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Kinetics, Thermodynamics, and Monomer Reactivities in Radical Polymerization of α-Acetoxystyrene

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ABSTRACT: The radical polymerization behavior of α-acetoxystyrene (ACOST) was investigated in toluene, using α,α′-azobis(isobutyronitrile) (AIBN) as the initiator. The polymerization of ACOST is an equilibrium process with a ceiling temperature (T_c) of 47 °C at 1 mol/L of monomer due to the steric hindrance. The rate of polymerization (R_p) can be expressed by $R_p = k[\mathrm{AIBN}]^{0.45}([\mathrm{M}] - [\mathrm{M}]_e)^{1.0}$, considering the depolymerization process with an equilibrium monomer concentration of $[\mathrm{M}]_e$. The overall activation energy has been determined to be 116 kJ/mol. The enthalpy of polymerization and entropy of polymerization obtained from a linear relationship between ln $[\mathrm{M}]_e$ and $1/T$ are −26.5 kJ/mol and −82.6 J/(K·mol), respectively. The T_c is low because of the low ΔH_p but high enough to allow radical homopolymerization owing to the low ΔS_p, which is significantly lower than the typical values (−100 to −125 J/(K·mol)) for vinyl monomers. Monomer reactivity ratios of bulk copolymerization of ACOST (M_2) with methyl methacrylate (MMA, M_1) are $r_1 = 0.644$ and $r_2 = 0.754$, respectively, at 60 °C. The temperature dependence (50–80 °C) of the reactivity ratios has revealed that the copolymerization mechanism can be adequately described by the Mayo–Lewis model; a depolymerization process does not have to be taken into consideration in copolymerization. Q and e values of ACOST can be calculated as 0.82 and −0.45 from the reactivity ratios. Although the values seem to be reasonable, the serious steric effect makes their meaning obscure.

Introduction

Many publications are available on the polymerization behavior of α-substituted acrylates and related monomers. However, α-substituted styrene derivatives except for α-methylstyrene (MST) have attracted little attention presumably due to their low radical polymerizability. As a part of our research program on the structure–reactivity relationships of vinyl monomers, we have recently initiated investigations of the polymerization behavior of α-substituted styrenes.

We studied the radical reactivity of α-(trifluoromethyl)styrene (TFMST)[1] and determined the Alfrey–Price Q–e values for this monomer by combining the copolymerization analysis with the "mercury method".[2] This investigation has revealed that TFMST does not undergo radical homopolymerization even in bulk presumably due to the steric hindrance and that TFMST has a smaller Q (0.43) and a higher e (0.90) than styrene (ST). In spite of its low electron density on the β-carbon due to the strong electron-withdrawing effect of the CF_3 group, TFMST fails to undergo anionic polymerization primarily because of the S_N2' side reaction.[3]

We have next focused our attention on α-acetoxystyrene (ACOST). Marvel and Moon reported unsuccessful attempts of its polymerization in 1940.[4] Radical copolymerization of ACOST with acrylonitrile was reported by Chapin et al. in 1949.[5] Haas et al.[6] briefly discussed the radical polymerization of ACOST without providing any details. Monthéard and co-workers studied radical homo- and copolymerization of ACOST and its para-substituted derivatives.[7–11] Although they reported the monomer reactivity ratios of these monomers[9] as well as NMR spectra[9,11] and thermal/dielectric properties[7–9,11] of the polymers, detailed kinetic and thermodynamic data of the polymerization are not available. Thus, ACOST undergoes radical homopolymerization, while isomeric methyl α-phenylacrylate (α-carbomethoxystyrene) is very reluctant to homopolymerize by radical initiation.[12,13]

In this paper is reported the radical polymerization behavior of ACOST in detail. We are also interested in the thermal and acid-catalyzed conversion of poly(α-acetoxystyrene) (PACOST) to poly(phenylacetylene), which is reported elsewhere.[14]

Experimental Section

Materials. α,α′-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. Toluene was successively washed with concentrated sulfuric acid, diluted sodium hydroxide, and distilled water, dried over calcium chloride, and then distilled. Methyl methacrylate (MMA) was purified by the conventional method. The other reagents were used without further purification.

Preparation of α-Acetoxystyrene. Although Marvel and Moon prepared the monomer by reacting styrene bromohydrin with acetyl chloride followed by dehydrobromination,[4] we adopted the procedure of Noyce and Pollack,[15] which involves the reaction of acetophenone with isopropenyl acetate in the presence of acid. ACOST was obtained in 34% yield after redistillation: bp 120–122 °C/20 mmHg (lit.[16] bp 120–122 °C/20 mmHg); IR (NaCl) 1760 (C=O), 1640 cm^{-1} (C=C); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.5 (m, 2 H, aromatic H3), 7.4 (m, 3 H, aromatic H2 and H4), 5.52 (d, 1 H, β-CH cis to phenyl, J = 2.1 Hz), 5.07 (d, 1 H, β-CH trans to phenyl, J = 2.1 Hz), 2.27 (s, 3 H, CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 168.73 (C=O), 152.71 (α-C), 134.03 (C1), 128.56 (C4), 128.25 (C2), 124.60 (C3), 101.81 (β-CH_2), 20.58 (CH_3).

