Experimental and Modeling Studies on Styrene–Butyl Methacrylate Copolymerization Reaction

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SYNOPSIS

Radical-induced copolymerization of styrene and butyl methacrylate was studied. The effects of the initiator (benzoyl peroxide) concentration, reaction temperature, and poly(vinyl alcohol) amount on the rate of reaction and final product quality are also measured. Kinetics studies and optical microscopy of the reaction mixture indicate that the reaction exhibits autoacceleration behavior, which could be suppressed by reducing the reaction temperature. ^{1}H-NMR of the intermediate and final product samples reveals the monomer sequencing. The monomer reactivity ratios at various temperatures are estimated from the experimental data. The reaction is mathematically modeled by a Monte-Carlo simulation, and the results of this analysis are compared with observed data. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The importance of the copolymerization of styrene with acrylates stems from the fact that the product polymer finds application in speciality areas, mainly in the manufacture of recording tapes and toners for xerox machines.[1,2] Copolymerization of styrene and several derivatives of acrylates, namely, methyl acrylate, methyl methacrylate, and butyl methacrylate, have been studied thoroughly.[3-6] Generally, the polymerization reactions are carried out in the emulsion mode.

In this article, the radical-initiated copolymerization of styrene and butyl methacrylate is studied in a suspension mode. The effect of various parameters on the reaction is discussed. The kinetics of the reaction is studied by observing the changes in the concentration of the raw materials and also the buildup of molecular weight. ^{1}H-NMR studies of intermediate and final polymer samples reveal interesting insights into the monomer sequencing.

EXPERIMENTAL

Copolymerization of styrene and butyl methacrylate (BMA) is carried out by suspension polymerization. The reactor is purged with nitrogen, and a nitrogen blanket is maintained throughout the course of the reaction to avoid oxygen entry and formation of peroxides and peroxy radicals. Initially, micelles in water are formed with poly(vinyl alcohol) and a stabilizing agent like calcium phosphate. The monomer mixture is added to this medium to form droplets. The reaction is initiated with benzoyl peroxide. Since the initiator is soluble in the monomer mixture, the reaction proceeds at the same rate as that of bulk polymerization. Styrene and water form an azeotropic mixture boiling at 93°C, and the end of the reaction (approx. 4 h) is indicated by a rise in temperature. The product is in the form of small translucent beads of about 0.6 mm average diameter, which can be filtered from the reaction medium.
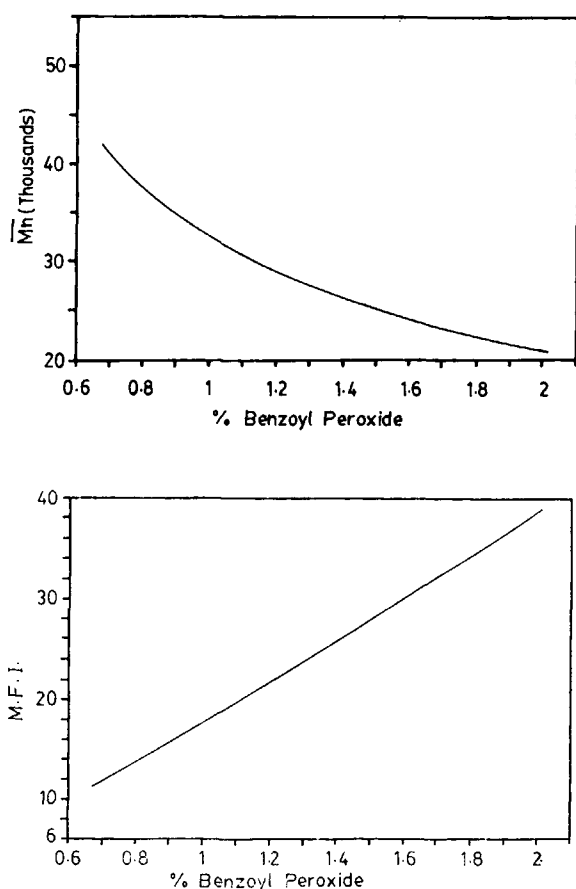
The kinetics of this copolymerization reaction is followed by collecting vapor and liquid samples at different times. The vapor contains water, styrene, and BMA. The concentrations of the individual monomers are determined by a gas liquid chro-
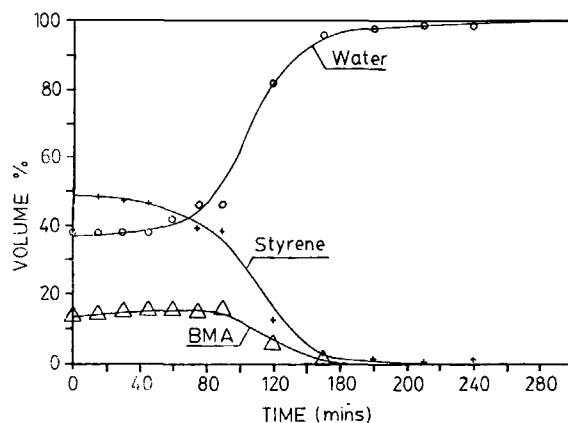
matographic (GLC) technique using an OV 17 column ($\frac{1}{8}$ in. i.d., 8 ft long; phase: 50% methyl, 50% phenyl silicone; model: GED 204 Pye Unicam) operated isothermally at 76°C with FID.

