

Emulsion Copolymers of Alpha-Methylstyrene and Styrene

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Synopsis

This article reports molecular weights and mechanical and processing properties of a series of styrene/alpha-methylstyrene copolymers produced by emulsion polymerization at various temperatures. Molecular weights were measured by solution viscosity, membrane osmometry, light scattering, and gel-permeation chromatography. Molecular weight development is controlled by chain transfer to monomer, but the molecular weight distributions are broader than would be expected for such reactions. This is attributed to polymer branching resulting from chain-transfer events. Molecular weight distributions of copolymers were multimodal. Thermal stability of the copolymers is somewhat lower than that of polystyrene, but addition of conventional antioxidants produces compositions with good stability in thermoplastic processing operations. Copolymers containing 25 wt. % of alpha-methylstyrene have usage temperatures about 12°C higher than that of polystyrene.

INTRODUCTION

The emulsion copolymerization behavior of alpha-methylstyrene and styrene has been reported in detail in a previous article,¹ in which it was shown that the reaction kinetics conformed quite well to the predictions of the Smith-Ewart-Gardon theory of emulsion polymerization of water-insoluble polymers which are miscible with their monomers. This appears to be the first test of this theory in a copolymerization system which meets all the postulates involved in the derivation of the model.

It was also demonstrated that the emulsion copolymerization of this monomer pair is consistent with the terminal copolymerization model,^{2,3} as expected from solution copolymerization studies.⁴

The copolymers made in this work are themselves of interest, since substitution of alpha-methylstyrene for some of the styrene produces an essentially styrenic polymer with higher usage temperatures than polystyrene. In this article we report the influence of emulsion reaction conditions on molecular weights of the product copolymers. This is a further test of the applicability of the "classical" emulsion polymerization model to a copolymer system.

Since poly(alpha-methylstyrene) is not as thermally stable as polystyrene, it was also of interest to compare the thermal stability of these copolymers with polystyrene.

A brief report is also included of the dependence of glass transition temperatures and mechanical properties on copolymer composition. These copolymers are the first reported radical-initiated styrene-alpha-methylstyrene polymers in which the molecular weights are sufficiently high that these properties are not dependent on molecular weight.

EXPERIMENTAL

Molecular Weight Measurements

Viscometry

Intrinsic viscosities $[\eta]$ were measured with Ubbelohde suspended level viscometers using toluene solutions at 25°C. Conventional plots according to the Huggins⁵ and Kraemer⁶ equations tended to be curved and not to yield identical $[\eta]$ values. This was not unexpected, since the molecular weights of these products are quite high. Good coincidence of extrapolated $[\eta]$ figures was obtained with the curvilinear least-squares technique of Rudin et al.⁷

Membrane Osmometry

The \bar{M}_n was measured by membrane osmometry at 22.5°C in toluene with deacetylated cellulose acetate membranes. Number-average molecular weights were obtained by linear least-squares fits to

$$\left(\frac{\pi}{c}\right)^{1/2} = \left(\frac{\pi}{c}\right)_0^{1/2} \left(1 + \frac{\Gamma_2}{2} c\right) \quad (1)$$

where π/c is the reduced osmotic pressure, the subscript zero denotes zero concentration, and Γ_2 is the second virial coefficient (in cm³/g). Equation (1) follows from the theoretical expression⁸

$$\frac{\pi}{c} = \left(\frac{\pi}{c}\right)_0 (1 + \Gamma_2 c + 0.25 \Gamma_2^2 c^2) \quad (2)$$

which is expected to hold for dilute $[\pi/c < 3(\pi/c)_0]$ solutions in good solvents.

Table I lists $[\eta]$, \bar{M}_n , and Γ_2 values, along with the compositions of copolymers formed from the initial reaction mixtures. The intrinsic viscosities of the three polystyrene homopolymers produced are equivalent to \bar{M}_v values of 1.1×10^6 , 2.0×10^6 , and 2.7×10^6 for the 69, 60, and 40°C polymers, respectively.⁹ The \bar{M}_n values of all copolymers are greater than 10^5 , which is a reasonably conservative estimate of the minimum number-average molecular weight needed for development of the full mechanical properties of styrenic thermoplastics.

The virial coefficients in Table I were obtained from data at six concentrations. The osmotic second virial coefficient for a 4.55×10^5 molecular weight polystyrene in toluene is reported to be 213 ± 27 cm³/g.¹⁰ Our three homopolymers average 249 cm³/g, which is in good agreement with the cited figure.

Goldwasser and Williams¹¹ found that second virial coefficients of 50/50 random anionic copolymers of styrene and alpha-methylstyrene were intermediate between those of the respective homopolymers at equivalent \bar{M}_n in toluene at 39°C. Our copolymer data compare quite closely with those of the authors cited.

The most important trend noticeable in the data in Table I is the decrease in second virial coefficient with increasing alpha-methylstyrene content in the copolymer. This compositional variation coincides with a decrease in \bar{M}_n , which in itself should cause Γ_2 to increase.¹² A likely reason for the decrease of second virial coefficients in toluene with increasing alpha-methylstyrene content is the poorer solvent power of the medium with increased aliphatic (methyl group) character of the copolymer.

