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Scale-Up Studies on Styrene−Butyl Methacrylate Copolymerization Reaction

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Abstract:

The scale-up of the radical-initiated copolymerization of styrene with butyl methacrylate is studied here. The reaction is scaled up from 3 to 100 L scale. The problems encountered during the scale-up are agglomeration, foaming, and material loss. The techniques employed to overcome these problems are discussed in detail. Kinetic studies indicate that the reaction exhibits autoacceleration behaviour, with induction time varying with reactor size. The effects of initiator concentration and reactor size on the molecular weight and melt flow index of the final sample are also studied.

Introduction

The scale-up of polymerization reactions poses several problems which are not generally encountered in normal organic reactions. One has to consider (i) aspects of uniform mixing for good temperature control and reactant homogeneity, by providing surface exposure and surface renewal; (ii) rheology; (iii) particle agglomeration; and (iv) foaming. These parameters can alter the final product specifications, namely, physical, electrical, and chemical properties during scaling up.

Scale-up of the radical-induced copolymerization of styrene with butyl methacrylate is described in this paper. The reaction is performed in a suspension mode with the aid of suspending agents. Here the scale-up is carried out from a laboratory scale of 3 L to a pilot scale of 100 L. This paper deals with the problems encountered during the scale-up of this reaction and the techniques employed to overcome them. This process is scaled-up in incremental stages to meet growing product development needs. This approach also provides an opportunity to observe the problems due to scale-up and can minimize risk at a lower scale of operation. Unlike organic reactions where high conversion and purity are the two desired criteria, in polymerization reaction the polymer product has to satisfy several specifications, viz., molecular weight and distribution, particle size and distribution, residual monomer content, melt flow index, etc.

The importance of this reaction stems from the fact that the ensuing polymer finds application in several specialty areas, such as the manufacture of audio tapes and also the preparation of toners for reprographic machines.[1,2] The estimated worldwide demand for styrene−methacrylate copolymers is 1.5 million tonnes in 1991, with a large portion taken up by styrene−butyl methacrylate. The relative ease of copolymerization of styrene with butyl methacrylate has made the latter the most favoured monomer when compared to other methacrylates and acrylates to be used with the former monomer. Copolymerizations of styrene with methyl acrylate,[3] methyl methacrylate,[4−6] butyl acrylate,[7,8] and acrylonitrile[9,10] have been studied in both emulsion and suspension modes. The effect of reaction conditions on the rate of the copolymerization reaction has been thoroughly examined. Young[11] compares the reactivity ratios of copolymerization and termination rate constants of various methacrylates and acrylates with styrene.

None of the papers deal with the problems of scale-up in copolymerization reactions. Schlegel[12] deals with the design of polymerization reactors and problems encountered during scale-up. Shinar and Church[13,14] have developed theoretical relations for breakup, coalescence, and suspension of droplets stabilised by surfactants in a stirred tank. Oldshue[15] provides correlations for average droplet size in agitated vessels and the minimum impeller speed required for dispersion.

Copolymerization Reaction

Copolymerization of styrene and butyl methacrylate is carried out here by suspension polymerization. The reactor is first purged with nitrogen, and later a nitrogen blanket is maintained throughout the course of the reaction, since oxygen can react with styrene to form peroxy radicals, which changes the polymer composition and molecular weight. Initially, water, poly(vinyl alcohol) (PVA), and a stabilising agent like calcium phosphate are taken in the reactor and stirred at 80 °C to form micelles. The monomer mixture is slowly added over a period of 15−30 min to this medium to form droplets. Foaming is observed if the monomer addition rate is fast. The reaction is initiated with benzoyl peroxide. Since the initiator is soluble in the monomer mixture, the reaction proceeds with the same rate as that of bulk polymerization. The reactor temperature is increased slowly. Styrene and water form an azeotropic mixture

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boiling at 93 °C, and the end of the reaction (approximately 4 h) is indicated by the rise in the vapour temperature (to 100 °C) when the monomers get consumed.

