

Emulsion Copolymers of α -Methylstyrene and Styrene

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Synopsis

The preparation of copolymers of α -methylstyrene and styrene in an emulsion system is described. At both 40 and 60°C, there was no evidence of deviation from simple kinetics. Polymers of high molecular weight and high α -methylstyrene content showed good thermal properties such as T_g and softening point. However, these polymers proved to be awkward to process due to a strong proclivity to degrade under shearing conditions.

INTRODUCTION

α -Methylstyrene (AMS) is known to polymerize and copolymerize sluggishly in free radical bulk and solution processes. This behavior has been attributed to steric restrictions on the placement of successive AMS monomer units (penultimate group effect),¹ reversibility of AMS polymerization,² degradative chain transfer to monomer,³ and kinetic factors.⁴ These kinetic factors include low propagation rate for AMS homopolymerization ($k_p = 26$ mol/L s vs. 176 mol/L s for styrene).

The emulsion copolymerization of AMS with styrene has been described by Rudin and Samanta^{5,6} at temperatures ranging from 40 to 69°C. They reported that high molecular weight products having useful mechanical properties could be obtained, provided that the monomer feed contained less than 50% AMS. In addition, they noted that most aspects of this copolymerization could be accommodated by the Smith-Ewart model for emulsion polymerization of water-insoluble monomers.

Copolymers of AMS and styrene have glass transition temperatures between those of the corresponding homopolymers, namely 100 and 174°C for styrene and AMS, respectively. As a result, these copolymers may be useful in applications in which enhanced thermal characteristics are desirable relative to polystyrene, while other properties remain similar in nature.

This paper describes the preparation and characterization of AMS-styrene copolymers prepared in an emulsion system, with particular focus on compositions containing more than 50% AMS. Some aspects of processing are also described as AMS polymers have been shown to degrade under conditions of high temperature and shear.⁷

EXPERIMENTAL

Materials

Dowfax 2A1 soap (sodium dodecylphenyloxide disulfonate) was obtained from the Dow Chemical Company in 45% wt/wt concentration and was diluted

to 3% wt/wt for use in the polymerizations. Other reagents were used as received.

Preparation of Activator

Trisodium phosphate (2.4 g) ethylenediaminetetraacetic acid (EDTA) (0.77 g) and Formapon (sodium formaldehyde sulfoxylate, 2.4 g) were dissolved in deionized distilled water (300 g) under constant nitrogen purge. Another solution containing ferrous sulfate (0.60 g) dissolved in deionized distilled water (200 g) was also prepared. When all the respective components had dissolved, the ferrous sulfate solution was added to the Formapon solution. The resulting mixture was clear and colorless, and was stored under nitrogen.

Polymerizations

Polymerizations were carried out in two different reactors. The first was a 500 mL round-bottomed flask, fitted with mechanical stirrer, thermometer, water-cooled condenser, gas inlet, and septum. The following general procedure was used. Water and surfactant solution were mixed and bubbled with nitrogen for 0.5 h and were then charged to the flask. The monomers were added with intensive agitation and the reactor was purged with nitrogen, brought to reaction temperature, and sealed with a septum. In cases where the redox initiator was used, 2 mL of a 1% wt/wt sodium hydrosulfite solution was added to the reaction medium as an oxygen scavenger, followed by the *p*-methane hydroperoxide (PMHP). Finally, the activator solution was added to the reactor to start the polymerization. In cases where the potassium persulfate was used, the time of persulfate addition was taken as the start of the reaction.

The second reactor was a 1-gal stainless steel vessel fitted with a hydraulic agitator and heating/cooling coils. The reactor was scrubbed and rinsed with the surfactant employed in the reaction. Surfactant, water, and monomers were pumped into the vessel and the system was purged with nitrogen. Finally, the reactor was pressurized to about 140 kPa nitrogen and sealed. The initiation procedure was similar to that used for the small scale reactions above. The polymerization recipes are given in Table I.

Upon completion of the reactions, the latexes were steam stripped to remove unreacted monomer, then coagulated by adding the product dropwise to a warm (70°C), 0.5% wt/wt calcium chloride solution at a ratio of solution : latex = 4 : 1. The polymer was washed thrice with water and then dried in a convection oven at 50°C.

Analysis

The conversion was followed gravimetrically. Small samples (2 mL) were withdrawn from the reaction mixture and placed in tared aluminum dishes. The weight of latex and dish were recorded, and a few drops of shortstop (*N,N*-diethyl hydroxylamine, DEHA) were added. The polymer was precipitated by the addition of a small amount of methanol and the samples were dried to constant weight in a vacuum oven at 40°C. Conversion was determined from the dry weight of the polymer.

