# Radical Copolymerization of Styrene with α-Methylene-δ-valerolactone: Role of Depropagation in the Mechanism

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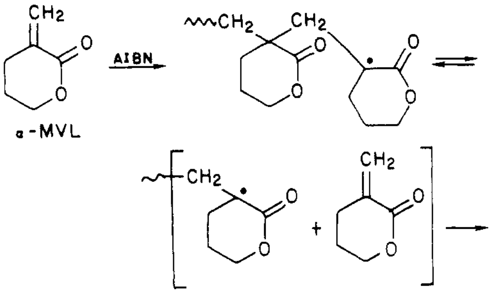
ABSTRACT: The radical copolymerization of styrene (St, $M_1$) with α-methylene-δ-valerolactone (α-MVL, $M_2$) has been investigated in dimethylformamide (DMF) from 45 to 80 °C with azobis(isobutyronitrile) as an initiator. Because α-MVL homopolymerizations exhibited a ceiling temperature of 83 °C, depolymerization of α-MVL groups from growing $M_2M_2\cdot$ chain ends was suspected to occur in analogy with α-methylstyrene copolymerizations. Therefore, copolymerization data were tested as a function of temperature with equations derived from three different copolymerization models: the Mayo–Lewis, the Lowry case I, and the Lowry case II equations. Surprisingly, the Mayo–Lewis equation was found to be adequate in describing the results. Apparently, the classic Mayo–Lewis model is an adequate description because the average sequence lengths of α-MVL ($M_2$) in the copolymers are very short. If very short $M_2$ sequences have higher ceiling temperatures than that of growing homopolymer chains, application of the Mayo–Lewis equation is readily understood. The reactivity ratios at 55 °C are $r_1 = 0.096$ and $r_2 = 1.44$. Derived $Q$–$e$ values are meaningless for this copolymerization due to the strong steric effects of α-MVL.

## Introduction

As a part of our research program on the structure–reactivity relationships of vinyl monomers in their radical polymerizations and copolymerizations,[1-8] our group has been studying the polymerization behavior of *exo*-methylene cyclic monomers.[4-6] Previously[6] we reported kinetic studies of the radical polymerization of α-methylene-δ-valerolactone (α-MVL). This investigation revealed that α-MVL has a ceiling temperature of $T_c = 83$ °C at a standard state corresponding to an α-MVL concentration of 1 mol/L. The rate of polymerization ($R_p$) followed the expression $R_p = k[\mathrm{AIBN}]^{0.44}([\mathrm{M}] - [\mathrm{M_e}])^{1.1}$ when the depropagation step was taken into account.[6] A low $T_c$ is expected based on steric constraints in this nonpolar lactone ring monomer.



The next target was to study the radical copolymerization behavior of α-MVL. In general, the simple Mayo–Lewis copolymer composition equation cannot be applied to the copolymerization of a monomer with a low ceiling temperature that is close to the polymerization temperature because of the effect of depropagation. To account for depropagation, several modified copolymer composition equations involving the depropagation step have been proposed to account for the deviations from the normal copolymer equation.[9-15] Lowry derived the basic theory for copolymerization with concomitant depropagation for three different sets of assumptions (cases I–III) about the depropagating ability of different terminal structures at the growing chain's end.[9]

In the Lowry case I model, only one of the two monomers undergoes depolymerization (i.e., $M_2$) and it does not depolymerize when attached to $M_1$ at the chain end (i.e., $M_1M_2\cdot$). However, $M_2$ has an appreciable tendency to depolymerize whenever it is attached to another $M_2$ unit. Case II differs from case I only in its condition that $M_2$ must be attached to two or more $M_2$ units to undergo depolymerization (i.e., $M_2M_2M_2\cdot$ depolymerizes but $M_1M_2M_2\cdot$ does not). In Lowry's case III both $M_1$ and $M_2$ can depolymerize when attached to two or more $M_2$ units. In all three cases the rate of additions (or removal) of a particular monomer unit to (or from) any given chain terminus is independent of the composition of the rest of the chain.

Lowry's equations provide a reasonable interpretation of the variation of copolymer composition in copolymerizations of a monomer with a low ceiling temperature. In particular, this treatment was applied to the copolymerization of α-methylstyrene (α-MSt) with other monomers over a wide temperature range.[10,11,13,16-19] Recently, different approaches to computer simulation of free radical copolymerizations with depropagation have been reported.[20] Unfortunately, other than in α-methylstyrene copolymerizations, very little experimental testing of various comonomer pairs has been carried out to determine what copolymerization–depropagation models actually apply in such copolymerizaitons. One reason for this situation is the complexity of the equations that must be used to describe the composition–conversion curves.[6,8] Second, the choice of which model best fits the data is not always going to be obvious, and a variety of treatments will be required to examine copolymerization data over a range of temperatures.[11]

In this paper, we report the results of the radical-initiated copolymerization of styrene with α-MVL over the temperature range 45–80 °C. In order to account for the copolymerization behavior, experimental results were examined by using three copolymer composition equations,

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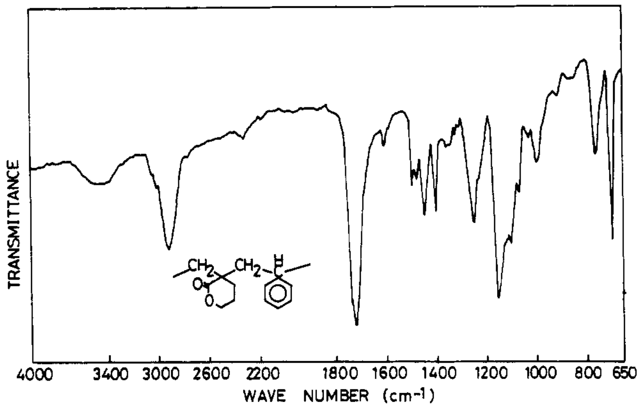


**Figure 1.** Infrared spectrum of the St-α-MVL copolymer (KBr). Mole ratio (St/α-mVL) = 0.46/0.54 in this copolymer.

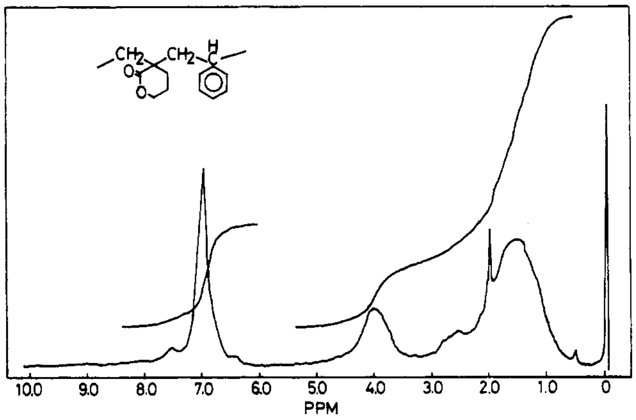
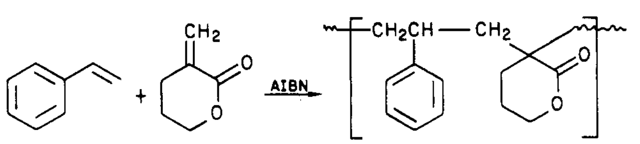


**Figure 2.** NMR spectrum of the St-α-MVL copolymer in $CDCl_3$ at 30 °C. Mole ratio (st/α-MVL) = 0.46/0.6 in this copolymer.

that is, the Mayo–Lewis equation and Lowry's case I and II equations.