TABLE I
Intrinsic Viscosities and Average Molecular Weights

Polymerization temp., °C	Code	Copolymer composition, mol fraction styrene	[η], ^a dl/g	Osmometry ^b		Light scattering ^c $\frac{M_w}{M_n} \times 10^{-5}$, g/mol
				$M_n \times 10^{-5}$, g/mol	Γ_2 , cm ³ /g	
69 ± 1	1C	1.0	2.61	5.81	232	13.3
	2C	0.922	1.87	2.75	74	—
	3C	0.843	1.64	2.29	58	—
	4C	0.763	1.11	1.83	45	—
	5C	0.680	0.95	1.52	33	3.0
	6C	0.594	0.69	1.32	53	—
60 ± 1	1B	1.0	3.96	6.85	232	—
	2B	0.922	3.01	4.27	115	—
	3B	0.843	2.11	2.77	128	7.74
	4B	0.763	1.53	2.62	113	6.79
	5B	0.680	1.28	1.88	92	—
	6B	0.594	1.06	1.78	71	—
40.7 ± 1	1A	1.0	5.00	8.40	282	20.0
	2A	0.922	5.43	4.32	134	22.7
	3A	0.843	4.74	3.91	137	—
	4A	0.763	2.58	2.35	96	—

^a Toluene solutions, 25°C.

^b Toluene solutions, 22.5°C.

^c Light scattering in chloroform, toluene, and benzene at 25°C.

The observed decrease of \bar{M}_n with increasing reaction temperature and alpha-methylstyrene feed content is qualitatively consistent with Smith-Ewart-Gardon^{13,14} kinetics of emulsion polymerization. If the average number of radicals per copolymer latex particle is 0.5, the rate of polymerization is¹⁵

$$R_p = \frac{N[M] K_{p1}K_{p2} [r_1f_1^2 + 2f_1f_2 + r_2f_2^2]}{2N_A [K_{p2}r_1f_1 + K_{p1}r_2f_2]} \frac{\text{mole}}{\text{cm}^3\text{s}} \quad (3)$$

where $[M]$ is the overall monomer concentration in the particles, N is the number of particles per unit volume of aqueous phase, N_A is Avogadro's constant, K_{p_i} is the propagation rate constant for monomer i which comprises mole fraction f_i of the feed, and r_1 and r_2 are the reactivity ratios. Also, the rate at which radicals enter particles (radicals/sec), r , is

$$r = 2\gamma N_A K_d [I] \quad (4)$$

where γ is the capture efficiency ($0 \leq \gamma \leq 1$) and K_d is the first-order decomposition rate constant of the initiator which is present at concentration $[I]$. The number-average degree of polymerization \bar{X}_n , is obtained by dividing the rate of polymerization (number of monomer molecules/particle/sec) by the rate (number of radicals/sec) at which radicals enter an active particle. That is,

$$\bar{X}_n = \frac{[M] K_{p1}K_{p2}[r_1f_1^2 + 2f_1f_2 + r_2f_2^2]N}{2[K_{p2}r_1f_1 + K_{p1}r_2f_2] \gamma N_A K_d [I]} \quad (5)$$

Since N is proportional¹³ to $(K_d)^{0.4}$, \bar{X}_n depends on $(K_d)^{-0.6}$. The activation energy E_d , for decomposition of $K_2S_2O_8$ in neutral solution is reported¹⁶ to be 31.4 kcal/mol, while that for propagation in both styrene and alpha-methylstyrene polymerizations, E_p , was taken to be equal to 7.4 kcal/mol.^{17,18} The overall activation energy for \bar{X}_n is equal to $E_p - 0.6E_d = -11.4$ kcal/mol according to eq. (5). The actual activation energies from Table I are, however, approximately -3 kcal/mol.

The foregoing calculation ignores the effects of chain transfer to monomers, and this accounts for the difference between the experimental values and those estimated from eq. (5). Reference 17 contains details of the magnitudes and temperature dependence of the transfer constants for each radical with either monomer in this system.

Light Scattering

Weight-average molecular weights of homopolymers can be calculated from light-scattering measurements by assuming that all polymeric species have the same refractive index. This is not true for copolymers in which the turbidity of a solution depends not only on the concentration, viewing angle, and mean molecular weight of the solute, but also on the heterogeneity of the chemical composition of the copolymer. \bar{M}_w of a binary copolymer can be determined in principle by measuring the scattering of light from at least three solvents with different refractive indices.^{19,20} The theory yields good values of \bar{M}_w , but the heterogeneity parameters which can also be estimated are usually not credible, at least for statistical copolymers.^{21,22} This difficulty has been attributed to the dependence of specific refractive index on polymer molecular weight and solvent.²³

Apparent \bar{M}_w values were measured in chloroform, toluene, and benzene solutions with 546-nm unpolarized light at nine angles between 30° and 145°. True \bar{M}_w averages were obtained as described elsewhere.²³ The procedure also yields estimates of the compositional heterogeneity of the copolymers. The magnitudes of these heterogeneity parameters were physically impossible in the present case. The probable reason has been mentioned above. \bar{M}_w figures are given in Table I.

Gel-Permeation Chromatography

The universal calibration method of Rudin and coworkers^{24,25} was used to establish the relation between effective hydrodynamic volume of the solute and elution volume in the particular GPC column set. This method yields the following expression for the hydrodynamic volume $V\epsilon$ of a polymer species with molecular weight M and intrinsic viscosity $[\eta]$ in a particular solvent:

$$V\epsilon = \frac{4\pi[\eta]M}{9.3 \times 10^{24} + 4\pi(N_{AC}([\eta] - [\eta]_{\theta}))} \quad (6)$$

where the units of concentration c and intrinsic viscosity are in g cm^{-3} and $\text{cm}^3 \text{g}^{-1}$, respectively. In eq. (6), V is the volume of an unperturbed molecule and ϵ is an expansion factor to allow for swelling by solvent. The intrinsic viscosity under analytical and theta conditions are denoted as $[\eta]$ and $[\eta]_{\theta}$, respectively, and can be calculated from the expressions

$$[\eta] = KM^{\alpha} \quad (7)$$

and

$$[\eta]_{\theta} = K_{\theta}M^{0.5} \quad (8)$$

where K and α are Mark-Houwink constants.

