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Copolymers of Styrene and Methyl α-(Hydroxymethyl)acrylate: Reactivity Ratios, Physical Behavior, and Spectral Properties

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ABSTRACT: Compositions of copolymers prepared in low conversion by bulk polymerization of methyl α-(hydroxymethyl)acrylate (MHMA) and styrene were determined by UV and ^{1}H NMR spectroscopy. Copolymers were further characterized by IR, ^{13}C NMR, DSC, and TGA. Reactivity ratios for both MHMA and styrene, determined by the methods of Kelen–Tudos and Tidwell–Mortimer, were found to be about 0.33. Joint confidence limits determined for the various methods indicate that the more precise estimates are those of Kelen–Tudos and Tidwell–Mortimer even though the monomer reactivity ratios determined by the methods of Fineman–Ross, Joshi–Joshi, and YBR were of comparable value. Physical properties were intermediate between those of homopolymers although glass transitions were found to be sensitive to MHMA composition and thermal history. An intramolecular cyclization with concurrent loss of methanol involving adjacent or near-neighbor MHMA units is proposed to account for the thermal behavior. Copolymers with high MHMA composition demonstrate reduced solubility in chloroform.

Introduction

The accurate estimation of copolymer composition and the precise determination of monomer reactivity ratios (MRR) are of importance for tailoring copolymers with desired physicomechanical properties. Acrylic copolymers have achieved great importance in a number of industrial applications; hence a knowledge of copolymer composition is an important step in the evaluation of their utility and properties. We have elsewhere reported the synthesis, purification, characterization, and polymerization of MHMA.[1]

The simple copolymer equation derived by Alfrey and Mayo, eq 1, describes the ratio of the instantaneous rates of consumption of the monomers as a function of the instantaneous monomer feed ratio and two reactivity ratios, r_1 and r_2:[2,3]

$$\mathrm{d[A]/d[B]} = ([\mathrm{A}]/[\mathrm{B}])[(r_1[\mathrm{A}] + [\mathrm{B}])/([\mathrm{A}] + r_2[\mathrm{B}])] = m_1/m_2 \quad (1)$$

where d[A]/d[B] is the ratio of the instantaneous rates of consumption of the monomers A and B (A = M_1 and B = M_2, $M_1/M_2 = x_0$) by chain propagation. d[A]/d[B] is approximated at low conversions by the copolymer composition, $m_1/m_2 = y$, since d[A]/d[B] cannot be measured easily.

There are a number of difficulties in using eq 1 to determine MRR values. The ratio of instantaneous monomer consumption is only approximated by the copolymer composition; most copolymers show drift in the molar feed ratio. Linearized forms which use linear least squares are biased, and conversion is not generally considered.[4]

Integrated forms of eq 1 do not suffer from these same disadvantages. However, they require tedious and extensive computations and are not useful without a computer.[4–6,17]

Methods using the differential equation (eq 1) to determine MRR values are varied and generally fall into several broad catagories: linear,[7,8] intersection,[3,9,10] curve fitting,[11,12] computational,[13,14] and NMR triad evaluation.[15] There have been a number of reviews[6,16,17] and computer programs[18] published concerning the use and relative merits of a large number of methods.

A good determination of MRR values must meet five criteria as defined by Tidwell and Mortimer:[16] (1) It must give an unbiased estimate of the parameters. (2) It should utilize all the information resident in the data. (3) MRR values should not depend on reindexing or other arbitrary factors. (4) It should give valid estimates of the errors involved. (5) It should be relatively easy to use. The only approach that fits these conditions is a nonlinear least-squares method such as that described by Tidwell and Mortimer.

The *Q–e* scheme is an attempt to quantify monomer reactivity by considerations of inherent resonance (*Q*) and polar (*e*) factors of the adduct radical; steric factors, however, are not considered.[19] Once determined experimentally, MRR values can be employed in the *Q–e* scheme to predict copolymer composition in copolymerizations with other monomers.

Experimental Section

MHMA was readily prepared from methyl acrylate and paraformaldehyde in the presence of catalytic amounts of 1,4-diazabicyclo[2.2.2]octane (DABCO) as previously described.[1] **WARNING**: Small amounts of a potent byproduct generated by this method cause severe contact dermatitis. Other esters have not shown this deleterious behavior. Styrene was purified by

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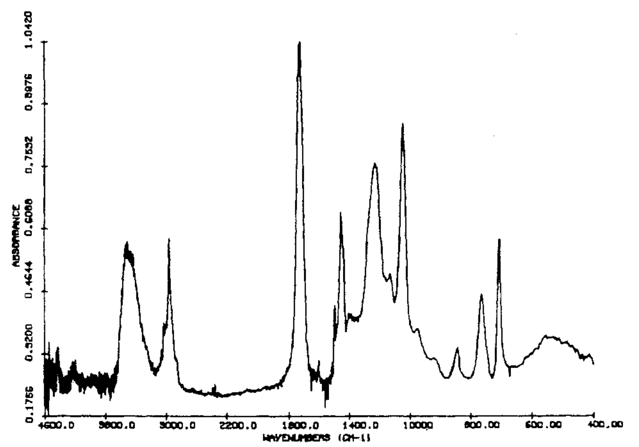
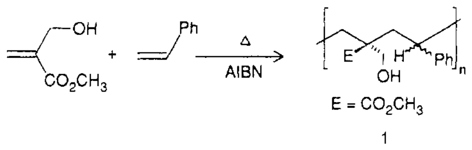


Figure 1. IR spectrum of a typical MHMA-*co*-styrene polymer with a 2:1 ratio of monomer units.

Scheme I
Proposed Lactone Formation Involving Adjacent MHMA Units



distillation and stored over 4A molecular sieves. AIBN was recrystallized from MeOH and stored in the dark in a refrigerator. Solvents and other reactants were reagent grade and used as obtained. IR analysis was performed on a Nicolet 5DX FT-IR. UV analysis was performed on a Perkin-Elmer 320 spectrophotometer. ^1H and ^{13}C NMR spectra were obtained on a Bruker MSL-200 spectrometer. Thermograms were obtained on a Du Pont 9900 equipped with 900 DSC and 910 TGA modules. Optical melting points were determined by using a Leitz Ortho-Pol polarizing microscope equipped with a Mettler FP5 hot stage.

General Polymerization Procedure. Carefully weighed quantities of styrene, MHMA, and AIBN were added to a 1-dram vial, cooled in an ice bath, degassed by bubbling nitrogen through the reaction mixture, sealed, and heated at 80 °C for a period sufficient to keep conversions low. The freeze–thaw method was found to be superior for degassing the samples prior to reaction and controlling conversion, although reactivity ratios should not be affected.

Polymeric material was precipitated by addition to diethyl ether containing a small quantity of hydroquinone. Products were further purified by precipitation, giving the polymers as white powders that were dried at 112 °C under vacuum.

Results and Discussion

Polymerization and Characterization. The copolymers (structure 1 in Scheme I) were readily obtained as white powders having optical softening points of about 140–160 °C. Spectral analysis confirmed copolymer formation.

For example, Figure 1 gives a typical IR spectrum showing an OH stretch at 3482 cm^{-1}, a CH stretch at 2951 cm^{-1}, a carbonyl stretch at 1722 cm^{-1}, a monosubstituted aromatic pattern at 759 and 706 cm^{-1}, and other major absorptions at 1450, 1224, 1038, and 839 cm^{-1}. Figure 2 shows typical ^{13}C NMR spectra with carbonyls at 175 ppm, aromatic carbons at 145, 128, and 126 ppm, the CH_2OH methylene at 61 ppm, the ester methyl at 51 ppm, and backbone absorptions from 50 to 39 ppm.