Bulk Radical Polymerization. ACOST (2.0 g, 12 mmol) and AIBN (4 mg, 0.024 mmol) were placed in a polymerization ampule and degassed by repeated freeze–thaw cycles. The ampule was sealed under vacuum. After 16 days of heating at 65 °C, the resulting colorless solid was dissolved in acetone, which was then poured into stirred methanol. The polymer was purified by repeated precipitation from acetone into methanol, filtered, and dried in vacuo at 60 °C for 48 h to give 50% yield (M_n = 25 000 and M_w = 59 000 (by GPC)): IR (film) 1740 cm^{-1} (C=O);

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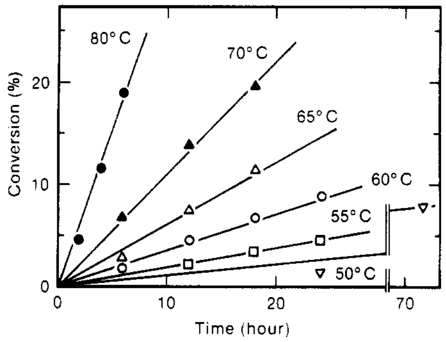

Figure 1. Time–conversion curves for polymerization of ACOST in toluene at various temperatures. [ACOST] = 5.69 mol/L; [AIBN] = 6.09 × 10^{-2} mol/L.

^{1}H NMR (250 MHz, $CDCl_3$) δ 7.6–5.7 (phenyl), 4.0–2.0 (β-CH_2), 2.0–0 (CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 170.0 (C=O), 140.6 (C1), 126.2 (C2, C3, C4), 85.5 (α-C), 44.6 (β-CH_2), 22.0 (CH_3). Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21. Found: C, 73.10; H, 6.28.

Kinetic and Thermodynamic Studies. Weighed amounts of ACOST, AIBN, and toluene were placed in polymerization ampules and degassed by repeating freeze–thaw cycles three times. The ampules sealed under vacuum were placed in a constant-temperature bath for a specified period of time. The ampules were then removed from the bath, and the polymer was precipitated into excess hexanes, filtered, dried in vacuo at 60 °C for 48 h, and weighed.

Copolymerization of ACOST with MMA. ACOST was copolymerized in bulk with MMA with 1.0 mol % of AIBN as the initiator at temperatures ranging from 50 to 80 °C in a fashion similar to those described for homopolymerization. All the copolymerizations were terminated at low conversions (<13%) and copolymer compositions determined by ^{1}H NMR.

Measurements. NMR spectra were recorded in deuteriochloroform ($CDCl_3$) on a Hitachi R-24B (60 MHz) or an IBM NR-250/AF (250 MHz) spectrometer. IR spectra were obtained with a JASCO IRA-1 spectrometer. Molecular weight determination was made by gel permeation chromatography (GPC) using a Waters Model 150 chromatograph equipped with 6 μStyragel columns at 30 °C in tetrahydrofuran (THF).

Results and Discussion

As reported by Monthéard et al.,[7] ACOST undergoes radical homopolymerization in bulk, which is in contrast with MST, α-methoxystyrene,[17] and methyl α-phenylacrylate.[12,13] While MST polymerizes by cationic or anionic initiation and methyl α-phenylacrylate by an anionic mechanism, α-methoxystyrene fails to provide polymer by either ionic or radical initiation. However, the polymerization of ACOST is slow, providing only ca. 50% conversion in more than 2 weeks, which is presumably due to the steric hindrance. The β-carbon of ACOST resonates at a significantly higher field (101.8 ppm) than that of ST (112.5 ppm) or MST (111.5 ppm), suggesting that ACOST is an electron-rich monomer, which may also contribute to its low radical polymerizability. Although methyl α-phenylacrylate is fairly electron-deficient, exhibiting its β-carbon resonance at ca. 2 ppm lower field than MMA,[13] the steric crowding of the carbomethoxy group appears to be more serious than that of the acetoxy group in radical homopolymerization. The lack of homopolymerizability in the case of α-methoxystyrene may be attributed to its high electron density ($e = -1.2$[17]) and the excess steric hindrance.