The elution volume in GPC is a function of the effective hydrodynamic volume of the dissolved species. At infinite dilution, M and $V\epsilon$ are related by

$$\ln M = \frac{\ln(9.3 \times 10^{24} V\epsilon_0/4\pi K)}{\alpha + 1} \quad (9)$$

where ϵ_0 is the expansion factor at zero concentration. A universal calibration curve can be established with sharp fractions of a standard polymer at finite concentrations, using eq. (6). This curve can be used to determine the molecular weights of components of a whole polymer by using eq. (9) provided the latter elute effectively at infinite dilution. This procedure reduces to the conventional Benoit method²⁶ if the elution volumes of the standard samples are not concentration dependent. Its usefulness depends on the GPC detector response being linear with weight concentration for all species in the particular sample. The usual detector is a differential refractometer which cannot function in the desired manner for copolymers in which the contribution of each comonomer to the refractive index of the polymer may differ. A 254 nm ultraviolet detector was used in combination with the differential refractometer.

The method for calculation of copolymer molecular weights was that of Runyon and coworkers,²⁷ in which it is assumed that the size of a copolymer molecule

is the sum of the sizes of the corresponding homopolymers weighted as to their relative proportions in the copolymer. That is to say,

$$\ln M_c = w_1 \ln M_1 + w_2 \ln M_2 \quad (10)$$

where M_c is the copolymer molecular weight at a given elution volume, w_1 and w_2 are the weight fractions of components 1 and 2 at that elution volume, and M_1 and M_2 are the respective homopolymer molecular weights at the same retention volume. The response factors²⁷ of polystyrene and a sample of cationically initiated poly(alpha-methylstyrene) were measured at different concentrations in chloroform, which was the GPC solvent. Peak areas were plotted against concentration. The weight fraction of monomer i in the copolymer which elutes at retention volume j is

$$w_{ij} = \frac{bF_{\mu j} - dF_{Rj}}{(b-a)F_{\mu j} + (c-d)F_{Rj}} \quad (11)$$

where F_{μ} and F_R are the signals from the ultraviolet spectrometer and differential refractive index detectors, respectively, and a to d are parameters from the response-concentration lines for the homopolymers.

GPC analyses were conducted in chloroform at 2.0–2.5 cm³/min flow rates. Sample concentrations were 2.5 g l.⁻¹, except for the response factor experiments, and 2-ml samples were injected.

The Mark-Houwink constants K and α for polystyrene were taken as 0.0122 cm³ g⁻¹ and 0.73, respectively.²⁸ K_{θ} was taken to be 0.08135 cm³ g⁻¹.²⁴

Mark-Houwink constants for the poly(alpha-methylstyrene)/chloroform system were not available in the literature. They were estimated by the following expedient. Kawai and Naito²⁹ have pointed out that the K and α values for a given polymer in various solvents lie on a common curve in which K decreases with increasing α . The K and α constants listed in the first edition of the *Polymer Handbook*³⁰ are plotted in Figure 1. It was assumed that α for poly-

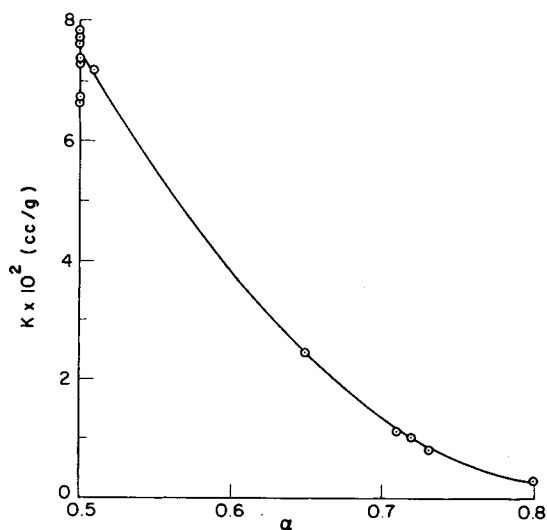


Fig. 1. Mark-Houwink constants for poly(alpha-methylstyrene) in various solvents. Data from ref. 30.

(alpha-methylstyrene)/chloroform solutions would be close to 0.7, by inference from polystyrene, which is chemically similar. The interpolated K for poly(alpha-methylstyrene) from Figure 1 is then $0.0136 \text{ cm}^3 \text{ g}^{-1}$.

Low-molecular-weight homologs of polymers do not generally have the same Mark-Houwink constants as higher-molecular-weight species. For polystyrene, $K = 1 \text{ cm}^3 \text{ g}^{-1}$ and $\alpha = 0.5$ for $M \leq 10,000$ in all solvents.³¹ These constants were used for the low-molecular-weight ranges of both homopolymers.

