POLYMERIZATION OF METHACRYLIC ACID IN THE PRESENCE OF ISOBUTYLALDEHYDE

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I. INTRODUCTION

Several reports for the effect of aldehyde on the polymerization of vinyl monomers have been so far presented. ROESN et al.[1] have already reported that the polymerization of vinylchloride was carried out in the presence of aldehydes and the obtained polymer was stereoregular. They considered that this stereoregulating effect of aldehydes was due to a complex formation in connection with the degree of polymerization. BURNETT et al.[2] have also reported the polymerization of acrylonitrile initiated by aldehyde peroxide. It is well known that aldehydes react with oxygen to produce peroxides by a free radical mechanism, and the peroxides are very efficient radical sources.

In the present work, non-catalyzed polymerization of methacrylic acid in the solvents such as benzene were carried out in the presence of isobutylaldehyde, and the effects of polymerization temperature, concentration of isobutylaldehyde and tacticity of the obtained polymer were investigated, and the characterization of this polymerization systems were elucidated.

II. EXPERIMENTAL

2.1. Reagents

Methacrylic acid of Wako Pure Chemical Industries, Ltd., was purified by distillation under reduced pressure before polymerization. Benzene, dioxane and n-buthanol of special grade of the same company were purified according to the ordinary way. Isobutylaldehyde was of reagent grade from the same company. Diazomethane was prepared by the reaction of p-toluenesulfonyl-N-methyl-N-nitrosoamide wth potassium hydroxide in diethyl ether.

2.2 Polymerization reaction

All polymerizations were carried out in sealed pyrex glass tubes which

were filled with the desired monomer, solvent and isobutylaldehyde. Before sealing, air was replaced by nitrogen with cooling.

The Polymerization was conducted at the desired tepmperatures and times. After polymerization, the polymers were precipitated in acetone, and then were dissolved in methanol, reprecipitated, washed and dried *i. vac.* for 24 hrs at 40°C.

2. 3.   Determination of degree of polymerization

Viscosities of methanol solutions of poly(methacrylic acid) (PMAA) were measured at 26°C using UBBELOHDE type viscometer and the intrinsic viscosity ($[\eta]$) was obtained by extrapolating the reduced viscosity to infinite dilution. The molecular weight of the polymer was calculated from the following equation[3]

$$[\eta] = 2.42 \times 10^{-3} \; \bar{M}_n^{0.51}$$

where $\bar{M}_n$ is the number average molecular weight.

2. 4.   Esterification of poly(methacrylic acid)

Esterification was carried out according to KATCHALSKY's method[4] with diazomethane; 0.2g of polymer was treated with 0.6g diazomethane in a 60% benzene/40% diethyl ether solution for 12hrs. The poly (methyl methacrylate) (PMMA) was precipitated with diethyl ether, washed and dried under vacum.
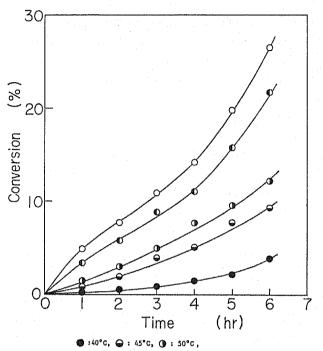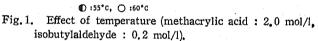
2. 5.   Determination of tacticity

For the determination of tacticity of polymers, the measurement of IR spectra was made on JASCO-IR-E spectrometer. The films used were prepared from benzene solution of PMMA by evaporating the solvent. The contents of syndiotactic diad (s-(diad)%) were calculated from the optical density ratio ($E_{9.45}/E_{7.25}$) of the absorption band at 9.45μ and 7.25μ by the method of BAUMANN *et al.*[5].
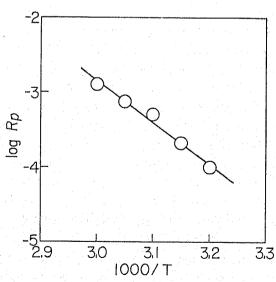

