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Free-Radical Copolymerization of Methacrylonitrile and α-Methylstyrene

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ABSTRACT: Copolymerization of methacrylonitrile and α-methylstyrene was studied at 60° with free-radical initiation. Copolymer composition was determined by monitoring rate of loss of monomers from toluene solution, using gas–liquid chromatography. The reactivity ratios are r_1(methacrylonitrile) 0.38, r_2(α-methylstyrene) 0.54. A simple copolymerization model fits the data, although the ceiling temperature of poly(α-methylstyrene) is 61°. Mean sequences of this monomer in the copolymer are short and have an effectively higher polymerization enthalpy and ceiling temperature than high molecular weight homopolymer. A comparison of these results and previous data for copolymerization of styrene and α-methylstyrene with other reports based on chemical analyses of high molecular weight copolymer suggests that α-methylstyrene may be accumulating in low polymer.

The free-radical polymerization and copolymerization of α-methylstyrene is slow and generally yields low molecular weight products at reaction temperatures commonly used in solution and bulk polymerizations. The choice of an appropriate model for the copolymerization behavior of this monomer is uncertain, despite the existence of a number of careful studies.

Free-radical copolymerizations with styrene in particular have been examined. Several investigators have measured reactivity ratios by applying the simple copolymer equation[1,2] in which it is assumed that reactivity of a growing polymer radical depends only on the nature of the terminal monomer unit and the relative reactivities and concentrations of adding monomers.[3–6]

It has also been suggested[7] that penultimate effects are involved in copolymerization of α-methylstyrene, because the bulky nature of the substituents on the 1-carbon atom in the vinyl grouping hinders head-to-tail addition of the monomer to another α-methylstyrene radical.

Poly(α-methylstyrene) has a ceiling temperature[8] of 61°.[9] This is the temperature above which it is not possible to produce long-chain homopolymer from monomer at unit or lower concentration. The ceiling temperature, T_c, is defined as

$$T_c = \Delta H_p/(\Delta S_p^\circ + R \ln [M]_e) \qquad (1)$$

where ΔH_p is the enthalpy of polymerization, ΔS_p° is the entropy increase for polymerization, referred to a standard state of unit monomer concentration, and $[M]_e$ is the concentration of monomer in equilibrium with high molecular weight polymer.

Modifications of the copolymer equation have been proposed to account for a temperature-dependent depropagation of sequences of a monomer with a ceiling temperature near the polymerization temperature.[10–12] In particular, the styrene–α-methylstyrene copolymerization has been reported to fit a model proposed by Lowry,[10] in which it is assumed that radicals terminating in three α-methylstyrene units may depropagate.[13] The copolymer equation in this case includes monomer feed concentrations and reactivity ratios, as in the simple Mayo–Lewis form, plus an equilibrium constant, ρ, for the reversible momomer addition step

$$\cdot(M)_n + M \longrightarrow \cdot(M)_{n+1}$$

Since the concentration of $\cdot(M)_n$ may be considered equal to that of $\cdot(M)_{n+1}$

$$\rho = [\cdot(M)_{n+1}]/[M][\cdot(M)_n] = 1/[M]_e \qquad (2)$$

where $[M]_e$ is the equilibrium concentration of the depropagating monomer. Thus, from eq 1 and 2

$$T_c = \Delta H_p/(\Delta S_p^\circ + R \ln (1/\rho)) \qquad (3)$$

If the enthalpy and entropy values derived from studies of anionically polymerized high molecular weight poly(α-methylstyrene) apply to sequences of this monomer in copolymers ρ can be calculated from eq 3 for a given reaction temperature.

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TABLE I
ANALYTICAL DATA[a]

Feed ratio[b] MAN/ αMS	Conversion, %	Wt fraction[c] T	Wt fraction[c] MAN	Wt fraction[c] αMS	Solvent[d]	Unreacted wt fraction[e] T	Unreacted wt fraction[e] MAN	Unreacted wt fraction[e] αMS	Copolym comp[f] MAN	Copolym comp[f] αMS	Copolym comp[g] MAN	Copolym comp[g] αMS
1.5/8.5	0	0.75525	0.03266	0.21209	1	0.75525	0.03266	0.21209				
	5	0.76449	0.03094	0.20453	0.98791	0.75525	0.03056	0.20206	0.00210	0.01003	0.17312	0.82688
5.0/5.0	0	0.73173	0.12502	0.14326	1	0.73173	0.12502	0.14326				
	5	0.74157	0.12129	0.13711	0.98672	0.73173	0.11968	0.13529	0.00533	0.00797	0.40075	0.59925
7.0/3.0	0	0.73710	0.17631	0.08659	1	0.73710	0.17631	0.08659				
	5	0.74715	0.17129	0.08182	0.98655	0.73710	0.16899	0.08072	0.00732	0.00587	0.55497	0.44503
8.5/1.5	0	0.77243	0.18929	0.03828	1	0.77243	0.18929	0.03828				
	5	0.78143	0.18352	0.03504	0.98847	0.77243	0.18141	0.03464	0.00789	0.00364	0.68430	0.31570