PACOST obtained by radical initiation is syndiotactic-rich.[14] Its conversion to poly(phenylacetylene) is reported in detail elsewhere.[14]

Kinetics of Polymerization. Time–conversion relationships are shown in Figure 1 for polymerization of ACOST in toluene initiated with AIBN (1.1 mol %) at temperatures ranging from 50 to 80 °C. The plots are all linear without exhibiting any induction period and allow calculation of the rate of polymerization (R_p) from the slope. The results are summarized in Table I. The dependence of R_p on the initiator concentration was investigated at 60 °C, which is presented in Table II. A plot of log R_p vs. log [AIBN], shown in Figure 2, is a straight line with a slope of 0.45. Table III summarizes the relationships between R_p and the monomer concentration in solution polymerization at various temperatures. Plots of log R_p against log [ACOST] deviate from linearity espe-

Table I
Relationship between Conversion and Polymerization Time[a]

temp, °C	polymn time, h	yield, %	$R_p \times 10^6$, mol/(L·s)
50	12	0.5	
50	18	0.9	
50	24	1.3	
50	72	7.9	1.73
55	12	2.2	
55	18	3.4	
55	24	4.5	3.03
60	6	1.8	
60	12	4.5	
60	18	6.7	
60	24	8.9	6.19
65	6	3.0	
65	12	7.5	
65	18	11.6	11.3
70	6	6.8	
70	12	13.9	
70	18	19.8	
70	24	26.6	17.2
80	2	4.5	
80	4	11.6	
80	6	18.9	
80	12	34.4	46.6

[a] [AIBN] = 6.09 × 10^{-3} mol/L; [ACOST] = 5.69 mol/L; solvent, toluene.

Table II
Relationship between R_p and Initiator Concentration[a]

[AIBN] × 10^3, mol/L	yield, %	$R_p \times 10^6$, mol/(L·s)
7.31	3.1	2.23
16.4	4.3	3.10
29.2	5.9	4.25
62.1	8.0	5.76
121.2	10.0	7.20

[a] [ACOST] = 6.22 mol/L; solvent, toluene; polymerization time, 24 h; temperature, 60 °C.

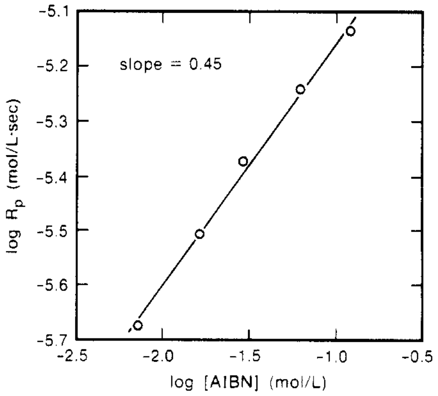

Figure 2. Plot of log R_p vs log [AIBN] for homopolymerization of ACOST in toluene at 60 °C. [ACOST] = 6.22 mol/L.

Table III
Relationship between R_p and Monomer Concentration[a]

temp, °C	[ACOST], mol/L	polymn time, h	yield, %	$R_p \times 10^6$, mol/(L·s)
50	6.26	50	5.7	1.98
50	5.69	72	7.9	1.73
50	3.13	72	6.3	0.761
50	2.50	72	5.7	0.550
50	2.09	72	4.4	0.355
60	5.69	24	8.8	5.80
60	5.22	24	9.1	5.50
60	5.22	24	8.9	5.38
60	4.81	24	8.7	4.84
60	4.17	24	7.9	3.81
60	3.48	24	7.3	2.94
60	3.22	24	6.6	2.46
60	2.50	24	4.8	1.39
60	2.09	24	3.9	0.943
70	4.81	9	8.9	13.2
70	3.22	9	7.0	6.96
70	2.72	10	5.4	4.08
70	2.50	10	4.6	3.19
80	5.69	3	8.8	46.4
80	4.81	3	7.4	33.0
80	4.17	3	6.1	23.6
80	3.13	3	2.4	6.96
80	2.85	3	1.4	3.69

[a] [AIBN] = 6.09 × 10^{-2} mol/L; solvent, toluene.

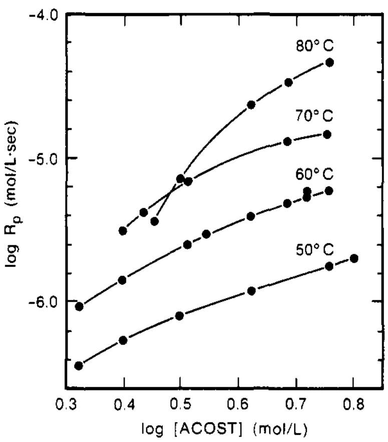

Figure 3. Plots of log R_p vs log [ACOST] for homopolymerization of ACOST in toluene at 50, 60, 70, and 80 °C. [AIBN] = 6.09 × 10^{-2} mol/L.

cially at higher temperatures, as Figure 3 indicates. The deviation is apparently due to a depropagation process that competes with the propagation reaction.

Since the radical polymerization of ACOST in solution appears to be an equilibrium process, equilibrium monomer concentrations ($[M]_e$) have been estimated by extrapolating the plots of R_p vs [ACOST] to $R_p = 0$ as demonstrated in Figure 4 and are summarized in Table IV. The equilibrium ACOST concentration ranges from 1.1 mol/L at 50 °C to 2.6 mol/L at 80 °C.

