Radical-Initiated Homopolymerization and Copolymerization of α-Hydroxymethylacrylonitrile

As part of our continuing research program on the structure–reactivity relationships of vinyl monomers in their radical polymerizations and copolymerizations, our group have recently initiated the study of the polymerization behavior of vinyl monomers containing α-heteromethyl group.

In the preceding paper,[1] we reported the kinetic study of the radical polymerization of ethyl α-hydroxymethylacrylate (EHMA). This investigation revealed that (1) the radical hompolymerization of EHMA proceeded more rapidly than that of MMA, and (2) EHMA has a larger Q value than MMA, and (3) the value of e for EHMA is slightly smaller than that for MMA. This result was tentatively explained by the through-space interaction between the electrophilic polymer radical and the hydroxymethyl group.

To evaluate this phenomenon, the next target is to verify the radical polymerization of α-hydroxymethylacrylonitrile (HMAN) as an analog of EHMA. The present paper describes kinetic studies of the radical polymerization of HMAN and properties of the resulting polymers.

EXPERIMENTAL

Materials

$α,α'$-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. N-Methyl-2-pyrrolidone (NMP) was dried over calcium hydride, was purified by vacuum distillation, and stored over 4 Å molecular sieves. Styrene (St) was purified by the usual method.

Preparation of α-Hydroxymethylacrylonitrile (HMAN)

Diethyl cyanomethylphosphonate was prepared by the reported procedure[2] in 80% yield from triethyl phosphite and chloroacetonitrile; bp 102–104°C/0.5 mm Hg (lit.[2] 132–135°C/1.2 mm Hg).

To a mixture of diethyl cyanomethylphosphonate (43.7 g, 0.247 mol) and 35% aqueous solution of formaldehyde (140 g) was added slowly with stirring a saturated solution of potassium carbonate (75 mL). The temperature of mixture reached 45–50°C during the addition of potassium carbonate solution and stirring was continued for 1 h. Then saturated ammonium chloride solution (110 mL) was added and the mixture was extracted with ether. The combined organic layers were dried with magnesium sulfate, the solvent was evaporated under *vacuum*, and the remaining oil was distilled. The product was further purified by column chromatography on silica gel (benzene : ethyl acetate = 95 : 5) in order to remove a small amount of impurity. Yield was 6.2 g (30%); bp 55–56°C/0.45 (mm Hg (lit.[3] 94–95°C/6–7 mm Hg).

IR (NaCl): $ν$ = 3390 (O—H), 2230 (C=N), 1640 cm^{-1} (C=C).

^{1}H-NMR (CDCl$_3$): $σ$ = 6.00 (2H, m), 4.20 (2H, d, J = 6 Hz), 3.15 ppm (1H, t, J = 6 Hz).

^{13}C-NMR (CDCl$_3$): $σ$ = 62.0 (CH$_2$), 117.0 (C=N), 130.5, 122.3 ppm (C=C).

MS (m/e): 83 (M$^+$).

Hompolymerization of HMAN

Bulk Polymerization of HMAN: HMAN (1.1 g, 9.4 × 10^{-3} mol) and AIBN (4.3 mg, 2.6 × 10^{-5} mol) were charged into a polymerization tube, followed by degassing (three vacuum–thaw cycles) and sealing. Polymerization was conducted at 60°C for 2.5 h and proceeded in heterogeneous. The tube was cooled, opened, and the resulting polymer was dissolved in NMP. The polymer was purified by reprecipitation from NMP into ether, filtration, and drying *in vacuo* at

40°C for 48 h to give 0.06 g (5.5%) of poly(HMAN). The inherent viscosity of the polymer in NMP was 0.57 dL/g, measured at a concentration of 0.5 g/dL at 30°C.

ANAL. Calcd for C_4H_5NO: C, 57.82%; H, 6.07%; N, 16.87%. Found C, 57.53%; H, 7.02%; N, 17.11%.

Solution Polymerization of HMAN: HMAN (2.0 g, 0.024 mol), AIBN (9.5 mg, 5.8×10^{-4} mol), NMP (13 mL) were charged into a polymerization tube and degassed. The tube was sealed and reacted at 60°C for 24 h and opened. The solution was poured into ether giving a white polymer in 39% yield: The inherent viscosity of the polymer was 0.88 dL/g, measured at a concentration of 0.5 g/dL in NMP at 30°C.

Kinetics

Weighted amounts of HMAN, NMP, and AIBN were charged into polymerization tubes. These solutions were degassed with three alternating freeze–thaw cycles. The tubes were then sealed and placed in a thermostated bath. The course of polymerization was followed by means of gas chromatography. Toluene was used as an internal reference.

