(8) We have carried out calculations based upon Karad and Schneider's data[7] for the fumaronitrile–styrene copolymerization and have shown that the predicted sequence distributions are indeed different for the two models.
(9) Here, only the 1 units will be considered. The treatment for 0 units is exactly the same but the 0's exchanged for 1's and vice versa.
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Synthesis and Homopolymerization Kinetics of α-Methylene-δ-valerolactone, an Exo-Methylene Cyclic Monomer with a Nonplanar Ring System Spanning the Radical Center

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ABSTRACT: α-Methylene-δ-valerolactone (α-MVL) has been synthesized and homopolymerized by bulk and solution methods. The poly(α-MVL) is soluble in DMF and Me_2SO at room temperature. Thermogravimetric analysis of poly(α-MVL) showed a 10% weight loss at 280 °C in air. The α-MVL has a low ceiling temperature, $T_c = 83$ °C at the standard state of 1 mol/L of monomer. Kinetics of α-MVL homopolymerization have been investigated in DMF solutions using azobis(isobutyronitrile) (AIBN) as an initiator. Depolymerization was competitive with polymerization. The rate of polymerization (R_p) followed the expression $R_p = k[\mathrm{AIBN}]^{0.44}\cdot([\mathrm{M}] - [\mathrm{M}]_e)^{1.1}$, considering the depolymerization step. The overall activation energy was calculated to be 79.5 kJ/mol. The heat of polymerization (ΔH_p) and entropy of polymerization ($\Delta S^\circ{}_p$), obtained from a linear relationship between ln $[M]_e$ vs. $1/T$, were −38.8 kJ/mol and 108.8 J/(K·mol), respectively. The low ΔH is most likely a reflection of the low ceiling temperature of the polymerization. A low T_c is expected based on steric constraints in this nonplanar lactone ring monomer.

Introduction

A large number of polymerization studies of alkyl methacrylates and related compounds have been reported.[1-5] However, very little attention has been paid to the polymerization of their cyclic analogues, except for the synthesis of poly(α-methylene-γ-butyrolactone) (α-MBL).[6] As part of our research program on the study of structure–reactivity relationships of vinyl monomers in their radical polymerizations and copolymerizations, our group has recently begun an investigation of the polymerization behavior of exo-methylene cyclic monomers. In an earlier paper, we reported kinetic studies of the radical polymerization of α-MBL.[7] This investigation revealed that α-MBL polymerization follows the normal vinyl free-radical polymerization mechanism. The Q and e values for α-MBL were larger than those of methyl methacrylate (MMA). The planarity of α-MBL results in a favorable approach between the growing radical and the monomer, and planarity favors delocalization into the carbonyl group.

The next target is to verify the radical polymerizability of α-methylene-δ-valerolactone (α-MVL), an analogue of α-MBL, which has a nonplanar lactone ring spanning the α positions. The present paper describes the synthesis of poly(α-MVL), properties of the polymer obtained, and kinetic studies of the radical polymerization of α-MVL. In addition, homo- and copolymers of α-MVL are currently being studied for potential lithographic resist applications.

Experimental Section

Materials. Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. *N,N*-Dimethylformamide (DMF) was purified as follows. Reagent grade 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. Other reagents were used as received.

Monomer. Preparation of α-Methylene-δ-valerolactone (α-MVL). This monomer was prepared according to the procedure of Ksander et al.[8] First, α-ethoxalyl-δ-valerolactone was prepared in 88% yield from diethyl oxalate and δ-valerolactone in the presence of sodium ethoxide in ethanol. This compound was used in the next step without purification. IR (NaCl) ν(C═O) 1740, 1640 cm^{-1}; NMR (in $CDCl_3$) δ = 1.25 (m, 3 H), 1.90 (m, 2 H), 2.75 (t, 2 H), 3.40 (q, 2 H), 4.25 (m, 2 H), 13.15 (s, 1 H). To a 1-L three-necked flask equipped with a mechanical stirrer, condenser, and dropping funnel were added sodium hydride (2.9 g, 0.12 mol) and 300 mL of THF. To this mixture was added