Representative GPC chromatograms are depicted in Figure 2. The curves shown are ultraviolet recorder traces. Polystyrene emulsion homopolymers (not shown) all had unimodal molecular weight distributions. Samples 3A, 3B, and 3C all contain 0.825 weight fraction styrene and were polymerized at 40.7, 60, and 69°C, respectively. The main peak is located at progressively lower molecular weights (higher elution volumes) with increasing reaction temperature. Subsidiary, lower-molecular-weight peaks are also more prominent at higher polymerization temperatures. The occurrence of multimodal molecular weight distributions during this copolymerization is not consistent with either the Smith-Ewart-Gardon emulsion polymerization model or the simple copolymerization theory. Both these models account reasonably well for the other observations in this study.¹

Table II lists the characteristics of the molecular weight distribution chromatograms. The breadth of the distribution is conveniently considered as the ratio of the standard deviation to the arithmetic mean of either the number or

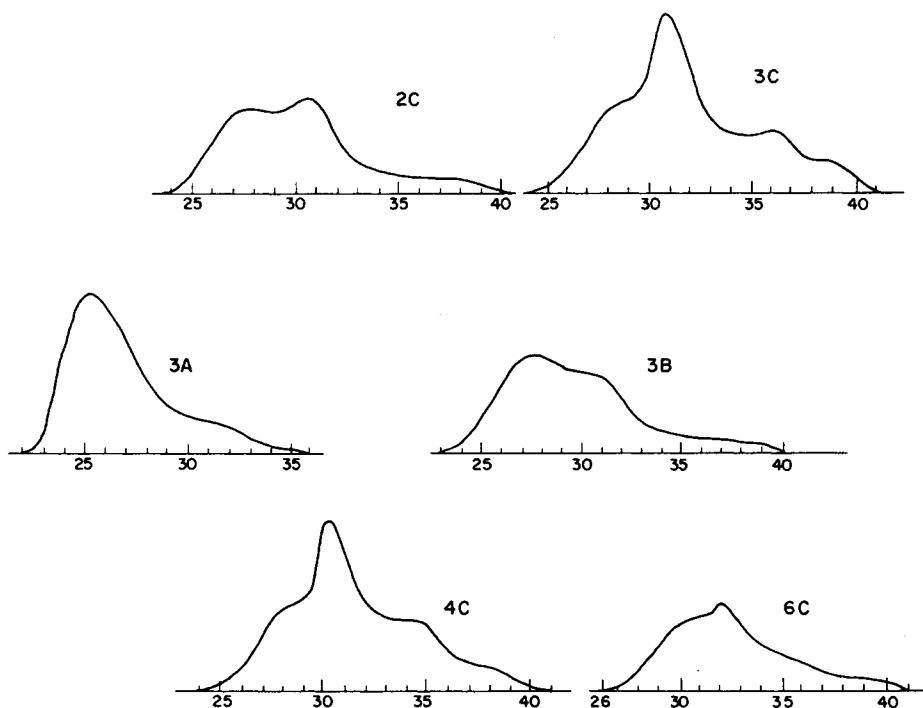


Fig. 2. GPC chromatograms (uv response) for various copolymers as characterized by weight fraction styrene, \bar{M}_w , and polymerization temperature, respectively: 2C, 0.912, 6.0×10^5 , 69°C; 3C, 0.825, 3.5×10^5 , 69°C; 3A, 0.825, 24.9×10^5 , 40.7°C; 3B, 0.825, 7.8×10^5 , 60°C; 4C, 0.739, 3.1×10^5 , 69°C; 6C, 0.564, 2.0×10^5 , 69°C.

weight distribution.³² The breadth of the number distribution (S_n/\bar{M}_n in Table II) is not noticeably sensitive to the polymerization temperature or the monomer feed composition. The weight distribution breadth (S_w/\bar{M}_w) is likewise insensitive to feed composition but may be slightly less broad at the lowest polymerization temperature.

Table II also compares the copolymer composition calculated from the simple copolymer equation and the reactivity ratios of Rudin et al.³³ and the composition calculated by summing w_{ij} [eq. (10)]. The two sets of values do not agree very well, although analytical and nmr measurements show that these reactivity ratios do indeed predict the polymer composition correctly.¹ The somewhat poorer agreement in this case probably reflects the fact that the specific refractive index increment which is recorded in the differential refractometer response is not independent of molecular weight, as assumed. For polystyrene, for example, Chau and Rudin²³ found that the specific refractive index increment increased with molecular weight up to $M > 10,000$, for some solvents. Errors as great as 15 or 20% can arise for this reason in estimates of the composition of low-molecular-weight species.³⁴ Styrene and alpha-methylstyrene have quite similar response factors, and relatively slight uncertainties in the assignments of a to d can have significant effects on calculations with eq. (10) in this case.

This same similarity which hinders accurate estimates of copolymer composition by GPC facilitates the measurement of molecular weight distributions. In this case, a polystyrene calibration produced average molecular weights which differed little from those obtained as described above with allowance for the copolymeric nature of the polymer.

It is tempting to use dual-detector GPC analysis to measure copolymer composition as well as molecular weight distributions. The experience recorded here suggests that the composition calculations may be reliable only if the copolymers do not contain appreciable quantities of low-molecular-weight species.

Molecular weight measurements from various methods are compared in Table III. The GPC \bar{M}_n values are generally significantly lower than those from membrane osmometry, but the \bar{M}_w data from light scattering and GPC are in good agreement. A possible explanation for the discrepancy in \bar{M}_n results involves leakage of low-molecular-weight species through the osmometer membrane.³⁵ The discrepancy between GPC and osmometric \bar{M}_n figures would be expected to increase, then, with increasing polymerization temperature, since this results in more low-molecular-weight species. This trend is seen in the data compiled in Table III. It should also be mentioned that the GPC values are calculated without any correction for band broadening, which would tend to produce \bar{M}_n data which are somewhat too low.³⁶

In this copolymerization the molecular weight is controlled by transfer reactions. Thus for sample 4B the rate of termination is 0.16×10^{-7} mol/l. of aqueous phase, while the overall rate of transfer reactions to monomer is 10-fold greater, 1.6×10^{-7} mol/l.¹⁷ Under these circumstances, the number distribution is random (i.e., Flory most-probable distribution) and $\bar{M}_w/\bar{M}_n = 2$.^{37,38} This is equivalent to $S_n/\bar{M}_n = 1$ and $S_w/\bar{M}_w = 1/\sqrt{2}$. These measures of the breadth of the molecular weight distribution recorded in Table II are wider than the expected values.