The overall rate of polymerization involving depropagation can be expressed as follows:[18]

$$R_p = k_p(fk_d/k_t)^{0.5}[I]^{0.5}([M] - [M]_e)$$

where k_p, f, k_d, and k_t are the propagation rate constant, the initiator efficiency, the rate constant of initiator (I) decomposition, and the termination rate constant, respectively. Table V summarizes relationships between log R_p and log ($[M] - [M]_e$), which give straight lines as shown in Figure 5 with slopes of 1.0, 0.97, 0.98, and 1.0 at 50, 60, 70, and 80 °C, respectively. The rate equation may be given, therefore, as

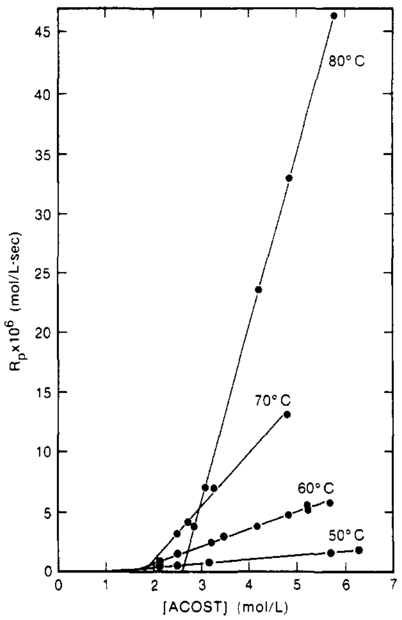

Figure 4. Plots of R_p vs [ACOST] for polymerization of ACOST in toluene at 50, 60, 70, and 80 °C. [AIBN] = 6.09 × 10^{-2} mol/L.

Table IV
Equilibrium Concentration of ACOST Monomer

temp, °C	$1/T \times 10^3$, K^{-1}	$[ACOST]_e$,[a] mol/L	ln $[ACOST]_e$, mol/L
50	3.10	1.1	0.095
60	3.00	1.5	0.405
70	2.92	1.8	0.588
80	2.83	2.6	0.955

[a] $[ACOST]_e$ = equilibrium monomer concentration.

$$R_p(50\ °C) = k[AIBN]^{0.45}([M] - [M]_e)^{1.0}$$

$$R_p(60\ °C) = k[AIBN]^{0.45}([M] - [M]_e)^{0.97}$$

$$R_p(70\ °C) = k[AIBN]^{0.45}([M] - [M]_e)^{0.98}$$

$$R_p(80\ °C) = k[AIBN]^{0.45}([M] - [M]_e)^{1.0}$$

These equations are close to that expected for the normal radical polymerization of vinyl monomers involving depolymerization.

The Arrhenius plot was evaluated by considering the equilibrium monomer concentration at each temperature. The temperature dependence of log k, calculated rom the above equations, is summarized in Table VI, and the Arrhenius plot is presented in Figure 6. The overall activation energy ΔE_a can be obtained from the slope to be 116 kJ/mol. This value is larger than that for ST (100 kJ/mol[19]).

Thermodynamics of Polymerization. The thermodynamic characteristics of polymerization are important in understanding the effect of the monomer structure on its polymerization behavior. The relationship between the equilibrium monomer concentration $[M]_e$ and the ceiling temperature T_c is expressed by the equation

$$\ln [M]_e = \frac{\Delta H_p}{RT_c} - \frac{\Delta S_p}{R}$$

where ΔH_p and ΔS_p are the enthalpy and entropy changes per monomer unit. Figure 7 indicates that the plot of ln $[M]_e$ against $1/T$ is in fact linear, from which T_c is determined to be 47 °C at an initial monomer concentration

Table V
Relationship between log R_p and log ([ACOST] - $[M]_e$)[a]

temp, °C	[ACOST], mol/L	[ACOST] - $[M]_e$, mol/L	log R_p, mol/(L·s)	log ([ACOST] - $[M]_e$), mol/L
50	6.26	5.16	-5.70	0.713
50	5.69	4.59	-5.76	0.662
50	3.13	2.03	-6.12	0.307
50	2.50	1.40	-6.26	0.146
50	2.09	0.99	-6.45	-0.004
60	5.69	4.19	-5.24	0.622
60	5.22	3.72	-5.27	0.571
60	5.22	3.72	-5.26	0.571
60	4.81	3.31	-5.32	0.520
60	4.17	2.67	-5.42	0.427
60	3.48	1.98	-5.53	0.297
60	3.22	1.72	-5.61	0.236
60	2.50	1.00	-5.86	0.000
60	2.09	0.59	-6.03	-0.229
70	4.81	3.01	-4.88	0.479
70	3.22	1.42	-5.16	0.152
70	2.72	0.92	-5.39	-0.036
70	2.50	0.70	-5.50	-0.155
80	5.69	3.09	-4.33	0.490
80	4.81	2.21	-4.48	0.344
80	4.17	1.57	-4.63	0.196
80	3.13	0.53	-5.16	-0.276
80	2.85	0.25	-5.43	-0.602

[a] $[M]_e$ = equilibrium monomer concentration of ACOST.