The monomers in the liquid samples, collected from the reaction pot, are once again estimated by GLC, whereas the polymer is precipitated out and analyzed by gel permeation chromatography (GPC) using μ-styragel columns of 10^5, 10^4, and 10^3 Å and THF as solvent with a refractive index detector. Polystyrenes were used as the standards for estimating the molecular weights of the polymer samples.

One of the bulk properties of the polymer is the melt flow index (MFI), which is a measure of the amount of polymer that flows through a capillary under controlled conditions of temperature and pressure, and it is a function of the polymer characteristics, such as viscosity and molecular weight. The MFI is measured (International Engineering Industries, Bombay) at 150°C over a period of 10

Figure 2 Kinetics of copolymer reaction at 93°C.

min under a weight of 5 lbs. The proton NMR studies of polymer samples are carried out with an ac 80 MHz Bruker dual probe instrument at 25°C with $CDCl_3$ as solvent.

RESULTS AND DISCUSSION

Poly(vinyl alcohol) (PVA)

This emulsifying agent reduces the surface tension of water and produces stable micelles. The degree of hydrolysis of PVA determines its solubility in water and also the amount to which the surface tension of water could be reduced. The PVA used in these studies reduces the surface tension from 72 to a value of 46 dynes/cm^2 for a PVA concentration of 0.02% (wt/wt). The amount of PVA used during the experimental work is greater than the critical micellar concentration.

Benzoyl Peroxide

This is a well-known initiator used in polymerization reactions, which initiates the reaction by decomposing to radicals. The effect of benzoyl peroxide concentration on the number-average molecular weight (M_n) is shown in Figure 1(a). Increase in initiator concentration decreases M_n according to the following power law relation:
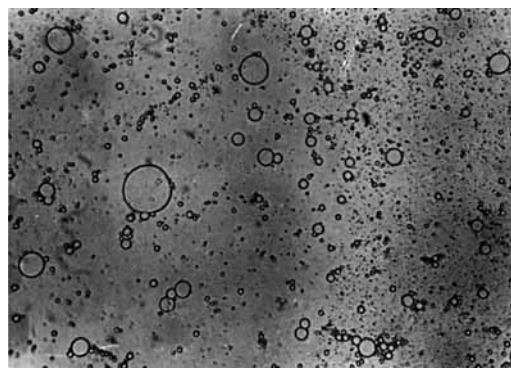
$$M_n = 30032[I_0]^{-0.635} \qquad (1)$$

Conversely, increase in benzoyl peroxide concentration increases the MFI [Fig. 1(b)], in the following manner:
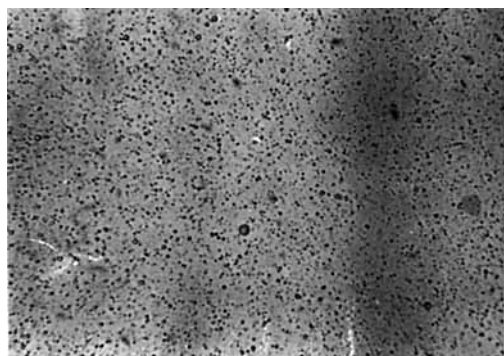
$$MFI = 19.46[I_0]^{1.131} \qquad (2)$$

Figure 1 Effect of benzoyl peroxide concentration on (a) molecular weight (M_n) and (b) MFI.