Copolymer Composition Analysis. The accurate determination of copolymer composition is of paramount importance to the accurate estimation of MRR values. The mole fraction of styrene in the copolymers were determined by UV absorption or proton NMR spectroscopy. Drying is a critical step needed to remove residual solvent and monomers. Copolymers having high MHMA compositions demonstrate reduced solubility in chloroform. This results in entries 18–21 of Table I being eliminated from evaluation because of inaccuracies inherent in analysis using hexafluoroisopropyl alcohol (HFIP) as the solvent.

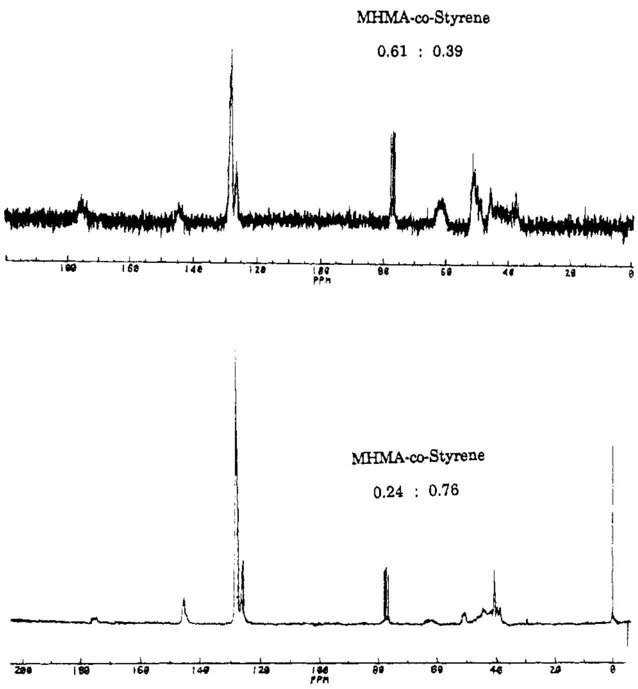


Figure 2. ^{13}C NMR spectra of typical MHMA-*co*-styrene polymers.

Copolymer Composition by NMR Spectroscopy. NMR offers a simple and rapid evaluation technique for copolymer composition based on the distinctive adsorption for the phenyl group. ^1H NMR spectra of several copolymers are given in Figure 3. They all show a distinctive and well-separated aromatic absorption at about 7.3 ppm and MHMA and backbone protons from about 4.0 to 1.5 ppm.

NMR copolymer compositions were easily determined. A quantity of polymer was dissolved in a volume of chloroform-d_1 containing TMS as the chemical shift standard, the spectrum obtained and integrated, and the composition determined by using

$$X_s = A_a/((A_b - 3A_a)/8) \tag{2}$$

where X_s is the mole fraction of styrene in the copolymer, A_a is the integrated area of the aromatic protons, and A_b is the integrated area of the styrene backbone plus MHMA protons.

Copolymer Composition by UV Spectrophotometry. UV spectrophotometric methods require that the constituent units have structurally different absorptions, and this requirement is met by the MHMA-*co*-styrene polymers. The molar absorptivity, ϵ, of polystyrene was determined from a plot of absorption vs polystyrene concentration. It was found to be 242.13 L/(mol·cm) with a linear least-squares correlation coefficient of 0.999. A carefully weighed quantity of copolymer was dissolved in a known volume of chloroform and the spectrum obtained by using pure chloroform in the reference cell. The mole fraction of styrene in the copolymer was determined from

$$X_s = (A_{abs}/\epsilon)/[(A_{abs}/\epsilon) + [m_g/V_L - \mu_s(A_{abs}/\epsilon)]/\mu_M] \tag{3}$$

where X_s is the mole fraction of styrene in the copolymer, A_{abs} is the absorption of the copolymer, ϵ is the determined

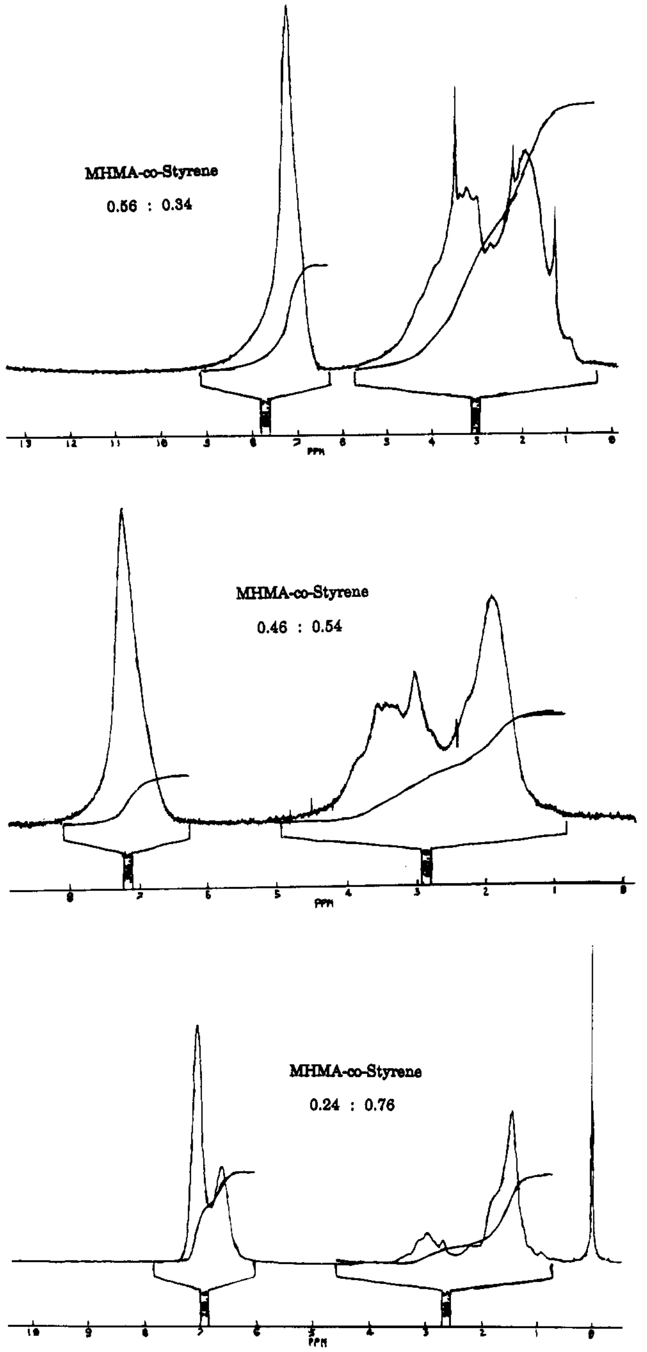


Figure 3. ^{1}H NMR spectra of typical MHMA-*co*-styrene polymers.

molar absorptivity of polystyrene, m_g is the mass of the copolymer in grams, V_L is the volume in liters, and μ_s and μ_M are the molecular weights of the styrene and MHMA repeat units.

Table I gives the wt % conversion and composition of the various copolymers isolated and analyzed. Values obtained by UV and NMR determinations were in relatively good agreement. Average values for both copolymer composition methods were used to determine MRR values.

Monomer Reactivity Ratios. Reactivity ratios for the MHMA/styrene system were calculated by using a number of well-known procedures. The behavior of the MHMA/styrene system was evaluated through a plot of copolymer composition vs feed composition (Figure 4). Both reactivity ratios are less than unity and of similar magnitude, as shown by an azeotropic composition at approximately 50% MHMA feed. A tendency toward alternation and no long homopolymeric blocks is expected.[20]

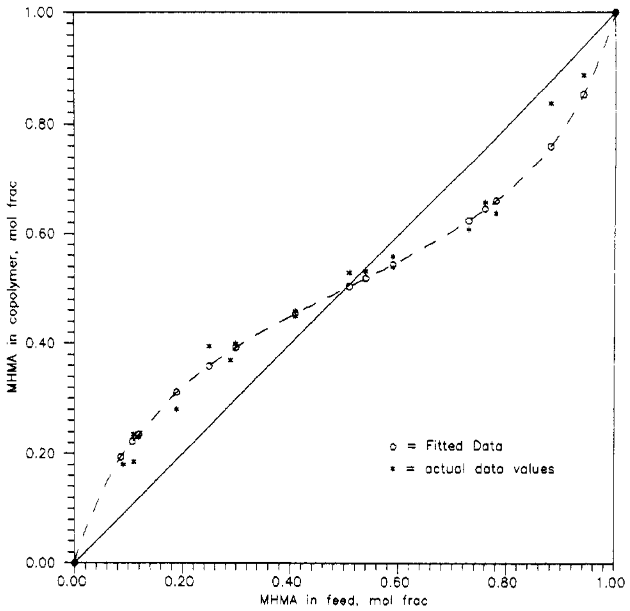


Figure 4. Copolymer composition vs feed composition (both in mole fractions).