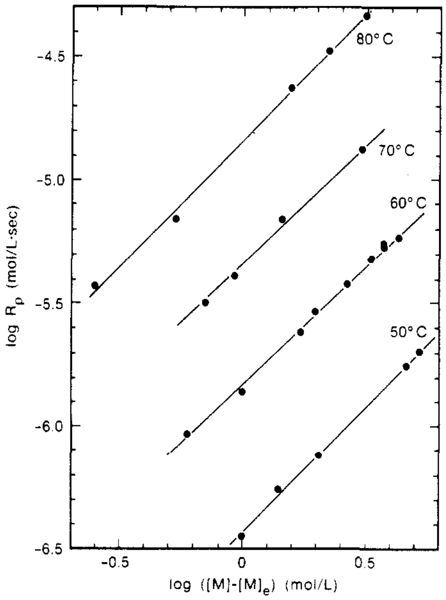

Figure 5. Plots of log R_p vs log ([M] - $[M]_e$) for polymerization of ACOST in toluene at 50, 60, 70, and 80 °C. [AIBN] = 6.09 × 10^{-2} mol/L.

of 1.0 mol/L. The heat of polymerization obtained from the slope is ΔH_p = -26.5 kJ/mol, and the corresponding value of the entropy obtained from the intercept is ΔS_p = -82.6 J/(K·mol). The thermodynamic constants of the radical polymerization of ACOST are indicated in Table VII together with those of selected vinyl monomers.

It is well-known that the entropy of polymerization for a wide variety of vinyl monomers is within the limit of -100 to -125 J/(K·mol) and little affected by the steric hindrance in the polymer, whereas the heat of polymerization varies over a wide range for different monomers. The ΔS_p value of ACOST (-82.6 J/(K·mol)) is significantly smaller than those of typical vinyl monomers such as MMA, ST, and MST. Therefore, the much lower T_c of ACOST than that of ST results from the profoundly reduced ΔH_p of ACOST (less than half of that of ST). ACOST has a higher T_c than MST in anionic polymerization (47 vs 7.7 °C[28]) although they have similar ΔH_p values (-26.5 vs -29.1 kJ/mol[28]), which is due to the much smaller ΔS_p of ACOST (-82.6 vs -103.8 J/(K·mol[28])). α-Methylene-δ-valerolactone (MVL), a cyclic analogue of MMA, has a low T_c of 83 °C due to its low ΔH_p (-38.8 kJ/mol), while its ΔS_p (-108.8 J/(K·mol)) is within the range of typical vinyl monomers.[18] Variations in the heat of polymerization arise from differences in bond, delocalization, and strain energies between monomer and polymer. In most cases, steric hindrance is the main reason for the low ΔH_p of α,α-disubstituted ethylenes since steric crowding of the α-substituents is greater in the polymer than in the monomer. The low ΔH_p for formation of PACOST apparently results from the sterically hindered phenyl and α-acetoxy groups. However, ACOST undergoes radical homopolymerization in contrast to MST owing to its higher T_c, which, in turn, arises from its lower ΔS_p. The situation is a little different from that of certain substituted quinodimethanes,[29] which have a low ΔH_p (-22 to -26 kJ/mol) and an extremely low ΔS_p (-37 to -38 J/(K·mol)), giving rise to a high T_c (301-442 °C at 1 mol/L). However, radical polymerization of these quinodimethanes is affected by depropagation due to their low solubility in polymerization solvents.

Copolymerization of ACOST with MMA. To study the reactivity of ACOST, we carried out copolymerizations of ACOST with MMA in bulk at 60 °C with 1 mol % of AIBN. The results are given in Table VIII. All copolymerizations were terminated at low conversions (<13%) to allow use of the differential form of the Mayo-Lewis equation, and the copolymer compositions were determined by ^{1}H NMR. Monomer-copolymer composition curves are shown in Figure 8. Monomer reactivity ratios (r_1 and r_2) were obtained by a nonlinear least-squares fitting program that employed a modified Marquardt method.[30] With ACOST defined as M_2, the ratios were determined as r_1 = 0.644 and r_2 = 0.754 at 60 °C. Thus, the cross-propagation reactions are faster than the self-propagation reactions because ACOST and MMA are electron-rich and electron-deficient, respectively. The Alfrey-Price Q-e values of ACOST, calculated from the reactivity ratios, are 0.82 and -0.45, respectively, indicating that the PACOST radical is resonance stabilized and that ACOST is electron-rich. The Q and e values calculated from the reactivity ratios reported by Monthéard et al.[9] for copolymerization of ACOST with ST and para-substituted styrenes range from 0.72 to 0.95 and from -0.63 to -0.78, respectively. These values appear to be reasonable, at least qualitatively. However, their meaning is obscure as will be discussed in the following section.