Feed ratio MAN/αMS	Mol fraction in feed MAN	Mol fraction in feed αMS	Mol ratio in feed MAN	Mol ratio in feed αMS	Mol fraction in copolymer MAN	Mol fraction in copolymer αMS	Mol ratio in copolymer MAN	Mol ratio in copolymer αMS
1.5/8.5	0.2145	0.7855	0.2731	3.6620	0.2694	0.7306	0.3688	2.7117
5.0/5.0	0.6074	0.3926	1.5470	0.6464	0.5408	0.4592	1.1780	0.8489
7.0/3.0	0.7831	0.2169	3.6101	0.2770	0.6871	0.3129	2.1964	0.4553
8.5/1.5	0.8976	0.1024	8.7642	0.1141	0.7924	0.2076	3.8183	0.2619

[a] MAN, methacrylonitrile; αMS, α-methylstyrene; T, toluene; 60°. [b] Monomer feed ratio by volume. [c] Of volatiles. [d] Internal standard factor of solvent.[15] [e] Of reaction mixture. [f] Weight fractions of reaction mixture. [g] Weight fractions of copolymer.

A previous report from this laboratory[14] dealt with free-radical copolymerization of styrene and α-methylstyrene at two temperatures. The reactivity ratios were estimated from rate of monomer loss, as measured by gas–liquid chromatography.[15] This technique has some advantages over conventional analyses of copolymer formed in reactions, such as those of α-methylstyrene, in which the product has low molecular weight and may be lost in the operations used to remove residual monomer. It was concluded that the simple copolymer equation described the relative rates of reaction of the comonomers. Production of oligomeric copolymers was ascribed to kinetic, rather than thermodynamic factors, because the ceiling temperature of relatively short α-methylstyrene sequences in the copolymer is significantly higher than that of high molecular weight poly(α-methylstyrene). The reactivity of α-methylstyrene was found to be significantly higher than in previous studies in which the simple copolymer model was reported applicable. These results are compared in Table III. This difference was ascribed to the effective inclusion of low molecular weight species in the gas chromatographic analysis of residual monomer and their loss in other techniques which rely on analysis of isolated high polymer.

The free-radical copolymerization of methacrylonitrile and α-methylstyrene reported here was studied to test and extend the above conclusions. Fordyce and coworkers[16] reported r_1(methacrylonitrile) 0.35 and r_2(α-methylstyrene) 0.12, from free-radical-initiated mass polymerization at 80°. Copolymers were analyzed for nitrogen by a micro-Dumas method which required an empirical correction for discrepancies between analyzed and theoretical nitrogen content of polymethacrylonitrile. A survey article by Young[17] quotes $r_1 = 0.15$, $r_2 = 0.21$ (80°) from unpublished data of A. F. Roche and G. Corey. The most recent collection of $Q - e$ values[18] yields estimates of $r_1 = 0.212$ and $r_2 = 0.062$. The present results show a higher reactivity of α-methylstyrene, as in the case of copolymerization with styrene.[14] Some of the styrene–α-methylstyrene copolymerization data reported previously are also reexamined in this report, using more sophisticated computational methods.

Experimental Section

α-Methylstyrene and methacrylonitrile were obtained as middle cuts in reduced-pressure distillation. The monomers were stored cold under nitrogen prior to their use. The initiator (azodiisobutyronitrile, ADIB) and reaction terminator (hydroquinone) were used as received. Polymerizations were carried out in toluene solution at 60° for designated times, to produce conversions of up to about 10% of the monomer charge. Copolymerization was terminated by addition of a saturated solution of hydroquinone in toluene. Reaction mixtures were analyzed for residual monomers by injecting aliquots into a gas chromatographic column equipped with a glass wool precolumn unit to trap copolymer and other nonvolatiles. A Carle Model 9000 gas chromatograph with hydrogen flame detector and equipped with a column of 8% dinonyl phthalate on Anakrom ABS was used at 95 ± 2°.

Details of the analytical method and calculations were as described elsewhere.[15] Each reaction mixture was analyzed in quadruplicate. Four different feed mole ratios of comonomers were used. Eight replicate mixtures of each feed were prepared and polymerized for different times. Unreacted weight fraction of each monomer was plotted against reaction time and the data at a specified time were read off the best-fit line through these points. Between 10 and 20 standard solutions of monomers were analyzed at random intervals during the analyses of the eight samples of each feed. These standards served to calibrate the monomer peaks and check the consistency of the gas chromatographic detector sensitivity. Reactivity ratios were calculated for 5% conversion. The values obtained were insensitive to extent of reaction up to 10%.