## Experimental Section

**Materials.** α,α′-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. Reagent grade *N*,*N*-dimethylformamide (DMF) (750 mL) was mixed with 90 mL of benzene and 40 mL of water and distilled at atmospheric pressure. Then it was distilled at reduced pressure under nitrogen. The other reagents were used without further purification. The monomer, styrene (St), was purified by usual methods. The preparation of α-methylene-δ-valerolactone (α-MVL) was previously described.[6]

**Copolymerizations.** Weighed amounts of monomer, DMF, and AIBN (total amount of solution was 11 mL) were charged into polymerization tubes and degassed by three alternate freeze–pump–thaw cycles. After the tubes were sealed, they were placed in a constant-temperature bath for a specific time. Then the tubes were removed from the bath, and the polymer was precipitated by pouring the mixture into excess methanol. The polymer was filtered, dried in vacuo at 60 °C for 48 h, and weighed. The compositions of the copolymers were calculated from elemental analyses for carbon content. The experimental error was determined by repeated analyses to be ±0.3% per sample. Careful repetitions were not employed for the polymers prepared at 65 °C where the sum of the monomer concentrations was 0.5 mol/L, due to the small amounts of polymer available. However, repetition under all other conditions confirmed that the $M_1/M_2$ composition could be rather accurately determined due to reproducibility of analyses for the percentage of carbon and due to the large percentage difference of carbon in the two monomers (α-MVL, 64.29% C; styrene, 92.31% C).

**Measurements.** The infrared spectra were recorded on a Jasco IRA-1 spectrophotometer and the NMR spectra on a Hitachi R-24B (60 MHz) instrument. Thermogravimetry (TG) was performed with a TG-20B thermal balance. Molecular weights of copolymers were determined by gel permeation chromatography (GPC). The chromatograms were obtained with a Toyo-Soda HLC-802A instrument fitted with a refractive index detector. A 1.2-m column bed of TSK-GEL G-5000H and G-300H polystyrene gel was employed with a universal calibration procedure. The gels employed had pore diameters of 17 and 13 μm, respectively, and the resolving range of the columns was $10^2$ to $4 \times 10^6$ daltons. DMF was employed as the eluting solvent for GPC and in [η] measurements.

## Results and Discussion

**Copolymer Characterization.** Copolymerizations of styrene (St) with α-methylene-δ-valerolactone (α-MVL) were initiated by AIBN at temperatures from 45 to 80 °C in DMF. Typical copolymerization results at low conversions are summarized in Table I. The copolymers were white solids of which brittle transparent films could be cast from chloroform solution. The copolymers were very soluble in chloroform, acetonitrile, dimethyl sulfoxide, and DMF and insoluble in methanol, *n*-hexane, benzene, and toluene. The infrared spectrum of a 54/46 α-MVL/styrene copolymer (run no. 13, Table I), shown in Figure 1, was in accord with its structure. The C=O stretching band at 1270 $cm^{-1}$, from the α-MVL units, and the C–H out-of-plane bending (monosubstituted phenyl group of styrene) at 760 and 700 $cm^{-1}$ were observed for the copolymer. The NMR spectrum of a 60/40 α-MVL/styrene copolymer (run no. 31, Table I) (Figure 2) in $CDCl_3$ exhibited characteristic broad peaks at δ 7.0 and 4.0, which were due to the aromatic protons (St) and the methylene protons adjacent to the oxygen of the lactone (α-MVL). Clearly copolymers were formed. The weight-average molecular weights obtained from the GPC measurements for the copolymers (run no. 21 and 30) were $5.5 \times 10^4$ and $3 \times 10^4$, respectively.

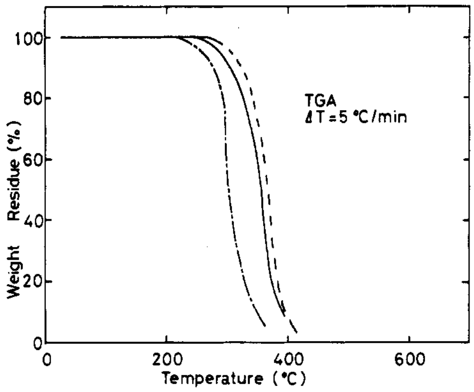


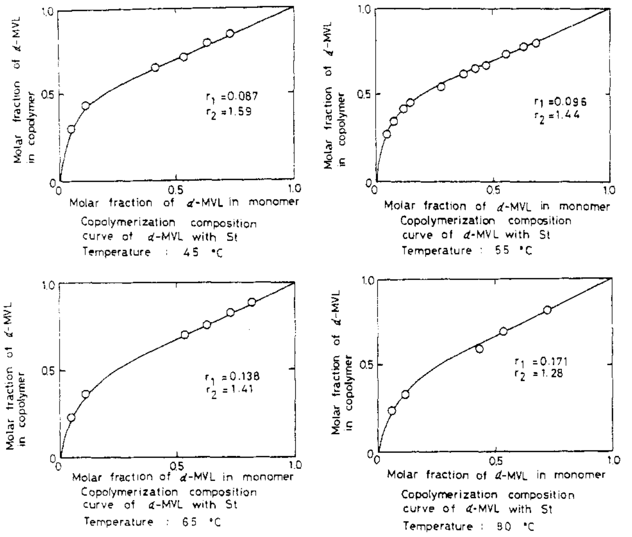
**Figure 3.** TGA traces for a St-α-MVL copolymer and for poly(α-MVL). Mole ratio (St/α-MVL) = 0.66/0.34: St-α-MVL copolymer in air (—); St-α-MVL copolymer in $N_2$ (- - -); poly(α-MVL) in air (-·-).

Thermogravimetry (TG) was carried out both in air and in $N_2$ at heating rates of 5 °C/min. The thermogram of the 34/66 α-MVL/styrene copolymer (run no. 17) is shown in Figure 3, where a thermogram for poly(α-MVL) is included for comparison. The degradation temperature corresponding to a 10% weight loss increased with increasing content of the St unit in the copolymer.