This is circumstantial evidence for the production of branched polymers because of chain transfer to polymer (unlikely) or through polymerization through

TABLE II
GPC Analyses of Copolymers

Polymerization temp., °C	Code	Copolymer composition, wt. fraction styrene		$\bar{M}_n \times 10^{-5}$	$\bar{M}_w \times 10^{-5}$	$\bar{M}_z \times 10^{-5}$	Standard deviation, $\times 10^{-5}$		S_w/\bar{M}_w	
		Calc.	Obs.				Number distribution, S_n	Weight distribution, S_w		
69 ± 1	1C	1.0	1.0	3.0	10.6	22.6	4.8	11.3	1.6	1.1
	2C	0.91	0.68	1.8	6.0	14.6	2.8	7.2	1.5	1.2
	3C	0.83	0.70	1.3	3.5	9.4	1.7	4.5	1.3	1.3
	4C	0.74	0.53	0.82	3.1	9.0	1.4	4.3	1.7	1.4
60 ± 1	6C	0.56	0.65	0.53	2.0	4.8	0.89	2.4	1.7	1.2
	1B	1.0	1.0	4.3	17.2	—	—	—	—	—
	2B	0.91	0.81	3.0	13.7	31.2	5.7	15.5	1.9	1.1
	3B	0.83	0.84	2.1	7.8	18.7	3.5	9.2	1.6	1.2
40.7 ± 1	4B	0.74	0.54	1.8	6.3	16.7	2.9	8.1	1.6	1.3
	5B	0.65	0.56	1.5	4.0	9.5	1.9	4.7	1.3	1.2
	6B	0.56	0.43	1.2	3.7	8.1	1.7	4.1	1.5	1.1
	1A	1.0	1.0	7.8	33.7	53.4	14.0	26.0	1.8	0.8
	2A	0.91	0.71	5.4	23.2	41.3	9.8	20.5	1.8	0.9
	3A	0.83	0.77	4.8	24.9	46.8	9.8	23.4	2.1	0.9
4A	0.74	0.68	3.1	13.1	27.2	5.6	13.6	1.8	1.0	

TABLE III
Comparison of Measured Average Molecular Weights

Polymerization temp., °C	Code	Copolymer Composition, wt. fraction styrene	$\bar{M}_n \times 10^{-5}$		$\bar{M}_w \times 10^{-5}$		\bar{M}_n (osm.)/ \bar{M}_n (GPC)
			Osmometry	GPC	Light scattering	GPC	
69 ± 1	1C	1.0	5.8	3.0	13.3	10.6	1.9
	2C	0.19	2.8	1.8	—	—	1.6
	3C	0.83	2.3	1.3	—	—	1.8
	4C	0.74	1.8	0.8	—	—	2.3
	6C	0.59	1.3	0.5	—	—	2.6
	1B	1.0	6.9	4.3	—	—	1.6
60 ± 1	2B	0.91	4.3	3.0	—	—	1.4
	3B	0.83	2.8	2.1	7.8	7.8	1.3
	4B	0.74	2.6	1.8	6.8	6.3	1.4
	5B	0.68	1.9	1.5	—	—	1.3
	6B	0.59	1.8	1.2	—	—	1.5
	1A	1.0	8.4	7.8	20.0	33.7	1.1
40.7 ± 1	2A	0.91	4.3	5.4	22.7	23.2	0.8
	3A	0.83	3.9	4.8	—	—	0.8
	4A	0.74	2.4	3.1	—	—	0.8

terminal vinyl groups. These unsaturated ends could arise from transfer to alpha-methylstyrene monomer involving loss of a hydrogen atom from the alpha-methyl group. (If there is substantial long-chain branching, the GPC calibration will be in error for higher-molecular-weight species.)

Thermogravimetric Analyses

The thermogravimetric behaviors of anionic and emulsion polystyrenes have been compared in an earlier publication.³⁹ Degradation in nitrogen was generally zero order for about the first 25% of the reaction and first order thereafter. Anionic and emulsion polymers differed significantly in thermal stability. Degradation of emulsion polymers proceeded more slowly and with higher activation energies in both the zero- and first-order regions. The differences in thermal stability were attributed to differences in end groups in the two polymer types. For this reason, the copolymers of the present study are most directly comparable with the emulsion polystyrenes.

Thermogravimetric experiments were carried out with a DuPont 950 balance attached to a model 900 differential thermal analysis unit. The heating rate was about 18°C/min, and samples were heated from ambient temperatures to 450°C under a 20 ml/min flow of dry nitrogen. Sample weights were between 1.8 and 2.6 mg. Thermogravimetric kinetic parameters are not affected by sample size in this range.³⁹

The data were treated as discussed elsewhere.³⁹ The primary thermogram was differentiated with computer assistance and some 10–15 data points were selected for a least-square fit to the equation

$$\ln \left(-\frac{dW}{dt} \right) = \ln A - \frac{E}{RT} + \ln W \quad (11)$$

In eq. (11), W is the weight of active material remaining at time t for a particular reaction with order n . A and E are the pre-exponential factor and activation energy, respectively, for the reaction in question. The regression analysis yields best-fit values of A , E , and n along with the 95% confidence limits or other statistical measures of the precision of these estimated values.