It is known that β-carbon (and proton) chemical shifts of vinyl monomers reflect electron densities on the double bonds and therefore e values of the monomers. For example, Herman and Teyssié[31] have derived two equations to calculate e values from β-carbon chemical shifts for vinylic and styrenic monomers. If ACOST is treated as a styrene derivative, the calculation gives an e value of -3.9 based on the β-carbon chemical shift (101.8 ppm). However, if one considers ACOST to be a substituted vinyl acetate, an e parameter (-0.53) much closer to our experimental value is obtained from the chemical shift.

In general, the simple Mayo-Lewis equation[32] cannot be applied to copolymerization carried out at a temperature that is close to T_c of one of the comonomers because of the depropagation process. The ceiling temperature of ACOST is 47 °C at 1 mol/L, which is very close to

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	[ACOST] − $[M]_e$, mol/L	$k \times 10^6$	ln *k*
50	3.10	1.73	0.086	1.09	4.60	1.33	-13.5
55	3.05	3.03	0.239	1.27	4.42	2.41	-12.9
60	3.00	6.19	0.385	1.47	4.22	5.16	-12.2
65	2.96	11.3	0.525	1.69	4.00	9.97	-11.5
70	2.92	17.2	0.663	1.94	3.75	16.2	-11.0
80	2.83	46.6	0.924	2.52	3.17	51.8	-9.87

[a] $[ACOST]_e$ = 5.69 mol/L; [AIBN] = 6.09 × 10^{-2} mol/L; solvent, toluene; $R_p = k[AIBN]^{0.45}([ACOST] - [ACOST]_e)^{1.0}$.

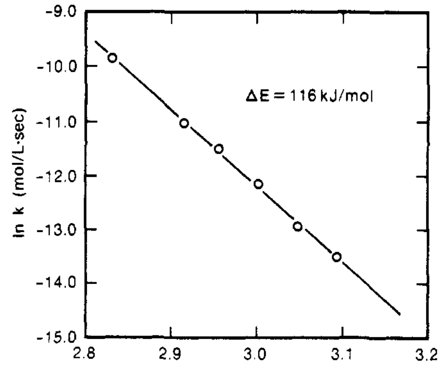

Figure 6. Arrhenius plot of log *k* vs $1/T$ for polymerization of ACOST.

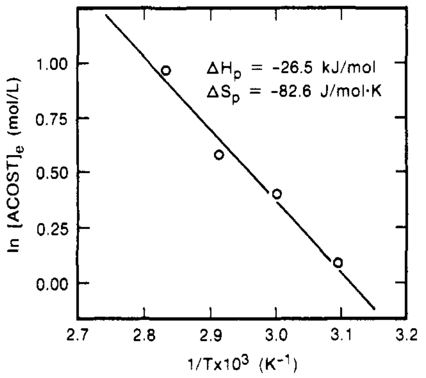

Figure 7. Plot of log $[ACOST]_e$ vs $1/T$ for polymerization of ACOST in toluene.

Table VII
Thermodynamic Constants for Polymerization of Selected Monomers

monomer	T_c,[a] °C	ΔH_p, kJ/mol	ΔS_p, J/(K·mol)	ref
ACOST	47	-26.5	-82.6	this work
MMA	160	-55.6	-117	20–23
EMA[b]		-59.4		22
MA[c]		-78.6		22
ST		-69.8	-105.4	24, 25
MST	7.7	-29.1, -35.1	-103.8, -110	26–28
MVL	83	-38.8	-108.8	18
quinodimethanes	301–442	-22 to -26	-37 to -38	29

[a] 1 mol/L. [b] EMA = ethyl methacrylate. [c] MA = methyl acrylate.

Table VIII
Copolymerization of ACOST with MMA[a]

feed				mol % of ACOST	
[MMA] × 10^3, mol	[ACOST] × 10^3, mol	polymn time, h	yield, %	in feed	in copolym
		At 50 °C			
1.55	6.19	67.5	8.6	80.0	76.0
2.65	6.19	39.3	5.0	70.0	68.3
4.13	6.19	26	3.0	60.0	61.1
6.19	6.19	24.8	3.0	50.0	54.0
9.39	6.26	24	3.0	40.0	43.0
9.39	4.02	24	3.8	30.0	37.3
9.39	2.35	15.5	1.1	20.0	22.9
9.39	1.04	12	3.5	10.0	15.5
		At 60 °C			
1.55	6.19	8	5.4	80.0	76.7
2.65	6.19	12	6.3	70.0	68.6
4.13	6.19	12	5.4	60.0	60.0
6.19	6.19	6	1.9	50.0	52.4
9.39	6.26	13	4.0	40.0	42.0
9.39	4.02	13	4.2	30.0	37.2
9.39	2.35	18	7.0	20.0	23.0
9.39	1.04	20	7.8	10.0	13.6
		At 70 °C			
1.55	6.19	6.5	6.8	80.0	76.0
2.65	6.19	6	6.8	70.0	68.2
4.13	6.19	6	7.1	60.0	60.4
6.19	6.19	6	7.7	50.0	52.0
9.39	6.26	5	6.4	40.0	42.3
9.39	4.02	4	6.3	30.0	34.5
9.39	2.35	3	6.0	20.0	23.6
9.39	1.04	2	5.7	10.0	12.2
		At 80 °C			
1.55	6.19	4	13.0	80.0	76.8
2.65	6.19	3.5	11.8	70.0	69.3
4.13	6.19	3	10.5	60.0	57.7
6.19	6.19	3	8.4	50.0	53.0
9.39	6.26	2.5	7.8	40.0	40.4
9.39	4.02	2	9.2	30.0	34.6
9.39	2.35	1	5.0	20.0	23.4
9.39	1.04	0.75	5.7	10.0	12.2