**Determination of the Reactivity Ratios.** In order to clarify the copolymerization mechanism, the following three copolymer composition equations were tested:

(a) Mayo–Lewis Equation[21]

$$d[M_1]/d[M_2] = ([M_1]/[M_2])(r_1[M_1] + [M_2])/([M_1] + r_2[M_2]) \quad (1)$$



Copolymerization composition curve of α-MVL with St Temperature : 45 °C

Copolymerization composition curve of α-MVL with St Temperature : 55 °C

Copolymerization composition curve of α-MVL with St Temperature : 65 °C

Copolymerization composition curve of α-MVL with St Temperature : 80 °C

**Figure 4.** Copolymerization of St with α-MVL at 45, 55, 65, and 80 °C. $\sum[\mathrm{St}] + [\alpha\text{-MVL}] = 1.0$ mol/L (Mayo–Lewis mechanism).

where $r_1 = k_{11}/k_{12}$, $r_2 = k_{22}/k_{21}$, and $d[M_1]/[M_2]$ denotes the instantaneous molar ratios of two monomer units incorporated into the copolymer formed from a feed containing the monomers at concentrations $[M_1]$ and $[M_2]$.

Lowry's equations for cases I and II were derived on the assumption that only one of monomers involved (e.g., α-MVL) is sufficiently near its ceiling temperature to have a significant rate of depropagation.[9]

(b) Lowry's Case I Equation

$$\frac{d[M_2]}{d[M_1]} = \frac{[M_2][1/(1-\alpha)]}{r_1[M_1] + [M_2]} \tag{2}$$

where $\alpha$ is defined by

$$\alpha = ([1 + \rho[M_2] + (\rho/r_2) \times [M_1]] - \{[1 + \rho[M_2] + (\rho/r_2)[M_1]]^2 - 4[M_2]\}^{1/2})/2$$

and $\rho$ is the equilibrium constant for the equilibrium expressed in the form

$$\sim\!\! M_1M_2M_2^* \rightleftarrows \sim\!\! M_1M_2^* + M_2$$

(c) Lowry's Case II Equation

$$\frac{d[M_2]}{d[M_1]} = \frac{\beta\gamma - 1 + [1/(1-\beta)]^2}{[(r_1[M_1]/[M_2]) + 1][\beta\gamma + [\beta/(1-\beta)]]} \tag{3}$$

where $\beta$ and $\gamma$ are defined by

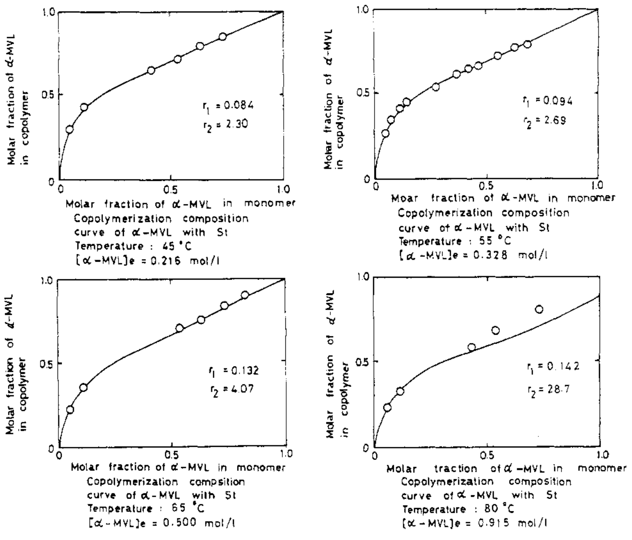
$$\beta = ([1 + \rho[M_2] + (\rho/r_2) \times [M_1]] - \{[1 + \rho[M_2] + (\rho/r_2)[M_1]]^2 - 4\rho[M_2]\}^{1/2})/2$$

$$\gamma = \{\rho[M_2] + (\rho/r_2)[M_1] - \beta\}/\rho[M_2]$$

and $\rho$ is the equilibrium constant for the equilibrium expressed in the form

$$\sim\!\! M_1M_2M_2M_2^* \rightleftarrows \sim\!\! M_1M_2M_2^* + M_2$$

In this paper, St is designated as $M_1$, and α-MVL as $M_2$. Equilibrium concentrations for α-MVL at several temperatures are listed in Table II. These values were determined by the method we previously reported.[6]



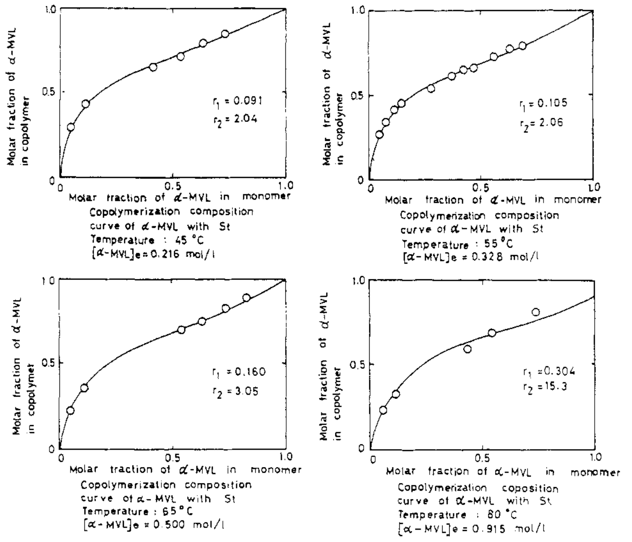
Copolymerization composition curve of α-MVL with St Temperature : 45 °C [α-MVL]e = 0.216 mol/l

Copolymerization composition curve of α-MVL with St Temperature : 55 °C [α-MVL]e = 0.328 mol/l

Copolymerization composition curve of α-MVL with St Temperature : 65 °C [α-MVL]e = 0.500 mol/l

Copolymerization composition curve of α-MVL with St Temperature : 80 °C [α-MVL]e = 0.915 mol/l

**Figure 5.** Copolymerization of St with α-MVL at 45, 55, 65, and 80 °C. $\sum[\mathrm{St}] + [\alpha\text{-MVL}] = 1.0$ mol/L (Lowry case I mechanism).



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Copolymerization composition curve of α-MVL with St Temperature : 80 °C [α-MVL]e = 0.915 mol/l

**Figure 6.** Copolymerization of St with α-MVL at 45, 55, 65, and 80 °C. $\sum[\mathrm{St}] + [\alpha\text{-MVL}] = 1.0$ mol/L (Lowry case II mechanism).