The reaction order in polystyrene degradation is close to unity in the 25–100% degradation region. The statistical analysis is improved if n is set identically equal to unity in this second degradation region.³⁹ This was not done with styrene-alpha-methylstyrene copolymers because there is no independent evidence that the reaction order is unity with these polymers.

The extent of degradation at which the reaction order changes from zero to close to unity is easily determined from the linearity of the plot of $\ln(-dW/dt)$ against $1/T$, which has slope $-E/R$ and intercept $\ln A$ when n in eq. (11) equals zero.

The primary thermograms of a polystyrene, a cationic poly(alpha-methylstyrene), and five emulsion copolymers are shown in Figure 3. The thermal stability of these copolymers evidently decreases with increased alpha-methylstyrene content. Kinetic degradation parameters are summarized in Table IV. As with polystyrene, the overall reaction order changes from zero to first order at about 25% degradation. The temperature at which this change in order is noticed is labeled $T_{0.1}$ in the table. This temperature decreases as the copolymer

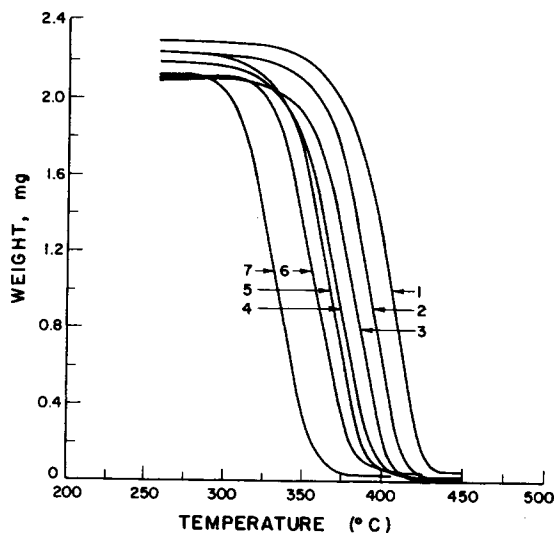


Fig. 3. Primary thermograms: 1, polystyrene; 2, copolymer, 0.910 weight fraction styrene; 3, copolymer, 0.825 weight fraction styrene; 4, copolymer, 0.740 weight fraction styrene; 5, copolymer, 0.650 weight fraction styrene; 6, copolymer, 0.564 weight fraction styrene; 7, cationic poly(α -methylstyrene) (from ref. 40).

becomes richer in α -methylstyrene. This reflects the fact that the 20–25% degradation level is reached at a lower temperature, at fixed heating rate, with lower styrene contents.

The maximum decomposition rate V_M does not show any clear relation with copolymer composition. The temperature for maximum decomposition rate T_M is, however, linear in copolymer composition. Figure 4(a) shows a plot of these data, in which the same line encompasses all the copolymer samples, as well as the two homopolymers. The temperature for half-weight loss T_w also fits a common relationship [Fig. 4(b)].

The thermal stability of these copolymers does not appear to be significantly affected by their polymerization temperature (cf. 3A, 3B, and 3C in Table IV).

It has been noted previously that the calculated E and A values are highly correlated with the estimate of n .³⁹ Sharp swings in E result from the form of the mathematical model and experimental error rather than from real variations in the degradation mechanism. The kinetic parameters listed in Table IV do not represent any particular reactions but are characteristic of kinetic change processes in which the overall order was observed to be zero or close to unity with respect to polymer weight.

Without venturing into mechanistic speculations, it can be seen from this study that the copolymers behave essentially like modified polystyrenes. Since polystyrene melts are quite stable at their processing temperatures, this suggests that the copolymers would also probably not present any processing stability problems. Capillary melt extrusion experiments at 210°C and 225°C verified this conclusion.

Samples for these melt viscosity measurements were emulsion products which had been coagulated in saturated, acidified brine, washed to remove salt and dried

TABLE IV
Thermal Decomposition of Styrene-Alpha-Methylstyrene Copolymers^a

Polymer-ization Temp., °C	Copolymer Composition, wt fraction styrene	$\bar{M}_n \times 10^{-5}$	Sample weight, mg	Heating rate, °C/min	T_M , °C	T_W , °C	$T_{0.1}$, °C	V_m , %/min	Extent of reaction, % decomposition	n	E , kcal/mol	A , min ⁻¹
69	1.0	5.8	2.25	18.3	405	402	385	40.7	1.4-24	0	35.7 ± 1.4	3 × 10 ¹¹ ±1
69	0.912	2.8	2.21	18.5	395	389	370	40.5	24-99	1.0	64.3 ± 4.5	5 × 10 ²⁰ ±2
60	0.825	2.8	2.11	18.5	385	380	365	44.9	1-20	0	42.5 ± 2.2	1.2 × 10 ¹⁴ ±
60	0.739	2.6	1.86	18.4	378	369	350	37.0	20-97	0.92 ± 0.05	49.9 ± 3.6	2.3 × 10 ¹⁶ ±1
60	0.652	1.9	1.88	18.2	370	365	340	39.0	2-23	0	44.9 ± 4.3	1.3 × 10 ¹⁵ ±2
60	0.564	1.8	2.07	18.6	360	357	340	43.2	23-96	1.3 ± 0.1	67.3 ± 8.2	2.7 × 10 ²² ±2
Cationic ^b	0	0.6	2.25	18.6	305	—	—	38.0	1-26	0	39.2 ± 0.9	2.2 × 10 ¹³ ±1
40.7	0.825	3.9	1.96	18.1	385	384	370	37.6	26-99	1.3 ± 0.9	56.0 ± 5.9	9.7 × 10 ¹⁸ ±2
69	0.825	2.3	2.03	18.2	400	392	375	40.4	1-20	0	44.2 ± 2.3	2 × 10 ¹⁵ ±1
									20-98	1.3 ± 0.10	58.1 ± 5.9	9 × 10 ¹⁹ ±2
									3-19	0	45.6 ± 0.7	9.5 × 10 ¹⁵ ±2
									19-96	1.3 ± 0.2	54.1 ± 14.6	5 × 10 ¹⁸ ±5
									0-34	3.5	64	—
									34-100	1.4	37	—
									5-27	0	36.4 ± 2.4	1 × 10 ¹² ±1
									27-99	1.3 ± 0.1	64.8 ± 10.1	2.6 × 10 ²¹ ±3
									0.7-21	0	41.1 ± 2.4	3 × 10 ¹³ ±1
									21-99	1.3 ± 0.2	62.0 ± 9.4	9 × 10 ¹² ±6