Kinetic Studies

Figure 2 shows the change in concentration of the monomers and water in the vapor sample with time. The reaction seems to be an autoacceleration type with the concentration of monomers falling slowly up to a time of 90 min, and then the reaction is completed instantaneously by the total consumption of the monomers. The water concentration correspondingly rises, the large jump in concentration occurring at 90 min. A few monomers like methyl methacrylate and acrylic acid are known to exhibit this type of behavior during homopolymerization,[7] which is due to a decrease in the rate at which the polymer molecules diffuse through the viscous medium, thus lowering the ability of two long-chain radicals to come together and terminate. Because of
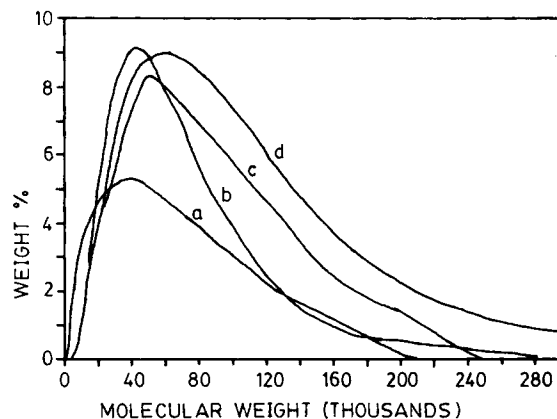

Figure 4 Molecular weight distribution with time at reaction temperature 93°C: (a) 30; (b) 80; (c) 120; (d) 180 min.

Figure 3 Optical microscopy of reaction mixture (A) before and (B) after foaming.

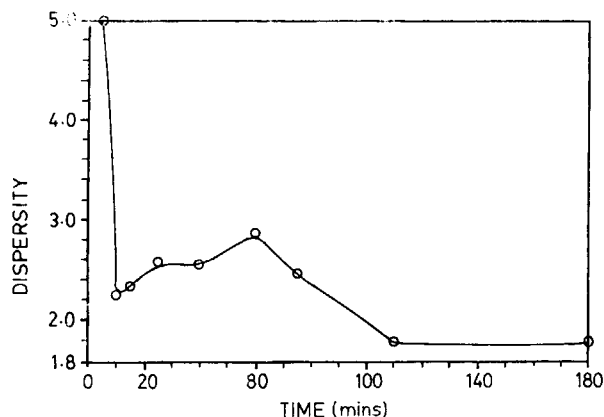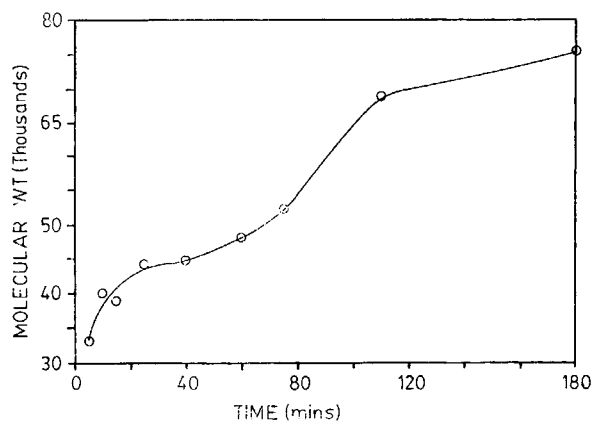the sudden jump in the rate of reaction, foaming is also observed at that time.