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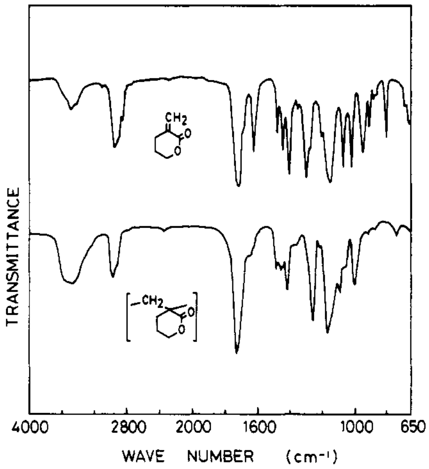
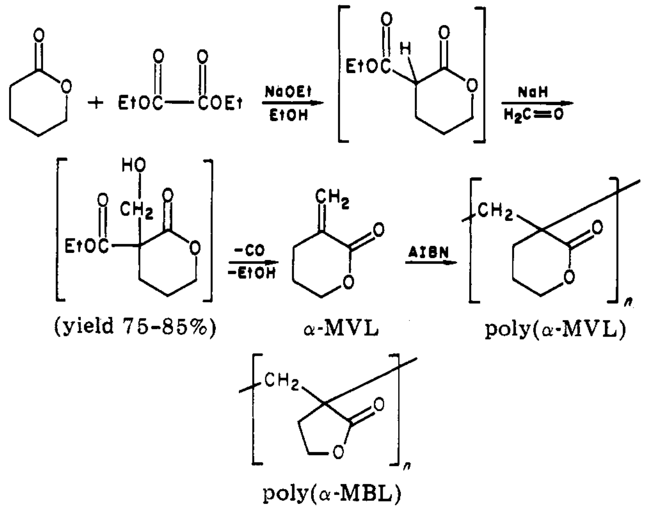


Figure 1. Infrared spectra of α-MVL (NaCl) and poly(α-MVL) (film).

Scheme I



dropwise α-ethoxalyl-δ-valerolactone (26 g, 0.13 mol) in 300 mL of THF with stirring over a period of 1 h at room temperature, and the stirring was continued for 2 h at this temperature. Then gaseous formaldehyde (obtained by thermal cracking of paraformaldehyde (8 g, 0.27 mol) was bubbled in under a slow nitrogen sweep. The reaction mixture was filtered, and the solvent was removed under reduced pressure. The residue was taken up in methylene chloride (50 mL) several times. The combined methylene chloride extracts were stirred with 200 mL of saturated aqueous $NaHCO_3$ for a few minutes. The organic layer was decanted and the aqueous phase was again extracted with 50 mL of methylene chloride. The combined methylene chloride layer was dried ($MgSO_4$), concentrated under reduced pressure, and fractionated. After redistillation, 11-12 g (75-85%) of α-MVL was obtained: bp 59 °C (0.1 mmHg) [lit.[8] bp 56.5 °C (0.07 mmHg)]; IR (NaCl) ν(C=O) 1720, ν(C=C) 1620 cm^{-1}; NMR (in $CDCl_3$) δ = 1.95 (m, 2 H), 2.63 (m, 2 H), 4.28 (t, 2 H), 5.45 (m, 1 H), 6.25 (m, 1 H); UV (95% ethanol) λ_{max} 208.3 nm.

Bulk Polymerization. α-MLV (2 g, 0.018 mol) and AIBN (0.005 g, 3×10^{-5} mol) were charged into a polymerization tube, and the tube was then degassed and sealed. After 48 h of heating at 60 °C, the tube was cooled and opened, and the resulting colorless solid block was dissolved in DMF. The polymer was purified by repeated reprecipitation from DMF into methanol, filtration, and drying in vacuo at 60 °C for 48 h to give 1.6 g (80%) of poly(α-MVL), which exhibited [η] = 1.24 dL/g in DMF at 30 °C. The IR spectrum exhibited ν(C=O) 1720 cm^{-1}. Anal. Calcd: C, 64.27; H, 7.19. Found: C, 63.7; H, 7.2.

Solution Polymerization. α-MVL (1.06 g, 9.45 mmol), AIBN (3.9 mg, 2.38×10^{-2} mmol), and 9 mL of DMF were charged into a polymerization tube and degassed. The tube was sealed and heated at 55 °C for 10 h and then opened, and the solution was poured into excess methanol with vigorous stirring. A white polymer obtained in 8.4% yield exhibited [η] = 0.3 dL/g in DMF at 30 °C.