Measurements

The IR spectra were recorded on a JASCO IRA-1 spectrophotometer. NMR spectra were obtained on Hitachi R-24B (60 MHz) and Hitachi R-90H (90 MHz) instruments. Thermogravimetry (TGA) and differential thermal analysis (DTA) of polymer samples were performed with a Seiko SSC 5000-TG/DTA 200 instrument at heating rates of 10°C/min.

RESULTS AND DISCUSSION

α-Hydroxymethylacrylonitrile (HMAN) was prepared by the reaction of α-chloromethylacrylonitrile with potassium hydroxide or the hydrolysis of α-acetoxymethylacrylonitrile.[3,4] But, these synthetic procedure are tedious and afforded unsatisfactory yields.[4] Recently, a simple method for the preparation of ethyl α-hydroxymethylacrylate was reported involving the Wittig–Horner reaction of triethyl phosphonoacetate with paraformaldehyde in the presence of saturated aqueous potassium carbonate.[5] This method was applied to prepare HMAN. The synthetic pathway is outlined in eq. (1):

$$(EtO)_3P + ClCH_2CN \longrightarrow (EtO)_2\underset{\underset{O}{\|}}{P}CH_2CN$$

$$(EtO)_2\underset{\underset{O}{\|}}{P}CH_2CN + HCHO \xrightarrow[K_2CO_3]{} CH_2{=}\underset{\underset{CN}{|}}{\overset{\overset{CH_2OH}{|}}{C}} \tag{1}$$

HMAM

Diethyl cyanomethylphosphonate (DCP) was prepared by heating triethyl phosphite with chloroacetonitrile and was used in the Wittig–Horner reaction. Thus, the treatment of the mixture of DCP and formaldehyde with a aqueous saturated solution of potassium carbonate afforded HMAN in 30% yield.

The IR spectrum of HMAN had a characteristic OH absorption at 3390 cm^{-1}, a strong C≡N absorption at 2230 cm^{-1}, and a C=C absorption at 1640 cm^{-1}. The NMR spectrum of HMAN consisted of two multiplets for vinyl protons at σ 4.2 and 6.0; a multiplet for methylene protons adjacent to the hydroxyl group at σ 4.2; and a triplet for the hydroxyl proton at σ 3.15.

Homopolymerization of HMAN

Bulk and solution polymerizations were readily carried out with AIBN as an initiator. Polymerization proceeded in heterogeneous in bulk, but in homogeneous in solution polymeriza-
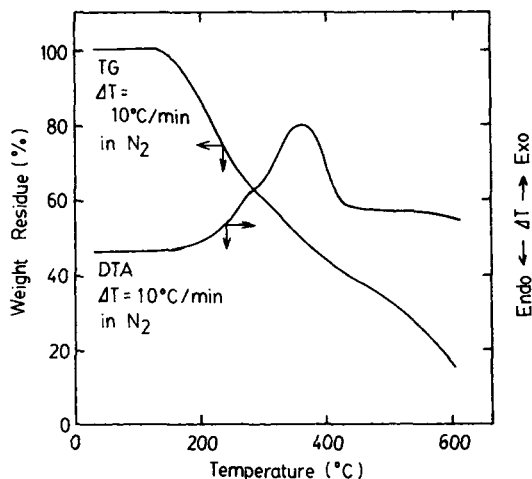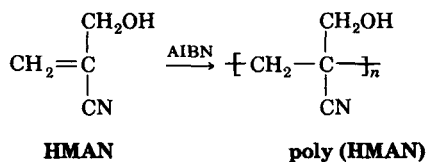
Fig. 1. TGA and DTA curves of poly(HMAM) in nitrogen.

tion. This polymer is easily soluble in polar aprotic solvents, such as NMP, DMAc, and DMF, but is insoluble in ether and alcohol.

$$CH_2=\underset{\underset{CN}{|}}{\overset{\overset{CH_2OH}{|}}{C}} \quad \xrightarrow{AIBN} \quad +CH_2-\underset{\underset{CN}{|}}{\overset{\overset{CH_2OH}{|}}{C}}\frac{}{}_n$$

HMAN   **poly (HMAN)**

The homopolymer gave a satisfactory elemental analysis. The IR spectrum of poly(HMAN) exhibited a characteristic hydroxy absorption at 3400 cm^{-1} and a nitrile absorption at 2215 cm^{-1}, but, no trace of C=C stretching peak found in the monomer. Thermogravimetry (TGA) and differential thermal analysis (DTA) on poly(HMAN) were carried out under nitrogen at heating rate of 10°C/min. A typical thermogram is shown in Figure 1. The DTA curve of poly(HMAN) exhibited an exotherm at ca. 150°C which correlated well with TGA, confirming that decomposition started at about this temperature.