Optical microscopy of liquid samples taken just before and after the foaming [Fig. 3(a) and (b)] shows a dramatic change in the characteristics: The former shows the presence of a large number of liquid droplets, and the latter, the absence of them and the appearance of solid polymer fine particles.

Figure 4 shows the change in molecular weight distribution with time. Initially, a low molecular weight product is formed, which builds up to the final value in a very short period of time. The plot of M_w with time [Fig. 5(a)] also indicates a quick buildup to the final value, whereas the polydispersity, which is a ratio of weight-average to number-average molecular weights (M_w/M_n) is very high initially and later reduces to a final value of 2.3 [Fig. 5(b)].

Interestingly, kinetics at 80°C show an absence of autoacceleration behavior, with the concentration of monomers smoothly diminishing (Fig. 6). Also, foaming, which is observed at a reaction temperature of 93°C, is absent at this temperature. The reaction time at the lower temperature increases by about 25%. M_w increases with decrease in reaction temperature, as seen in Figure 7, whereas the product size remains unchanged, with an average particle diameter of 0.6 mm.
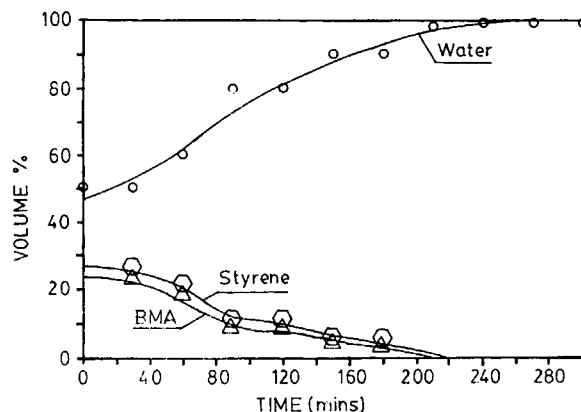
Proton NMR Studies

Figure 2 indicates that concentration of styrene decreases faster than that of BMA, which may be due to the ease of production of these radicals more than to BMA radicals. This is also seen in the proton
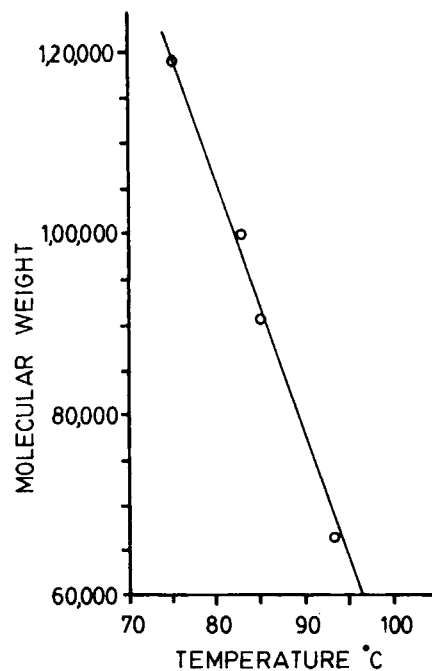
Figure 6 Kinetics of copolymer reaction at 80°C.

Figure 5 Kinetic study at 93°C: (a) molecular weight and (b) dispersity change with time.

the styrene units has the same configuration as that of the central ester unit) occurs in the lowest-field resonance area (atactic). Based on this interpretation, the probability that two styrene units and a BMA unit have same configuration (isotactic) in this copolymer is .1. The probability that at least one styrene and a BMA unit placed adjacent to each other has the same configuration in this copolymer is .65. The monomer block configuration of the intermediate polymer sample also appears to be the same as that of the final product.