[a] [AIBN] = 1 mol %.

typical polymerization and copolymerization temperatures. To test the applicability of the Mayo–Lewis equation to the ACOST copolymerization, we copolymerized ACOST with MMA at temperatures ranging from 50 to 80 °C. The results are summarized in Table VIII. The theoretical instantaneous copolymerization curves (solid lines) based on the Mayo–Lewis equation are presented in Figure 8 along with the experimental points at various temperatures. The Mayo–Lewis equation predicts closely the observed instantaneous copolymerization behavior over the entire temperature range.

Before accepting the Mayo–Lewis model, however, one should further consider the work by Wittmer,[33,34] who pointed out that the curve-fitting approach alone in his studies was not sufficient to discern the proper copolymerization model. He has demonstrated that the copolymerization behavior of MST with MMA can be adequately described via the composition curves at 20–100 °C generated either with the Mayo–Lewis equation or with an equation that he derived by taking a depropagation step into account. Therefore, to achieve a more sensitive probe to distinguish between these mechanisms, Wittmer used Arrhenius plots of the reactivity ratios to decide which model best describes the copolymerization

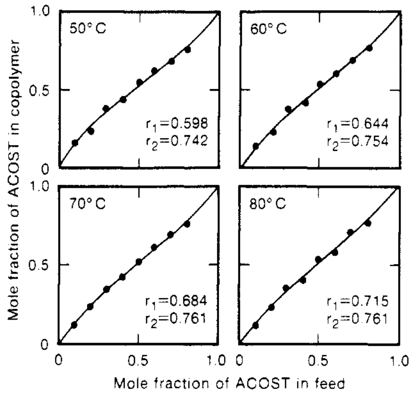

Figure 8. Copolymerization of ACOST (M_2) with MMA (M_1) at 50, 60, 70, and 80 °C.

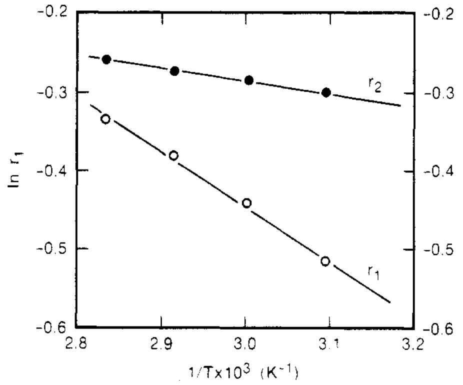

Figure 9. Arrhenius plots of reactivity ratios for ACOST/MMA copolymerization.

data for the MST/MMA system.

$$r_1 = \frac{k_{11}}{k_{12}} = \frac{A_{11}}{A_{12}} \frac{\exp(E_{12} - E_{11})}{RT}$$

In this equation, E_{11} and A_{11} are the propagation activation energy and frequency factor for M_1 radical adding to M_1 monomer, respectively, and E_{12} and A_{12} are the corresponding values for M_1 radical adding to M_2 monomer. According to the Mayo–Lewis model, the reactivity ratios must exhibit linear relationships between ln r and $1/T$. When a strong curvature exists in these plots, the Mayo–Lewis model may then be discarded.

In Figure 9 are shown plots of ln r vs $1/T$ for the ACOST/MMA copolymerization. The Arrhenius plots are linear over the temperature range we studied. Thus, this treatment further supports the applicability of the Mayo–Lewis model to the ACOST/MMA copolymerization system. The Mayo–Lewis model adequately describes the bulk copolymerization of ACOST with MMA; that is, the low T_c of ACOST does not play a role in the copolymerization. We have reported[35] the radical copolymerization of ST with MVL which has a low T_c of 83 °C,[18] where the copolymerization data as a function of temperature were tested against equations derived from three copolymerization models: the Mayo–Lewis, the Lowry case I, and the Lowry case II equations.[36] In this case, the Mayo–Lewis model has been found to be adequate in describing the results. We conclude that the Mayo–Lewis model is an adequate description of the copolymerization of ACOST with MMA in bulk because average sequence lengths of ACOST in the copolymers are very short. Such short M_2 sequences have higher T_c than growing homopolymer chains according to Joshi and Zwolinski.[37]