Kinetic Study

The solution homopolymerization of HMAN in NMP was initiated with AIBN at temperatures from 50–70°C. The time–conversion curves, shown in Figure 2, were linear and without introduction period. Table I shows the relationship between R_p and initiator concentration at 60°C. A plot of log R_p against log[AIBN] (Fig. 3), gives a straight line with a slope 0.54. Table II summarizes the relationship between Rp and monomer concentration for polymerization at 60°C. A plot of log R_p vs. log[HMAN] (Fig. 3) gives a slope of 1.03. The rate equation for the homopolymerization of HMAN in NMP may be given, therefore, as

$$R_p = k[\text{AIBN}]^{0.54}[\text{HMAN}]^{1.03} \tag{2}$$

where k is the overall rate constant. Equation (2) is close enough to that expected for the normal vinyl free-radical polymerization mechanism that the following simple kinetic scheme may be written to describe this polymerization:
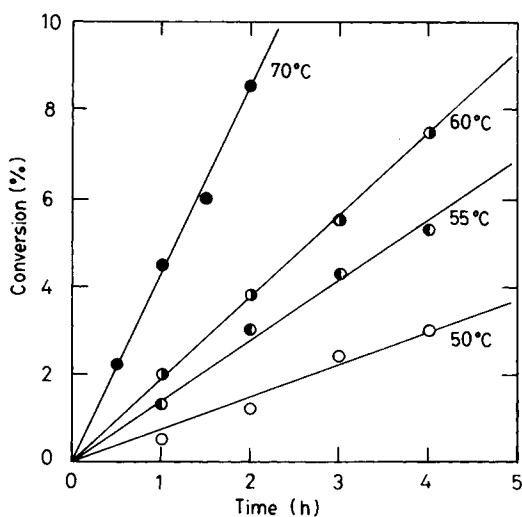
$$R_p = k[\text{AIBN}]^{0.5}[\text{HMAN}]^{1.0} \tag{3}$$

Fig. 2. Time–conversion curves for solution polymerization of HMAN at various temperatures: [HMAN] = 2.2 mol/L, [AIBN] = 3.7 × 10^{-3} mol/L.

TABLE I
Relationship between R_p and Initiator Concentration[a]

[AIBN] × 10^{-3} (mol/L)	Yield (%)	R_p × 10^5 (mol/L s)	R_p/[I]$^{0.54}$ × 10^4
14.7	9.10	2.78	2.71
5.73	5.35	1.63	2.65
3.70	3.70	1.13	2.32
1.40	2.01	0.64	2.23

[a][HMAN] = 2.2 mol/L, polymerization time: 7200 s, solvent: NMP, temperature: 60°C.
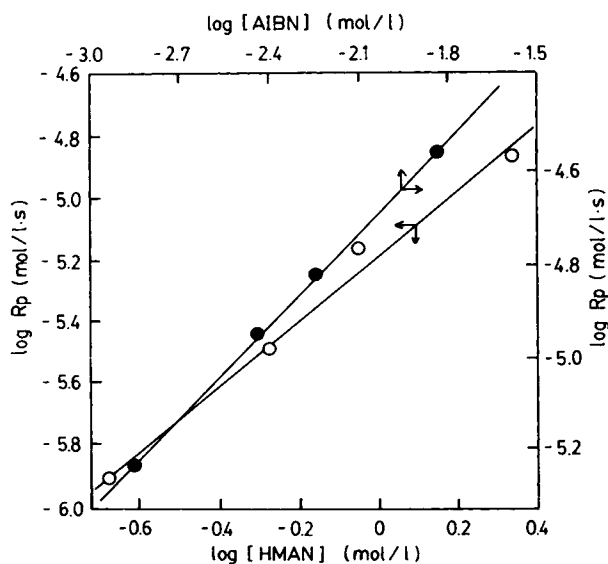
Fig. 3. Plot of log R_p vs. log[AIBN] or log[HMAN] for hompolymerization of HMAN in NMP at 60°C.