TABLE I
Polymerization Recipes

Reagent	Experiment		
	A	B	C
Temperature (°C)	60	40	40
Water (g)	180	100	800
Surfactant (g)			
3% Dowfax 2A1		170	1360
SDS	3.49		
Monomers (g)	100	150	1200
Initiator			
K ₂ S ₂ O ₈ (g)	0.86		
PMHP (mL)		0.75	4.8
Activator (mL)		15	96
1% Sodium hydrosulfite (mL)		7.5	60
		^a	^b
Time (h)	24	24	12

^a At 3.5 h, 20 h add 0.45 mL PMHP, 3.0 mL activator.

^b At 3.5 h, 7.0 h add 1.2 mL PMHP, 24 mL activator.

Changes in monomer feed composition were determined by gas chromatography. Samples of latex (about 0.3 mL) were withdrawn from the reactor and placed in a preweighed vial. The sample weight was recorded, 5 mL of tetrahydrofuran containing 1% toluene as internal standard, and 500 ppm hydroquinone as shortstop was added. When the polymer had dissolved, the solution was analyzed using a Shimadzu GC-9A instrument fitted with precolumn trap for nonvolatile materials and a Quadrex capillary column. The injection port was maintained at 220°C and the column temperature was 120°C. The relative amount of each monomer present in the sample was calculated using previously constructed calibration curves.

The amount of each monomer in the copolymers was determined by two methods. First, proton NMR spectra were obtained using a Bruker WP250 spectrometer. The amounts of AMS and styrene were determined by comparing the peak due to the α -methyl group at 0.3 ppm with the peaks arising from the aromatic protons in the 6.5–7.1 ppm region or the polymer backbone methane peak at 1.5 ppm. The second method was based on mass balance, knowing the feed composition via GC. In general, the two methods were in good agreement.

The molecular weight of the copolymers was measured using a Hewlett-Packard 1090 GPC with PL-gel columns and THF at 40°C as eluent. The calibration curve was constructed using narrow molecular weight distribution polystyrene standards.

Differential scanning calorimetry (DSC) and thermogravimetric (TGA) results were obtained using a DuPont 9900 thermal analyzer at scanning speeds of 10 and 20°C/min, respectively.

Capillary Rheometry

The rheology of the products was tested using a Goettfert Rheograph 2001 instrument fitted with 1 × 30 mm and 3 × 30 mm dies.

Physical Testing

To prepare the polymers for processing, samples were devolatilized by passing through a Haake Rheocord System 40 extruder fitted with a vacuum port. This was performed at 240–260°C and 30–60 rpm. The extrudate was chopped into fine pellets.

Samples for physical testing were prepared by compression molding at 240°C or injection molding using a Minijector injection molding machine. The conditions are given below:

Barrel temperature	240–260°C
Mold temperature	32–43°C
Heating time	1–2 min
Injection time	15 s
Cooling time	45 s

Measurement of tensile strength, tensile modulus, and elongation were carried out on type IV dumbbells as described in ASTM D632. Fragments of these dumbbells were used for Vicat softening point test (ASTM D1525). Heat deflection temperature under load (DTUL) and Izod impact tests were performed according to ASTM D648. Finally, melt flow index values (ASTM D1238) were determined using condition T (2.16 kg load, 250°C).

Particle Size Distribution

Average particle size of the latexes was determined using a Niacomp 680 particle size analyzer. The calculation procedure for number of particles is given by Rudin and Samanta.⁵

RESULTS AND DISCUSSION

Preparation of AMS/Styrene Copolymers

The first series of reactions was conducted at 60°C, as described by Rudin and Samanta.⁵ Monomer feeds ranging in composition from AMS/styrene = 20/80 to 70/30 by weight were polymerized under the conditions given in Table I, series A. The results for reactions A-1–A-6 are summarized in Table II. It is evident from the conversion vs. time plot (Fig. 1) that, as the AMS content of the feed increases, the copolymerization rate decreases. This effect is most pronounced in the reactions having AMS/styrene ratio greater than 1. The molecular weights of these copolymers decreased significantly with increasing AMS/styrene feed ratio. This is also reflected in the physical and mechanical properties (Table II).

The results of series A indicate that, in order to prepare copolymers having a softening point significantly greater than that of polystyrene while maintaining attractive mechanical properties, the synthetic variables would have to be modified to allow higher conversion of AMS-rich monomer feeds.

The low conversion and low molecular weights of the polymers obtained from reactions A-5 and A-6 could be attributed to phenomena such as depropagation of AMS units, or penultimate group effects due to the steric restrictions

TABLE II
Series A Copolymerization Results: Physical Properties of Series A Copolymers

Experiment number	A-1	A-2	A-3	A-4	A-5	A-6
Mole fraction AMS feed	0.170	0.269	0.370	0.468	0.567	0.673
Mole fraction AMS product	0.180	0.240	0.340	0.425	0.335	0.460
% Conversion	98.5	92.0	78.2	70.0	54.5	11.6
Reaction time (h)	5.9	7.8	9.7	10.8	26.1	25.1
$M_n \times 10^{-3}$	300	213	130	66.2	33.1	13.8
M_w/M_n	2.62	3.25	2.87	2.80	2.07	3.07
Average particle size (nm)		58			45	
N , number particles/mL, aqueous phase		4.7×10^{15}			6.9×10^{15}	
Vicat softening temp ($^{\circ}\text{C}$) ^a	111	121	127	131	—	—
Tensile strength (MPa) ^a	40.7	38.0	31.8	15.7	—	—

^a Samples compression molded at 240 $^{\circ}\text{C}$.

on the placement of successive AMS units in the copolymer. These effects, reported to result in significant deviations from simple Mayo-Lewis copolymerization kinetics,^{8,9} would be more prevalent in these reactions which contained large proportions of AMS in the feed.