The approximation method of Burfield and Savariar,[21] eq 4, gives a fast estimate of a reactivity ratio. It does have a number of serious disadvantages. For instance, it can only evaluate one monomer at a time, can only be used at very high monomer feed ratios, does not allow an evaluation of how well the data fit eq 4, assumes no deviation from eq 4, gives no estimate of the error structure, and requires very high precision in the analysis of copolymer composition to be accurate.

$$\ln([M_1]_t/[M_1]_0) = r_1 \ln([M_2]_t/[M_2]_0) \qquad (4)$$

MRR values estimated by eq 4 were found to be approximately 0.29 for r_{MHMA} and 0.38 for r_{styrene}. Considering the inherent difficulties, these cannot be considered very accurate, although the relative ranges should be close to the actual values.

The two linear methods most often used are the Fineman–Ross and Kelen–Tudos procedures, both of which are biased due to disregard of the error structure.[22] The amount of bias depends on the actual values of r_1 and r_2, the extent of reaction, and the number of experimental points.[12,23] The Fineman–Ross equation[7] (eq 5) is one of the earliest attempts to linearize eq 1 by defining new dependent and independent variables.

$$G = r_1F - r_2 \qquad (5)$$

G is defined as $x_0(1 - 1/y)$ and F as x_0^2/y, where y is the mole ratio of monomers in the copolymer and x_0 is the mole ratio of monomers in the feed. The slope of G vs F gives r_1, whereas the intercept is $-r_2$.

Behnken[23] and Tidwell and Mortimer[12] pointed out that linearization transforms the error structure in the observed copolymer composition with the result that the new errors no longer have zero mean and constant variances. This means that such transformed variables do not meet the requirements for least squares. This transformation also has the unfortunate consequence that eq 5 is no longer symmetrical with respect to the definition of which monomer is 1 and which is 2; this is referred to as reindexing error. It also suffers from a number of other disadvantages. Specifically, certain experimental points have abnormal and inappropriate weights in the Fineman–Ross plot; thus, experiments made at the lowest comonomer concentrations (M_2) have points the furthest from the vertical axis and with the greatest influence on the slope of the line. Fur-

Table I
Monomer Feed and Copolymer Composition Ratios (Mole Fraction)

				polymer composition					
		monomer feed		NMR		UV		averaged	
charge	conversion[a]	MHMA	st[b]	MHMA	st	MHMA	st	MHMA	st
1	4.5	0.09	0.91	0.19	0.81	0.18	0.82	0.18	0.82
2	2.9	0.11	0.89	0.18	0.82	0.19	0.81	0.19	0.81
3	10.1	0.11	0.89	0.20	0.80	0.27	0.73	0.24	0.76
4	6.8	0.12	0.88	0.23	0.77	0.24	0.76	0.23	0.77
5	9.2	0.19	0.81	0.28	0.72	0.29	0.71	0.28	0.72
6	16.2	0.25	0.75	0.38	0.62	0.41	0.59	0.40	0.60
7	22.1	0.29	0.71	0.38	0.62	0.37	0.63	0.37	0.63
8	6.7	0.30	0.70	0.42	0.58	0.38	0.62	0.40	0.60
9	4.8	0.41	0.59	0.51	0.49	0.44	0.56	0.46	0.54
10	4.8	0.41	0.59	0.49	0.51	0.44	0.56	0.45	0.55
11	14.8	0.51	0.49	0.53	0.47	0.53	0.47	0.53	0.47
12	8.1	0.54	0.46	0.53	0.47	0.54	0.46	0.53	0.46
13	11.3	0.59	0.41	0.55	0.45	0.56	0.44	0.56	0.44
14	8.2	0.59	0.41	0.56	0.44	0.53	0.47	0.54	0.46
15	9.1	0.73	0.27	0.60	0.40	0.62	0.38	0.61	0.39
16	23.6	0.76	0.24	0.67	0.33	0.65	0.35	0.66	0.34
17	5.1	0.78	0.22	0.62	0.38	0.66	0.34	0.64	0.36
18[c]	37.9	0.78	0.22	0.84	0.16	0.78	0.22	0.81	0.19
19[c]	44.9	0.87	0.13	0.92	0.08	*d*	*d*	*d*	*d*
20[c]	29.8	0.88	0.12	*d*	*d*	0.84	0.16	*d*	*d*
21[c]	31.5	0.94	0.06	0.89	0.11	*d*	*d*	*d*	*d*

[a] Wt % conversion. [b] Styrene. [c] NMR obtained in HFIP have inherent inaccuracy due to overlap of solvent peaks with peaks to be integrated. [d] Values not determined.

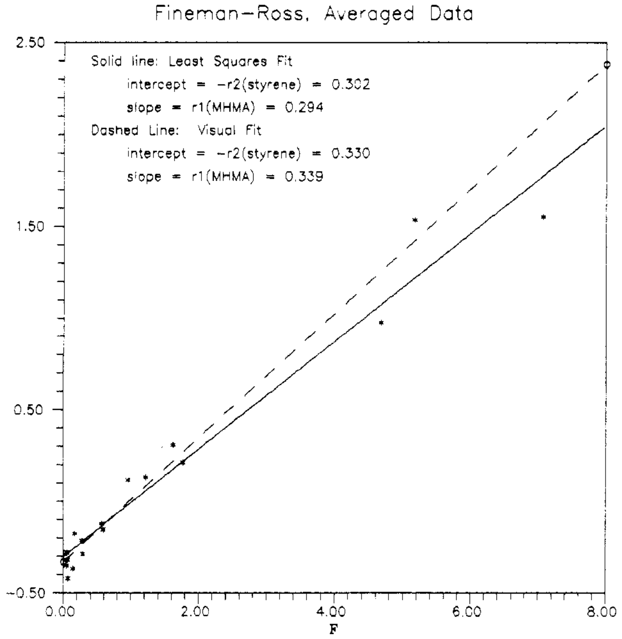


Figure 5. Fineman-Ross plot, averaged data.

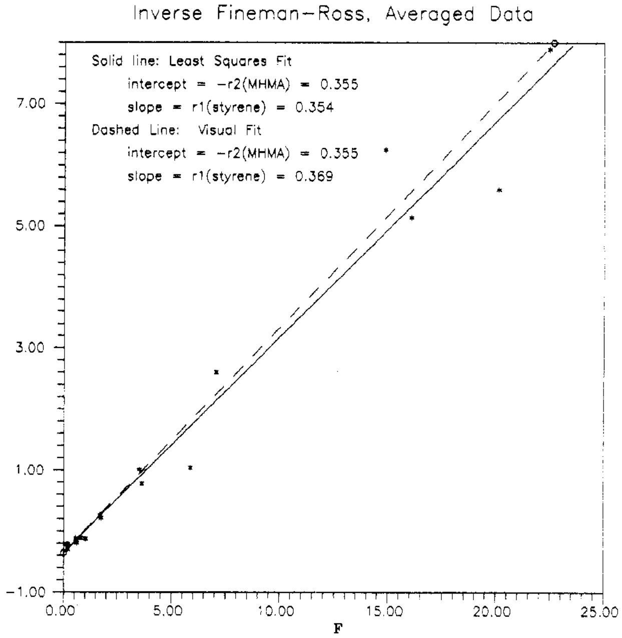


Figure 6. Reindexed Fineman-Ross plot, averated data.

thermore, eq 5 does not provide visual confirmation of eq 1, and degrees of conversion which affect y have been ignored. In general, the Fineman-Ross method is no longer considered appropriate except as a fast approximation of MRR values for use in more accurate procedures. Because of the various problems associated with the Fineman-Ross method it is recommended that the slope (which is affected least by subjective error) of the best visual fit of both the Fineman-Ross and reindexed Fineman-Ross plots be used to determine MRR values.[6] Figures 5 and 6 show the Fineman-Ross and reindexed Fineman-Ross plots for the MHMA/styrene system. MRR values determined from the best visual slopes are found to be 0.34 for MHMA and 0.37 for styrene.