The gas chromatographic technique has certain advantages in this application. Errors due to loss of low polymer and systematic errors which have plagued chemical analyses of nitrile-containing polymers[16,19] are avoided. The method is, however, not necessarily more accurate than chemical techniques since it is based on analysis of small differences in concentrations of monomers before

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TABLE II
REACTIVITY RATIOS, 60° POLYMERIZATION[a]

Method	r_1[b]	r_2
Fineman–Ross[c]	0.403 ± 0.028	0.544 ± 0.011
Reciprocal Fineman–Ross[c]	0.345 ± 0.016	0.353 ± 0.165
Joshi–Kapur[d]	0.388 ± 0.067	0.524 ± 0.362
Integrated Mayo–Lewis[e]	0.382 ± 0.046	0.542 ± 0.074
Best fit[f]		
Linear least squares	0.383	0.545
Nonlinear least squares	0.382	0.544

[a] M_1, methacrylonitrile; M_2, α-methylstyrene. [b] ±standard deviation. [c] See ref 21. [d] See ref 22. [e] See ref 1. [f] Best fit for differential Mayo–Lewis equation (ref 1).

and after copolymerization. The resulting uncertainty can be minimized by carrying out reactions to high conversion and estimating reactivity ratios from integrated, rather than differential forms of a suitable copolymer equation.[20] This is not possible with copolymerizations of α-methylstyrene, however, because the kinetic chain length is so low that an impossibly high initiator concentration would be needed to achieve a high monomer conversion. Reactivity ratios reported here were therefore calculated from low conversion data, although both differential and integrated forms of the copolymer equations were used in these estimates.

Reactivity Ratios

(a) Simple Copolymerization Model. Table I lists the experimental results obtained. Table II includes reactivity ratios estimated by applying different calculation methods to the experimental results. The Fineman–Ross, reciprocal Fineman–Ross,[21] and Joshi–Kapur method of intersecting slopes[22] employ arithmetically correct linear forms of the differential copolymer equation. A linear least-squares fit of the data is obtained for these equations. This can result in inadvertent errors, because data points furthest from the origin have the greatest influence on the slope and intercept of the best-fit line.[23] The first two entries in Table II are examples of such uncertainties. Another computational method (which is not practical without use of a computer) involves a simple curve fitting of the copolymer–monomer compositions. Reactivity ratios calculated by these methods are listed in Table II as "best fit" values. The linear least-squares fit is to a straight line through the four compositions involved in this case. The nonlinear least-squares fit does not assume that the relation between mole fraction of a given monomer in the copolymer and feed is necessarily linear. The computer program which was written for this calculation is essentially equivalent to the computations described by Tidwell and Mortimer.[23] The data were also fitted to an integrated form of the copolymer eq 1, using a linear least-squares computer program.[24] The reactivity ratios calculated from the integrated equation and the two best-fit techniques agree closely (last three entries in Table II). Calculations based on linear best fits to linear forms of the differential copolymer equation (first three entries) result in reactivity ratios which are subject to more uncertainty. This observation agrees with the conclusions reached in previous comparisons of the different estimation procedures.[25,26]

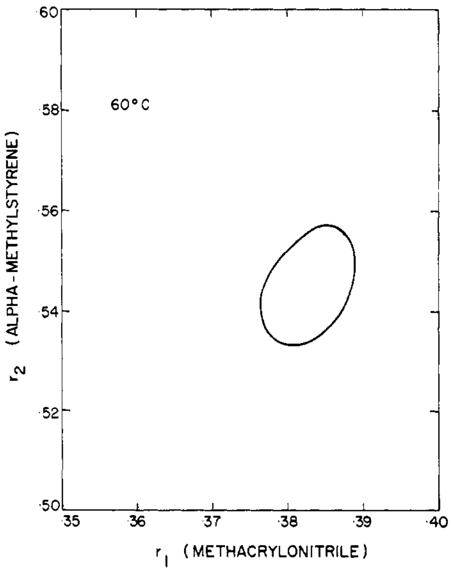

Figure 1. Joint 95% confidence limits for free-radical copolymerization of methacrylonitrile (r_1) and α-methylstyrene (r_2) at 60°.