^a Symbols as follows: T_M , temperature for maximum decomposition rate; T_W , temperature for half-weight loss; $T_{0.1}$, temperature for reaction order transition; V_m , maximum decomposition rate; n , order of reaction; E , activation energy; A , frequency factor.

^b Data of Chiang (ref. 40).

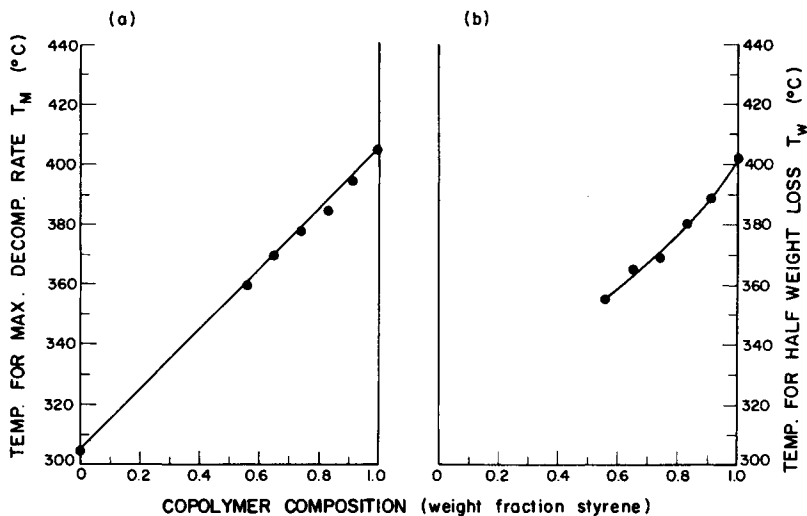


Fig. 4. (a) Temperature at which decomposition rate T_M is a maximum at a heating rate of $18^\circ\text{C}/\text{min}$. (b) Temperature for loss of half the initial sample weight at a heating rate of $18^\circ\text{C}/\text{min}$.

at 40°C in a vacuum oven. Stabilizer was added to the dry, powdery polymers by tumbling for 24 hr with 0.3% (w/w) 2,6-di-*tert*-butyl-4-methylphenol antioxidant. This concentration is more than enough to stabilize polystyrene itself in experiments of this type.⁴¹ Smaller concentrations would be used in commercial processing operations, where the residence time of the material at elevated temperatures is much less than in our experiments. No attempt was made here to find the minimum antioxidant level for processing stability under laboratory conditions.

All samples, including the emulsion-polymerized styrene homopolymers, developed a yellow-brown discoloration during the pressing operation. Further heat treatment in the capillary rheometer made no significant change in this color. Ordinary bulk-polymerized polystyrene shows no color change under comparable conditions, and it is believed that the problem is due to heat sensitivity of the particular surfactant which was used in this work.

Melt viscosity data are not recorded here because it is not possible to generalize about the effects of copolymer content without compensating for variations in molecular weight distributions between the various samples made in this study. The important conclusion in the present context is that solution viscosities measured before and after extrusion at the cited temperatures revealed no evidence of thermal degradation.

It is clear from the TGA and extrusion experiments that copolymers with substantial alpha-methylstyrene contents are sufficiently stable to be processed as styrenic thermoplastics. The ceiling temperature for high-molecular-weight alpha-methylstyrene homopolymer is 61°C ,⁴² but the enthalpy of polymerization is an inverse function of chain length at low molecular weights.⁴³ The alpha-methylstyrene sequence lengths in the present copolymers with styrene are so short that there is no direct reflection of the relative thermal stabilities of the two corresponding homopolymers.^{44,45} By analogy with the behavior of blends of the homopolymers,⁴⁶ it seems likely that the lowered thermal stability which

is observed in the copolymers reflects the initial generation of alpha-methylstyrene radicals which can abstract tertiary H atoms from polystyrene sequences to cause the progressive degradation of the latter components. The tabulated V_m (maximum decomposition rates) are not such as to indicate significant increases in direct unzipping to monomer in copolymers which are richer in alpha-methylstyrene.

Dynamic-Mechanical Properties

A Rheovibron dynamic viscoelastometer was employed in these studies. This apparatus subjects solid samples to a sinusoidally varying strain and measures the strain and the corresponding stress. The strain amplitude varies slightly with temperature and is about $0.3 \times 10^{-2}\%$ under ambient conditions. All measurements were made at 11 Hz unless otherwise noted. Specimens were cut from compression-molded sheets to the dimensions specified in the Rheovibron user's manual. The required thickness (0.3 mm) is quite low, and it was found that useful samples could be cut with a scalpel from the flash from compression-molded tensile bars.