NMR of polymer samples collected at intermediate and final times (Fig. 8). The ^{1}H-NMR shows that the concentration of styrene monomer in the intermediate sample is almost 50% more than that of the final sample. The final polymer sample has a styrene-to-BMA mol ratio of 1 : 0.82. The methoxy proton resonance is distributed between three bands that have been assigned to the ester monomeric units (M), adjacent in the chain to none (II), one (III), and two (IV) isotactically oriented phenyl groups of the styrene (S), respectively.[8,9] Further, based on the interpretation of Crompton,[10] the highest-field methoxy resonance is due to SMS triads in which both styrene units have the same configuration (isotactic) on the central BMA unit. The central methoxy resonance area is due to the methoxy molecules of the ester units centered in SMM and SMS triads, where one of the styrene units has the same configuration (syndiotactic) as that of the central BMA unit. The resonance of the remaining methoxy protons (MMM and SMM or SMS, where none of
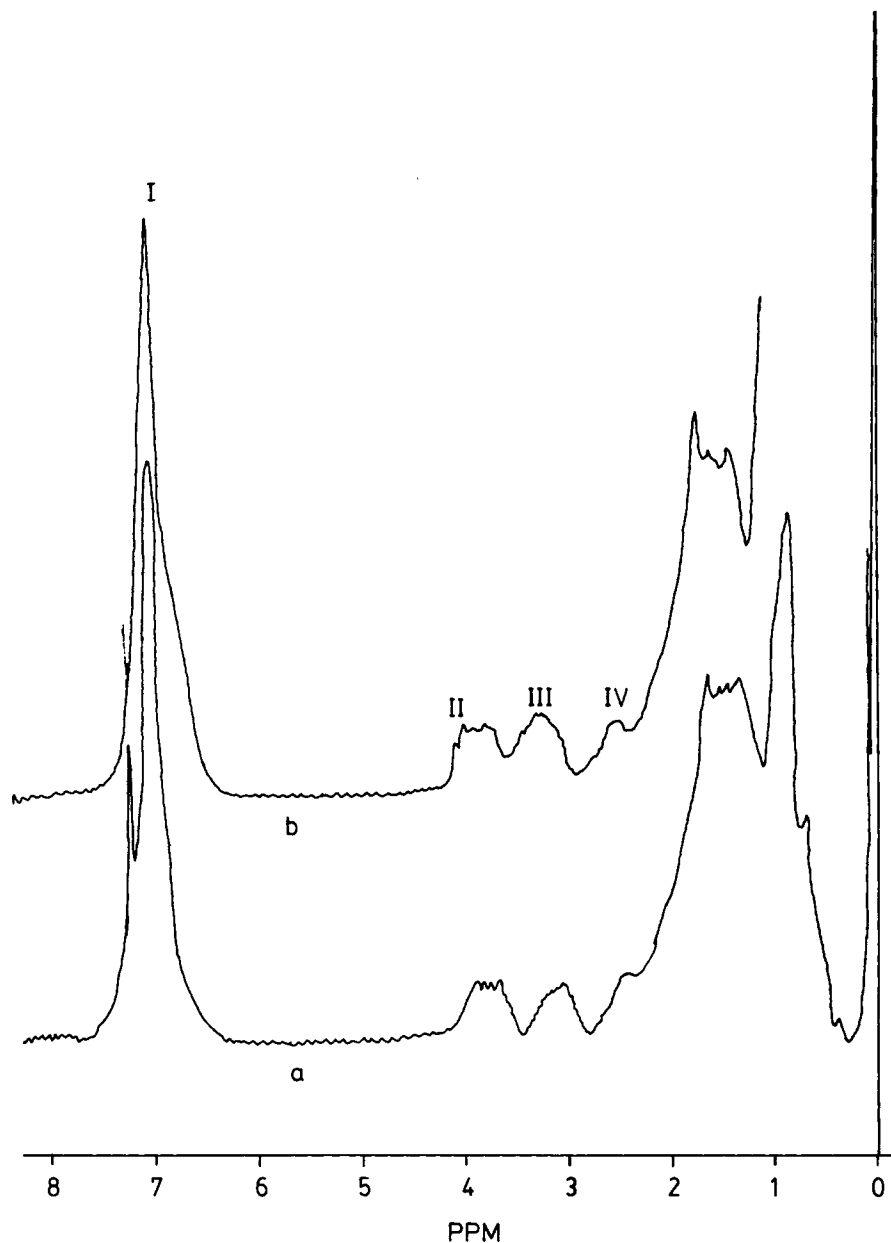

Figure 7 Effect of reaction temperature on molecular weight (M_w).