The intersection method (originated by Mayo and Lewis[3]) is based on a rearrangement of eq 1 to give eq 6, so that the intersections of a family of lines, each representing one copolymerization experiment on an r_1 vs r_2 plot, give unique reactivity ratios. Its numerous disadvantages are that it requires a subjective estimate of the best intersection, does not give visual validation of eq 1, requires extensive calculation, does not give a quantitative estimate of error, and ignores the extent of conversion.

$$r_1 = r_2(1/F) + G/F \qquad (6)$$

The best procedure for determining the statistical intersection was proposed by Joshi and Joshi.[10] The procedure described is a least-squares analysis of eq 5 such that each experimental point is weighted by the factor $1/(1 + m_i^2)$ prior to doing a linear least-squares analysis of the data. This is a nongraphical procedure which gives the point of intersection as the one that is statistically closest to all the experimental intersections and which, if it were not for experimental errors, would lie on every line of the

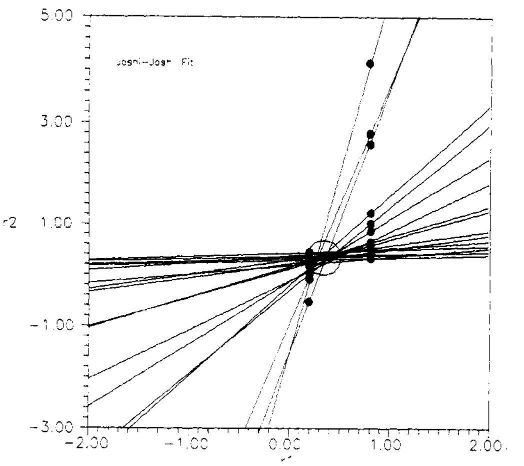


Figure 7. Joshi–Joshi/Mayo–Lewis plot, averaged data.

Mayo–Lewis plot, resulting ideally in a unique intersection point. It is not subject to reindexing errors and allows confidence limits to be determined. However, it has the same disadvantages as any other linear least-squares procedure and ignores the effect of conversion.

Despite the fact that this method has been found to be unsatisfactory in yielding a rational solution,[6] reactivity ratios for the MHMA/styrene system have been determined, $r_{\mathrm{MHMA}} = 0.363 \pm 0.069$ and $r_{\mathrm{styrene}} = 0.346 \pm 0.162$, and are graphically illustrated in Figure 7.

A numeric procedure, originated by Yezrielev, Brokhina, and Roskin[13] (YBR), is the result of a symmetrical transformation of eq 5 to give eq 7.

$$r_1 F^{0.5} - r_2 F^{-0.5} - G F^{-0.5} = 0 \tag{7}$$

This method is not subject to reindexing errors and gives a valid estimate of the confidence limits. However, it does have the same disadvantages of any linear least-squares procedure, and conversion has been ignored. Reactivity ratios for MHMA and styrene determined by the YBR method were $r_{\mathrm{MHMA}} = 0.326 \pm 0.032$ and $r_{\mathrm{styrene}} = 0.349 \pm 0.016$.

The Kelen–Tudos equation (eq 8) symmetrically transforms eq 5 by introducing new parameters η and ξ and a symmetry parameter α defined as $(F_{\min}/F_{\max})^{0.5}$, where $F_{\min}$ and $F_{\max}$ represent the lowest and highest values of F that are calculated.

$$\eta = \xi(r_1 + r_2/\alpha) - r_2/\alpha \tag{8}$$

The transformed variables are defined as $\eta = G/(\alpha + F)$ and $\xi = F/(\alpha + F)$, where the variable ξ can take any possible value in the interval of 0 and 1. A plot of η vs ξ gives a straight line, which on extrapolation to $\xi = 0$ and $\xi = 1$ gives $-r_2/\alpha$ and r_1, respectively.

Kelen and Tudos modified this equation for high conversion by redefining F and G as follows: $\mathrm{F} = (m_1/m_2)/(\log z_1/\log z_2)^2$ and $G = (m_1/m_2 - 1)/(\log z_1/\log z_2)$, where $z_1 = M_{1\mathrm{F}}/M_{10}$ and $z_2 = M_{2\mathrm{F}}/M_{20}$. M_{10}, $M_{1\mathrm{F}}$, and M_{20}, $M_{2\mathrm{F}}$ represent the initial and final concentrations of monomer 1 and monomer 2, respectively. This procedure does not suffer from reindexing errors and, with this modification, can be used with relatively high conversions. Furthermore, it gives the data symmetrically located along the interval of the independent variable and gives a visual evaluation of the applicability of eq 1. Its principal disadvantages are the same as any linearized form of eq 1.

Figure 8 of the conversion-extended Kelen–Tudos plot gives $r_{\mathrm{MHMA}} = 0.325 \pm 0.047$ and $r_{\mathrm{styrene}} = 0.326 \pm 0.046$ with a correlation coefficient of 0.975. The calculations required for an extended Kelen–Tudos analysis are described in detail in the Appendix.

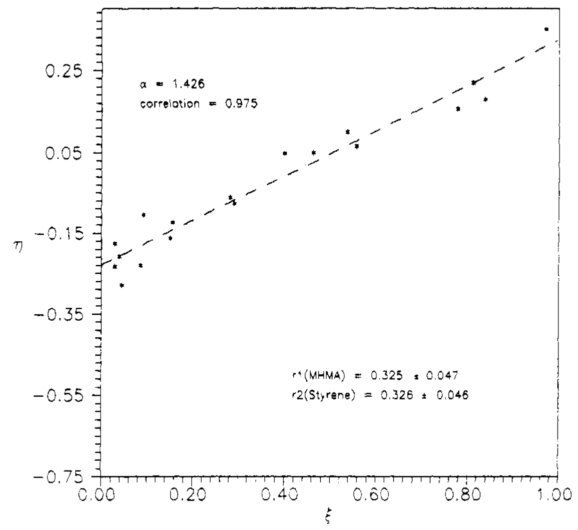


Figure 8. Extended Kelen–Tudos plot, averaged data.

Table II
Summary of Monomer Reactivity Ratios

method	r_{MHMA}	r_{styrene}
approximation	0.29	0.38
Fineman–Ross[a] reindexed	0.34	0.37
Joshi–Joshi	0.363 ± 0.069	0.346 ± 0.162
YBR	0.326 ± 0.032	0.349 ± 0.016
Kelen–Tudos	0.325 ± 0.047	0.326 ± 0.046
Tidwell–Motimer	0.326	0.330

[a] Values given are of the slopes of the best visual fits.