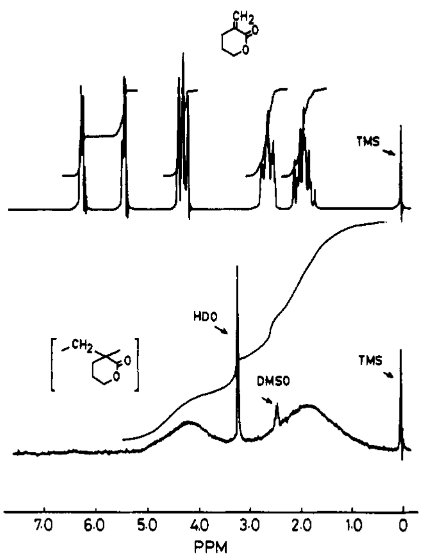


Figure 2. NMR spectra of α-MVL in $CDCl_3$ and poly(α-MVL) in $(CD_3)_2SO$ at 30 °C.

Kinetics. Weighed amounts of monomer, solvent, and initiator were charged into polymerization tubes and degassed by three alternate freeze-thaw cycles. After the tubes were sealed, they were placed in a constant-temperature bath for a specified time. Then the tubes were removed from the bath, and the polymer was precipitated by pouring the mixture into excess methanol, filtered, dried in vacuo at 60 °C for 48 h, and weighed. The accuracy of the yield measurements was ±2%.

Measurements. Infrared spectra were recorded on a Jasco IRA-1 spectrophotometer, ultraviolet spectra on a Hitachi Model 100-60 spectrophotometer, and NMR spectra on a Hitachi R-24B (60 MHz) instrument. Differential thermal analysis (DTA) and thermogravimetry (TGA) were performed with a Shimadzu DT-20 instrument and TG-20B thermal balance, respectively.

Results and Discussion

The synthesis of α-MVL in 75-85% yields was conducted, as shown in Scheme I, by using a method similar to that of Ksander et al.[8] (see Experimental Section). Bulk homopolymerizations were readily carried out with AIBN as the initiator. The homopolymer was a white solid. Transparent films of poly(α-MVL) could be cast from DMF solutions. The homopolymer was essentially insoluble in many organic solvents but it was soluble in both DMF and Me_2SO at room temperature. Its solubility resembles that reported for poly(α-methylene-γ-butyrolactone) (α-MBL).[7] The homopolymer of α-MVL gave a satisfactory elemental analysis, and its infrared spectrum, shown in Figure 1, was in accord with its structure. The infrared spectra of both monomer and polymer are compared in Figure 1. The C=O bond stretching at 1720 cm^{-1} and C=C bond stretching at 1620 cm^{-1} are clearly observed for α-MVL, whereas poly(α-MVL) exhibited a C=O absorption at 1720 cm^{-1} and no trace of a C=C stretching band.

The NMR spectra of α-MVL (Figure 2) in $CDCl_3$ at 30 °C consisted of two multiplets for vinyl protons (δ = 6.25, 5.45), a triplet for the methylene protons adjacent to oxygen (δ = 4.28), and two multiplets for methylene protons (δ = 2.63, 1.95). The NMR spectra of poly(α-MVL) at 30 °C in $(CD_3)_2SO$ (3-4 wt %) exhibited two broad peaks at δ = 4.2 (2 H) and δ = 1.8 (6 H). These results suggested that α-MVL polymerized via the double bond without the ring opening.

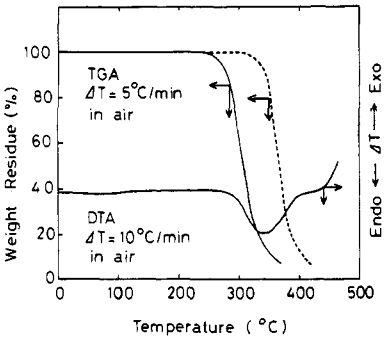


Figure 3. TGA and DTA curves of (—) poly(α-MVL) and (- - -) poly(α-MBL).