The depropagation phenomenon is a temperature-dependent process¹⁰ and, thus, a reduction in the reaction temperature should improve the yield and molecular weight of the products in reactions using AMS-rich feeds, if depropagation were indeed occurring.

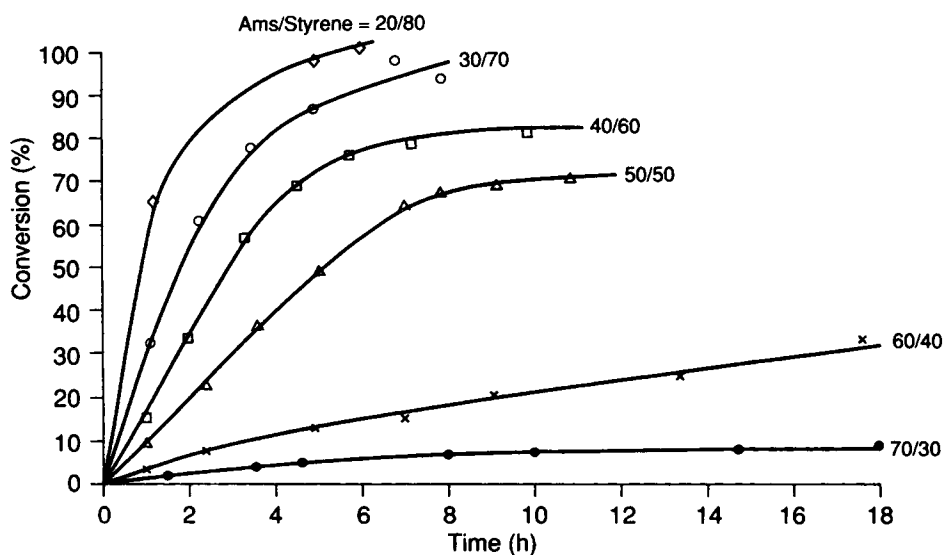


Fig. 1. Conversion vs. time for series A, 60 $^{\circ}\text{C}$. Run number is shown.

TABLE III
Series B Copolymerizations—Results

Experiment number	B-1	B-2	B-3	B-4	B-5	B-6
Mole fraction AMS feed	0.170	0.227	0.370	0.563	0.670	0.773
Mole fraction AMS product	0.157	0.193	0.333	0.510	0.580	0.640
% Conversion final	91	88	85	84	67	53
Reaction time (h)	2.5	4.5	5.0	20	20	20
$M_n \times 10^{-3}$	147,000	212,000	161,700	100,000	85,000	71,000
M_w/M_n	2.167	2.147	1.915	2.100		
Average particle size (nm)		36.4		30.8		
N , number particles/mL, aqueous phase		1.9×10^{16}		3.1×10^{16}		

Therefore, a second series of reactions was conducted at 40°C with monomer feeds ranging from AMS/styrene = 20/40 to 80/20 by weight. Reaction conditions are given in Table I, series B. The results (Table III and Fig. 2) indicate that, in general, the polymerizations were faster than the analogous reactions at 60°C. This is probably related to the number of particles, as discussed below. The differences are more striking in the AMS-rich cases, comparing, for example, the yields and molecular weights of reactions A-5 with B-4 and A-6 with B-5. The formation of copolymers containing predominantly AMS having high molecular weights was achieved with good yields in reactions B-4, B-5, and B-6.

A number of synthetic variables were changed in series B. These included initiator (potassium persulfate vs. redox), surfactant (sodium dodecyl sulfate