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 molecular weight and molecular weight distribution of the polymer are determined analytically by a GPC (gel permeation chromatography) technique using μ Styragel columns of 10^5, 10^4, and 10^3 Å and THF as solvent with a refractive index detector. Polystyrene is used as the standard. The kinetics of the reaction are followed by collecting liquid and vapour samples from time to time. The water in the condensate is measured and removed by layer separation. The quantity of individual monomers is determined by a gas liquid chromatographic technique using an OV 17 column operated isothermally at 76 °C. The composition of the individual monomers in the polymer is determined by ^{1}H NMR.

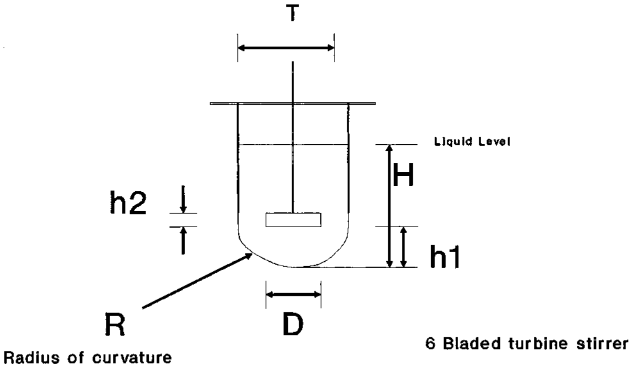
The emulsifying agent, PVA, reduces the surface tension of water and produces stable micelles. The degree of hydrolysis of PVA determines its solubility in water and also the amount to which the surface tension of water could be reduced. The PVA used in these studies reduces the surface tension from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

One of the bulk properties of the polymer is the melt flow index (MFI), which is a measure of the mass rate of flow of the polymer through a specified capillary under controlled conditions of temperature and pressure, and it is a function of polymer characteristics like viscosity, molecular weight, etc. The MFI of the polymer produced in various reactors is measured with a MFI indicator (International Engineering Industries, Bombay, India). The melt flow index is determined at 150 °C and is the amount of polymer flowing out of the orifice over a period of 10 min under a weight of 2.271 kg (5 lb).

The polymer particle size is measured using a Horiba LA50 laser particle size analyzer, and the monomer droplet size is determined from optical microscopy.

Table 1. Dimensions of reactors and stirrers used for scale-up studies

system	reactor vol (L)	stirrer diam (mm)	diam of stirrer/ diam of reactor	rpm	tip velocity (cm/s)	tip Reynolds no. (10^4)
1a	3	100	0.66	500	41.6	2.06
1b	3	80	0.53	750	50	2.0
2	10	100	0.41	505	42.1	2.1
3	100	210	0.5	110	19.25	2.02



All measurments in mm

V (ltr.)	T	H	R	D	h1	h2
3	150	70	103	80/100	18	11.5
10	195	153	103	100	20	32
100	420	300	332	210	87.5	55

Figure 1. Schematic diagram of reactors and stirrers used in scale-up.

Lab and Scale-Up Reactors

The first lab scale reactor consists of a 150 mm diameter 200 mm long cylindrical flanged glass vessel, with a glass multinecked flange for stirrer shaft, condenser, and solids addition. The reactor volume is 3 L. The reactor is heated with an oil bath. The stirrer motor is a variable speed dc motor. A reflux condenser also acts as an additional heat removal system. The second lab scale reactor is a 10 L stainless steel (ss) vessel of 240 mm diameter fitted with a flat multinecked mild steel plate at the top. The reactor is heated electrically. The third semitechnical reactor is a 420 mm diameter and 660 mm long ss vessel with a steam jacket. The total reactor volume is 100 L. It consists of a stainless steel shell and tube type condenser. The reactor contents could be emptied by opening a drain valve. The stirrer motor is a constant speed dc motor, whose revolutions per minute (rpm) could be varied in steps with the help of a pulley block. The details of the various reactors and diameters of the stirrers considered for the scale-up studies are listed in Table 1 and Figure 1. Six-bladed turbine type stirrers with the blades making an angle of 30° to the vertical are used in all the reactors. Two different-sized stirrers were employed in the 3 L reactor to study the effect of stirrer to reactor diameter on the product quality. The selection of the ratio of the impeller diameter to diameter of the tank is very important. In industrial applications, ratios from 0.25 to 0.65 are used for common impellers, while larger ratios are used for anchors, gates, and helical impellers.[16] If the process requires flow rather than turbulence, ratios of 0.4−0.6 are chosen (as in this case, Table 1). For processes requiring turbulence and micro mixing (intimate mixing), ratios of 0.25−0.35 would be selected and impellers would be operated at higher speeds than in the previous case. The suspension polymerization process takes place in a noncoalescing system. Mixing for these systems should provide dispersion and suspension because coalescence is virtually absent. Mean drop size decreases and the droplets are better suspended as impeller speed increases. Also, the time to reach a completely dispersed condition is short in a small vessel and long in a large vessel (mixing times in 3, 10, and 100 L reactors are 1, 2.3, and 7.1 s, respectively), so one ends up comparing completely dispersed droplets in smaller vessels with partly dispersed droplets in large vessels. Hence, agitation speed has to be increased in larger vessels to produce droplet sizes equivalent to those made in miniplants. But increasing the rpm increases power consumption as power is proportional to the cube of rpm.