Although standard deviations of reactivity ratios are also listed in the conventional manner in Table II, such a method of estimating the uncertainty in the results is not statistically sound. The errors in r_1 and r_2 are coupled, since both are derived from the same experimental data. A better procedure involves the calculation of joint confidence limits, within which the correct values are believed to coexist, with stated probability. The technique of Tidwell and Mortimer[23] was used to approximate these limits (this is not an exact calculation), at 95% confidence, as shown in Figure 1. The values used to compare predicted and experimental copolymer compositions were $r_1 = 0.383$, $r_2 = 0.545$.

The extreme values in the joint confidence limit ellipse in Figure 1 include $0.378 < r_1 < 0.388$ and $0.534 < r_2 < 0.554$. Some of the values from the first three estimation procedures listed in Table II are thus excluded, despite the reasonable standard deviations calculated by conventional linear least-squares data fitting. It should be noted that the joint confidence limits are based on a comparison with the Snedecor statistical *F* distribution. The estimate of variance is strongly affected by the small number of composition points, and the approximate joint confidence limits are correspondingly generous.

Table III lists styrene–α-methylstyrene reactivity ratios quoted from an earlier reference.[14] Nonlinear least-squares best fit values have been added to the original data, which did not include results of this estimation method. A slight error in r_2 at 90° has been corrected (the initial report listed this as 0.272 instead of 0.296 for linear least-squares best fit to the simple copolymer equation).

Figure 2 shows 95% joint confidence limits for the 90° copolymerization of styrene and α-methylstyrene, based on $r_1 = 0.788$, $r_2 = 0.297$. In this case reactivity ratios from all estimation methods are enclosed in the confidence limit loop. The joint confidence limits for the 60° copolymerization are shown in Figure 3, based on $r_1 = 1.124$, $r_2 = 0.627$ values from a nonlinear least-squares fit to the copolymer equation. The joint confidence limit loop includes all the reactivity ratio values estimated by the various methods listed in Table III. It does not encompass any of the literature values cited, which are based on isolation and analysis of copolymer of sufficiently high molecular weight to be insoluble in methanol.

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TABLE III

REACTIVITY RATIOS, STYRENE–α-METHYLSTYRENE

Estimation method	60°		90°	
	r_1[a]	r_2[b]	r_1	r_2
Fineman–Ross[c]	1.049 ± 0.079	0.563 ± 0.020	0.793 ± 0.006	0.294 ± 0.001
Reciprocal Fineman–Ross[c]	1.133 ± 0.012	0.627 ± 0.033	0.805 ± 0.005	0.311 ± 0.018
Joshi–Kapur[d]	1.112 ± 0.214	0.603 ± 0.109	0.798 ± 0.016	0.297 ± 0.039
Integrated Mayo–Lewis[e]	1.125 ± 0.044	0.603 ± 0.059	0.795 ± 0.011	0.298 ± 0.021
Best fit[f]				
Linear least squares	1.080	0.570	0.784	0.296
Nonlinear least squares	1.124	0.627	0.788	0.297

[a] Literature values of r_1: 1.20,[3] 1.20,[4] 1.25,[5] 0.71.[6] [b] Literature values of r_2: 0.35,[3] 0.35,[4] 0.25,[5] 0.14.[6] [c] See ref 21. [d] See ref 22. [e] See ref 1. [f] Best fit to differential Mayo-Lewis equation (ref 1).

TABLE IV

METHACRYLONITRILE–α-METHYLSTYRENE COPOLYMERIZATION AT 60°

(a) Best Fit to Simple Copolymer Equation; $r_1 = 0.383$, $r_2 = 0.545$

Feed comp,[a] MAN/αMS	Feed comp, *M*		Mol ratio in copolym	
	MAN	αMS	Exptl	Calcd
1.5/8.5	1.0519	3.8529	2.7117	2.7126
5.0/5.0	3.5063	2.2664	0.8489	0.8491
7.0/3.0	4.9088	1.3599	0.4553	0.4831
8.5/1.5	5.9607	0.6799	0.2619	0.2438
Mean absolute deviation				0.0118

(b) Best Fit to LII Mechanism[b]

Feed comp,[a] MAN/αMS	Feed comp, *M*		Mol ratio in copolym				
	MAN	αMS	Exptl	LII[c]	LII[d]	LII[e]	LII[f]
1.5/8.5	1.0519	3.8529	2.7117	1.9006	1.9027	1.9403	1.9462
5.0/5.0	3.5063	2.2664	0.8489	0.8555	0.8473	0.8600	0.8642
7.0/3.0	4.9088	1.3599	0.4553	0.4684	0.4587	0.4555	0.4574
8.5/1.5	5.9607	0.6799	0.2619	0.2230	0.2161	0.2095	0.2100
Mean absolute deviation				0.2174	0.2150	0.2088	0.2087

(c) Best fit to LI mechanism[g]