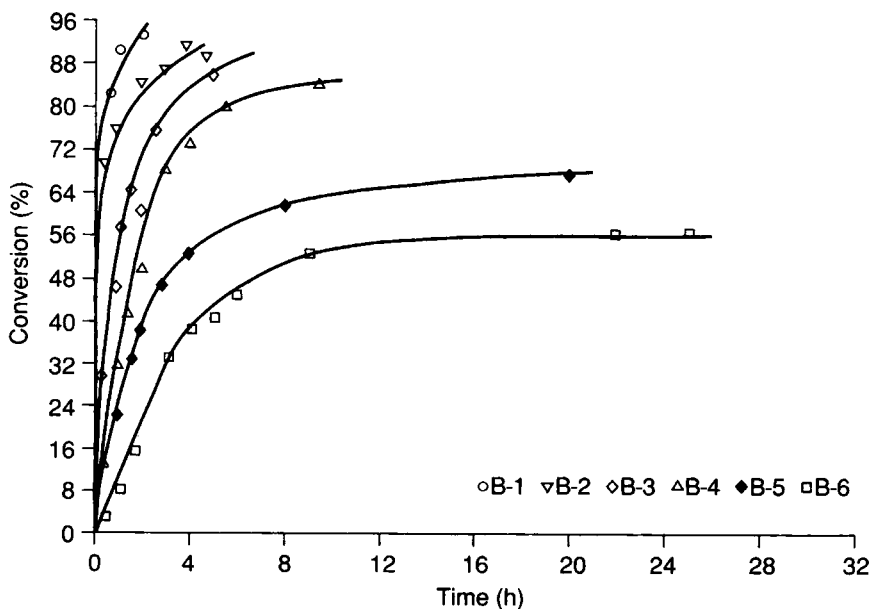


Fig. 2. Conversion vs. time for series B, 40°C. Run number is shown.

vs. DOWFAX 2A1) and reaction temperature, which, as discussed previously, may influence the copolymerization kinetics. The effect of changing reaction temperature on the course of the copolymerizations was examined by determining if the copolymerizations followed Mayo–Lewis kinetics. Reactivity ratios were estimated from the integrated Mayo–Lewis equation developed by Meyer and Lowry¹¹ and Skeist¹² to predict the drift in monomer composition during the copolymerization. The integrated Mayo–Lewis equation relates conversion and instantaneous feed composition:

$$m = 1 - \left[\frac{f_1}{f_{10}} \right]^\alpha \left[\frac{f_2}{f_{20}} \right]^\beta \left[\frac{f_{10} - \delta}{f_1 - \delta} \right]^\gamma \quad (1)$$

where f_{i0} and f_i are the initial and instantaneous proportion of monomer i in the feed at conversion m , r_1 , and r_2 are the reactivity ratios and

$$\alpha = r_2 / (1 - r_2)$$

$$\beta = r_1 / (1 - r_1)$$

$$\delta = (1 - r_1 r_2) / [(1 - r_1)(1 - r_2)]$$

$$\gamma = (1 - r_2) / (2 - r_1 - r_2)$$

Equation (1) was fitted separately to the data at 40 and 60°C using the nonlinear regression method of Marquardt. However, within each of these data sets, the model was not fitted to the data arising from any one initial feed composition in the derivation of r_1 and r_2 . This latter practice has been shown to be of limited value.¹³ The reactivity ratio estimates were similar for the two temperatures and the regression was performed again with the data from 40 and 60°C combined. A 95% confidence contour for the overall estimates of the reactivity ratios was calculated using the method of Box et al.¹⁴ (Fig. 3). Our values ($r_1 = 1.300$, $r_2 = 0.264$, styrene = r_1 , AMS = r_2) are compared with those reported by Golubeva et al.,¹⁵ and Rudin et al.¹⁶ and are shown to differ significantly.

If a copolymerization is adequately described by the Mayo–Lewis model, the data relating the variation of monomer composition with conversion should be randomly scattered around the curve predicted by the Skeist equation. If a trend in the residuals between the experimental and calculated points is observed, the Mayo–Lewis model does not provide an adequate representation of the polymerization.¹⁷

A comparison of the predicted and experimental data obtained at 40 and 60°C is given in Figures 4 and 5. Examination of the plots shows that the model fits the data reasonably well at both temperatures with there being random scatter about a line of slope = 1. Therefore, there is no evidence to indicate that the simple copolymerization model is inappropriate at either temperature. This in turn suggests that any depropagation or penultimate effects were not significant.⁴ As a result, the improvements observed in the production of AMS-rich copolymers at 40°C must have been due to the changes in the other synthetic variables. Let us now consider the effect of changing surfactant type and