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Polymer fouling is generally a problem in suspension polymerization. During scale-up, supplemental heat transfer area in the form of coils is avoided. To reduce fouling of reactors by polymer, the following techniques are generally adopted:[12] (i) use of glass-lined vessels; (ii) use of a suspension formulation modification that minimizes polymer buildup; (iii) more attention paid to the metal-surface finish, including special polishing techniques; and (iv) use of simplified cleaning systems with solvents, as well as high-pressure water and detergents. Baffles are also eliminated to prevent polymer deposition; this decreases the mixing in the reactor. Also, polymer agglomeration can lead to its deposition on the reactor walls.

Scale-Up

Several problems were encountered during the scale-up of the copolymerization reaction and they are as follows.

Agglomeration of product during the course of the reaction caused product outside specifications and fouling of the reactor. This was overcome by a suitable choice of the stirrer diameter and rpm of the stirrer so that the scale-up was based on a constant Reynolds number. Also the ratio of the stirrer diameter to reactor diameter was reduced during scale-up from a value of 0.66 to a value of 0.5 to reduce the power consumption. The only way one particle catches up with another in a mixing vessel is by having a different velocity vector. Thus, shear rate is a measure of velocity gradients. On scale-up, operating speed (average speed) drops while velocity gradient usually increases, hence there is generally a greater range of shear rates in a larger tank than there is in a small tank, which could lead to more particle agglomeration in the former than in the latter.[15] Agglomeration was also caused by large temperature gradients in the reactor because the softening point of the polymer is low (68 °C).

Foaming occurs at approximately 90 min after the addition of the initiator benzoyl peroxide. The cause of the foaming and how it was eliminated are described in the later sections of the paper.

It was necessary to clean the reactor with solvent after a few batches to remove the polymer coating formed on the walls of the vessel. The coating not only reduced the heat transfer coefficient but also resulted in production of larger sized polymer beads. The use of solvent for reactor cleaning resulted in increased raw material cost. The need for reactor cleaning was partially eliminated by decreasing foaming and maintaining the reactor temperature constant with a steam and water combination.

Agitation provides shear to disperse the monomer into discrete droplets, and suspending agents prevent agglomeration. As mentioned above, the stirrer diameters and the rpm were chosen so that the tip Reynolds number ($D^2N\rho/\mu_c$) was maintained constant in all cases. Also, the ratio of the diameter of the stirrer to that of the reactor was reduced considerably in a systematic manner. The tip velocity (ND) for all cases is given in Table 1. As the reactor size increases, the average fluid velocity decreases. Here both the dimensional and dynamic similarity cannot be maintained. As an agitator is scaled up under constant Reynolds number, maximum shear rate (occurs near the blade tip) increases, average shear rate decreases, and the reactor turnover rate (impeller pumping capacity per unit volume) and superficial velocity decrease (Table 2).

Table 2. **Expected performance of stirrers listed in Table 1**[a]

system	$P \propto N^3D^5$ $\times 10^{16}$	P/V $\times 10^{16}$	$Q \propto ND^3$ $\times 10^8$	Q/V $\times 10^8$	superficial velocity: Q/reactor area	N_m
1a	125	83.3	5	3.3	0.022	446
1b	138.2	92.1	3.8	2.5	0.0169	720
2	128.8	25.8	5.1	1	0.0089	446
3	54.4	1.1	10.2	0.2	0.0059	90

[a] P = power. N = stirrer rpm. D = diameter of the stirrer, in mm. V = volume of the liquid in the vessel, in L. Q = pumping capacity.