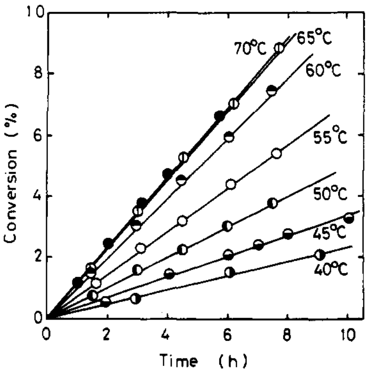


Figure 4. Time–conversion curves for solution polymerization of α-MVL at various temperatures. [α-MVL] = 0.891 mol/L; [AIBN] = 2.37 × 10^{-3} mol/L; solvent, DMF.

Thermogravimetry (TGA) and differential thermal analysis (DTA) were carried out at heating rates of 5 and 10 °C/min in air, respectively. Thermograms are shown for poly(α-MVL) in Figure 3, where a thermogram of poly(α-MBL) is also included for comparison. The DTA curve of poly(α-MVL) exhibited an endotherm at about 250 °C, which correlated well with TGA, confirming that the depolymerization occurred at about this temperature. Poly(α-MVL) is less stable than poly(α-MBL).[7] The activation energy of the depolymerization steps, E_d, is expected to equal the sum of the activation energy for the propagation reaction in polymerization, E_p, plus the heat of polymerization, ΔH_p:[9]

$$E_d = \Delta H_p + E_p \qquad (1)$$

Since E_p is usually about 21 kJ/mol, the value of E_d is largely determined by that of ΔH_p; that is, the lower the heat of polymerization, the more completely decomposition will proceed in the direction of the monomer. Also decomposition will be favored at lower temperature. Therefore, the lower decomposition temperature of poly(α-MVL) vs. that of poly(α-MBL) is explained by the lower heat of polymerization for α-MVL, and this is discussed later.

Table I
Relationship between R_p and Initiator Concentration[a]

[AIBN] × 10^4, mol/L	polymerization time, h	yield, %	R_p × 10^6, mol/(L·s)
4.87	20.0	11.0	1.68
9.44	14.0	9.4	2.05
28.0	8.0	8.6	3.28
73.1	3.0	5.4	5.49

[a] [α-MVL] = 1.10 mol/L; solvent, DMF; temperature, 55 °C.

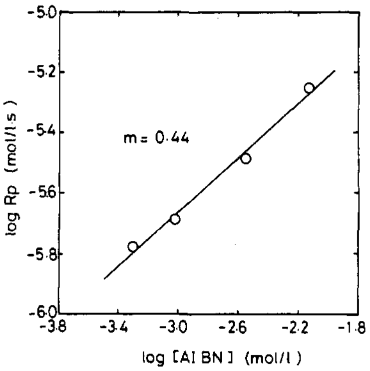


Figure 5. Plot of log R_p vs. log [AIBN] for homopolymerization of α-MVL in DMF at 55 °C. [α-MVL] = 1.10 mol/L.

Table II
Relationship between R_p and Monomer Concentration[a]

[α-MVL], mol/L	polymerization time, h	yield, %	R_p × 10^6, mol/(L·s)
4.48	1	1.79	22.3
3.47	2	3.15	15.2
2.78	2.75	4.16	11.7
1.99	3.5	4.70	7.42
1.86	2.83	3.99	7.30
1.36	4	4.48	4.21
1.28	4.5	5.54	4.39
1.24	7.5	8.33	3.81
0.956	6.5	6.88	2.81
0.982	7.5	7.60	2.77
0.898	5	4.62	2.30
0.815	7	6.03	1.95
0.605	13.25	8.34	1.06
0.562	11.53	6.99	0.947
0.569	7	4.06	0.917
0.439	15.72	5.59	0.434
0.458	7.5	2.74	0.466
0.367	7	0.86	0.125
0.360	18	2.47	0.137
0.322	30	2.34	0.0698

[a] [AIBN] = 2.64 × 10^{-3} mol/L; solvent, DMF; temperature, 55 °C.