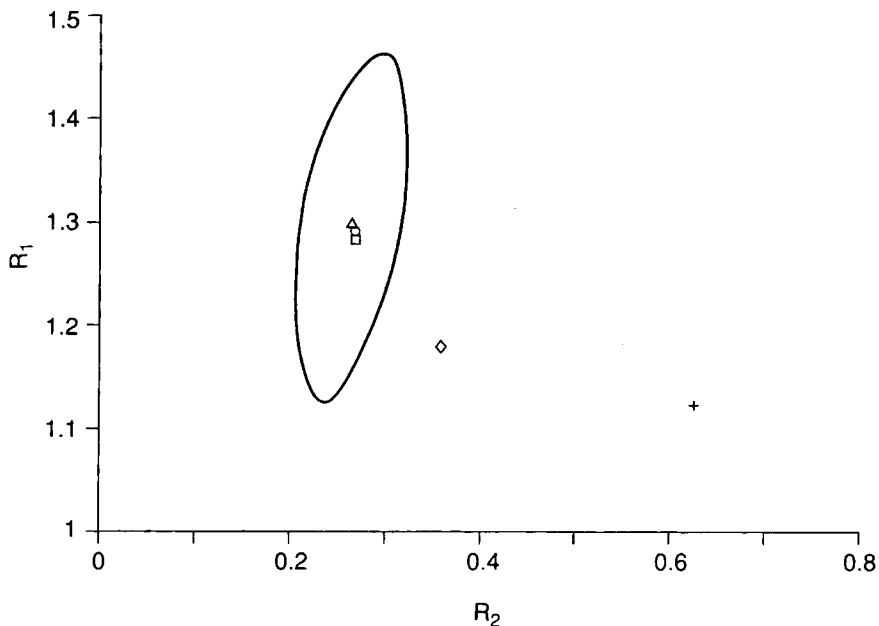


Fig. 3. Reactivity ratios obtained from 40°C data (\square), 60°C data (\triangle), and combined data (\circ). Estimates from Rudin (+) and Golubeva (\diamond) are also shown along with the 95% confidence contour for our combined data estimate.

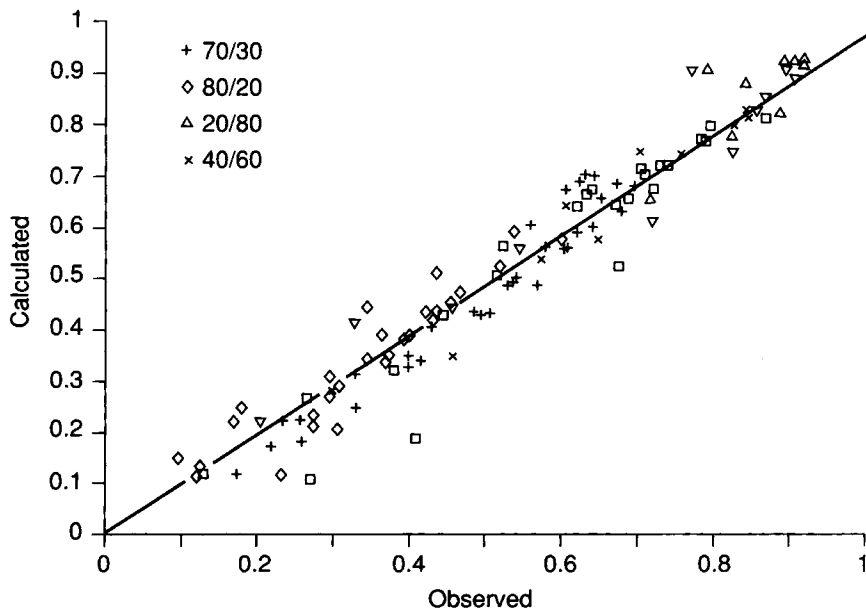


Fig. 4. Predicted vs. observed data for series B, 40°C.

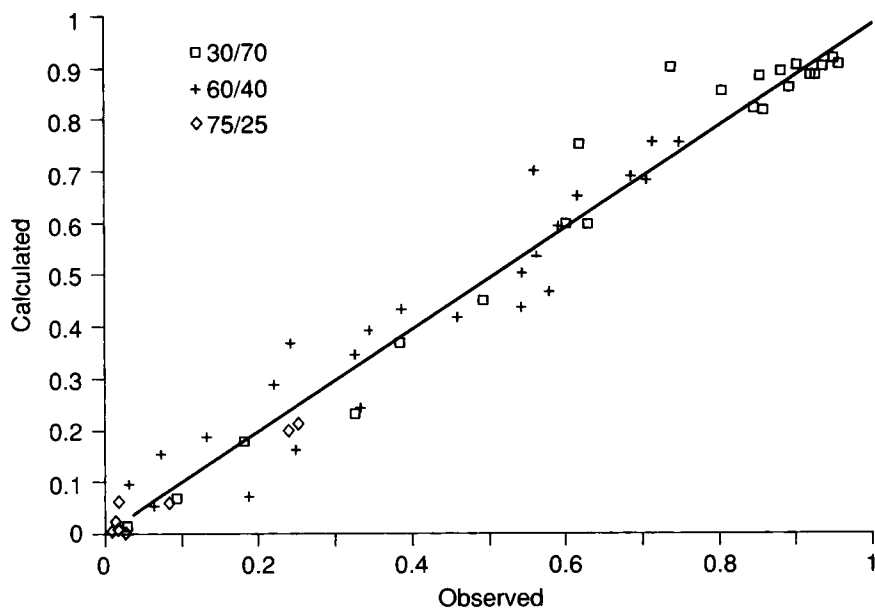


Fig. 5. Predicted vs. observed data for series A, 60°C.

concentration and initiator type on the number of particles produced and the implications with respect to kinetics.

