Studies on the Polymerization of Acrolein Oxime. II. Thermal Polymerization

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ABSTRACT: The same values of the monomer reactivity ratios are experimentally obtained for both the thermal and catalyzed copolymerizations of acrolein oxime with vinyl compounds such as acrylonitrile, methyl methacrylate, and styrene, the catalyst being *n*-butyllithium. On the basis of these data, it is proposed that thermal polymerization of the oxime proceeds by an anionic mechanism, and that the initiating species is an anion, $\text{CH}_2=\text{CH}-\text{CH}=\text{N}-\text{O}^\ominus$, arising from the dissociation of the molecular aggregates of the oxime. In the thermal polymerization at 60°C, the product is a white, hygroscopic and powdery polymer having a low molecular weight of 1000—2000. The polymer consists of two or more types of structural units and this may be explained in terms of the resonance phenomenon and the migration of a proton at the growing chain end.

KEY WORDS Acrolein Oxime / Thermal Polymerization / Thermal Copolymerization / Anionic Mechanism / Structures of Polymer / *Syn—Anti* Isomerization /

Numerous papers have described the thermal polymerization of vinyl compounds as a reaction which generally proceeds by a radical mechanism. In our previous paper,¹ however, we suggested that a nonradical mechanism is operative in the case of acrolein oxime (AOM). This suggestion is based mainly on the following two facts: (1) Neither the presence nor the absence of azobisisobutyronitrile (AIBN) or *p*-benzoquinone affects the velocity of the polymerization of AOM. (2) AOM is an efficient inhibitor of radical polymerizations. In order to elucidate further the mechanism of the thermal polymerization, a comparative study of the thermal and the catalyzed copolymerizations of AOM with acrylonitrile (AN), methyl methacrylate (MMA), or styrene (ST) was undertaken.

EXPERIMENTAL

Materials

AOM was prepared by the same method as described in the previous paper²; bp 44°C (14 mm), and *O*-methyl acrolein oxime (MAOM)

by the method of Ioffe and Zelenin³; bp 70—72°C/760 mmHg. AN, MMA, and ST were purified by the ordinary methods and distilled prior to use.

Polymerization Procedure

Thermal polymerization and thermal copolymerization were carried out at 60°C in sealed tubes. The copolymerization by the use of initiators was carried out at 0°C under agitation in a glass tube provided with a rubber plug through which a solution of *n*-butyllithium in *n*-hexane or concentrated hydrochloric acid was injected. Reactor tubes were opened after a designated time; those contents were brought together with large amount of ether so that the polymers precipitated as a result. The polymers were washed with appropriate solvents, dried under reduced pressure, and weighed.

Analyses of Acrolein Oxime Polymer (PAOM) and Copolymers

The composition of resulting copolymers was determined by elementary analysis, and the monomer reactivity ratio was estimated by the

Fineman and Ross method.⁴ The molecular weights of PAOM and copolymers were determined using dimethylformamide (DMF) as the solvent at 70°C by a vapor pressure osmometer (Hitachi Perkin-Elmer, model 115). The oxime group in PAOM was reduced to the primary amine with hydrogen in the presence of a Raney Nickel catalyst,⁵ and then the amount of the amine was determined by the Van Slyke method.⁶ The content of carbon—carbon double bond was calculated by determining the iodine value.⁷

PAOM was hydrolyzed in the following way: 0.71 g PAOM was dissolved in 10 ml of a 1:1-methanol—water mixture containing 5-% potassium hydroxide, then heated at 60°C for 3 hr. After neutralization of the solution, the resulting potassium chloride was removed, the hydrolysis product was identified by gas chromatography under the same conditions as described above.² The ratio of the *syn* and *anti* forms in AOM was also measured by gas chromatography.

The NMR spectrum was obtained with a JOEL PS-100 spectrometer (100 MHz) at 21°C using deuterated dimethyl sulfoxide (DMSO- d_6) as the solvent and tetramethylsilane (TMS) as the internal standard. The polymer concentration was approximately 7.6% (wt/vol).