The nonlinear least-squares procedure as outlined by Tidwell and Mortimer[12] is considered to be one of the most accurate and unbiased procedures for the determination of MRR values.[16] The method is a modification of the curve-fitting procedure such that the sum of the squares of the difference between the observed and computed polymer compositions is minimized. The computation procedure is basically a Gauss–Newton nonlinear least-squares method with a modification by Box[24] to assure rapid convergence to a pair of values. A brief description of the method consists of the following: given initial estimates of r_1 and r_2, a set of computations is performed yielding the sum of the squares of the differences between the observed and computed polymer compositions; the sum is then minimized by iteration yielding unique reactivity ratios. Tidwell and Mortimer[12] recommend that monomer feeds that result in copolymer compositions of 30–70% give maximum reliable information of the MRRs of a copolymerization system. This procedure gives unique r_1 and r_2 values and provides means of evaluating how well the reactivity ratios have been estimated and if the data are consistent with eq 1.

Nonlinear least-squares procedures such as that of Tidwell and Mortimer are considered to be the only statistically accurate means of determining reactivity ratios from data obtained at low conversions.[25] Nonlinear least squares is most suitable when the following conditions are met: (1) errors in the dependent variable are random and statistically independent from observation to observation with constant variance, (2) the independent variable contains no measurement error, and (3) the copolymerization model is consistent with the experimental data.[17]

Reactivity ratios calculated by the method of Tidwell and Mortimer for the MHMA/styrene are 0.326 for r_{MHMA} and 0.330 for r_{styrene}. The computations required to obtain Tidwell and Mortimer estimates are described in detail in the Appendix.

Table III
Comparable Reactivity Ratios[26]

monomer	r_{acrylate}	r_{styrene}
methyl acrylate	0.20	0.75
ethyl acrylate	0.48	0.80
butyl acrylate	0.21	0.82
methyl methacrylate	0.35	0.35
ethyl methacrylate	0.29	0.65
butyl methacrylate	0.64	0.54
MHMA	0.33	0.33

Table II summarizes the reactivity ratios determined by the above methods. It is evident that both r_{MHMA} and r_{styrene} are about 0.33 as determined by both the extended Kelen–Tudos and the Tidwell–Mortimer procedures. One of the referees pointed out that the Tidwell–Mortimer method is not accurate for results obtained at higher conversions, which applies to some of the data in Table I. This is because monomer composition changes with conversion (except at the azeotropic feed composition) and drifts away from the azeotropic composition. Experiments 3 and 16, which were obtained at high conversions and are located relatively far from the 50% (azeotropic) composition, may have a serious effect on the MRR. However, most of the data points were obtained at lower conversions, and some of the high conversion data points are close to the azeotropic composition, where the drift is not so serious. Therefore, we conclude that the reactivity ratios do not change much if conversion drift is neglected in this data set for the Tidwell–Mortimer calculation. It has been reported previously that under proper conditions the Kelen–Tudos procedure can be used with almost as much confidence as a nonlinear least-squares procedure.[25]

Considering the joint confidence limits (discussed in detail in a later section), the other procedures used are not as accurate, and the reactivity ratios obtained using them are less reliable despite their low apparent errors. In summary, it is recommended that a nonlinear least-squares or Kelen–Tudos procedure be used to determine reactivity ratios.

Overall Copolymer Structures. The reactivity ratios of 0.33 indicate that at equal monomer concentrations the adduct radical of either monomer is about 3 times more likely to react with the other monomer relative to its own monomer. This would indicate a random copolymer with a strong tendency toward alternation. Long blocks of homopolymer are therefore not expected to any extent in the copolymers except at feed ratios far from 1. This conclusion coincides with Figure 4, which graphically shows this behavior. These reactivity ratios may be compared to reactivity ratios calculated for other acrylate/styrene systems (Table III) under similar conditions.[26] The reactivity of MHMA is essentially identical with that of methyl methacrylate.

Confidence of Experimental Design. It has been shown by Tidwell and Mortimer[12,16] that experiment design plays a significant role in the determination of reactivity ratios and joint confidence limits. Kelen and Tudos introduced a quantitative measure of the confidence δ, which is defined by the relative values of confidence intervals

$$\delta = (\Delta r_1 \Delta r_2)/(r_1 r_2) \tag{9}$$

for systems consistent with the simple binary copolymerization model of eq 1.

A class 1 system is defined by Kelen and Tudos[8] as one that is strictly linear and describable by the two-parameter binary system and has a δ value less than 0.1. Class 1(!) systems are linear and still describable by the two-parameter model but giving poorer parameter estimates because of a greater dispersion of experimental points. The borderline between class 1 and class 1(!) systems is not very sharp, and the η vs ξ plot must be considered to judge the classification of intermediate systems. A δ of 0.02 was calculated for the MHMA/styrene system by using the reactivity ratios determined by the Kelen–Tudos procedure. Figure 8 gives a correlation coefficient of 0.975 and indicates that this is a class 1 copolymerization.

Kelen and Tudos proposed that a well-planned experiment has $\Delta r_1 = \Delta r_2/\alpha$, $\alpha_{\text{exptl}} = \alpha_{\text{theor}}$, and $\Delta r_1/r_1 = \Delta r_2/r_2$, where $\alpha_{\text{theor}} = r_2/r_1$. With these considerations in mind, Kelen and Tudos introduced a parameter Q_{KT} that allows a quantitative evaluation of the design of an experiment

$$Q_{\text{KT}} = \exp[-|\ln (r_2/(r_1\alpha))|] \tag{10}$$

Q_{KT} has a maximum value of 1 since it was shown that in ideally planned experiments the auxiliary paramter α is equal to the ratio of the copolymer parameters r_2/r_1.[8] A low Q_{KT} value, obtained when α_{exptl} is significantly different from the ideal, indicates an improperly designed experiment. Although general conclusions could not be reached by Kelen and Tudos, they reported that class 1 determinations are associated with high values of Q_{KT}.

The following parameters were calculated by using reactivity ratios and confidence intervals for the MHMA–styrene system that were determined by the extended Kelen–Tudos procedure:

$$\alpha_{\text{exptl}} = 1.426 \qquad \Delta r_1/r_1 = 0.145 \qquad \Delta r_2/r_2 = 0.141$$
$$Q_{\text{KT}} = 0.702$$

Considering all of these parameters, it can be concluded that the experimental design of the MHMA/styrene system is qualitatively a good one.

Joint Confidence Limits. Simple intervals do not clearly convey the message of which pair of parameters are consistent with the data since estimates of the reactivity ratios must be simultaneously determined and therefore cannot be considered statistically independent. The specification of joint confidence limits, within which the correct values are believed to exist, properly conveys some idea of the "goodness" of the experiment and data. The smaller the experimental error and the better the experimental design, the smaller the area of uncertainty.

It should be noted that confidence limits are not necessarily symmetric about the least-squares estimate with functions having nonlinear parameters. This is illustrated in Figure 9, where the area delimited by the rectangle containing the values of r_1 and r_2 that the simple confidence intervals imply is consistent with the data even though only those values of r_1 and r_2 contained within the ellipse are considered to be consistent with the data at a given probability level, β.

The $100(1-\beta)$% joint confidence limits are delimited by the set of values, r_1^* and r_2^*, which satisfy

$$S_c = [\textstyle\sum(d_i)^2]_{\min} + 2s^2F_{\beta(2,h)} \tag{11}$$

where $F_{\beta(2,h)}$ is the critical value of F taken from the tabulated F distribution,[27] s^2 is an estimate of the experimental error variance σ^2 having h degrees of freedom, and $[\sum(d_i)^2]_{\min}$ is the sum of the squared differences between experimental copolymer compositions and those calculated with the most probable r values of $r_1°$ and $r_2°$. S_c is defined as

$$S_c = \textstyle\sum[[m_{2i}/(m_{2i} + m_{1i})] - G(M_{2i},r_1^*,r_2^*)]^2$$

where the values r_1^* and r_2^* are the set of r values that satisfies eq 11.