Dowfax 2A1 was used in the reactions at 40°C rather than SDS in order to facilitate emulsifier removal from the polymer when coagulated in warm calcium chloride solution.¹⁸

The type and concentration of surfactant has a direct effect on N , the number of particles in an emulsion polymerization, which in turn directly affects the rate of polymerization (R_p) and the molecular weight of the material produced. According to Smith-Ewart kinetics, N is given by eq. (2) which, as Rudin⁵ demonstrated, describes the emulsion copolymerization AMS and styrene:

$$N = 0.37(p_i/\mu)^{0.4}(a_s[S])^{0.6} \quad (2)$$

where p_i = rate of radical generation, μ = rate of particle volume growth, a_s = adsorbed area/surfactant molecule, and $[S]$ = surfactant concentration.

SDS has a molecular weight of 288.38 g/mol. The surface area/molecule adsorbed on polystyrene latex particles, which are quite similar to the particles produced in the current reactions, is $60 \times 10^{-20} \text{ m}^2$.¹⁹ The concentration of SDS employed in the series A reactions was $6.66 \times 10^{-2} \text{ mol/L}$. By comparison, Dowfax 2A1 has a molecular weight of 569 g/mol. This surfactant was employed in the series B reactions at a concentration of $3.06 \times 10^{-2} \text{ mol/L}$, one-half the concentration of the SDS in the series A reactions. The surface area/adsorbed molecule is unknown for this particular reagent, but given the fact that the molecule is doubly charged, one would expect a significantly larger a_s than is observed for SDS.

To determine the influence of changing surfactant type and concentration on the AMS/STY copolymerizations, reaction A-2 was repeated except that

the SDS was replaced with Dowfax 2A1, at one-half the concentration. This particular reaction was found to reach 95% conversion in 6 h, yielding a copolymer with a number average molecular of 224,000. The average particle size of the latex was 60 nm. These results are very similar to those obtained in reaction A-2, except that a slightly higher molecular weight copolymer was produced. This implies that the change in surfactants between series A and B reactions had little effect on the outcome of the reactions, provided that Dowfax 2A1 was used at one-half the concentration of SDS. It appears then that the major cause of the different results obtained in the series A and B reactions was the type of initiator employed. In the reactions carried out at 60°C, $K_2S_2O_8$ was used as the initiating species. At 60°C, p_i is approximately 2.0×10^{13} radical/s mL with a half-life of 33 h.²⁰ However, the redox initiator, originally designed to operate at temperatures of 5–15°C, was employed at a temperature of 40°C in the series B reactions. This resulted in such a rapid initial rate of radical generation, p_i , that incremental addition of this reagent was required at 3.0 and 7.0 h to prevent premature stoppage of the polymerization due to depletion of the initiator. These facts suggest that during the particle nucleation stage of the emulsion copolymerization (conversion 0–20%), p_i was larger in the redox initiated systems at 40°C than the persulfate initiated reactions at 60°C. This would result in an increase in N , and a smaller particle size in the series B reactions, which was observed. This resulted in a significant increase in R_p for the series B reactions when compared with their series A analogues, since R_p is proportional to N in an emulsion polymerization. If p_i was constant in the series B reactions, the higher rate of radical generation, while giving rise to a greater rate of polymerization would produce a reduction in the molecular weight of the products produced. This is a result of the two relations $N \propto P_i^{0.4}$ while $M_w \propto N/p_i$. Typically, an increase in both R_p and molecular weight in an emulsion polymerization is achieved by increasing the surfactant concentration. This approach was not explored in this instance, as this would have promoted greater discoloration of the plastic upon processing. In the series B reactions, the small increments of added initiator were probably not large enough to raise p_i to the level achieved at the beginning of the synthesis. Thus, the ratio of N/P_i is larger than would normally be expected in the case where p_i is more or less constant over the course of the reaction, as in the series A experiments. However, the subsequent reduction in p_i during the course of the polymerization allowed for the observed increase in molecular weight.

Finally, reactions B-4 and B-5 only achieved conversions of 67 and 53%, respectively. Chromatographic analysis of the residual monomer remaining in the reaction media at these points indicated that the supply of the more reactive monomer styrene was virtually depleted at this point. The mole fraction of styrene remaining in the monomer feeds of B-4 and B-5 were 0.107 and 0.091, respectively. The manner in which these two conditions are linked is unknown at present.

Properties of AMS/STY Copolymers

The physical characteristic of the copolymers prepared in series A are given in Table II. The data, obtained from samples compression molded at 240°C, show that, as the amount of AMS in the copolymers increases, the softening

point of the copolymers increases. However, the mechanical strength of the copolymers decreases from reaction A-1 to A-4, mirroring the decrease in molecular weight of the copolymers.

Some of the series B copolymerizations yielded copolymers having high molecular weights and greater than 50% AMS. Three of these reactions, namely B4, B5, and B6 were scaled up, as described in Table I, series C. The copolymers were isolated and injection molded using a ram feed injection molding machine. The physical characteristics of these materials is summarized in Table IV. The data demonstrate that the copolymers have mechanical properties similar to that of polystyrene, but with markedly enhanced thermal properties. The AMS/STY copolymers are brittle in nature, as demonstrated by the Izod impact strength values, while having tensile strengths ranging between 50 and 28 MPa. The glass transition temperatures and Vicat softening points of the copolymers are 24–30°C higher than polystyrene. The melt flow index (MFI) measurements suggest that the copolymers may have high melt viscosities at temperatures of 250°C.

