and as a result, particle diameter decreases. In both cases, particles were found to be polydisperse. Molecular weight measurements showed a slight decrease with increasing amount of stabilizer (Table II). It is not clear that the concentration of stabilizer affects molecular weight. As varying particle size does not cause a significant variation in the ratio of different reactants contained in each particle, it is speculated that molecular weight would not exhibit any significant change.

Results of polymerization reactions with different amounts of AIBN initiator are shown in Figure 3. As seen here, increasing amount of initiator led to earlier reaction completion. While the amount of initiator did not affect particle size, there was a large difference in molecular weight. As initiator amount increases, more radicals form, and as a result, reaction rate increases. In suspension polymerization, molecular weight is an inverse function of the square root of initiator concentration. Our results indicate that change in number weight average molecular weight is in the approximate range of this variation, though there is a considerable deviation in weight average molecular weight.

Conclusion

Polystyrene particles were synthesized by suspension polymerization in the aqueous phase with TCP as stabilizer. In order to minimize interfacial tension between TCP and monomer, and TCP and water, a small amount of SLS was added. The reaction was sensitive to the amount of initiator and stabilizer. We observed that 5 wt% of stabilizer and 0.4 wt% initiator were minimum amount necessary to form polymeric particles. Formed particles were polydisperse, ranging from 5 to 50 μm. In order to obtain narrower particle size distribution, we suggest that careful control of costabilizer is crucial. Glass transition was found to be independent of reaction temperature and the amount of stabilizer. Increased amount of initiator accelerated reaction rate, and molecular weight was found to be inversely proportional to the square root of initiator concentration.

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