Feed comp,[a] MAN/αMS	Feed comp, *M*		Mol ratio in copolym				
	MAN	αMS	Exptl	LI[h]	LI[i]	LI[j]	LI[k]
1.5/8.5	1.0519	3.8529	2.7117	1.3040	1.3326	1.3657	1.3824
5.0/5.0	3.5063	2.2664	0.8489	0.7644	0.7657	0.7895	0.7993
7.0/3.0	4.9088	1.3599	0.4553	0.4919	0.4827	0.4969	0.5009
8.5/1.5	5.9607	0.6799	0.2619	0.2658	0.2561	0.2635	0.2646
Mean absolute deviation				0.3832	0.3741	0.3622	0.3568

[a] By volume. [b] Reference 10. $-M_2M_2M_2\cdot$ sequences may depropagate, $\rho = 0.0935$ l./mol. [c] $r_1 = 0.45$, $r_2 = 0.96$. [d] $r_1 = 0.47$, $r_2 = 1.0$. [e] $r_1 = 0.50$, $r_2 = 1.22$. [f] Best fit. $r_1 = 0.50$, $r_2 = 1.25$. [g] Reference 10. $-M_1M_2M_2\cdot$ and $-M_2M_2M_2\cdot$ sequences may depropagate, $\rho = 0.0935$ l./mol. [h] $r_1 = 0.33$, $r_2 = 0.65$. [i] $r_1 = 0.35$, $r_2 = 1.00$. [j] $r_1 = 0.34$, $r_2 = 1.60$. [k] $r_1 = 0.34$, $r_2 = 2.27$.

(b) Reversible Copolymerization Model. The equilibrium constant, ρ, required for estimates of reactivity ratios according to this model[10] was calculated from the high polymer entropy and enthalpy data of Worsfold and Bywater[9] to be 0.0935 l. mol^{-1}. The reactivity ratios for reversible copolymerization were obtained by minimizing the mean absolute deviation of experimental values of copolymer compositions and values predicted by assuming either that $M_1M_2M_2\cdot$ and $M_2M_2M_2\cdot$ sequences may depropagate (LI case) or that only $M_2M_2M_2\cdot$ sequences are subject to reversible polymerization (LII case).[10] Table IV lists results for various reactivity ratios for both cases, compared to the simple copolymer model. (The computer curve-fitting procedure involved selection of initial r_1 and r_2 values and variation of both in 0.01 increments about the starting points to minimize the sum of the absolute deviations between predicted and observed copolymer compositions at all feed compositions.) The best fit to the LII case produced $r_1 = 0.50$, $r_2 = 1.25$, but the mean deviations between experimental and predicted copolymer compositions are much larger than for the conventional copolymer model. The correlation with the LII model is only slightly improved by quite large changes in reactivity ratios. This effect is even more apparent in the LI case, where r_1 is quite constant at 0.34, but variations in r_2 between 0.65 and 2.27 did not produce much improvement in the mean deviation. Similar observations were recorded previously in the copolymerization of α-methylstyrene with styrene.[14]

Choice of Copolymerization Model. The conventional copolymer equation is seen to predict polymer composition more accurately than models which assume reversible polymerization of α-methylstyrene. The correlation between experimental and calculated copolymer composition in the former case seems to be sufficiently close that additional parameters, as in a penultimate effect model, need not be invoked for this system.

Although prediction of experimental copolymer compositions is a necessary condition for validity of a copolymeriza-

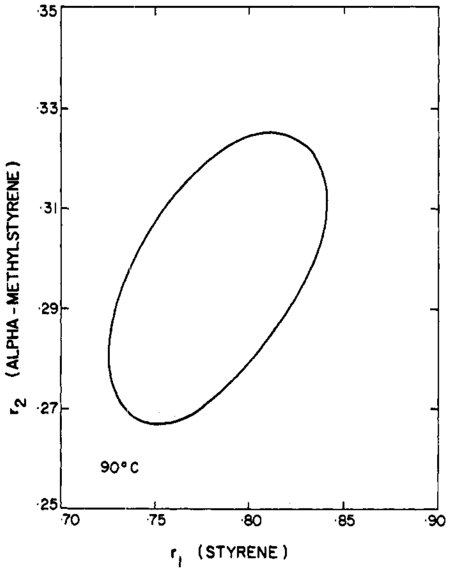

Figure 2. Joint 95% confidence limits for free-radical copolymerization of styrene (r_1) and α-methylstyrene (r_2) at 90°.

tion model, it has been pointed out that this in itself may not always be sufficient.[25] The model should be shown to give unbiased estimates which are independent of extent of reaction or feed composition. A simple diagnostic test for this condition is a plot of feed compositions against the deviations between calculated and experimental copolymer compositions. Figure 4 is such a plot for styrene-α-methylstyrene copolymerization at 60° and Figure 5 records the corresponding data for the methacrylonitrile system. The deviations between experimental copolymer compositions and those predicted by the simple copolymer equation tend to be randomly distributed, with no evidence of a trend with changing feed composition. The related test with degree of conversion as the abscissa cannot be applied to this system because the initial data are extracted from a plot of unreacted mole fraction of each monomer as a function of extent of reaction.