Kinetic Study. Solution polymerizations of α-MVL were performed in DMF at temperatures from 40 to 70 °C. Time–conversion curves, shown in Figure 4, were linear without an induction period. However, the rates of polymerization, R_p, did not increase above 65 °C. The dependence of R_p on the concentration of monomer and initiator was investigated at 55 °C. Table I shows the relationship between R_p and initiator concentration. A plot of log R_p vs. log [AIBN], shown in Figure 5, is a straight line with a slope of 0.44. The rather low value of the initiator concentration dependence (0.44) is probably not due to primary radical termination. α-MVL is a conjugated monomer with a large Q value ($Q > 2$). Also the homopolymer viscosities were not low. All of this indicates that the probability of primary radical termination is low.

Table II summarizes the relationship between R_p and monomer concentration in the polymerization at 55 °C. A plot of log R_p vs. log [α-MVL] (Figure 6) is not a straight line. Figure 7 shows an Arrhenius plot of R_p vs. $1/T$, which deviates greatly from linearity above 65 °C.

These results strongly suggested that the decrease of rate at higher temperatures may be caused by the depolymerization. Recently, Yamada et al.[10] and Yuki et al.[11] separately proposed a procedure for determining the ceiling temperature T_c in radical polymerization by extrapolation of $k_p/k_t^{1/2}$ vs. $1/T$ and DSC. The value of T_c may be estimated from plots of R_p vs. T (Figure 8). Extrapolation to zero rate gives T_c = 81 °C. Another method is to plot the equilibrium monomer concentration, $[M]_e$, vs. $1/T$,

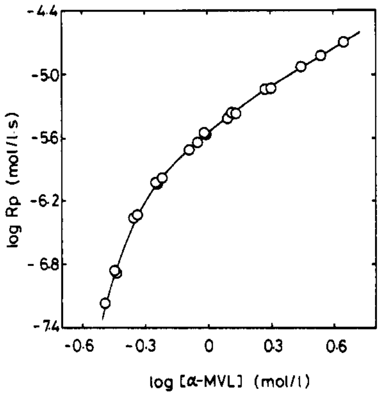


Figure 6. Plot of log R_p vs. log [α-MVL] for homopolymerization of α-MVL in DMF at 55 °C. [AIBN] = 2.64×10^{-3} mol/L.

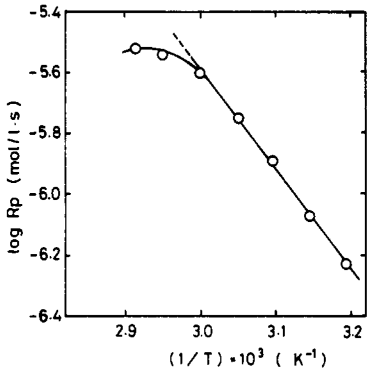


Figure 7. Plot of log R_p vs. $1/T$ for polymerization of α-MVL.

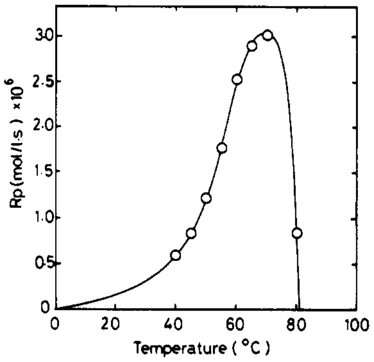


Figure 8. Plot of R_p vs. temperature for polymerization of α-MVL.

Table III
Equilibrium Concentration of α-MVL Monomer

temp, °C	$1/T \times 10^3$, K^{-1}	[α-MVL],[a] mol/L	ln [α-MVL], mol/L
55	3.05	0.324	−1.13
70	2.91	0.631	−0.460
80	2.83	0.899	−0.106

[a] $[\alpha\text{-MVL}]_e$ = equilibrium monomer concentration.

according to eq 2,[12] where ΔH_p and $\Delta S°_p$ are the entropy

$$\ln [M]_e = \Delta H_p/RT_c - \Delta S°_p/R \qquad (2)$$

and enthalpy changes per monomer unit. When the polymer chains are long, these quantities are identical with the heat and entropy changes of polymerization. The values of $[M]_e$ at various temperatures were determined by the following method. The equilibrium concentrations of monomer, $[M]_e$, at 55, 70, and 80 °C were estimated by the extrapolation of the R_p vs. [α-MVL] plots at these temperatures to $R_p = 0$ (Figure 9). The $[M]_e$ values for α-MVL at 55, 70, and 80 °C are summarized in Table III.