III.   RESULTS and DISCUSSION

3. 1.   Effect of polymerization conditions

The polymerization of methacrylic acid in benzene was conducted in the range of the temperatures of 40°C to 60°C. The time-conversion curves are shown in Fig. 1. It is found that the rate of polymerization increased with time in earier stage of the reaction. The initial acceleration is due to the reaction progress in heterogeneuos system because the resulting polymer is insoluble in benzene. The rate of polymerization were determined at the temperatures of 40, 45, 50, 55 and 60°C at the fixed concentration of mono-

Fig. 1. Effect of temperature (methacrylic acid : 2.0 mol/l, isobutylaldehyde : 0.2 mol/l).

Fig. 2. ARRHENIUS plot of the rate of polymerization (methacrylic acid : 2.0 mol/l, isobutylaldehyde : 0.2 mol/l).

mer of 2.0 mol/l and of isobutylaldehyde of 0.2mol/l. The ARRHENIUS plot of polymerization is shown in Fig. 2. The apparent activation energy was 24.2 kcal/mol. This value is similar to the activation energy of a common radical polymerization. The reaction was also inhibited by the addition of hydroquinone.
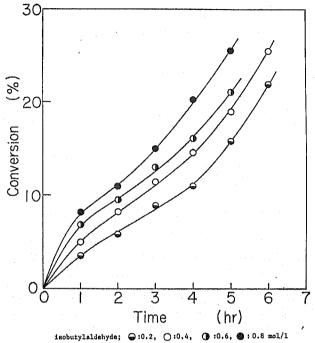
From the fact presented above, it is expected that the reaction proceeds by a radical mechanism. The molecular weight had a tendency to increase gradually in the earlier stages of the reaction and levelled off to a constant value with the progress of the reaction. This behavior is the characteristics of a heterogeneous polymerization. The results of polymerization at the temperature of 55°C are summarized in Table 1.

Table 1. Polymerization of methacrylic acid in benzene at 55°C.

Sample No.	Time (hr)	Conversion (%)	$\overline{M}_n \times 10^{-4}$	$\overline{DP} \times 10^{-3}$
MB-1	1	3.6	56.7	6.6
MB-2	2	6.1	67.9	7.9
MB-3	3	9.3	72.0	8.4
MB-4	4	11.0	79.4	9.2
MB-5	5	15.4	81.9	9.5
MB-6	6	22.5	77.5	9.0

Next, we were examined the effect of concentrations of isobutylaldehyde. The rate of polymerization were determined under various concentrations of isobutylaldehyde of 0.2 to 0.8 mol/l at fixed monomer concentration of 2.0 mol/l and 55°C. The time-conversion curves are shown in Fig. 3. The plot on the logarithm of the rate of polymerization versus that of the concentration of isobutylaldehyde is shown in Fig. 4. The rate of polymerization is proportional to the 0.67 power of the concentration of isobutylaldehyde. If isobutylaldehyde acts as initiator, this value is greater than a common initiator concentration exponent, that is, 0.5. These fact was explained by considering a unimolecular termination by occlusion of a part of propagating radical in a clump of polymer molecules, which appears in heterogeneous polymerization.

3.2. Initiation mechanism using isobutylaldehyde

It is well known that aldehyde reacts with oxygen to produce peroxides. We found that peroxide of 1.8% was contained in using isobutylaldehyde by iodine method. BURNNET et al.[2] proposed the following kinetic scheme.

isobutylaldehyde; ●:0.2, ○:0.4, ◑:0.6, ●:0.8 mol/l

Fig. 3.   Effect of isobutylaldehyde concentration
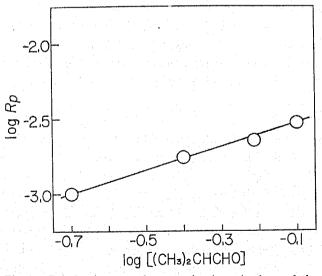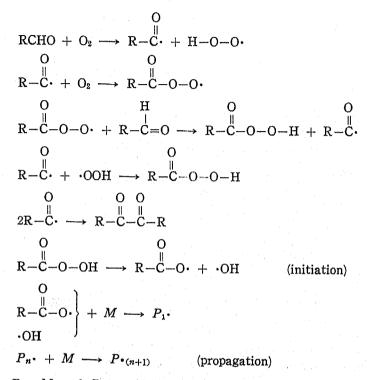(methacrylic acid : 2.0 mol/l, 55°C).