The direct readout of $\tan \delta$ provided by the Rheovibron can be in error and a correction^{47,48} was applied to the data reported here.

Figure 5 shows loss modulus-temperature curves for various emulsion polymers in the temperature range -50 to 130°C . These results are best compared to the behavior of polystyrene, since the copolymers are essentially styrenic polymers with higher softening points. The major peak at temperatures $>100^\circ\text{C}$ corresponds to the main glass transition temperature. The weaker peak is variously reported in the 25 – 60°C region and merges into the main transition region at higher frequencies.⁴⁹⁻⁵²

The glass transition peak (at 11 Hz) shifts to higher temperatures as the

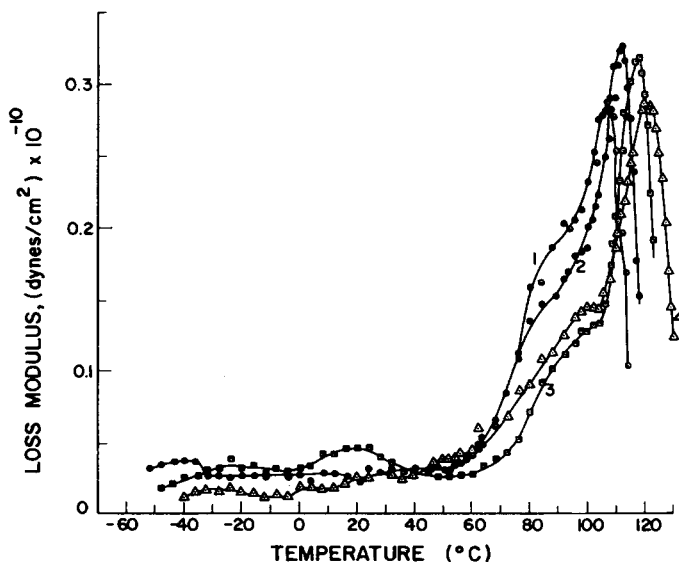


Fig. 5. Loss modulus-temperature curves (11 Hz) for 60°C polymerized samples: 1, polystyrene; 2, 0.912 weight fraction styrene; 3, 0.825 weight fraction styrene; 4, 0.739 weight fraction styrene.

alpha-methylstyrene content of the copolymer increases. The dynamic-mechanical transition temperature for polystyrene is about 108°C, while that of a copolymer containing 0.27 weight fraction of alpha-methylstyrene is 120°C. The weaker peak also shifted to higher temperatures and merged into the main peak as the copolymer became richer in alpha-methylstyrene.

The frequency dependence of the main glass temperature was investigated with the copolymer containing 0.088 weight fraction alpha-methylstyrene. The activation energy in the region of 3.5–35 Hz was 111 kcal/mol, which is as expected from other studies of styrenic polymers.⁵³

The T_g values were essentially the same for copolymers made at 60 and 69°C.

Glass transition temperatures were also measured by differential thermal analysis (DTA) as described by Rudin and Burgin.⁵⁴ The T_g values from the two methods are compared in Table V. The 11-Hz dynamic-mechanical T_g figures are about 8°C higher than the DTA values, which were extrapolated to a heating rate of 1°C/min.

The dependence of T_g on copolymer composition is expressed quite well in this case by

$$\frac{1}{T_g} = \frac{w_A}{T_{gA}} + \frac{w_B}{T_{gB}} \quad (12)$$

where w_i is the weight fraction of component i in the copolymer and T_{gi} is the glass transition temperature of its high-molecular-weight homopolymer.

Tensile data were obtained on eighth-inch compression-molded samples with the dimensions given as Type I in ASTM method D638-61T.⁵⁵ The properties of the copolymers were much like those of styrene homopolymers, except for tensile modulus increases of up to about 10%. Tensile strengths were in the range of 80–90 MN/m², Youngs' moduli were in the neighborhood of 280–300 MN/m², and maximum elongations were of the order of 2.5–3.0% at room temperature and elongation rates of 0.5 cm/min.

CONCLUSIONS

The observed number-average molecular weights are not predicted by emulsion polymerization theory because the development of \bar{M}_n is controlled by chain transfer to monomer.¹⁷ The number distribution of molecular weights is, however, not random, as would be expected under such circumstances. It seems most likely that this observation reflects the production of some branched

TABLE V
Glass Transition Temperatures from Rheovibron and DTA Experiments

Copolymer composition, wt. fraction		T_g , °C			
		Rheovibron, 11 Hz for polymerization temp.		DTA for polymerization temp.	
Styrene	Alpha-Methyl Styrene	60 ± 1°C	69 ± 1°C	60 ± 1°C	69 ± 1°C
1	0	107	109	100	100
0.912	0.088	112	110	105	108
0.825	0.175	118	117	109	~109
0.739	0.261	120	119	~112	~111

polymers produced by polymerization through terminal vinyl groups, which themselves resulted from chain transfer to alpha-methylstyrene monomer. The reasons for the multimodal nature of the GPC chromatograms are, however, not clear.

Thermogravimetric and capillary extrusion experiments show that copolymers with up to at least 0.40 weight fraction alpha-methylstyrene are sufficiently stable for conventional thermoplastic processing operations. As expected, glass transition temperatures of the copolymers are direct functions of alpha-methylstyrene contents.

This report and a preceding article¹ show that emulsion copolymerization of styrene and alpha-methylstyrene yields high-molecular-weight, mechanically useful polymers at fast rates. For most practical purposes the copolymers produced behave like polystyrenes with higher usage temperatures than conventional styrenics.

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