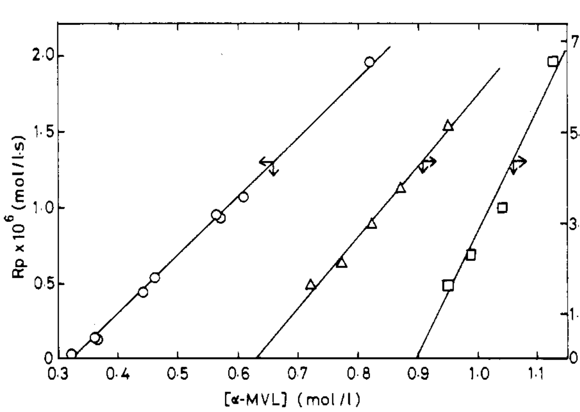


Figure 9. Plot of R_p vs. [α-MVL] for polymerization of α-MVL. [AIBN] = 2.64×10^{-3} mol/L; solvent, DMF; 10^{-3} mol/L; temperature, 55 (○), 70 (△), and 80 °C (□).

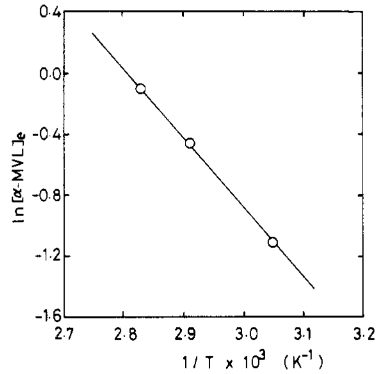


Figure 10. Plot of ln $[\alpha\text{-MVL}]_e$ vs. $1/T$ for polymerization of α-MVL.

Table IV
Ceiling Temperature

monomer	[M], mol/L	T_c, °C	ref
α-MVL	0.891	80.5	
	1.00	83	
MMA	1.00	160	14
α-MeSt[a]	1.00	7.5	15

[a] α-MeSt = α-methylstyrene.

Table V
Relationship between log R_p and log ([α-MVL] − $[M]_e$)

[α-MVL], mol/L	[α-MVL] − $[M]_e$, mol/L	log R_p, mol/(L·s)	log ([α-MVL] − $[M]_e$), mol/L
4.48	4.16	−4.65	0.619
3.47	3.15	−4.82	0.498
2.78	2.46	−4.93	0.390
1.99	1.67	−5.13	0.222
1.86	1.54	−5.14	0.186
1.36	1.04	−5.38	0.0154
1.28	0.956	−5.36	−0.0195
1.24	0.916	−5.42	−0.0381
0.956	0.632	−5.55	−0.199
0.982	0.658	−5.56	−0.182
0.898	0.574	−5.64	−0.241
0.815	0.491	−5.71	−0.309
0.605	0.281	−5.98	−0.551
0.562	0.238	−6.02	−0.623
0.569	0.245	−6.04	−0.611
0.439	0.115	−6.36	−0.939
0.458	0.134	−6.33	−0.873
0.367	0.043	−6.90	−1.37
0.360	0.036	−6.86	−1.44

[a] $[M]_e$ = equilibrium concentration of α-MVL at 55 °C.

Figure 10 shows that a linear relationship exists for ln $[M]_e$ vs. $1/T$ as was expected from eq 2. From this plot, T_c is determined to be 80.5 °C with an initial monomer

Table VI
Relationship between log k and Polymerization Temperature[a]

temp, °C	$1/T \times 10^3$, K^{-1}	$R_p \times 10^6$, mol/(L·s)	ln $[M]_e$, mol/L	$[M]_e$, mol/L	[α-MVL] − $[M]_e$, mol/L	$k \times 10^5$	log k
40	3.19	0.587	−1.80	0.165	0.721	1.19	−4.92
45	3.14	0.841	−1.56	0.210	0.681	1.83	−4.74
50	3.09	1.28	−1.38	0.252	0.639	2.99	−4.52
55	3.05	1.77	−1.14	0.320	0.571	4.68	−4.33
60	3.00	2.46	−0.910	0.403	0.488	7.74	−4.11
65	2.96	2.91	−0.720	0.487	0.404	11.3	−3.95
70	2.91	3.02	−0.540	0.583	0.308	15.7	−3.80

[a] [α-MVL] = 0.891 mol/L; [AIBN] = 2.37×10^{-3} mol/L; solvent, DMF; $R_p = k[\mathrm{AIBN}]^{0.44}([\alpha\text{-MVL}] - [\alpha\text{-MVL}]_e)^{1.1}$.