The minimum impeller speed necessary for uniform dispersion of an organic chemical in water for a turbine agitator is given by Skelland and Seksania[15] as

$$N_m = 2.838D^{-2.15}(\mu_c/\mu_d)^{1/9}\sigma^{0.3}\Delta\rho^{0.25} \tag{1}$$

The values for different reactor sizes are also given in Table 2. It can be seen that the operating speeds (see Table 1) in all cases are greater than the minimum speed required for dispersion.

A correlation produced by Love and Rushton[15] relates the average droplet size to the reactor geometry as

$$d \propto N^{-2.56}D^{-4.17}T^{1.88} \tag{2}$$

which means that the average droplet sizes produced in 3, 10, and 100 L reactors are related as 1:1.5:16.

In our studies the pumping capacity per unit volume is expected to decrease by a factor of 15, the superficial velocity by a factor of 4, and the tip velocity by a factor of 2 when scale-up is carried out from 3 to 100 L scale. (Tip velocity is a measure of movement in the radial direction, while the superficial velocity is the measure of movement in the axial direction.) The advantages in maintaining a constant Reynolds number during scale-up are (i) decrease in power consumed per unit volume with increasing reactor size, which is highly desirable from the point of view of operating costs; (ii) achievement of similar heat transfer; (iii) reduced velocity gradient and shear stress; and (iv) equal surface motion and vortex. Advantages ii and iii help in reducing agglomeration and foaming.

Experimental Procedure

The copolymerization reaction is carried out in 3, 10, and 100 L (systems 1b, 2, and 3) and also with two different stirrers in the 3 L reactor (systems 1a and 1b). The effect of scale-up was studied on the following: (a) molecular weight, molecular weight distribution, and particle size; (b) benzoyl peroxide requirement; (c) MFI; (d) apparent reaction kinetics at 93 and 80 °C.

Results and Discussion

Molecular Weight. The effect of the stirrer diameter for constant reactor size (system 1a vs 1b) on the copolymerization is seen in Figure 2. Although the weight average molecular weight remains the same (M_w = 69 500), the

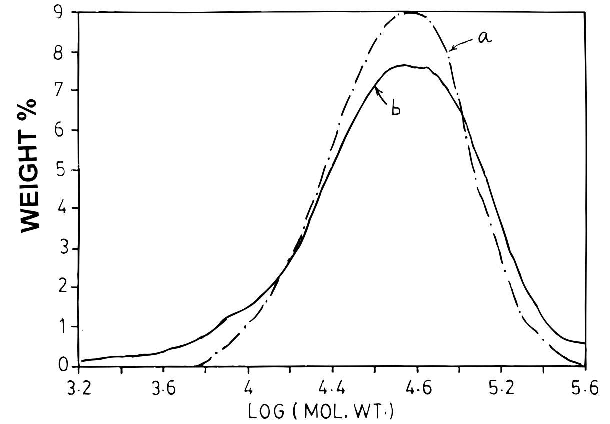

Figure 2. **Effect of stirrer size on molecular weight distribution in 3 L reactor at 93 °C (six-bladed turbine reactor): (a) 100 mm diameter; (b) 80 mm diameter.**

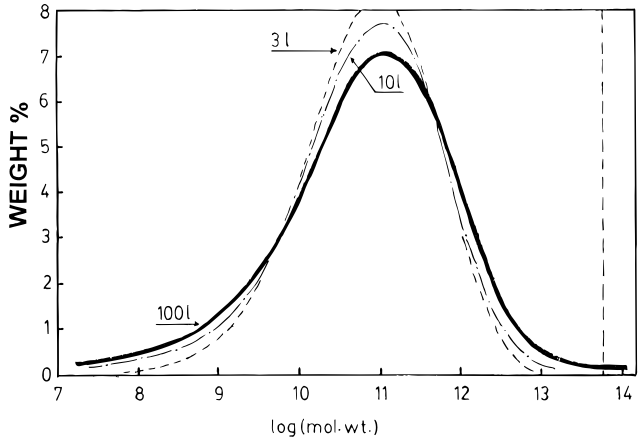

Figure 3. **Effect of reactor size on molecular weight distribution at 93 °C: (a) 3 L; (b) 10 L; (c) 100 L. (Refer to Table 1 for stirrer dimensions.)**