Previous researchers have suggested that AMS polymers and copolymers may have stability problems under thermoplastic processing conditions, (high temperature and shear). TGA thermograms of copolymer C-1 (mole fraction AMS = 0.51, M_n = 111,500) and C-2 (mole fraction AMS = 0.56, M_n = 88,700) are given in Figures 6 and 7. The thermograms show that, as the AMS content of the copolymers increases, the onset of decomposition as determined by extrapolation, decreases from 359 to 336°C. More realistically, the first evidence of weight loss for the copolymers occurs at lower temperatures (C-1, approx. 320°C; C-2 approx. 300°C). These values are the upper limits of temperature which can be used to process those copolymers.

Processing Behavior of AMS/STY Copolymers

Capillary rheology experiments, using AMS/STY copolymers C-1 and C-2, confirmed the initial data pertaining to the melt viscosity. Figure 8 shows the

TABLE IV
Mechanical Properties of AMS/STY Copolymers

Experiment number	C-1	C-2	C-3	Polysar Polystyrene 201 resin
Mole fr. AMS	0.51	0.56	0.64	0
M_n	111,500	88,700	78,100	175,000
M_w/M_n	2.30	2.07	1.97	
T_g (°C)	128	136	139	100
Tensile strength (MPa)	50.2	39.6	27.7	50.0
Elongation (%)	5	5	5	2.0
Tensile modulus (MPa)	2340	2670	2,590	3,100
Melt flow (g/10 min)	0.30 ^a	0.37 ^a	0.60 ^a	1.6 ^b
Vicat (°C)	130	133	129	106
Impact strength notched Izod (1/4 in. bar ft lb/in. notch)	0.27	0.20	—	—

^a Condition T.

^b Condition G.

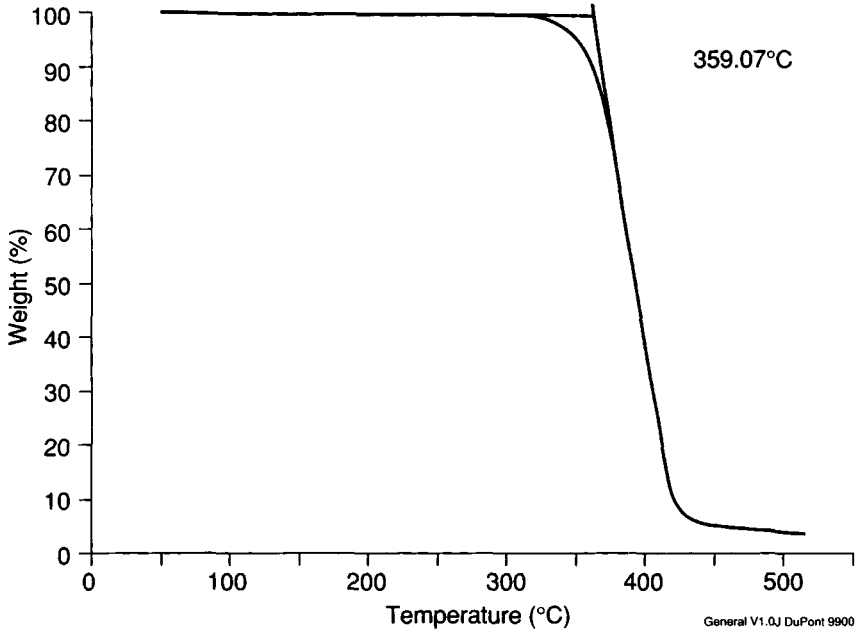


Fig. 6. TGA of C-1 copolymer.

relationship between apparent viscosity and apparent shear rate for copolymers D-1 and D-2 at 240°C, over a range of shear rates. For comparison, similar data are also shown for Polysar Polystyrene 201 resin at 200 and 240°C. It is