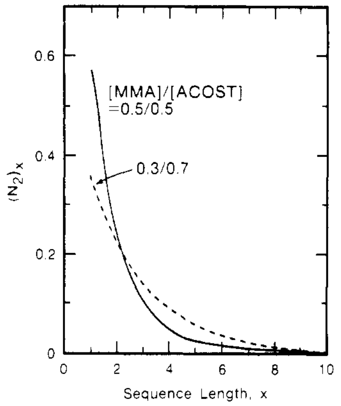

Figure 10. Sequence length distributions of ACOST in ACOST/MMA copolymers. r_2 = 0.754 (60 °C); feed ratio, [MMA]/[ACOST] = 0.5/0.5 and 0.3/0.7.

In accord with the description of the ACOST copolymerizations given above, it would be useful to determine the sequence length distributions in the ACOST/MMA 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[38]

$$(N_1)_x = P_{11}^{\,x-1}P_{12} \qquad (N_2)_x = P_{22}^{\,x-1}P_{21}$$

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 ACOST/MMA copolymerization at 60 °C with r_1 = 0.644 and r_2 = 0.745 are shown in Figure 10 for the feed compositions of ACOST/MMA = 0.5/0.5 and 0.7/0.3. The average sequence length of ACOST is 1.8 and 2.8, respectively. Therefore, the observation that the depropagation effects are not of practical importance in our ACOST/MMA copolymerization may be interpreted in terms of the short average sequence lengths of ACOST.

Q–e Values. The Alfrey–Price Q–e scheme is based on the assumption that steric factors can be neglected. If this assumption is valid, the interpretation of the monomer reactivity based on activation energies is meaningful. Meyer[38] obtained the following equation describing monomer reactivity ratios in his studies of copolymerization of ST with MMA from 30 to 132 °C by applying the Arrhenius expressions

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

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

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

From the slopes of the Arrhenius plots of the reactivity ratios in Figure 9, the differences in the activation energies, $E_{11} - E_{12}$ and $E_{22} - E_{21}$, were calculated to be 5.63 and 1.19 kJ/mol, respectively, for the ACOST/MMA copolymerization. From the intercepts, the differences in the frequency factors, ln A_{11} − ln A_{12} and ln A_{22} − ln A_{21}, were obtained as 1.59 and 0.145, respectively. In terms of transition theory, the temperature dependence of the monomer reactivity ratios may be written as

$$\ln r_1 = \frac{\Delta S^\dagger_{11} - \Delta S^\dagger_{12}}{R} - \frac{\Delta H^\dagger_{11} - \Delta H^\dagger_{12}}{RT}$$

$$\ln r_2 = \frac{\Delta S^\dagger_{22} - \Delta S^\dagger_{21}}{R} - \frac{\Delta H^\dagger_{22} - \Delta H^\dagger_{21}}{RT}$$

where $\Delta S^\dagger$ represents the entropy of activation and $\Delta H^\dagger$ the enthalpy of activation. For our ACOST/MMA copolymerization system, the differences in the entropy of activation are $\Delta S^\dagger_{11} - \Delta S^\dagger_{12} = 13.3$ J/(K·mol) and $\Delta S^\dagger_{22} - \Delta S^\dagger_{21} = 1.27$ J/(K·mol). The difference between the two values is relatively large, though smaller than in the case with the MVL/ST copolymerization (39.7 vs −12.9 J/(K·mol)), which suggests that the steric effect cannot be neglected in the ACOST/MMA copolymerization. Accordingly, we conclude that the calculated *Q–e* values have little meaning.

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On the Kinetic Model for the Radical Copolymerization of Methyl Acrylate and Sulfur Dioxide

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ABSTRACT: Composition data for the copolymerization of sulfur dioxide and methyl acrylate at −78 and 0 °C were obtained and analyzed using a nonlinear least-squares optimization routine. In the model which was found to be adequate to describe experimental data the reactions of methyl acrylate addition to the growing chain are irreversible. Sulfur dioxide can be added only to the macroradicals having methyl acrylate as a terminal and a penultimate monomeric unit, and this reaction is highly reversible even at −78 °C. On the basis of the results obtained, several kinetic parameters are estimated and factors determining the reactivity of sulfur dioxide in propagation and depropagation reactions are discussed.

Introduction

The free-radical copolymerization of sulfur dioxide with many olefinic compounds leads to the formation of polysulfones having a regular alternating structure, which is independent of the monomer feed ratio.[1,2] In contrast, several vinyl monomers such as styrene,[3] vinyl chloride,[4] chloroprene,[5] acrylamide,[6] or alkyl acrylates[7] form polysul-

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