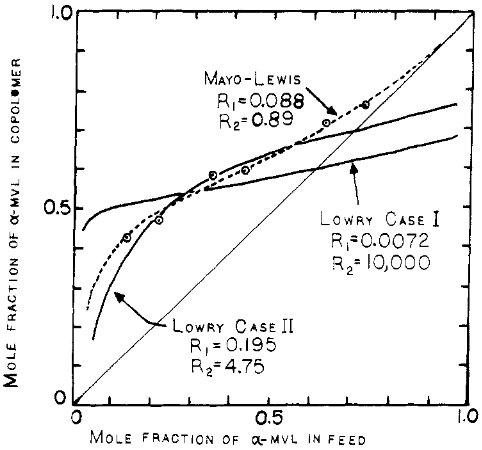


**Figure 7.** Copolymerization of St with α-MVL at 100 °C. Comparison of the Mayo–Lewis to the Lowry case I and II models. $\sum[\mathrm{St}] + [\alpha\text{-MVL}] = 1.0$ mol/L.

The theoretical curves for the instantaneous copolymer composition vs. monomer feed composition for copolymerizations at various temperatures were calculated for the classic Lewis–Mayo and Lowry Case I and II mechanisms using eq 1, 2, and 3, respectively. The results are shown as the calculated (solid) curves that are plotted vs. the experimental points in Figures 4–7. Figure 4 gives the Mayo–Lewis predictions, Figure 5 the Lowry case I predictions, and Figure 6 the Lowry case II predictions for the results obtained at 45–80 °C. Figure 7 shows the

**Table I**
**Copolymerization of Styrene (St) with α-MVL**

| | condns[a] | | | | | mol fraction of α-MVL, mol % | |
|---|---|---|---|---|---|---|---|
| no. | [St] × $10^3$, mol | [α-MVL] × $10^3$, mol | polymn time, h | copolym yield, % | elem anal., %C | in feed | in copolym |
| | | | At 45 °C[b] | | | | |
| 1 | 2.50 | 6.83 | 6.0 | 4.3 | 68.3 | 73.2 | 84.7 |
| 2 | 3.36 | 5.82 | 5.0 | 3.0 | 69.8 | 63.4 | 79.0 |
| 3 | 4.28 | 4.94 | 4.0 | 2.6 | 71.9 | 53.6 | 71.2 |
| 4 | 5.01 | 3.58 | 5.5 | 2.5 | 73.6 | 41.7 | 65.0 |
| 5 | 7.68 | 1.02 | 8.0 | 1.7 | 79.7 | 11.7 | 43.0 |
| 6 | 8.17 | 0.46 | 8.0 | 2.0 | 83.5 | 5.4 | 29.7 |
| | | | At 55 °C[c] | | | | |
| 7 | 2.80 | 6.14 | 4.0 | 5.5 | 69.7 | 68.7 | 79.4 |
| 8 | 3.45 | 5.86 | 3.0 | 5.1 | 70.2 | 62.9 | 77.6 |
| 9 | 3.80 | 5.21 | 4.0 | 6.3 | 71.5 | 57.8 | 72.7 |
| 10 | 4.91 | 4.36 | 3.0 | 4.1 | 73.2 | 47.1 | 66.5 |
| 11 | 5.22 | 3.84 | 3.5 | 5.2 | 73.7 | 42.4 | 64.6 |
| 12 | 5.72 | 3.38 | 3.5 | 4.9 | 74.5 | 37.1 | 61.7 |
| 13 | 6.72 | 2.61 | 3.0 | 3.5 | 76.6 | 28.0 | 54.1 |
| 14 | 8.01 | 1.45 | 4.0 | 3.6 | 79.0 | 15.3 | 45.5 |
| 15 | 8.20 | 0.43 | 4.0 | 2.8 | 84.3 | 5.0 | 27.0 |
| 16 | 8.39 | 1.11 | 4.5 | 3.6 | 80.2 | 11.7 | 41.3 |
| 17 | 8.82 | 0.74 | 6.0 | 6.4 | 82.2 | 7.7 | 34.3 |
| | | | At 65 °C[d] | | | | |
| 18 | 1.63 | 7.76 | 2.0 | 5.3 | 67.2 | 82.6 | 88.8 |
| 19 | 2.51 | 6.92 | 2.5 | 7.5 | 68.8 | 73.4 | 82.8 |
| 20 | 3.43 | 5.86 | 2.5 | 7.8 | 70.8 | 63.1 | 75.3 |
| 21 | 4.21 | 4.88 | 3.0 | 9.3 | 72.2 | 53.7 | 70.1 |
| 22 | 7.69 | 0.97 | 4.3 | 7.2 | 81.7 | 11.2 | 36.0 |
| 23 | 8.03 | 0.42 | 4.5 | 7.0 | 85.5 | 5.0 | 22.8 |
| | | | At 65 °C[e] | | | | |
| 24 | 1.39 | 3.51 | 4.5 | 11.2 | 68.8 | 71.7 | 82.8 |
| 25 | 2.15 | 2.58 | 4.8 | 13.7 | 71.9 | 54.6 | 71.2 |
| 26 | 2.42 | 2.05 | 6.5 | 17.1 | 73.2 | 45.9 | 66.5 |
| 27 | 3.42 | 1.16 | 4.8 | 5.7 | 76.9 | 25.3 | 53.0 |
| 28 | 3.90 | 0.69 | 4.8 | 5.5 | 79.6 | 15.1 | 43.4 |
| | | | At 80 °C[f] | | | | |
| 29 | 2.56 | 6.90 | 1.0 | 7.6 | 69.1 | 72.9 | 81.7 |
| 30 | 4.27 | 4.92 | 1.5 | 13.1 | 72.4 | 53.5 | 69.4 |
| 31 | 5.09 | 3.91 | 1.5 | 11.9 | 75.1 | 43.4 | 59.5 |
| 32 | 7.67 | 1.01 | 2.0 | 9.7 | 82.5 | 11.6 | 33.2 |
| 33 | 8.12 | 0.54 | 2.5 | 9.7 | 85.1 | 6.2 | 24.2 |

[a] Solvent: DMF; $\sum[M_1] + [M_2] = 1.0$ mol/L for all cases except the second set of data at 65 °C. [b] [AIBN] = $2.46 \times 10^{-3}$ mol/L. [c] [AIBN] = $2.37 \times 10^{-3}$ mol/L. [d] [AIBN] = $2.35 \times 10^{-3}$ mol/L. [e] [AIBN] = $2.51 \times 10^{-3}$ mol/L; $\sum[M_1] + [M_2] = 0.5$ mol/L. [f] [AIBN] = $2.60 \times 10^{-3}$ mol/L.