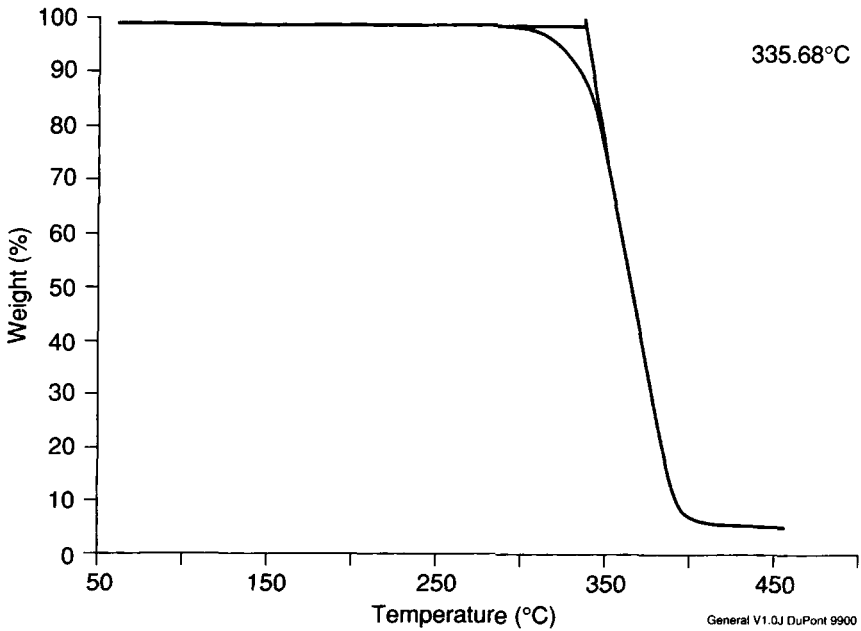


Fig. 7. TGA of C-2 copolymer.

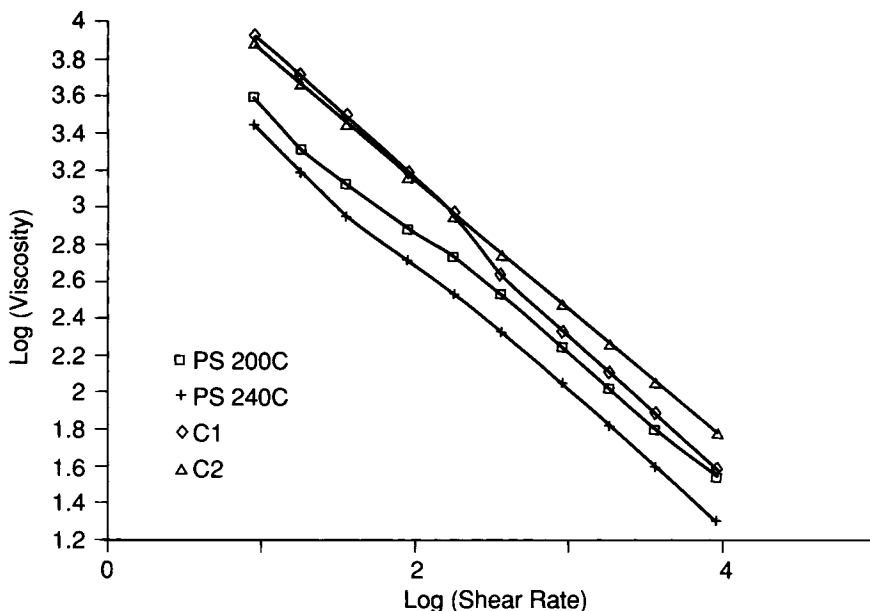


Fig. 8. Apparent viscosity vs. apparent shear rate for C-1 (\diamond) and C-2 (Δ) polymers at 240°C. Comparative data are shown for Polysar Polystyrene 201 at 200°C (\square) and 240°C (+).

not unexpected that the viscosities of the copolymers are higher than that of the polystyrene at 240°C. However, the copolymer viscosities are higher than those of polystyrene when the materials are both about 100°C above T_g . Thus, the AMS copolymers are more viscous at 240°C than the polystyrene at 200°C. This suggests further that processing the AMS copolymers may be problematic.

Although the copolymers demonstrate high melt viscosities, the thermal stability of the materials under high shear conditions was still not defined. Some insight into this question was obtained by recycling experiments using the capillary rheometer. Under conditions of 260°C and shear rates of 1800 and 3600 s^{-1} , an AMS/STY copolymer was recycled on the capillary rheometer. Although the time frame of this experiment is short compared to typical injection molding times (about 0.1 s in the rheometer experiment vs. seconds in an injection molding process), significant information may still be obtained. The results are given in Table V. It is obvious that the copolymer is degraded appreciably by a combination of temperature of 260°C and a shear rate of 3600 s^{-1} . At a shear rate of 1800 s^{-1} , the decrease in molecular weight is not as large. Processing conditions should be chosen to avoid such a decrease in molecular weight upon processing, if possible. This typically is achieved by increasing the processing temperature, but the TGA data indicate that there is not much flexibility in this regard. As a result, the AMS/STY copolymers, with their sensitivity to high shear conditions, must be classified as difficult to process.

CONCLUSIONS

We have shown that, by appropriate selection of reaction conditions, AMS-styrene copolymers having high molecular weight and good thermal properties

TABLE V
Thermal Stability of Copolymer C-1 during Capillary Rheometry

Cycle	Shear rate (s ⁻¹)	
	1800	3600
0	$M_n = 111,500$ P.D. ^a = 2.30	111,500 2.30
1	$M_n = 98,470$ P.D. = 2.44	79,100 2.654
2	$M_n = 101,600$ P.D. = 2.30	72,100 2.713
3	$M_n = 87,340$ P.D. = 2.55	

^a Polydispersity M_w/M_n .

can be prepared in an emulsion system. Sensitivity to shear degradation at high temperatures suggests some difficulty in processing under conditions of conventional fabrication.

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