RESULTS AND DISCUSSION

Copolymerization of AOM with Vinyl Compounds

AOM thermally reacted with anyone of the substances, AN, MMA, and ST, at 60°C. This substance was in every case insoluble in benzene, but easily soluble in both acidic and basic aqueous solutions. This solubility behavior indicates that the product is, in all cases, not a mixture of polymers arising from the independent polymerizations of AOM and some other starting substance. Obviously, it is a copolymer; this conclusion is also supported by the infrared spectroscopic data on these products. The spectra exhibit a nitrile peak at 2240, a carbonyl peak at 1735 and phenyl peaks at 765 and 710 cm^{-1} for the systems of AOM—AN, AOM—MMA, and AOM—ST, respectively.

Figures 1—3 show monomer—copolymer composition curves for the present three systems. In every system the curve for the thermal co-

polymerization almost completely coincides with that for the anionic copolymerization in the presence of *n*-butyllithium. The addition of AIBN never once affected the velocities of the thermal copolymerizations as well as the compositions of the resulting substances. However, AOM is found to be an efficient inhibitor of

Figure 1. Copolymerization diagram for AOM—AN system: ○, thermal copolymerization at 60°C; ●, anionic copolymerization in the presence of BuLi at 0°C.

Figure 2. Copolymerization diagram for AOM—MMA system: ○, thermal copolymerization at 60°C; ●, anionic copolymerization in the presence of BuLi at 0°C.

Figure 3. Copolymerization diagram for AOM—ST system: ○, thermal copolymerization at 60°C; ●, anionic copolymerization in the presence of BuLi at 0°C; ◐, cationic copolymerization in the presence of HCl at 0°C.

Table I. Monomer reactivity ratios in copolymerizations of AOM with reference monomers

M ₁	M ₂	Initiator	r ₁	r ₂
AOM	AN	None	1.0	0.1
		BuLi	1.0	0.1
AOM	MMA	None	1.4	0
		BuLi	1.4	0
AOM	ST	None	9.8	0
		BuLi	9.8	0
		HCl	30	0.01

radical polymerizations as described in our previous paper.¹ These facts indicate that an anionic mechanism is operative in the thermal polymerization of AOM.

Monomer reactivity ratios measured in these copolymerization systems are summarized in Table I, which obviously indicates that in all cases the active ends of the growing chains react more readily with AOM than with any of the comonomers. The molecular weights of the resultant copolymers were all about 1000, almost the same as or lower than that of the PAOM formed by the thermal polymerization of AOM.

MAOM has a structure arising from substitution of a methyl group for the hydrogen atom of the hydroxyl group in AOM, and does not polymerize by itself, but rather copolymerizes with AOM on heating. The infrared spectrum of the resulting polymer shows absorption peaks at 1700 and 1610 cm⁻¹; the former peak is assigned to the C=N stretching vibration in the MAOM structural unit, and the latter to that in the AOM unit. Thus the hydrogen atom of the hydroxyl group of AOM seems to play an important role in the thermal polymerization of AOM.

Syn—Anti Isomerization of AOM

AOM is ordinarily an equilibrium mixture of two isomers, about 17% of the *syn* and 83% of the *anti* forms, which can be separated into their pure states by gas chromatographic means.² The content of *anti* form in the unpolymerized portion of the AOM that had been enriched in the *syn* form component varied with time during the thermal polymerization in an atmosphere of nitrogen as shown in Figure 4. The isomerization seemed to attain equilibrium eventually when the *anti* form content became about 17%. This isomerization, as is often the case with oximes, seems to take place during the liberation of the proton from the hydroxyl group.⁸

Also, any oxime molecules can associate with each other to form cyclic aggregates by hydrogen bonds of the two types, O—H—N and O—H—O.⁹ The infrared spectrum of AOM shows an OH peak at 3250 and a C=N peak at 1610 cm⁻¹, indicating the shifts of frequencies from those which would be measured when AOM is expected to be in a monomeric form at a very dilute concentration. The apparent molecular weight of AOM in benzene at a molality of 0.86 was cryoscopically determined to be 160, which gives an estimate of 2.3 for the aggregation factor, *i.e.*, the number of molecules per an aggregate.

Thus, those anions which initiate the thermal polymerization of AOM are probably produced by dissociation of the aggregates:

Figure 4. *Syn-anti* isomerization of AOM: ●, 45°C; ○, 60°C; ●, 70°C.

where $(\text{AOM})_1$ and $(\text{AOM})_{2-3}$ represent the free AOM and the AOM aggregate with the aggregation factor of 2 or 3, respectively. The AOM anion has three resonance structures formulated as

Isomerization between the *syn* and *anti* forms of AOM seems to proceed *via* structures [II] and [III], because the free rotation about the carbon-nitrogen bond is favorable for only these two structures.