Figure 8   NMR of polymer samples: (a) ^{1}H-NMR of intermediate sample; (b) ^{1}H-NMR of final sample; I, aromatic proton; II, III, and IV, methoxy proton.

Monomer Reactivity Ratios

The copolymer equation based on the radical process is given by[11]

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]} \qquad (3)$$

where $[M_1]$ and $[M_2]$ are mol fractions of the two monomers, and r_1 and r_2, the monomer reactivity ratios: the ratios of the rate constant for a given

radical adding to its own monomer to the rate constant for it adding to the other monomer. Hence,

$$r_1 = k_{11}/k_{12} \qquad \text{and} \qquad r_2 = k_{22}/k_{21}$$

k_{11} and k_{22} are rate constants corresponding to radical M_1^* added to monomer M_1, and radical M_2^*, to monomer M_2, respectively. The monomer reactivity ratios can be estimated by fitting eq. (3) to the experimental data, and Figure 9 makes such a comparison for the reaction carried out at 93°C. The
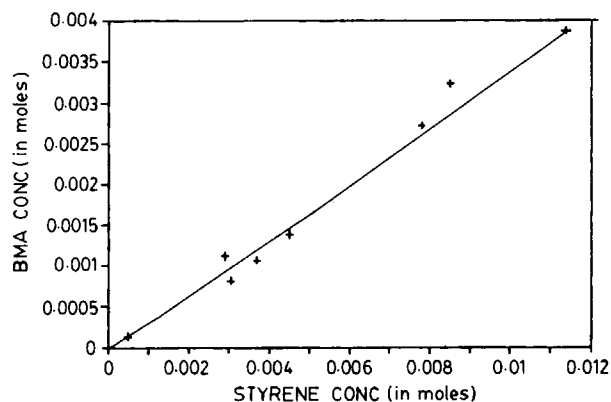
Figure 9   Comparison of model and experiment at 93°C. Continuous line = model.

pairs of monomer reactivity ratios estimated at 93 and 80°C, respectively, are 0.44, 0.74 and 0.475, 0.49, where r_1 refers to BMA, and r_2, to styrene. Although the monomer reactivity ratio for BMA remains reasonably constant with change in temperature, for styrene, the ratio increases, which indicates that increase in temperature favors the styrene radical reacting with another styrene molecule more than with the BMA molecule. The monomer reactivity ratios for the same system at 60°C with 2,2'-azoisobutyronitrile as initiator are found in the literature[9] to be 0.4 and 0.56, respectively.

Mathematical Modeling

The copolymerization reaction between styrene and BMA is mathematically modeled by the Monte-Carlo simulation approach. The simulation procedure consists of the following steps for each time step:

1. Let N_S and N_B be the number, respectively, of styrene and BMA molecules taking part in the reaction giving rise to N_P, polymer molecules of different lengths.
2. Choose a random number between 1 and N_P, the polymer molecule where the next monomer is going to be added.
3. Choose a random number (X) between 0 and 1.
4. (a) If the present monomer molecule is BMA and $X < r_1$, the next monomer will also be BMA. If $X > r_1$, the next monomer will be styrene. (b) If the present monomer molecule is styrene and if $X < r_2$, the next monomer will also be styrene; else, it will be BMA.

5. Choose a random number (D) between 0 and 1.
6. Select the direction of the monomer: If $D < 0.5$, the direction is upward; else, it is downward.

Figure 10(A) simulates the conversion of the monomers as a function of time at 93 and 80°C. The r values for both the cases were given in the previous section. At 93°C, styrene is consumed faster than is BMA (curve 1a vs. 1b). This is also seen in the experiments. At 80°C, the conversions of both the monomers are almost the same (although conversion of BMA is slightly higher than that of styrene: curves 2b and 2a). The time values mentioned on the X axis have no significance. Figure 10(B) shows the ratio of BMA to styrene in the product. As seen experimentally through ^{1}H-NMR at 93°C, the amount of styrene is twice that of BMA (BMA/styrene = 0.5) in the polymer, whereas the BMA to styrene reaches 0.85 at the completion of the reaction. At 80°C, the model predicts that the BMA-to-styrene ratio remains almost equal to 1 throughout the reaction, finally dropping down to 0.85.