Equation 11 is extremely laborious and difficult to use because of the extensive iterations that are required to give the locus of roots of r_1^* and r_2^* that will satisfy this

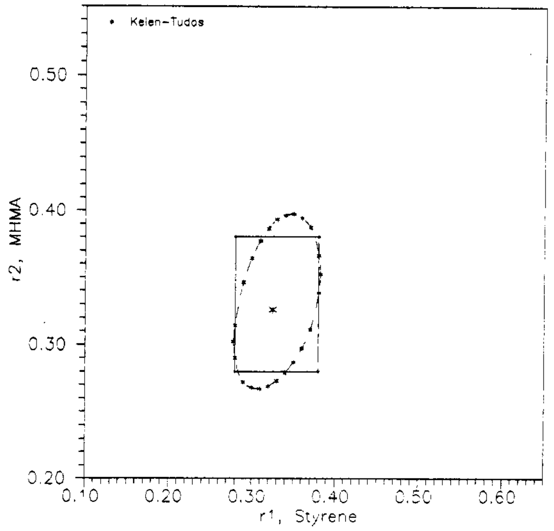


Figure 9. Joint confidence limit/simple confidence interval for extended Kelen–Tudos data.

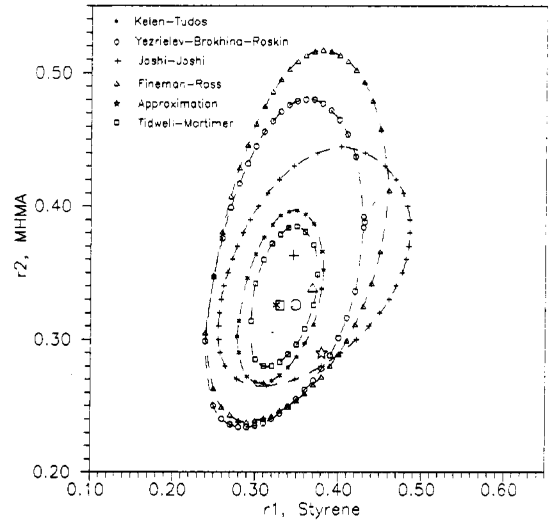


Figure 10. Joint confidence limits for all methods.

equation. A satisfactory approximation of the locus of roots t_1^* and t_2^* that satisfies a quadratic approximation of the $100(1-\beta)\%$ joint confidence limit for t_1° and t_2°, the natural log of the least-squares estimates of r_1° and r_2° is defined by

$$(t_1^* - t_1^\circ)^2 a_{11} + 2(t_1^* - t_1^\circ)(t_2^* - t_2^\circ)a_{12} + (t_2^* - t_2^\circ)^2 a_{22} = 2s^2 F_{\beta(2,h)} \quad (12)$$

where

$$a_{11} = (r_1^\circ)^2 \sum[(\partial G_i/\partial r_1)^2]$$
$$a_{12} = (r_1^\circ r_2^\circ) \sum[(\partial G_i/\partial r_1)(\partial G_i/\partial r_2)]$$
$$a_{22} = (r_2^\circ)^2 \sum[(\partial G_i/\partial r_2)^2]$$
$$t_i^* = \ln r_i^*; \qquad t_i^\circ = \ln r_i^\circ$$

The applicability of the approximation is dependent on the magnitude of the experimental error and the experimental conditions used to generate the data. If the experimental error is reasonably small and the data are collected under reasonably good experimental design, then the approximation is remarkably good. A more detailed discussion of the procedures for obtaining joint confidence limits is given in a number of publications.[12,16,28]

Figure 10 shows the joint confidence limits evaluated here for each pair of reactivity ratios determined for MHMA and styrene. As expected, the Tidwell–Mortimer procedure gives the most precise estimate, although this estimate is only slightly better than that obtained by the Kelen–Tudos procedure. The estimates derived by using the Fineman–Ross, Joshi–Joshi, and the YBR methods are much less precise, and the reactivity ratios determined by using these methods are less reliable. However, it should be noted that all computed r_1 and r_2 pairs (except those by approximation) lie within the joint confidence limits derived for the Tidwell–Mortimer estimates. Evaluation of the joint confidence limits for the Kelen–Tudos estimates using eq 12 is described in detail in the Appendix.

Table IV
Q-*e* Values[26]

monomer	*Q*	*e*
methyl acrylate	0.60	0.42
ethyl acrylate	0.52	0.22
methyl methacrylate	0.74	0.40
ethyl methacrylate	0.73	0.52
butyl methacrylate	0.78	0.51
allyl alcohol	0.048	0.36
MHMA[a]	0.89	0.66

[a] Computed by using the extended Kelen–Tudos estimates.

Table V
Glass Transition Data (°C)

	heating cycle		
charge	first	second	third
1	114.1	113.8	114.3
2	114.3	114.7	113.9
3	116.7	117.8	117.3
4	112.3	111.9	112.0
5	118.7	117.5	
6	126.9	127.8	128.0
7	125.8	126.2	128.5
8	125.2	125.3	123.4
9	132.4	131.2	137.9
10	134.6	134.4	139.2
11	134.6	133.8	145.8
12	136.6	136.1	145.6
13		162.4	158.8
14	132.9	168.5	158.8
15	138.0	139.2	173.4
17	140.4	142.6	171.8
18	137.4		
20	139.3	142.9	
21	136.0	142.6	
22[a]	145.6	203.7	203.7

[a] Poly(MHMA).

***Q*-*e* Scheme.** The semiquantitative *Q*-*e* scheme is a well-known method of classifying the general reactivity of a given monomer. It is used in much the same way the Hammett σ-ρ equation is used in organic chemistry to predict rates and equilibria.[29] Each monomer is characterized by a resonance stability factor *Q* and a polarity characteristic *e*. Under conditions where eq 1 operates, the *Q*-*e* scheme can be used to predict the reactivity ratios for a copolymerization reaction. It should be noted, however, that the validity and limitations of the *Q*-*e* scheme are many, and these limitations have been well documented.[30] Despite these limitations, *Q* and *e* values for the MHMA were determined and compared to other monomers (Table IV).

The *Q*-*e* values allow a few generalities concerning MHMA: it is a polar molecule with an electron-deficient double bonds, the *Q* value indicates a high resonance stability of the adduct radical, and the reactivity of MHMA is similar to that of styrene and methyl methacrylate.

Glass Transitions of Copolymers. MHMA modifies the thermal properties of MHMA-*co*-styrene polymers. Table V gives the glass transitions as determined by DSC