AOM can easily polymerize in the presence of either an anionic or cationic catalyst. Therefore, both of the anion and cation, concurrently arising from the ionic dissociation of the AOM aggregates, can be the initiator of the thermal polymerization of AOM. When *n*-butyllithium was added to AOM at a temperature below 0°C, the evolution of butane was clearly detected by gas chromatography, which apparently is indication of the occurrence of the following reaction.

Therefore, the anion, $\text{CH}_2=\text{CH}-\text{CH}=\text{N}-\text{O}^\ominus$, also seems to be an initiator in addition to the butyl anion for the anionic polymerization in the presence of *n*-butyllithium. Considering this conclusion together with the above-described data on the copolymerization, we can reasonably assume that the AOM anion is the initiator in the thermal polymerization of AOM.

The AOM cation would also take part in the termination process

and the chain transfer would occur only between the growing chain end and AOM aggregates.

Chemical Structure of PAOM

The initial rate of the thermal, bulk polymerization of AOM at 60°C was 2.73×10^{-4} mol/l sec. The resulting polymer is a white, hygroscopic powder, and soluble in both acidic and basic aqueous solutions and insoluble in most organic solvents except for DMF. On

being allowed to stand in air, the polymer gradually becomes insoluble. The number-average molecular weight value is within the range of 1000–2000.

When AOM is added to a growing chain,

there are five possible paths, respectively, which lead to the structures of chain unit: (A) 1,2-addition, (B) 3,4-addition, (C) 1,4-addition, (D) and (E) hydrogen transfer. The last two were suggested by Breslow, *et al.*¹⁰

A sample PAOM (M_w , 2100) contained 42% of the structural units having a carbon–carbon double bond per unit, 46% of those having a pendant oxime per unit, and 12% of unknown structural units.

If the polymerization proceeds by path (A), the pendant oxime remains unchanged, and hence the content of [IV] is 46% in the resultant PAOM. Paths (B), (C), and (E) can yield respectively the carbon–carbon double bond units. But the path (B) is compared with path (A), unlikely to occur owing to the instability of the resulting anion and the steric

hindrance. Vinyl peaks at 1405, 990, and 925 cm^{-1} are seen in the infrared spectrum of PAOM, but they are very small compared with those in the case of AOM. These smaller peaks can be attributed to the vinyl group of the AOM monomer unit located at the chain end. Thus the carbon–carbon double bonds in PAOM should arise only from paths (C) and (E), and 12% of the structural units, mentioned above as unknown, seems to come about by path (D). The phenomenon of resonance and the migration of a proton at the end of the growing chain appear to govern the contents of the structural units in the resulting polymer. The growing-chain end has two resonance forms, [IV]' and [VI]', each of which is in equilibrium with its tautomeric anion as shown in Figure 5. The actual ratio of structure [IV] to [VII] in the resulting polymer seems to depend on the equilibrium concentrations of [IV]' and [VII]'. If the same value of equilibrium constant is assumed for the interchange between [VI]' and [VIII]', the C=C structural units, totaling 42% as mentioned above, should consist of the 33.3% [VI] and 8.7% [VIII] structures. From these data, the distribution of structural units for the PAOM with a $\bar{P}_n$ value of 30 is determined as

Figure 5. Resonance and equilibria for growing chain end.

Figure 6. NMR spectrum of PAOM.

The data on both the hydrolysis and NMR spectroscopy of PAOM show that it contains $\text{CH}_2=\text{CH}-\text{CH}=\text{N}-\text{O}-$ as its terminal unit. The hydrolysis gave AOM, which can not be produced from any of the above-described structural units other than the terminal one. As shown in Figure 6, the NMR spectrum has a multiplet at around 11 ppm, which becomes faint when heavy water is added. The multiplet seems to indicate the presence of $-\text{NH}-$ as

well as OH groups. The peaks at 7.71, 7.04, 6.40, and 5.50 ppm are assigned to the protons of the end group, $\text{CH}_2=\text{CH}-\text{CH}=\text{N}-$.² The other peaks are due perhaps to the backbone of the polymer, but the exact assignment is difficult because of the structural complexity.

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