Figure 11 simulates the sequencing of the two monomers in the polymer at 93 and 80°C. At 93°C, the model predicts that the fraction of isotactic configurations (central BMA unit and two styrenes on either side have same configuration) initially reaches a maximum of 0.15 and decreases to 0.11 and remains almost at that value and, finally, reaches a value of 0.04 (curve i_1). The syndiotactic fraction, where only one styrene has the same configuration
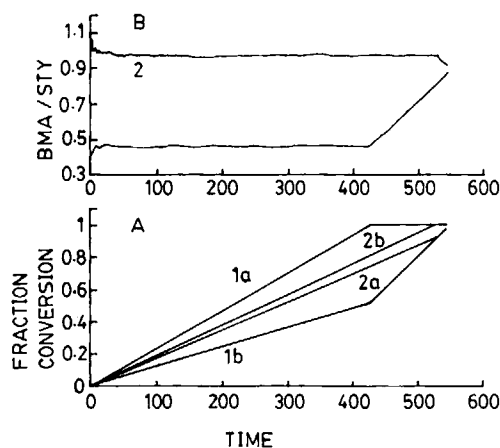
Figure 10   Monte-Carlo simulation results: (A) fraction conversion of the monomers; (B) fraction of BMA/styrene in the product polymer as a function of dimensionless time. (1) 93 and (2) 80°C; (a) styrene; (b) BMA.
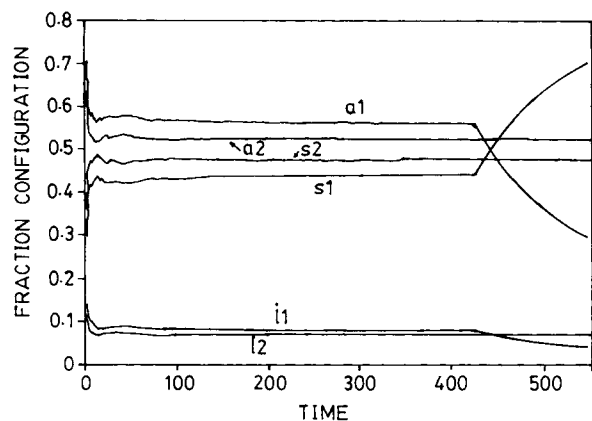
Figure 11 Monte-Carlo simulation of monomer configuration as a function of dimensionless time at 93 and 80°C. (1) 93 and (2) 80°C; i, isotactic; s, syndiotactic; a, atactic.

as that of the BMA configuration, remains at 0.42, finally increasing to 0.7 (curve S_1). The fraction of atactic configuration (curve a_1) initially remains at 0.58, finally dropping down to 0.26. NMR analysis of the intermediate polymer product reveals ratios of 0.1, 0.65, and 0.25 for isotactic, syndiotactic, and atactic configurations, respectively.

CONCLUSIONS

The free-radical-induced suspension copolymerization of styrene and BMA was studied. PVA was used to reduce the surface tension of water and also to produce micelles. The concentration of PVA used was more than the critical micelle concentration. Increase in concentration of benzoyl peroxide decreased M_n and increased MFI. Kinetics of the reaction revealed an autoacceleration type of behavior at 93°C, where the monomer concentration drops suddenly after an initial induction period. This also caused foaming. The autoacceleration was eliminated by reducing the reaction temperature to a value less than 89°C. From the kinetics and ^{1}H-NMR studies, it was observed that the styrene con-

sumption rate at intermediate reaction times was higher than the rate of consumption of BMA. The NMR analysis also gave some idea about the monomer sequencing and their relative configuration to each other in the final and intermediate polymers. From the monomer reactivity ratios estimated at two different temperatures, it can be concluded that increase in reaction temperature favors styrene radical reactivity to the styrene monomer more than to the BMA monomer. Decrease in reaction temperature increased M_w. Monte-Carlo simulation studies match well with experimental data.

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