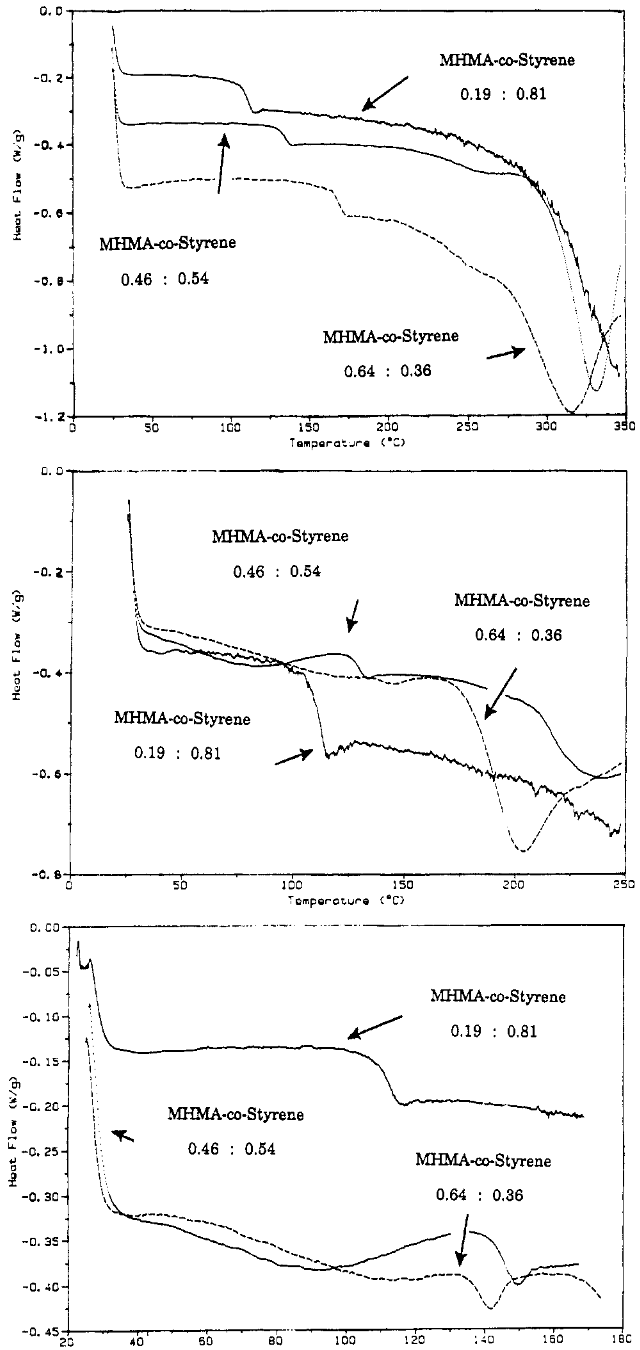


Figure 11. DSC thermograms of typical MHMA-*co*-styrene polymers; first cycle on top, last on bottom.

(see Figure 11). The DSC analysis procedure used consisted of first heating the polymer to 175 °C, cooling in an ice bath to about 25 °C, heating to 250 °C, cooling again, and finally heating to 350 °C. Most polymers showed some decomposition on the final heating cycle. This was confirmed by TGA (Figure 12), which showed decomposition beginning at ca. 310–350 °C.

Figure 13 shows the T_g values determined on the first heating cycle. Glass transitions are seen to increase in a relatively linear manner up to about 60 mol % MHMA, where a plateau is achieved. T_g values measured on the second heating cycle were about the same as those on the first heating cycle with the exception of a couple of points which were raised in value.

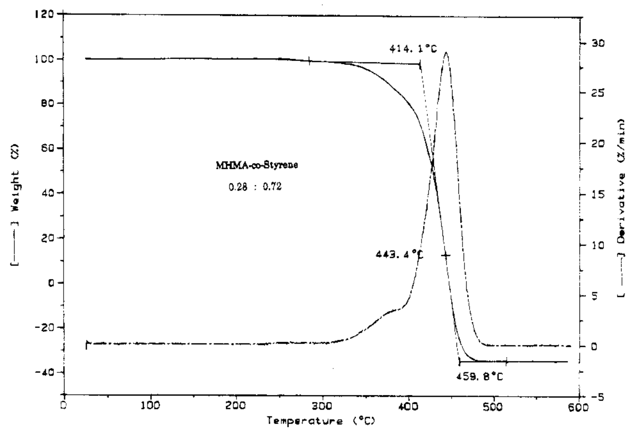


Figure 12. TGA thermogram of a typical MHMA-*co*-styrene polymer.

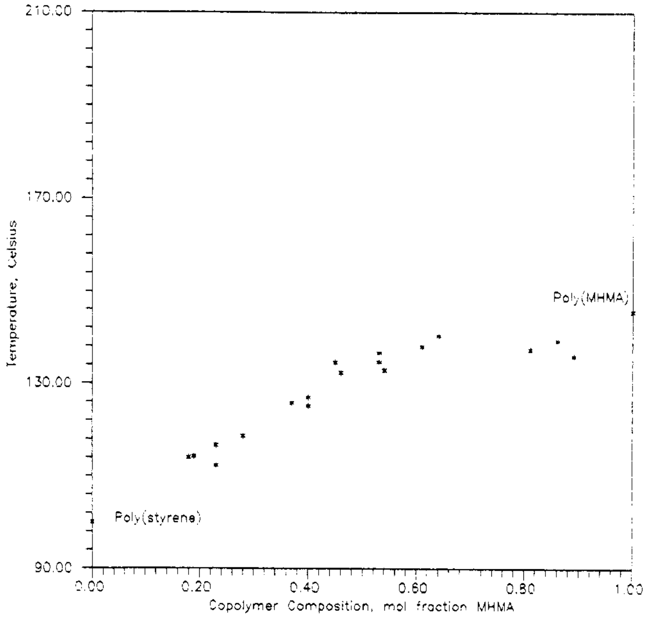


Figure 13. Glass transitions determined from the 25–175 °C heating regime.

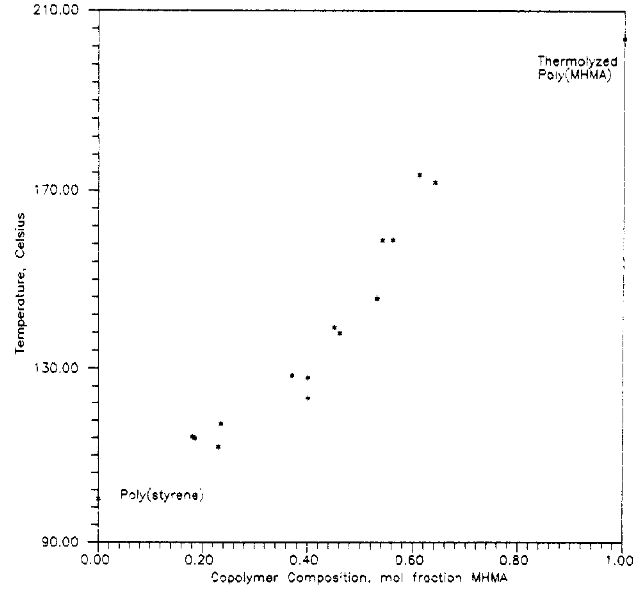
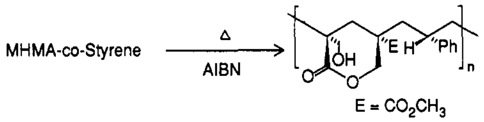


Figure 14. Glass transitions determined from the 25–350 °C heating regime.

Figure 14 shows the T_g values obtained on the third heating cycle. The effect of heating to 250 °C is larger for copolymers high in MHMA composition, resulting in drastically increased values. Samples with lower MHMA incorporation were affected little. We propose an intramolecular cyclization between adjacent or near-neighbor MHMA units leading to formation of lactones (structure

Scheme II
Copolymer Formation from Styrene and MHMA



2

2 of Scheme II) with loss of methanol to account for the observations. Obviously, those copolymers of highest MHMA content are those most likely to react in this manner.

The thermolysis of homopolymer poly(MHMA) at ca. 220 °C shows about 22% weight loss, or about 80% of theoretical for complete lactonization. This material has a T_g of about 205 °C. Interestingly enough, materials with similar T_g values are obtained when homopolymers of EHMA, BHMA, or EHMA-MHMA copolymers are thermolyzed under similar conditions. BHMA and EHMA are the corresponding butyl and ethyl esters of MHMA, respectively. Weight losses were about 60–80% of the theoretical for all samples. The thermal behavior of these polymers is attributed to a similar reaction leading to loss of alcohol and lactone formation that is essentially identical in all cases. Thermolyzed polymers were insoluble, indicating cross-linking via transesterification as well as lactonization.

Conclusions

Reactivity ratios for MHMA and styrene were determined by a variety of procedures. Both the Kelen–Tudos and Tidwell–Mortimer procedures gave values for both monomers of about 0.33. The joint confidence limits confirmed that Kelen–Tudos and Tidwell–Mortimer estimates are more reliable and precise than those given by Fineman–Ross, Joshi–Joshi, and YBR methods. It should be remembered that these are only estimates of the relative reactivities even though the recent trend has been to consider the determination of MRR values to be quantitative.[16] The criteria given by Kelen–Tudos indicate that this is a class I linear polymerization consistent with the simple binary equation and with relatively good experimental design.