Table VII
Thermodynamic Constants for Polymerization of Selected Monomers

monomer	ΔH_p, kJ/mol	$\Delta S°_p$, J/(K·mol)	ref
α-MVL	−38.8	−108.8	
MMA	−54.4	−101.7	16–18
EMA[a]	−59.4, −57.7		19
MA[b]	−77.7, −84.5		19
St	−69.8	−105.4	20, 21
α-MeSt[c]	−35.1	−103.8	22, 23

[a] EMA = ethyl methacrylate. [b] MA = methyl acrylate. [c] α-MeSt = α-methylstyrene.

concentration of 0.891 mol/L. This T_c is in good agreement with the value of 81 °C obtained for this term from the plots of R_p vs. T (Figure 8). The ceiling temperatures for α-MVL, MMA, and α-methylstyrene are compared in Table IV.

From the above results, it is obvious that one would have to take into account the depolymerization step to determine the rate equation. Radical polymerization mechanisms involving depolymerization can be summarized as follows:

Initiation

$$\mathrm{I} \xrightarrow{k_d} 2\mathrm{I}\cdot$$

$$-\mathrm{d}[\mathrm{I}]/\mathrm{d}t = k_d[\mathrm{I}] \qquad (3)$$

$$\mathrm{I}^0 + \mathrm{M} \xrightarrow{k_i} \mathrm{M}\cdot$$

$$-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k_i[\mathrm{I}][\mathrm{M}] = 2fk_d[\mathrm{I}] \qquad (4)$$

Propagation

$$\mathrm{M}^0 + \mathrm{M} \underset{k_{-p}}{\overset{k_p}{\rightleftharpoons}} \mathrm{M}\cdot$$

$$-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k_p[\mathrm{M}\cdot][\mathrm{M}] - k_{-p}[\mathrm{M}\cdot] \qquad (5)$$

Termination

$$2\mathrm{M}\cdot \xrightarrow{k_{tc}} \mathrm{P}$$

$$2\mathrm{M}\cdot \xrightarrow{k_{td}} 2\mathrm{P}$$

$$-\mathrm{d}[\mathrm{M}\cdot]/\mathrm{d}t = k_t[\mathrm{M}\cdot]^2 \qquad (6)$$

where $k_t = k_{tc} + k_{td}$. At equilibrium, the rates for the propagation reaction and the depolymerization reaction are equal; i.e., $-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = 0$ or

$$k_p[\mathrm{M}]_e = k_{-p} \qquad (7)$$

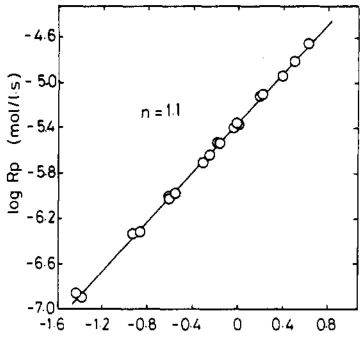


Figure 11. Plot of log R_p vs. log ([α-MVL] − $[\alpha\text{-MVL}]_e$) for polymerization of α-MVL. [AIBN] = 2.64×10^{-3} mol/L; solvent, DMF; temperature, 55 °C.

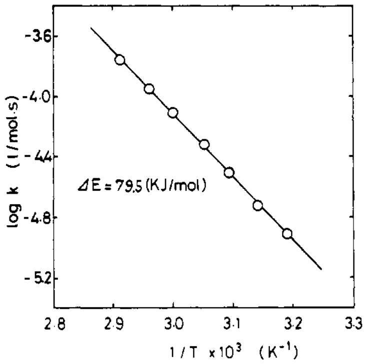


Figure 12. Plot of log k vs. $1/T$ for polymerization of α-MVL.