**Table II**
**Equilibrium Concentrations of α-Methylene-δ-valerolactone as a Function of Temperature**

| temp, °C | $1/T \times 10^3$ | [α-MVL]$_e$[a], mol/L |
|---|---|---|
| 45 | 3.14 | 0.216 |
| 55 | 3.05 | 0.328 |
| 65 | 2.96 | 0.500 |
| 70 | 2.91 | 0.631 |
| 80 | 2.83 | 0.915 |

[a] [α-MVL]$_e$ = equilibrium monomer concentration. ln [α-MVL]$_e$ = $(-4.66 \times 10^3)/T_c + 13.1$.

results at 100 °C for all three models. In this treatment $[M_e]$ is held fixed.

Values of the reactivity ratios, $r_1$ and $r_2$, were obtained for all three models by a nonlinear least-squares fitting computer program that employed a modified Marquardt method.[22] The program varied $r_1$ and $r_2$ by small increments over a large range of values to minimize the mean absolute deviation between the experimental points and the predicted composition for each of the copolymer equations, respectively. Fixed values of the equilibrium constant were employed. Monomer feed compositions were approximately constant since low conversions were employed. These reactivity ratios are summarized in Table III, and these are the values that were applied in generating the curves in Figures 4–8. The reactivity ratios calculated by using 2 and 3 (Lowry's cases I and II, respectively) were very large at 80 °C, indicating that these models are less effective at describing the copolymerization system at this temperature.

The reactivity ratios obtained with the classic Mayo–Lewis model, eq 1, illustrate that an increase in temperature results in a less selective copolymerization. Both reactivity ratios begin to approach unity due to a decreasing selectivity by either growing radical toward the two monomers. These results constitute a normal temperature dependence for *r* values. On the other hand, the values of both $r_1$ and $r_2$, obtained by employing the Lowry depropagation mechanisms for cases I and II, became large with increasing temperature. These results predict an unreasonable situation. They indicate that the α-MVL radical reacts preferentially with α-MVL monomer with increasing polymerization temperature, that is, with increasing equilibrium monomer concentration. This temperature dependence of the *r* values is abnormal.

Further evidence for the applicability of the Mayo–Lewis copolymerization model is observed in Figures 4–7. The

**Table III**
**Reactivity Ratios for St ($M_1$) and α-MVL ($M_2$)**

| $1/T \times 10^3$, $K^{-1}$ | $r_1$ | $r_2$ | $\ln r_1$ | $\ln r_2$ |
|---|---|---|---|---|
| | From Mayo–Lewis[a] | | | |
| 3.14 | 0.087 | 1.59 | -2.44 | 0.46 |
| 3.05 | 0.096 | 1.44 | -2.34 | 0.36 |
| 2.96 | 0.138 | 1.41 | -1.98 | 0.34 |
| 2.83 | 0.171 | 1.28 | -1.77 | 0.25 |
| | From Lowry Case I[a] | | | |
| 3.14 | 0.084 | 2.30 | -2.48 | 0.83 |
| 3.05 | 0.094 | 2.69 | -2.36 | 0.99 |
| 2.96 | 0.132 | 4.07 | -2.02 | 1.40 |
| 2.83 | 0.142 | 28.7 | -1.95 | 3.36 |
| | From Lowry Case II[a] | | | |
| 3.14 | 0.091 | 2.04 | -2.40 | 0.71 |
| 3.05 | 0.105 | 2.06 | -2.25 | 0.72 |
| 2.96 | 0.160 | 3.05 | -1.83 | 1.12 |
| 2.83 | 0.304 | 15.3 | -1.19 | 2.73 |
| | From Mayo–Lewis[b] | | | |
| 2.96 | 0.119 | 1.15 | -2.13 | 0.14 |
| | From Lowry Case I[b] | | | |
| 2.96 | 0.119 | 1.85 | -2.13 | 0.62 |
| | From Lowry Case II[b] | | | |
| 2.96 | 0.119 | 1.65 | -2.13 | 0.50 |

[a] [St] + [α-MVL] = 1.0 mol/L. [b] [St] + [α-MVL] = 0.5 mol/L.

Mayo–Lewis equations predict closely the observed instantaneous copolymer composition–monomer feed composition curves. Over the entire range of temperatures the Mayo–Lewis predictions are adequate and fit the experimental data more accurately than either the Lowry case I or case II models. However, the Lowry case I and II models do give reasonable fits at lower temperatures, and, when taken alone, these differences in fit might not be a totally convincing basis for choosing the Mayo–Lewis model. The Lowry models also give better fits when the values of $[M_e]$ are varied to much lower values. The Lowry models give increasingly poorer fits as the temperature increases. This is most strikingly illustrated in Figure 7. This figure shows the copolymer composition vs. monomer feed plots vs. the experimental points obtained in copolymerizations at 100 °C when calculated by each of the three models. Only the Mayo–Lewis model gives a good fit.

We examined the sensitivity of the Lowry cases I and II to the value of $K_{eg}$ and found that these models are indeed quite sensitive to $K_{eg}$. This can be briefly illustrated with the α-MVL copolymerization with styrene at 55 °C. Our data (Table III) show that the equilibrium concentration of α-MVL is 0.328 mol/L and that the Lowry case I model gives $r_1 = 0.094$ and $r_2 = 2.69$. If one varies the equilibrium concentration of α-MSV from 0.2 to 0.4 to 0.5 mol/L (holding $r_1 = 0.095$), the values of $r_2$ obtained are $r_2 = 2.01$, 3.34, and 4.92, respectively.

Indeed, a large number of calculations were carried out where the equilibrium concentration of α-MVL was varied stepwise over a large range. As the value of $[M_e]$ decreased the Lowry case I and II fits improved and often approached those of the Mayo–Lewis model. The sensitivity of "goodness of fit" to variation in $[M_e]$ varied with temperature. A thorough discussion of these details will not be attempted here other than to conclude that one can get consistently good fits with the Mayo–Lewis model without superimposing the search of $[M_e]$ values required of the Lowry cases.

Wittmer[10,11] has pointed out that the depropagation copolymerization models are not simply a function of the $M_1/M_2$ ratios but are also dependent upon the absolute value of the monomer concentrations. Thus, copolymerizations were carried out (65 °C) at different monomer concentrations {[$\sum$[St] + [α-MVL]) of 1.0 mol/L (Figures 4–6) and 0.5 mol/L (Figure 8)}. No difference in the quality of the fit by the different models was noticed. In retrospect studies at 70 or 75 °C over a monomer concentration range 0.1–2 mol/L would have been desirable, but the lower concentrations created experimental difficulties.