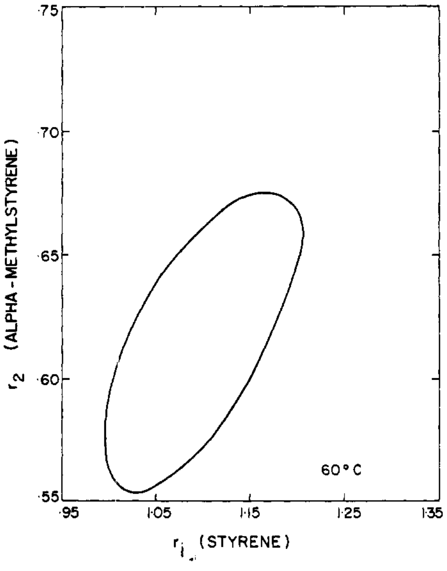

Figure 3. Joint 95% confidence limits for free-radical copolymerization of styrene (r_1) and α-methylstyrene (r_2) at 60°.

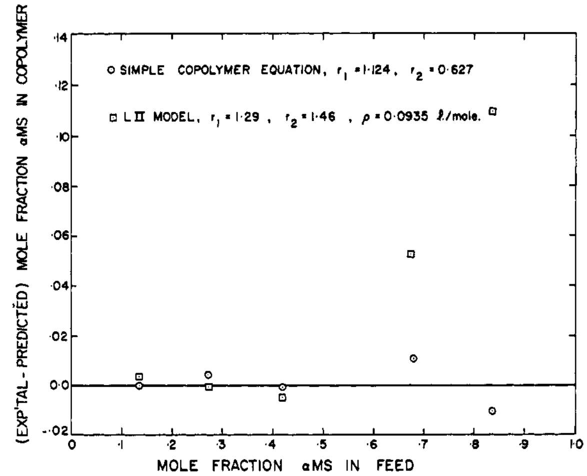

Figure 4. Styrene-α-methylstyrene at 60°, prediction of α-methylstyrene content in copolymer.

Discussion

The simple copolymer equation is clearly an adequate model for the free-radical copolymerizations of α-methylstyrene with styrene and with methacrylonitrile. It remains to explain why this should be so, when poly(α-methylstyrene) has a ceiling temperature at 61° and the reversible copolymerization model[10] is mathematically sound. It was suggested[14] that depropagation effects are not important in the copolymerization with styrene because the mean sequence lengths of α-methylstyrene in the copolymer are short. Such short sequences have higher polymerization enthalpies[27] and hence higher ceiling temperatures than high molecular weight homopolymer. Mean sequence lengths in the styrene-α-methylstyrene case were calculated from the reactivity ratios, using probabilities which pertain to high polymer.[28]

These calculations are not entirely appropriate because the α-methylstyrene copolymers tend to have low molecular weights. A more suitable sequence length calculation is summarized below, for the methacrylonitrile-α-methylstyrene

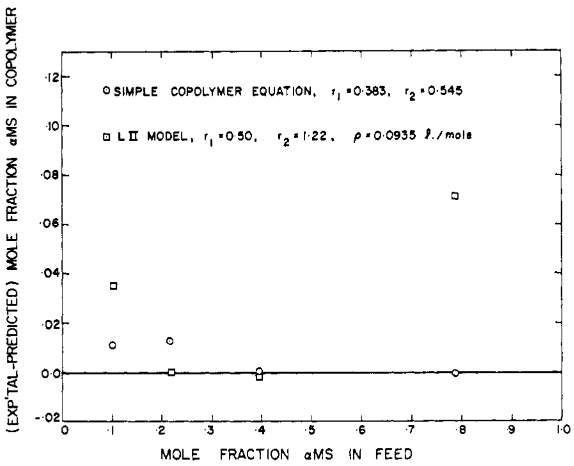

Figure 5. Methacrylonitrile-α-methylstyrene at 60°, prediction of copolymer composition.