Q–e considerations showed that MHMA is an electron-deficient, polar molecule, with a high degree of resonance stabilization of the adduct radical and a reactivity similar to that of styrene. For this system, a random copolymer having a strong tendence to alternate with little likelihood for long homopolymer blocks is formed in an essentially azeotropic polymerization.

Thermolysis of copolymers under controlled conditions resulted in the loss of methanol with concomitant lactone formation and cross-linking. This opens up the possibility of thermal curing of these copolymers in a variety of applications where increased T_g and insolubility are desired.

Acknowledgment. We gratefully recognize financial support for this project from the Division of Materials Research of the National Science Foundation and from the Office of Naval Research for a Department of Defense instrumentation grant for purchase of our Bruker MSL-200.

Appendix

The calculation procedures of Fineman–Ross,[7] Joshi–Joshi,[10] and YBR[13] have been well documented and will not be discussed in this section.

Extended Kelen–Tudos Method. The partial molar monomer conversions, ζ_1 and ζ_2, and the integral z are computed by using

$$\zeta_2 = m_g[(\mu + x_0)/(\mu + y)] \qquad \zeta_1 = \zeta_2 y/x_0$$
$$z = \log(1 - \zeta_1)/\log(1 - \zeta_2)$$

where x_0 is $[M_1]/[M_2]$, the initial mole ratio in the feed; y is m_1/m_2, the final mole ratio in the copolymer; w is the wt % copolymer conversion; and μ is $\mu_{\text{styrene}}/\mu_{\text{MHMA}}$, the molecular weight ratio of the monomers. The variables F and G and the plotting parameters η and ξ are then computed:

$$F = y/z^2 \quad \text{and} \quad G = (y - 1)/z$$

$$\eta = G/(\alpha + F) \quad \text{and} \quad \xi = F/(\alpha + F)$$

Confidence limits for the above estimates are easily determined by

$$\Delta r_1 = \pm t_{\beta(n-2)}([(S^2{}_{\min})/(n - 2)][\sum(1 - \xi_i)^2/D])^{1/2}$$
$$\Delta r_1 = \pm \alpha t_{\beta(n-2)}([(S^2{}_{\min})/(n - 2)][\sum(\xi_i)^2/D])^{1/2}$$

where $S^2{}_{\min}$ is the minimum value given by the expression S^2; r_1 and r_2 are the Kelen–Tudos reactivity ratio estimates, and D is defined as

$$D = \sum\xi_i{}^2\sum(1 - \xi_i)^2 - [\sum\xi_i(1 - \xi_i)]^2$$
$$S^2 = \sum[\eta_i - r_1\xi_i + (r_2/\alpha)(1 - \xi_i)]^2$$

The value $t_{\beta(n-2)}$ is obtained from the tabulated values of Student's distribution for n experiments at $n - 2$ degrees of freedom and at the desired β probability level.[27]

Tidwell–Mortimer Procedure. Given initial estimates of r_1 and r_2 obtained by some other method, G_i is calculated by

$$G_i = (r_2M_{2i}{}^2 + M_{1i}M_{2i})/(r_2M_{2i}{}^2 + 2M_{1i}M_{2i} + r_1M_{1i}{}^2) \tag{13}$$

The difference d_i, the partial derivatives $\partial G_i/\partial r_1$ and $\partial G_i/\partial r_2$, and the least-squares estimates b_1 and b_2 are determined by

$$d_i = m_{2i}/(m_{1i} + m_{2i}) - G_i \tag{14}$$

$$\partial G_i/\partial r_1 = -[M_{1i}{}^2(r_2M_{2i}{}^2 + M_{1i}M_{2i})]/p^2 \tag{15}$$

$$\partial G_i/\partial r_2 = M_{2i}{}^2(r_1M_{1i}{}^2 + M_{1i}M_{2i})/p^2 \tag{16}$$

where

$$p = r_2M_{2i}{}^2 + 2M_{1i}M_{2i} + r_1M_{1i}{}^2$$

$$b_1 = [\sum[(\partial G_i/\partial r_2)^2/(\partial G_i/\partial r_1)^2]\sum[d_i/(\partial G_i/\partial r_1)] - \sum[(\partial G_i/\partial r_2)/(\partial G_i/\partial r_1)]\sum[d_i(\partial G_i/\partial r_2)/(\partial G_i/\partial r_1)^2]]/C$$

$$b_2 = [n\sum[d_i(\partial G_i/\partial r_2)/(\partial G_i/\partial r_i)^2] - \sum[(\partial G_i/\partial r_2)/(\partial G_i/\partial r_1)]\sum[d_i/(\partial G_i/\partial r_1)]]/C$$

$$C = n\sum[(\partial G_i/\partial r_2)^2/(\partial G_i/\partial r_1)^2] - [\sum[(\partial G_i/\partial r_2)/(\partial G_i/\partial r_1)]]^2$$

Values of $S_k = [\sum(d_i)^2]_k$ for $r_1 = r_1{}^j + [(k - 1)/2]b_1$ and $r_2 = r_2{}^j + [(k - 1)/2]b_2$ are determined for values of k = 1, 2, and 3 and $S_4 = [\sum(d_i)^2]_4$ for $r_1 = r_1{}^j + Vb_1$ and $r_2 = r_2{}^j + Vb_2$, where

$$V = 0.5 + (S_1 - S_3)/[4(S_1 - 2S_2 + S_3)]$$

S_1 and S_4 (if $S_4 < S_1$) are evaluated by repeating this process with the new estimates of r_1 and r_2 being the r values calculated at S_4. If $S_4 > S_1$, then reevaluate V by first having b_1 and b_2. This process is repeated until the sum of the squares of the differences is minimized.

For most systems with a good initial estimate of reactivity ratios, only two or three iterations are required to obtain the minimum difference.

Joint Confidence Limits. Copolymer composition G_i is determined by using eq 13, the difference d_i (eq 14) is determined, and the parameter s^2 is computed by

$$s^2 = [\sum(d_i)^2]/(n - 2)$$

for n experimental points.

The critical value of F is taken from the tabulated F distribution for $100(1 - \beta)\%$ probability and $n - 2$ degrees of freedom.[27] $2s^2F_{\beta(2,n-2)}$, the right side of eq 12, can now be computed.

The partial derivatives (eq 15 and 16) are evaluated for each experiment, and the parameters a_{11}, a_{12}, and a_{22} are computed. Substitution into eq 12 for set values of t_1^* ($t_1^* = \ln r_1^*$) allows r_2^* values to be calculated from the resulting quadratic equation.

Symbols

A_{abs}	UV absorption
A_i	integrated area of i computed by ^{1}H NMR
e	monomer polarity factor
F, G	Fineman–Ross variables
G_i	computed mole fraction of monomer i in the copolymer
m_g	mass in grams
M_i	feed composition of monomer i
m_i	copolymer composition of monomer i
Q	monomer resonance factor
Q_{KT}	Kelen–Tudos experiment design parameter
Δr_i	simple confidence limit for monomer i
r_i°	calculated reactivity ratio for monomer i
r_i^j	estimated reactivity ratio for monomer i for the jth iteration
r_i^*	arbitrary r values used to compute joint confidence limits
V_L	volume in liters
x_0	initial mole ratio of monomers in the feed
y	mole ratio of monomers in the copolymer
z_i	ratio of final to initial concentration of monomer i in the feed
α	symmetrization parameter of Kelen–Tudos
β	percent error acceptable in the determination of simple confidence intervals or joint confidence limits
δ	Kelen–Tudos confidence parameter
ϵ	molar absorptivity
η, ξ	Kelen–Tudos transformed parameters
μ	molecular weight ratio
μ_i	molecular weight of monomer i
ζ_i	partial molar monomer conversion of monomer i

Registry No. MHMA, 15484-46-5; (MHMA)(styrene) (copolymer), 110118-29-1; styrene, 100-42-5.

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