TABLE II
Relationship between R_p and Monomer Concentration[a]

[HMAN] (mol/L)	Yield (%)	$R_p \times 10^6$ (mol/L s)	$R_p/[M]^{1.03} \times 10^6$
2.2	5.35	16.3	7.24
1.1	4.50	6.88	6.24
0.55	4.34	3.32	6.15
0.22	4.10	1.25	5.95

[a][AIBN] = 5.73×10^{-3} mol/L, polymerization time: 7200 s, solvent: NMP, temperature: 60°C.

Figure 4 shows an Arrhenius plot of R_p vs. $1/T$. From the slope of this plot, the overall activation energy E_a is estimated at 77.4 kJ/mol. In the presence of an initiator, the overall activation energy for the normal kinetic scheme is given by

$$E_a = 1/2E_d + \left(E_p - 1/2E_t \right) \tag{4}$$

where E_d, E_p, E_t are the activation energies for the initiation, propagation, and termination steps, respectively. Using the literature values of 128 kJ/mol in benzene for E_d,[6] we calculated a value of 13.4 kJ/mol for $E_p - 1/2E_t$ for HMAN in NMP. This value is smaller than that for MAN (37.6 kJ/mol).[7]

Copolymerization with Styrene

Copolymerizations of HMAN with styrene were carried out in NMP at 60°C. The results are given in Table III. The copolymerization compositions were determined by means of gas chromatography. The monomer-copolymer composition curve is shown in Figure 5. The values of r_1 and r_2 were obtained by the curve fitting method.[8] Defining HMAN as M_2, the values were $r_1 = 0.24$ and $r_2 = 0.55$. The reactivity of monomer can be illustrated by considering the inverse of its monomer reactivity ratio $(1/r)$. The value of $1/r_1$ is 4, thus, the styryl radical reacts preferentially with HMAN. The Q–e values for HMAN, calculated for monomer reactivity ratios,
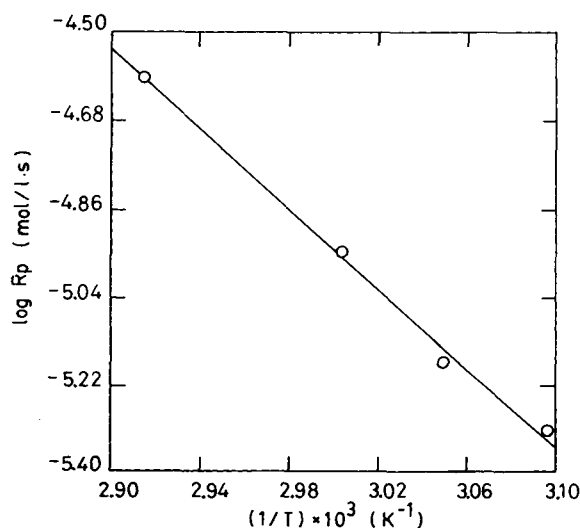

Fig. 4.   Plot of log R_p vs. $1/T$ for polymerization of HMAN.

TABLE III
Copolymerization of HMAN [M$_2$] and Styrene [M$_1$][a]

No.	Monomer		Polymerization time	Yield of copolymer (%)	HMAN content (mol%)
	[M$_1$] (mol%)	[M$_2$] (mol%)			
1	0.87	0.13	3 h 10 min	5.8	0.26
2	0.85	0.15	3 h 45 min	7.2	0.32
3	0.70	0.30	4 h	6.2	0.46
4	0.63[b]	0.37	4 h	6.8	0.53
5	0.52[b]	0.48	2 h 30 min	4.9	0.56
6	0.35[b]	0.65	2 h	5.2	0.64
7	0.24[b]	0.76	1 h 30 min	4.4	0.70
8	0.18[b]	0.82	1 h 30 min	4.6	0.78
9	0.11[b]	0.89	1 h 30 min	4.9	0.83

[a][AIBN] = 6.94 × 10^{-3} mol/L.
[b][AIBN] = 3.95 × 10^{-3} mol/L, solvent: NMP, temperature: 60°C.

are listed in Table IV, where the corresponding values of analogous acrylonitriles are shown in comparison.

The electron-withdrawing effects of the hydroxyl group is expected to increase Q and e values. HMAN was shown to have a larger Q value than methacrylonitrile (MAN) of acrylonitrile (AN).