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Table V

Sequence Distribution of α-Methylstyrene (αMS) in Copolymers

αMS units[a]	Mol fraction of αMS[b]	Mol fraction of αMS[c]	$\overline{\mathrm{DP}}_n$ (mol wt)	Conditions
1	0.4323	0.5500		60°,
2	0.2466	0.2475		MAN/αMS 3/7 (v/v),
3	0.1404	0.1114	27	[αMS] 3.173 *M*,
4	0.0798	0.0501		[MAN] 2.104 *M*,
5	0.0453	0.0226	(2800)	[AIBN] 0.036 *M*,
6	0.0257	0.0102		69 hr,
7	0.0145	0.0046		r_1 0.383, r_2 0.545
8	0.0082	0.0021		
9	0.0046	0.0009		
10	0.0026	0.0004		
1	0.6830	0.8712		60°
2	0.2166	0.1122	38	MAN/αMS 7/3 (v/v),
3	0.0687	0.0145	(3140)	[αMS] 1.360 *M*,
4	0.0217	0.0019		[MAN] 4.909 *M*,
5	0.0069	0.0002		[AIBN] 0.036 *M*,
6	0.0022			69 hr,
7	0.0007			r_1 0.383, r_2 0.545
8	0.0002			
9	0.0001			
			53	MAN homopolym,
			(3560)	[MAN] 7.33 *M*,
				[AIBN] 0.036 *M*,
				51 hr
			5.2	αMS homopolym,
			(620	[αMS] 4.53 *M*,
				[AIBN] 0.032 *M*,
				20 hr

[a] Number of αMS units in sequence. [b] $\overline{\mathrm{DP}}_n$ as given. [c] Infinite molecular weight.

system. These estimates requires a knowledge of the copolymer molecular sizes.

No attempt was made to produce controlled molecular weight samples in the reactions used to measure reactivity ratios. Initiator concentrations (which were 0.009–0.018 *M*) and polymerization times were adjusted to produce small conversions conveniently. Some copolymerizations were performed later with higher initiator concentrations, to produce enough polymer for molecular weight measurements. Reaction conditions and molecular weights are listed in Table V. The reaction mixtures were freeze-dried under vacuum until a dry solid remained. This residue was dissolved in *N,N*-dimethylacetamide and its number-average molecular weight was measured with a thermoelectric differential vapor pressure apparatus[29] calibrated against benzil and hydrazobenzene. The measured $\bar{M}_n$ values were converted to $\overline{\mathrm{DP}}_n$ figures from the measured copolymer compositions at the stated feed compositions. Molecular weights of copolymers produced in the initial reactivity ratio studies would be expected to be somewhat higher than those listed in Table V, because of the lower initiator concentrations. The greatest deviation would, however, only correspond to a factor of 2, assuming the usual inverse square root dependence of $\overline{\mathrm{DP}}_n$ on initial initiator concentration in free-radical reactions. The conclusions from sequence length calculations based on measured molecular weights will not be changed significantly by variations of this magnitude.

The appropriate calculations for low molecular weight copolymers involve use of finite Markov chains, in which the probability of a given sequence is not necessarily the same as that of its enantiomer. We use the formulation of Fueno and Furukawa[30] for chain-propagation steps of binary copolymerization. The probability of finding an M_2 unit at the end of a growing *n*-mer is

$$\Phi_{M_2}{}^{(n)} = \left[X - \frac{1 - P_{M_1}}{2 - P_{M_1} - P_{M_2}}\right](P_{M_1} + P_{M_2} - 1)^{n-1} + \left[\frac{1 - P_{M_1}}{2 - P_{M_1} - P_{M_2}}\right] \quad (4)$$

where X is the instantaneous mole fraction of monomer M_2 in the copolymer and the probability P_{M_i} is defined as

$$P_{M_i} \equiv \frac{K_{ii}[M_i]}{K_{ii}[M_i] + K_{ij}[M_j]} = \frac{[M_i]}{[M_i] + [M_j]/r_i} \quad (5)$$

with K_{ii} and K_{ij} the propagation rate constants in the copolymerization reaction. The calculations require specification of the exact positions of the monomers, as well as their relative positions, since the number of ways of forming a sequence of units of one type increases with increasing molecular size. The probability that a given sequence exists in a chain is equal to the sum of the probabilities of finding that sequence in any of its possible positions in the molecule. The particular monomer of interest may exist as units, dimers, trimers, and so on, in isolated sequences. The fraction in a particular sequence is the quotient of the probability of that sequence divided by the sum of the probabilities of all sequences up to the limit dictated by the size of the mean polymer chain. Table V lists results of such calculations as well as those in which an infinite molecular weight is assumed[28] and the number distribution of sequences of α-methylstyrene is given by

$$N(\alpha\mathrm{MS}, n_1) = P_{22}{}^{n_1 - 1}(1 - P_{22})$$

where $N(\alpha\mathrm{MS}, n_1)$ is the probability that an α-methylstyrene sequence picked at random contains n_1 units of this momomer and P_{22} is defined as

$$P_{22} = r_2[M_2]/([M_1] + r_2[M_2]) \quad (6)$$

These latter calculations were made with a computer program by Harwood.[31] It is clear that the longest α-methylstyrene sequence length which may be expected to occur to any significant extent contains eight monomer units, regardless of the mean molecular weight of the copolymer.