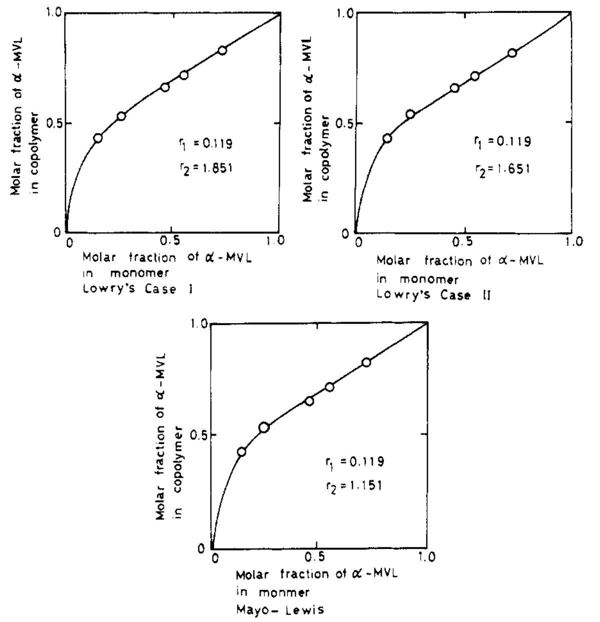
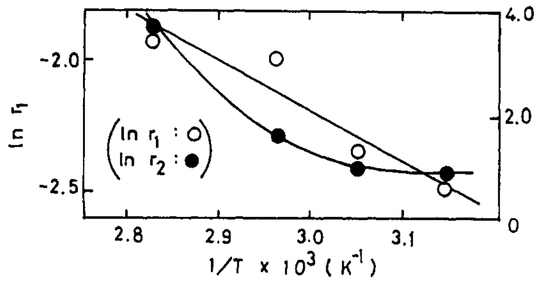


**Figure 8.** Copolymerization of St with α-MVL at 65 °C. Comparison of Mayo–Lewis, Lowry case I, and Lowry case II models. $\sum$[St] + [α-MVL] = 0.5 mol/L.

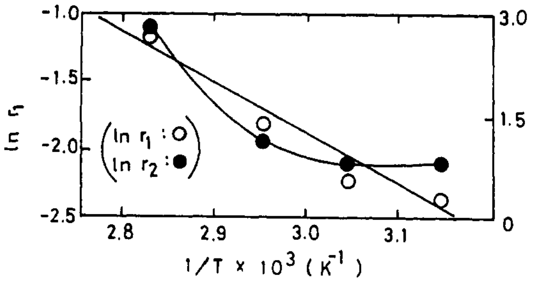
Before accepting the Mayo–Lewis model, one should further consider the work of Wittmer.[10,11] Wittmer pointed out that the curve-fitting approach, alone, in his studies was not sufficient to discern the proper copolymerization model. He showed that the copolymerization behavior of α-methylstyrene (α-MSt) with methyl methacrylate (MMA) can be adequately described via polymer composition–feed composition curves between 20 and 100 °C generated with either the Mayo–Lewis equation or an equation that he derived to take depropagation into account. Therefore, in order to achieve a more sensitive probe to distinguish between these mechanisms, Wittmer used Arrhenius plots of the reactivity ratios (see eq 4) to decide which model best describes the copolymerization data for the α-MSt/MMA system.

$$\mathrm{r}_1 = \frac{k_{11}}{k_{12}} = \frac{A_{11}}{A_{12}} \frac{\exp(E_{12} - E_{11})}{RT} \qquad (4)$$

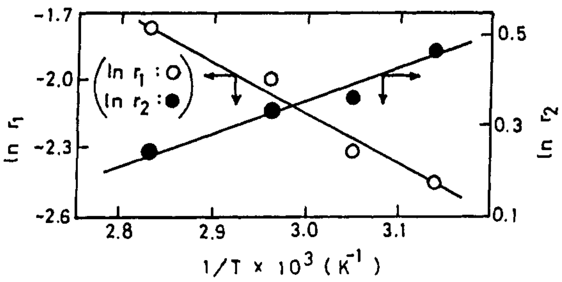
In eq 4, $E_{11}$ and $A_{11}$ are the propagation activation energy and frequency factor for $M_1$ radical adding $M_1$ monomer, respectively, and $E_{12}$ and $A_{12}$ are the corresponding values for $M_1$ radical adding $M_2$ monomer. The reactivity ratios must exhibit linear plots of log $r$ vs. reciprocal temperature. Therefore, these Arrhenius plots can be constructed from the values of $r$ predicted by each of the copolymerization models (i.e., Mayo–Lewis Lowry case I–III, etc.) and examined. When strong curvature exists in these plots, the copolymerization model may then be discarded. Wittmer[11] found that Arrhenius plots of $r_1$ values, which resulted from the Mayo–Lewis treatment, exhibited great curvature for α-MSt/MMA copolymerizations. However, linear plots of ln $r_1$ vs. $1/T$ were obtained with $r_1$ values from his depropagation model equation, thereby allowing him to discard the Mayo–Lewis



Reactivity ratios from Lowry's Case I



Reactivity ratios from Lowy's Case II



Reactivity ratios from Mayo-Lewis equation

**Figure 9.** Arrhenius plot of reactivity ratios for St–$\alpha$-MVL copolymerizations.

model for that copolymerization system.

Logarithmic plots of the values of $r$ vs. $1/T$ from the St/$\alpha$-MVL copolymerizations are shown in Figure 9. The plots using values of $r_1$ and $r_2$ calculated from Lowry's case I and II models were severely curved. However, the corresponding plots using values of $r_1$ and $r_2$ from the classic Mayo–Lewis model were linear. Therefore, this treatment further supports the applicability of the Mayo–Lewis model for the St/$\alpha$-MVL copolymerization. Both methods (Arrhenius plots of $r$ values and observing which model best fits polymer composition–feed composition plots) clearly argue that using the classic Mayo–Lewis copolymerization model is satisfactory.

The values of $r_1$ and $r_2$ at 55 °C from eq 1 were obtained by three approaches: computerized curve fitting and both the Fineman–Ross[23] and Kelen–Tüdös[24] methods. The best values were $r_1 = 0.096$ and $r_2 = 1.44$ (curve-fitting method). The $Q$–$e$ values for $\alpha$-MVL, calculated from monomer reactivity ratios, are listed in Table IV, but their meaning is entirely obscure. This reason will be discussed in a later section. The relative reactivity of monomers to the referential radical is seen from the inverse of the monomer reactivity ratios. The values of $1/r_1$ and $1/r_2$ are 10 and 0.7, respectively, which means that both the polystyryl and the $\alpha$-MVL radicals react preferentially with $\alpha$-MVL ($M_2$). This finding is in accord with the $\alpha$-MVL monomer being more reactive monomer than St.