On the other hand, the value of e for HMAN (0.63) is substantially smaller than that of either MAN (0.81) or AN (1.23). This is the same trend that is observed by comparing the Q–e values of MAN or AN with ethyl α-hydroxymethylacrylate (EHMA). The e value for EHMA (0.35) is smaller that that of ethyl methacrylate (EMA) (0.44). The e value is related to the electron density of the monomer and monomer's corresponding radical, and the linear relationship between e values and NMR chemical shifts of vinylic double bonds has been well established.[9] ^{13}C chemical shifts are a sensitive measure of electron density on carbon atoms. It was consequentially expected that ^{13}C chemical shift of the β-carbon of HMAN would be observed at higher field than that of MAN. However, no difference in their chemical shifts (HMAN : 130.5 ppm, MAN : 130.6 ppm) was observed. To explain these results, the through-space interaction in
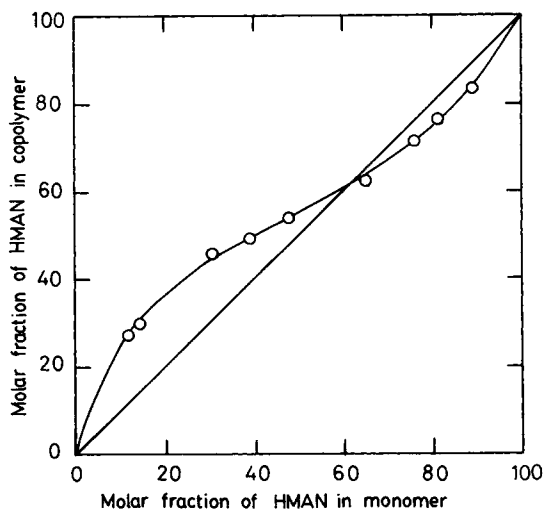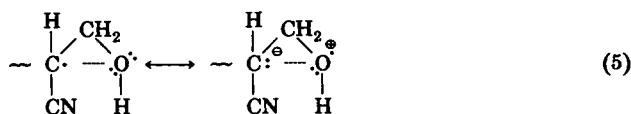

Fig. 5. Copolymerization of HMAN with St.

TABLE IV
Copolymerization Parameters

M_1	M_2	r_1	r_2	r_1r_2	Q_2	e_2
St	HMAN	0.24	0.55	0.13	1.35	0.63
St	MAN	0.29	0.23	0.067	1.12	0.81
St	AN	0.40	0.04	0.016	0.49	1.23

[a]St: $Q_1 = 1.00$, $e_1 = -0.80$.

addition to the through-bond interaction would be considered as in the case of EHMA. That is, the larger Q value and smaller e value for HMAN (versus MAN or AN) could be due to a polarization phenomenon wherein the electrophilic polymer radical (adjacent to the nitrile group) may be stabilized by the weak interaction of sp^2 orbital of radical on carbon with sp^3 orbital of lone pairs on oxygen (eq. 5):

$$\sim \underset{\underset{CN}{|}}{\overset{\overset{H}{|}}{C}}\cdot \overset{\overset{CH_2}{\diagup}}{---}\underset{\underset{H}{|}}{\overset{\overset{}{}}{O}}\cdot \longleftrightarrow \sim \underset{\underset{CN}{|}}{\overset{\overset{H}{|}}{C}}\overset{\ominus}{:} \overset{\overset{CH_2}{\diagup}}{---}\underset{\underset{H}{|}}{\overset{\overset{\oplus}{}}{O}} \tag{5}$$

Many more example monomers in this series should be accumulated to evaluate this through-space interaction more clearly. Such efforts is now progress in our laboratory.

References

1. M. Ueda, T. Koyama, M. Mano, and M. Yazawa, *J. Polym. Sci. Polym. Chem. Ed.*, in press.
2. N. D. Dowson and A. Burger, *J. Am. Chem. Soc.*, **74**, 5312 (1952).
3. G. W. Hearne and D. S. La France, U.S. Pat. 2,601,659 (1952).
4. J. B. Dickey and H. W. Coover, J., U.S. Pat. 2,682,527 (1954).
5. J. Villieras and M. Rambaud, *Synthesis*, 924 (1982).
6. A. V. Tobolosky and B. Baysal, *J. Polym. Sci.*, **11**, 471 (1953).
7. J. Brandrup and E. H. Immergup, Eds., *Polymer Handbook*, 2nd ed., Wiley, New York, 1975, p. II-451.
8. R. P. Bevington, *Data Reduction and Error Analysis for the Physical Science*, McGraw-Hill, New York, 1969.
9. J. J. Herman and Ph. Teyssie, *Macromolecules*, **11**, 839 (1978).

MITSURU UEDA
KAZUHIKO KAWAGUCHI
MOTOKAZU MANO

Department of Polymer Chemistry
Faculty of Engineering
Yamagata University
Yonezawa, Yamagata 992, Japan