Table 3. **Effect of reactor size on product quality (93 °C, six-bladed turbine stirrer)**

reactor vol (L)	wt av mol wt (M_w)	dispersity
3	68 800	1.95
10	71 300	2.6
100	79 700	3.45

dispersity (M_w/M_n) increases from 1.72 to 2.28 and the molecular weight distribution is also broader when the stirrer diameter is reduced from 100 to 80 mm. Although the tip velocity is higher in the case of system 1b when compared to system 1a, the superficial velocity (or the vertical mixing) is less in the former. Increased power input per unit liquid volume need not mean increased pumping per unit liquid volume but can lead to even decreased pumping (as seen in system 1b). The increase in dispersity here may be due to decreased pumping in the vertical direction.

The effect of reactor size on the molecular weight distribution is shown in Figure 3 (comparison of systems 1b, 2, and 3). As the reactor size is increased, the molecular weight and dispersity also increase (Table 3), indicating improper mixing since both the tip velocity and the superficial velocity decrease. These two effects mentioned above are mainly due to scale-up. While a microscopic property like molecular weight distribution is a function of scale-up, interestingly, a macroscopic property like particle size is not altered during scale-up. The average particle size and particle size distribution remain almost the same during scale-up (Figure 4) (0.656 and 0.721 mm in 3 and 100 L reactors, respectively, with 0.178 and 0.169 standard deviations). The particles formed in suspension polymerization are affected by shear rate and shear work, where shear work is related to the number of times a particle passes through a high shear region per unit time. If the flow in the vessel per unit volume is high, the particles formed will be small.

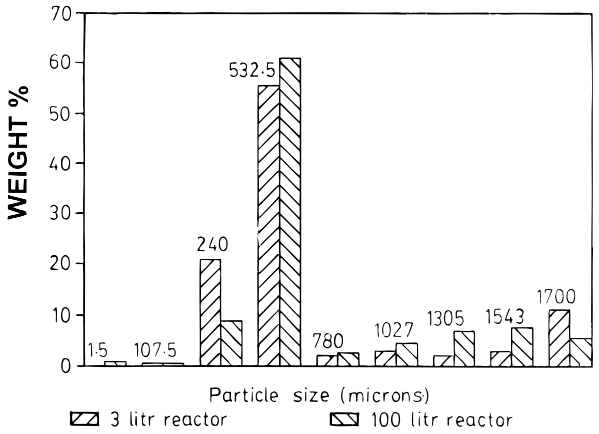

Figure 4. **Effect of reactor size on copolymer size distribution: (a) 3 L; (b) 100 L.**

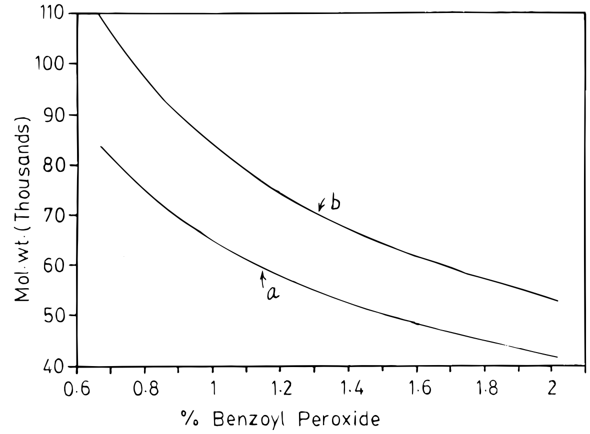

Figure 5. **Effect of benzoyl peroxide concentration on weight average molecular weight: (a) 3 L; (b) = 100 L.**

Benzoyl Peroxide. This is a well-known initiator used in polymerization reactions which initiates the reaction by decomposing into radicals and attacks the monomers' double bonds, thus forcing the active radical center onto the monomers. The effect of benzoyl peroxide concentration on the weight average molecular weight (M_w) for both 3 and 100 L reactors is shown in Figure 5. An increase in initiator concentration decreases M_w. Also, the quantity of benzoyl peroxide required in the larger reactor to achieve same molecular weight is more than the amount required in the smaller one. This may be due to improper distribution of the initiator in the former reactor leading to its nonavailability in certain parts of the solution.