Roberts and Jessup[27] have shown that the enthalpy of polymerization of low molecular weight thermally initiated poly(α-methylstyrene) decreases with increasing chain length, to a limit consistent with data reported for high molecular weight anionically polymerized homopolymer.[9] These data are supported by studies of low molecular weight polymer produced in cationic systems.[32,33] As calculated previously,[14] ΔH_p for an octamer of α-methylstyrene is 10.6 kcal/mol from the results of Roberts and Jessup.[27] Assuming that ΔS_p is -26.3 cal/(mol deg), as for high polymer, $[\alpha\mathrm{MS}]_e = 0.055$ mol/l. at 60° (from eq 1). The equilibrium monomer concentration for the longest α-methylstyrene sequence indicated is thus considerably lower than the actual feed concentration.

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These calculations are approximate. They take no account of the distribution of copolymer composition about the mean, in short-chain polymers,[34] nor of the effect of combinative termination on the mean enthalpy of polymerization. The effects will hardly be large enough to invalidate the conclusions that depropagation is not significant under particular experimental conditions used and that the simple copolymer model therefore describes the consumption of both monomers.

The reactivity ratios measured by gas chromatographic analysis for copolymerizations of α-methylstyrene (αMS) with styrene (S) and methacrylonitrile (MAN) at 60° are $r_{\mathrm{S}} = 1.12$, $r_{\alpha\mathrm{MS}} = 0.63$; $r_{\mathrm{MAN}} = 0.38$, $r_{\alpha\mathrm{MS}} = 0.54$. α-Methylstyrene is indicated by the present work to be more reactive than shown by literature reports or $Q - e$ predictions. It would appear also that the slow copolymerization rates and low molecular weight products are reflections mainly of a slow propagation rate of the stable α-methylstyryl radicals.

Since the present data differ from those reported by other workers, it was of interest to examine the internal consistency of the reactivity ratios we found for α-methylstyrene copolymerization with styrene and methacrylonitrile. The r_1r_2 product is smaller for the methacrylonitrile system, in which polarity differences and alternation tendency would be expected to be greater.

A comparison of the r_1 values for the two systems (α-methylstyrene is the common monomer 2) similarly leads to expected results. From the definition of a reactivity ratio

$$K_{12} = K_{\mathrm{p}}/r_1 \tag{7}$$

where K_{p} ($=K_{11}$) is the propagation rate constant for addition of monomer 1 to its own radical. The K_{p} values for styrene and methacrylonitrile polymerizations at 60° are 145 and 184 l./(mol sec), respectively.[35] Hence the rate constants for additions of α-methylstyrene monomer are 129 l./(mol sec) (polystyryl radical) and 338 l./(mol sec) (polymethacrylonitrile radical). These differences are consistent with the electron-poor character of the methacrylonitrile radical and electron-rich nature of the α-methylstyrene vinyl grouping and the styryl radical.

The ratios of rate constants for addition of styrene and methacrylonitrile to α-methylstyryl radical will be in the inverse ratio of the r_2 values if the simple copolymer model applies. This calculation indicates that methacrylonitrile adds 1.15 times as fast as styrene at 60°. The effect of polarity is less than when α-methylstyrene is the attacking monomer. This is consistent with the greater resonance stabilization of the α-methylstyrene radical, as discussed by Evans and coworkers.[36]

The r_2(α-methylstyrene) values reported in this work are considerably higher than those quoted by other workers cited. The r_1 figures (methacrylonitrile or styrene) are close to those from previous work. Although the methods of analysis and computation of reactivity ratios are different in our work, it is tempting to ascribe the main cause of this discrepancy to the fact that other workers analyzed only high polymer, whereas the gas chromatographic method reported here takes account of loss of monomer in all products. Qualitatively, it seems reasonable that the termination/propagation ratio will be higher for polymer radicals ending in α-methylstyrene units than in the other comonomers. This difference would be more pronounced for methacrylonitrile than for styrene polymerizations. We find, indeed, that our r_2 values exceed the high polymer figures reported by a greater factor in this case than when the comonomer is styrene. (The low polymer/high polymer r_2 ratios are approximately 0.54/0.12 and 0.63/0.35 for methacrylonitrile and styrene systems, respectively.) The weight of evidence from this and previous studies thus indicates that α-methylstyrene may accumulate significantly in low molecular weight polymer.

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