Fig. 4.   Relation between the rate of polymerization and the
concentration of isobutylaldehyde (methacrylic acid :
2.0 mol/l, 55°C).

$$RCHO + O_2 \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}\cdot + H-O-O\cdot$$

$$R-\overset{\overset{\displaystyle O}{\|}}{C}\cdot + O_2 \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-O-O\cdot$$

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-O\cdot + R-\overset{\overset{\displaystyle H}{|}}{C}=O \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-O-O-H + R-\overset{\overset{\displaystyle O}{\|}}{C}\cdot$$

$$R-\overset{\overset{\displaystyle O}{\|}}{C}\cdot + \cdot OOH \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-O-O-H$$

$$2R-\overset{\overset{\displaystyle O}{\|}}{C}\cdot \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-R$$

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-OH \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-O\cdot + \cdot OH \qquad \text{(initiation)}$$

$$\left.\begin{array}{l} R-\overset{\overset{\displaystyle O}{\|}}{C}-O\cdot \\[4pt] \cdot OH \end{array}\right\} + M \longrightarrow P_1\cdot$$

$$P_n\cdot + M \longrightarrow P\cdot_{(n+1)} \qquad \text{(propagation)}$$

where R, M and $P\cdot$ are isobutyl group, monomer and polymer chain, respectively.

As described in previous section, the reaction in this experiment was apparent to be the free radical polymerization since the activation energy of this polymerization was much greater than that of ionic polymerization and hydroquinone was found to inhibit the production of polymer. Therefore, the reaction in this experiment is expressed by the kinetic scheme proposed by BURNNET et al.[2].

3.3. Tacticity

The stereoregularity of polymer obtained using isobutylaldehyde was compared with that using benzoyl peroxide (BPO) under the same reaction conditions. The results are summarized in Table 2. Table 2 reveals that the increase of stereoregularity based on isobutylaldehyde in dioxane and n-buthanol is observed, but not in benzene. It can therefore be presumed that the end control of isobutylaldehyde is depressed by arising a interaction between benzene and isobutylaldehyde or benzene and the end of propagating chain. The effects of solvents on the polymerization in the presence of isobutylaldehyde need to be investigated further.

Table 2.   Comparison of stereoregularity of polymer obtained using
isobutylaldehyde with the using benzoyl peroxide (BPO)
under the same condition.

Sample No.	Solvent	$E_{9.45}/E_{7.25}$	s-(diad) (%)	Cat.
MP-1	dioxane	0.68	75	BPO
MO-1	dioxane	0.77	83	isobutylaldehyde
MP-2	benzene	0.69	76	BPO
MB-4	benzene	0.70	77	isobutylaldehyde
MP-3	n-buthanol	0.81	90	BPO
MA-1	n-buthanol	0.90	95	isobutylaldehyde

IV.   SUMMARY

Non-catalyzed polymerization of methacrylic acide in the presence of isobutylaldehyde were carried out in benzene.   The rate of polymerization increased as temperature increased in the range of 40 to 60°C and an apparent activation energy was calculated to be 24.2 kcal/mol. Hydroquinone inhibited the polymerization. These results indicated that the polymerization proceeded by free radical mechanism.   The rate of polymerization was proportional to the 0.67 power of the concentration of isobutylaldehyde and the molecular weight had a tendency to increase gradually in the earlier stages of the reaction and levelled off to a constant value with the progress of the reaction. This behavior is the characteristic of a heterogeneuos polymerization. By the measurements of IR spectra of poly(methyl methacrylate) prepared from esterification of poly(methacrylic acid),   the increase of stereoregularity based on isobutylaldehyde was observed in dioxane and n-buthanol,   but not in benzene.

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