Conversely, an increase in benzoyl peroxide concentration increases the MFI (Figure 6). It is seen that the MFI of the polymer produced in the 100 L reactor is less than that of the polymer produced in the 3 L reactor for the same initiator amount. The equations generated based on the experimental

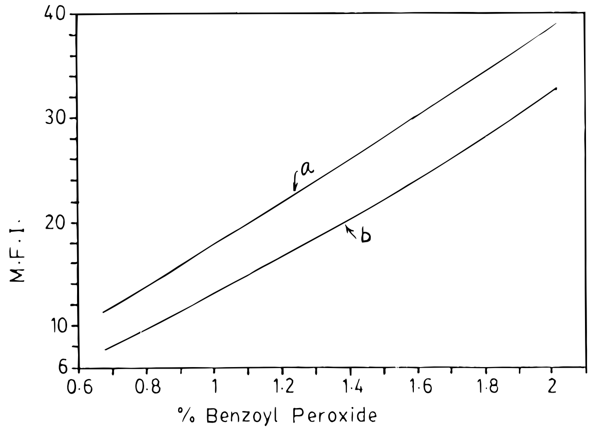

Figure 6. **Effect of benzoyl peroxide concentration on MFI: (a) 3 L; (b) 100 L.**

data relating benzoyl peroxide quantity to average molecular weight and MFI for both reactors are as follows.

3 L reactor:

$$M_w = 60061[I_0]^{-0.635} \tag{3}$$

$$\mathrm{MFI} = 19.46[I_0]^{1.131} \tag{4}$$

100 L reactor:

$$M_w = 98120[I_0]^{-0.658} \tag{5}$$

$$\mathrm{MFI} = 11.94[I_0]^{1.318} \tag{6}$$

Residence time distribution studies carried out in the two reactors indicate that 68% of the volume of the larger reactor resembles the smaller one, and the remainder of the volume is poorly mixed. The exponents of $[I_0]$ (initiator concentration) remain almost the same (−0.635 and −0.659 for 3 and 100 L reactors) in both cases, indicating that the mechanism corresponding to initiator generation is independent of reactor size, whereas the constant term in the equation for the 100 L reactor (eq 5) is 62% greater than the corresponding term for the 3 L reactor (eq 3), which matches well with the findings from the residence time distribution studies. Similar conclusions could be drawn by comparing eqs 4 and 6.

Kinetic Studies

Figure 7 shows the change in concentration of the monomers and water in the vapour sample with time in the 3 L reactor. The reaction seems to be an autoacceleration type with the concentration of monomers falling slowly up to a time of 90 min; 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 behaviour during homopolymerization, and it 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 (diffusion-controlled reaction). This acceleration is also known as the Trommsdorff effect.[17] Due to 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 shows a sudden change in the characteristics. The former sample shows the presence of a large number of liquid droplets, and the latter the absence of them and the appearance of solid fine polymer particles.[20] This observation from the liquid side once again confirms the sudden rise in polymerization rate at about 90 min in this reactor. The kinetic studies also indicate consumption of more styrene initially than butyl methacrylate, which may be due to the greater ease of production of its radical than of BMA radicals.

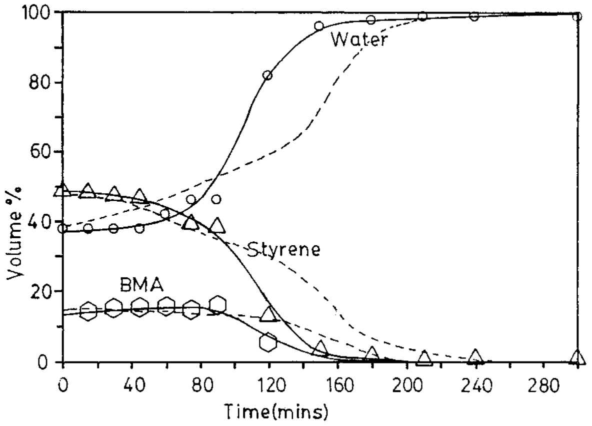

Figure 7. **Kinetics of copolymer reaction at 93 °C: vapour composition as a function of time (continuous lines, 3 L; dotted lines, 100 L).**