It is difficult to compare the copolymerizations of $\alpha$-MVL to other systems where depropagation is occurring because so few experimental studies have appeared. Wittmer studied $\alpha$-MSt copolymerizations with both MMA and acrylonitrile[10,11] and concluded that a depropagation model was the only treatment that fit the experimental data. However, Johnston and Rudin[25,26] concluded that copolymerizations of $\alpha$-MSt with MMA and with St (at both 60 and 90 °C) follow the simple Mayo–Lewis model (eq 1). They explained why this should be the case as follows: Depropagation effects are not important in the copolymerization because the sequence lengths of $\alpha$-MSt in the copolymer are short. These short sequences would have higher polymerization enthalpies, hence higher ceiling temperatures, than high molecular weight sequences found in homopolymerizations. This conclusion was derived from the report that the heat of polymerization of $\alpha$-MSt was a linear inverse function of molecular weight.[27]

**Table IV**
**Copolymerization Parameters at 55 °C**[a]

| $M_1$ | $M_2$ | $r_1$ | $r_2$ | $r_1r_2$ | $Q_2$ | $e_2$ |
|---|---|---|---|---|---|---|
| St[b] | $\alpha$-MVL | 0.096 | 1.44 | 0.138 | 3.27 | 0.61 |
| St[c] | $\alpha$-MVL | 0.0992 | 1.50 | 0.149 | 3.34 | 0.58 |
| St[d] | $\alpha$-MVL | 0.0967 | 1.42 | 0.137 | 3.35 | 0.61 |

[a] St: $Q_1 = 1.00$, $e_1 = -0.80$. [b] By curve-fitting method. [c] By Fineman–Ross method. [d] By Kelen–Tüdös method.

That short sequence lengths for the low ceiling temperature monomer can explain the applicability of eq 1 receives further credence from the work of Joshi et al.[28] They reported that steric strain in low ceiling temperature polymers is progressively built up. This, in turn, lowers the heat of polymerization per double bond consumed. For isobutene polymerizations the heat of polymerization falls ultimately to a value of 54 kJ mol$^{-1}$. This pattern of a diminishing value of the heat polymerization ($\Delta H_p$) with an increase in the chain length may, for isobutene, be empirically fitted to the equation

$$-\Delta H = 81.6 - 27.6(1 - 1/n^2)\ \text{kJ mol}^{-1} \qquad \text{for } n > 1$$

where $n$ is the number of hindered dimethyl segments. In copolymerizations, this situation is largely avoided. The steric strain due to the consecutive placement of three or more similar units is relieved in the copolymer due to an alternate or a semialternate arrangement of the two monomer segments. Furthermore, the C–C linkages in the chain backbone joining two dissimilar units presumably become strengthened if the nature of the substitutions in the two species complement each other.

In accord with the description of $\alpha$-MSt copolymerizations given above, it would be useful to determine the sequence-length distributions in the $\alpha$-MVL/styrene copolymers. The probabilities or mole fractions $(N_1)_x$ and $(N_2)_x$ of forming $M_1$ and $M_2$ sequences of length $x$ are given by[29]

$$(N_1)_x = P_{11}{}^{x-1}P_{12} \tag{5}$$

$$(N_2)_x = P_{22}{}^{x-1}P_{21} \tag{6}$$

where

$$P_{11} = \frac{r_1}{r_1 + ([M_2]/[M_1])} \qquad P_{12} = \frac{[M_2]}{r_1[M_1] + [M_2]}$$

$$P_{21} = \frac{[M_1]}{r_2[M_2] + [M_1]} \qquad P_{22} = \frac{r_2[M_2]}{r_2[M_2] + [M_1]}$$

The sequence-length distributions for the St/$\alpha$-MVL copolymerization at 55 °C with $r_1 = 0.096$ and $r_2 = 1.44$ for the two feed compositions St/$\alpha$-MVL = 0.5/0.5 and 0.3/0.7

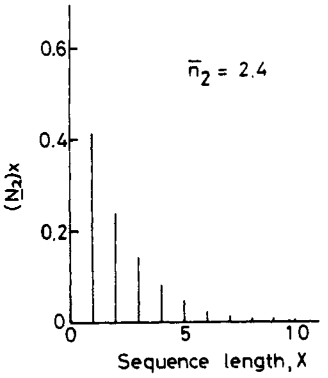


**Figure 10.** Sequence-length distributions for α-MVL in a St–α-MVL copolymer: temperature 55 °C; $r_2 = 1.44$; feed composition St/α-MVL = 0.5/0.5.

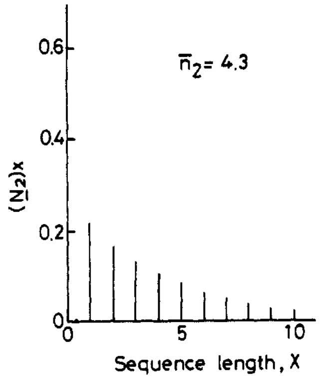


**Figure 11.** Sequence-length distributions for α-MVL in a St–α-MVL copolymer: temperature 55 °C; $r_2 = 1.44$; feed composition St/α-MVL = 0.3/0.7.

are shown in Figures 10 and 11. Other computer simulations of the copolymer composition formed under these conditions illustrate that the mean α-MVL sequence lengths are short even for a feed that is 70 mol % α-MVL. The observation that depropagation effects are not of practical importance in our St/α-MVL copolymerizations, therefore, may be interpreted in terms of the short average sequence lengths of α-MVL. These short α-MVL sequences have a higher ceiling temperature than the longer sequence lengths in the α-MVL homopolymer.

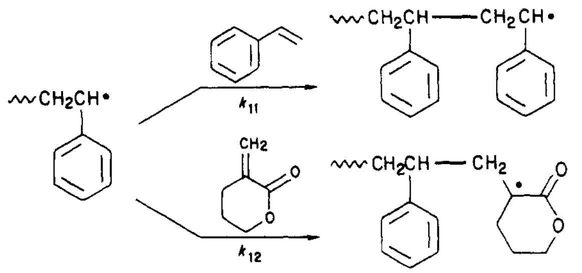
***Q–e* Values.** The *Q–e* scheme[30] is based on the assumption that steric factors can be neglected. If this assumption is valid, then the interpretation of the monomer reactivity based on activation energies is meaningful. Meyer[31] obtained the following equations describing monomer reactivity ratios in studies of the copolymerization of St–MMA from 30 to 132 °C by applying the Arrhenius expression (eq 4).

$$\ln r_1 = 0.04736 - (235.45/T)$$

$$\ln r_2 = 0.1183 - (285.36/T)$$

Meyer concluded that the differences in specific rate constants in this system are due primarily to the lower activation energies for the cross-polymerization steps rather than due to the differences in the frequency factors. Therefore, we investigated the effects of the frequency factors in the St/α-MVL copolymerization.