Then substituting (7) into (5)

$$-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k_p[\mathrm{M}]([\mathrm{M}] - [\mathrm{M}]_e) \qquad (8)$$

Assuming the steady-state condition, $2fk_d[\mathrm{I}] = k_t[\mathrm{M}\cdot]^2$; hence

$$[\mathrm{M}\cdot] = (2fk_d[\mathrm{I}]/k_t)^{1/2} \qquad (9)$$

Combining eq 8 and 9 gives the overall rate of polymerization.[13]

$$R_p = k_p(2fk_d/k_t)^{1/2}([\mathrm{M}] - [\mathrm{M}]_e) \qquad (10)$$

According to the linear relationship of ln $[\mathrm{M}]_e$ vs. $1/T$, $[\mathrm{M}]_e$ at 55 °C was calculated to be 0.324 mol/L. Table V summarizes the relationship between log R_p and log ([M] − $[\mathrm{M}]_e$). A plot of log R_p vs. log ([M] − $[\mathrm{M}]_e$) has a slope of 1.1 (Figure 11). The rate equation may be given, therefore, as

$$R_p = k[\mathrm{AIBN}]^{0.44}([\mathrm{M}] - [\mathrm{M}]_e)^{1.1} \qquad (11)$$

where k is an overall rate constant. Equation 11 is close to that expected for the normal vinyl free-radical polymerization mechanism.

The Arrhenius plot was reevaluated considering the

Table VIII
Kinetic Constants for α-MVL, α-MBL, and MMA[a]

monomer	E_a, kJ/mol	$A \times 10^{-9}$	$k \times 10^4$	$\Delta G^{\ddagger}$, kJ/mol	$\Delta H^{\ddagger}$, kJ/mol	$\Delta S^{\ddagger}$, J/(K·mol)	$\Delta S^{\ddagger}$,[b] J/(K·mol)
α-MVL[c]	79.5	0.200	0.774	107.9	76.6	94.1	85.4
α-MBL[d]	76.1	0.871	9.74	100.8	73.2	82.8	74.1
MMA[e]	83.2	3.7	3.25	104.2	80.3	71.5	62.8

[a] Temperature, 60 °C. [b] $\Delta H = E_a$. [c] $R_p = k[\text{AIBN}]^{0.44}[\alpha\text{-MVL}]^{1.1}$. [d] $R_p = k[\text{AIBN}]^{0.54}[\alpha\text{-MBL}]^{1.1}$. [e] $R_p = k[\text{AIBN}]^{0.5}[\text{MMA}]$.

equilibrium monomer concentration at each temperature. The relationship between log k, calculated from eq 11, and $1/T$ is summarized in Table VI. Figure 12 shows an Arrhenius plot of log k vs. $1/T$. From the slope, the overall activation energy and the frequency factor were calculated to be 79.5 kJ/mol and 2.00×10^8, respectively.

The heat of polymerization obtained from eq 2 (Figure 10) is $\Delta H_p = -38.8$ kJ/mol, and the corresponding value of the entropy is $\Delta S°_p = -108.8$ J/(K·mol). The thermodynamic constants in the polymerization of α-MVL are indicated in Table VII, together with those of the other monomers.

It is well-known that the entropy of polymerization for a wide variety of vinyl monomers is within the limits of 105–126 J/(K·mol) and little affected by the steric hindrance in the polymer.[9] Indeed, $\Delta S°_p$ of α-MVL is comparable to that of MMA. Therefore the much lower T_c of α-MVL vs. that of MMA may result from the low ΔH_p of α-MVL. Variations in the heats of polymerization arise from bond energy differences, the delocalization energy, and the strain energy differences between monomers and polymers. In most cases, steric hindrance is the main reason for the low heats of polymerization of the α,α-disubstituted ethylenes since steric crowding of the α groups is greater in the polymers than in the monomers. The low ΔH_p for the formation of poly(α-MVL) may result from the sterically hindered nonplanar lactone ring situated perpendicular to the plane of the backbone. This side-group steric hindrance serves to make ΔH_p more positive.

The activation free energy, $\Delta G^{\ddagger}$, activation enthalpy, $\Delta H^{\ddagger}$, and activation entropy, $\Delta S^{\ddagger}$, were calculated according to transition-state theory. The results are shown in Table VIII, where α-MBL and MMA are compared to α-MVL. The polymerization behavior of α-MVL, having a bulky nonplanar lactone ring, is characterized by a low frequency factor and a large negative activation entropy compared to those values for MMA and α-MBL.

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