Also, production of polymer particles increases the bulk viscosity. With an increase in viscosity the discharge from the impeller is less effective at inducing a recirculation motion. A predominantly axial flow pattern achieved with the turbine stirrer can change to a radial flow pattern with major recirculations above and below the impeller.[18] Since the stirrer operates at a highly turbulent region, the impeller loads are not dramatically affected by the bulk viscosity. Kinetics of the copolymerization reaction carried out in the 100 L reactor exhibit the same autoacceleration type of behavior, but the sudden drop in the monomer concentrations happens at a later time (at 120 min instead of at 90 min in the case of the 3 L reactor). This indicates that the reactor size has a profound effect on the apparent reaction kinetics.

The plot of weight average molecular weight (M_w) with time (Figure 8A) indicates a quick buildup to the final value in both reactors, while the dispersity, which is a ratio of weight average to number average molecular weights (M_w/M_n) is very high initially and later settles down to a final value of 2.3 (Figure 8B) in the 3 L reactor and 3.5 in the 100 L reactor. The figure also compares molecular weight buildup and dispersity changes with time in the 3 and 100 L reactors. Weight average molecular weight is higher and the polymer product more disperse at all time values in the larger reactor than in the smaller one.

Interestingly, the kinetics at 80 °C in the 100 L reactor show an absence of autoacceleration behaviour, with the concentration of monomers falling down smoothly (Figure

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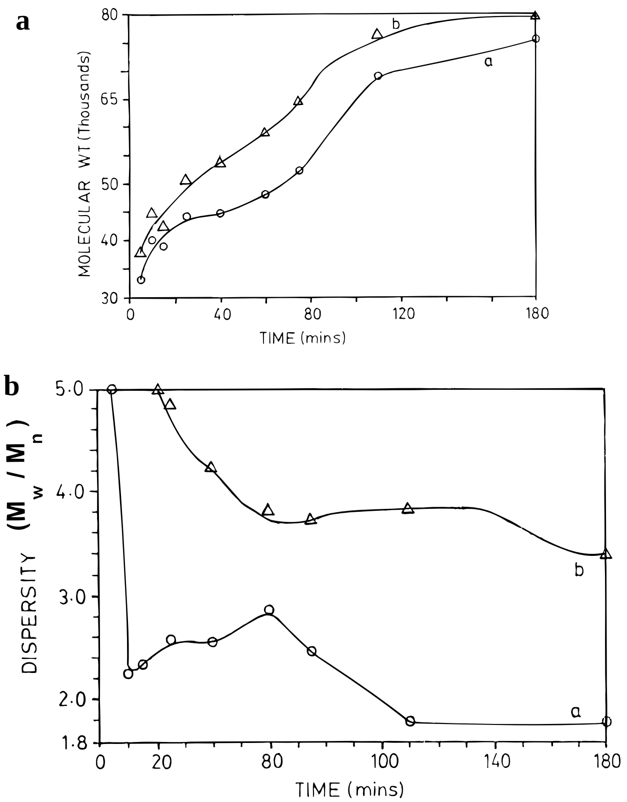

Figure 8. **Kinetic study at 93 °C: (A) weight average molecular weight and (B) dispersity buildup with time (a, 3 L; b, 100 L).**

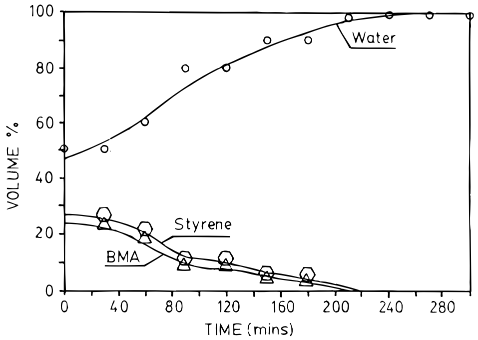

Figure 9. **Kinetics of copolymer reaction at 80 °C in 100 L reactor: vapour composition as a function of time.**

9). 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%. This may be due to the fact that a decrease in reaction temperature decreases the rate of reaction, thereby shifting the reaction from a diffusion-controlled to a kinetic-controlled regime.