Scheme I



From the slope of the Arrhenius plot of ln *r* vs. $1/T$ in Figure 9, the differences in the energies of activation, $E_{11} - E_{12}$ and $E_{22} - E_{21}$, were calculated to be 19.2 and −5.28 kJ mol$^{-1}$, respectively, for St/α-MVL copolymerizations. From the intercept, the differences in frequency factors, $\ln A_{11} - \ln A_{12}$ and $\ln A_{22} - \ln A_{21}$, were 4.78 and −1.55, respectively. In terms of transition theory, the temperature dependence of the monomer reactivity ratios may be expressed as

$$\ln r_1 = (\Delta S_{11}^{\dagger} - \Delta S_{12}^{\dagger})/R - (\Delta H_{11}^{\dagger} - \Delta H_{12}^{\dagger})/RT$$

$$\ln r_2 = (\Delta S_{22}^{\dagger} - \Delta S_{21}^{\dagger})/R - (\Delta H_{22}^{\dagger} - \Delta H_{21}^{\dagger})/RT$$

where $\Delta S^{\dagger}$ represents the entropy of activation and $\Delta H^{\dagger}$ the enthalpy of activation. For our St/α-MVL copolymerizations the differences in entropy of activation were $\Delta S_{11}^{\dagger} - \Delta S_{12}^{\dagger} = 39.7$ J/(K·mol) and $\Delta S_{22}^{\dagger} - \Delta S_{21}^{\dagger} = -12.9$ J/(K·mol). These entropy of activation differences are relatively large, which demonstrates that steric effects cannot be neglected in St/α-MVL copolymerizations. Accordingly, we can conclude that calculated *Q–e* values have little meaning in these copolymerizations.

It might be mentioned that Kang and O'Driscoll[32] have discussed the physical significance of reactivity ratios obtained by applying the Mayo–Lewis method to data from systems that were expected to polymerize with some depropagation.

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**Registry No.** St, 100-42-5; α-MVL, 42023-19-8; (St)·(α-MVL) (copolymer), 99281-02-4.

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# Stereochemical Configuration of Poly(methyl α-(*p*-chlorobenzyl)acrylate) and Poly(methyl α-(*p*-methoxybenzyl)acrylate) Synthesized by Radical Polymerization

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ABSTRACT: Methyl α-(*p*-chlorobenzyl)acrylate and methyl α-(*p*-methoxybenzyl)acrylate have been synthesized and polymerized at temperatures between 40 and 90 °C in benzene solutions with AIBN as the initiator. The stereochemical parameters of both polymers have been determined from the analysis of the $^1$H NMR $OCH_3$ and $^{13}$C NMR C=O and aromatic C* resonance signals. The results obtained indicate that the mechanism of the stereochemical additions of monomers to polymeric chain ends deviates from classical Bernoullian statistics.

## Introduction

It has been widely demonstrated that the syndiotactic and isotactic additions in the propagation step of free radical polymerization are markedly influenced by the chemical structure of substituents on the olefinic carbons.[1-3] In this sense, several authors[4-7] have stated that the presence of an α-$CH_3$ group in vinyl and acrylic monomers gives rise to polymers with atactic or syndiotactic stereochemical configurations. Other organic groups such as α-chloro or α-cyano[1] give rise to the formation of polymers with a predominant syndiotactic stereostructure. However, larger substituents in the α-position such as α-ethyl, α-*n*-propyl, α-phenyl, etc.[8] seem to favor the formation of atactic polymers.

In an earlier report[9] we analyzed the stereochemical configuration of poly(methyl α-benzylacrylates) prepared be free radical polymerization at several temperatures, being predominantly syndiotactic. However, the formation of isotactic sequences was favored in comparison with poly(methyl methacrylate) prepared under the same experimental conditions in such a way that the mechanism for the propagation step of the free radical polymerization of methyl α-benzylacrylate initiated by AIBN could be fitted to the first-order Markov model.

To obtain more information about the influence of the chemical structure of this kind of monomer on stereoregulation in the propagation step of the free radical polymerization, this article deals with the determination of the stereochemical configuration of polymers derived from methyl α-(*p*-chlorobenzyl)acrylate (CLBAM) and methyl α-(*p*-methoxybenzyl)acrylate (MBAM). The results obtained are compared with those of poly(methyl α-benzylacrylate) (BAM) and poly(methyl methacrylate).

## Experimental Section

Methyl α-(*p*-chlorobenzyl)acrylate and methyl α-(*p*-methoxybenzyl)acrylate were prepared from the condensation of dimethyl malonate with the corresponding para-substituted benzyl chloride as described elsewhere.[10]

Polymerizations were carried out in sealed glass ampules under high vacuum with benzene as the solvent and 2,2′-azobis(isobutyronitrile) (AIBN) as the initiator. The reaction temperature was regulated between 40 and 90 ± 0.05 °C in a thermostatic bath. The polymers were isolated by pouring the solution into excess methanol (CLBAM) or heptane (MBAM) and washing and drying the samples to constant weight. The polymers were analyzed by $^1$H NMR (Varian EM-390, 90 MHz) and $^{13}$C NMR (Bruker WP 80 SY, 20.15 MHz) spectroscopies using nitrobenzene, deuterated chloroform, and deuterated acetone as the solvents. The spectra in acetone or chloroform solutions were recorded at 60 °C and those in nitrobenzene at 120 °C. The stereochemical parameters were calculated from the areas of appropriate signals measured by triangulation and planimetry.

## Results and Discussion

As we have stated previously,[9] the $^1$H NMR spectrum of poly(BAM) recorded in deuterated chloroform does not give useful tacticity information because of the poorly resolved methoxy proton signals. However, the resonance pattern of methoxy protons splits into three rather well-resolved peaks at 3.47, 3.60, and 3.70 ppm from HMDS when nitrobenzene is used as the solvent. The splitting of the methoxy proton resonances in the presence of aromatic solvents has been explained by several authors[11,12] by taking into account the possible differences in the orientation of the methoxy groups with respect to the π-electron system of the aromatic ring of the solvent molecules for each of the three kinds of tactic triad stereosequences.

In a similar way, Figure 1 shows that the methoxy proton resonance pattern of poly(CLBAM) in chloroform solution is not adequately resolved to evaluate the relative concentration of tactic triads, but the spectra recorded in deuterated acetone or nitrobenzene contain well-resolved peaks at 3.54, 3.66, and 3.77 ppm from HMDS. These resonances have been assigned by comparison with the spectra of poly(BAM)[9] and poly(methyl methacrylate) recorded in aromatic solvents[13] to rr, (rm + mr), and mm triads, respectively. This assignment has been verified by the analysis of the decoupled $^{13}$C NMR spectrum recorded

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