Monomer Reactivity Ratios

The copolymer equation based on a radical process is given by[19]

$$\frac{f_1(1-2F_1)}{(1-f_1)F_1} = C_2 + \frac{f_1^{\,2}(F_1-1)C_1}{(1-f_1)^2F_1} \qquad (7)$$

where f_1 and F_1 are mole fractions of monomer 1 in feed and polymer, respectively. C_1 and C_2 are the monomer reactivity ratios, the ratios of the rate constant for addition of a given radical to its own monomer to the rate constant for its addition to the other monomer (i.e., $C_1 = k_{11}/k_{12}$ and $C_2 = k_{22}/k_{21}$). k_{11} and k_{22} are rate constants corresponding to radical $M_1^\bullet$ adding to monomer M_1 and radical $M_2^\bullet$ to monomer M_2, respectively. The monomer reactivity ratios are the slope and intercept of eq 7. Mole fraction of monomer in the feed is estimated by analyzing the liquid sample by GLC. The mole fraction of monomer in the polymer is estimated by analyzing the polymer sample by ^{1}H NMR.[20]

The monomer reactivity ratios, C_1 and C_2, estimated in the 3 L reactor at 93 °C and 80 °C respectively are 0.44 and 0.74, and 0.475 and 0.49, where C_1 refers to BMA and C_2 to styrene. The monomer reactivity ratio for BMA remains reasonably constant with changes in temperature, while for styrene, the ratio increases with increases in temperature, which indicates that an increase in temperature favours styrene radicals reacting with another styrene molecule more than with a BMA molecule. The monomer reactivity ratios for methyl methacrylate and styrene are found in the literature to be 0.46 and 0.52, respectively, at 60 °C, and for butyl methacrylate and styrene to be 0.64 and 0.54, respectively, at 70 °C,[19] which match fairly well with our findings.

Conclusions

The scale-up of the copolymer reaction of styrene and butyl methacrylate is studied in this paper. The reaction was carried out in 3, 10, and 100 L reactors. The product obtained in the 3 L reactor was found to be satisfactory with respect to molecular weight, dispersity, MFI, and particle size distribution. The main problems encountered during scale-up are particle agglomeration, foaming, and material loss. The particle agglomeration was eliminated without increasing the mixing energy by proper design of the stirrer and selection of the rpm. The peripheral speed in the larger reactors was kept low, by which the shear rates and the particle agglomeration were kept low. In all cases the stirrer tip Reynolds number was maintained constant.

An increase in reactor size also increased the weight average molecular weight and dispersity, while the average polymer particle size remained unaltered. A decrease in reaction temperature increased M_w. The copolymerization reaction proceeded through an autoacceleration type of sudden change in concentrations of the reactants with an initial induction period at a certain reaction time at 93 °C. During this period, foaming was observed. Below 80 °C foaming and autoacceleration phenomena were absent. In the 100 L reactor the sharp drop in the monomer concentrations happened at a later time when compared to the 3 L reactor, probably due to decreased mixing. An increase in the benzoyl peroxide concentration decreased the M_w and increased the MFI, and reactor scale-up reduced the availability of the initiator, thereby requiring more of it than in the smaller reactor to attain the same M_w.

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NOMENCLATURE

C_1	monomer reactivity ratio $= k_{11}/k_{12}$
C_2	monomer reactivity ratio $= k_{22}/k_{21}$
d	average droplet diameter
D	impeller diameter

$[I_0]$	initiator concentration (%)
k_{11}	rate constant of radical $M_1^{\bullet}$ reacting with monomer M_1
k_{12}	rate constant of radical $M_1^{\bullet}$ reacting with monomer M_2
k_{21}	rate constant of radical $M_2^{\bullet}$ reacting with monomer M_1
k_{22}	rate constant of radical $M_2^{\bullet}$ reacting with monomer M_2
MFI	melt flow index
M_w	weight average molecular weight
M_n	number average molecular weight
T	tank diamteter
μ_c, μ_d	viscosity of continuous and dispersed phases
ρ	liquid density
$\Delta\rho$	density difference
σ	surface tension

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