Studies on the Polymerization of Acrolein Oxime. III. Kinetics of the Thermopolymerization

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ABSTRACT: The effects of solvents on the overall rate of thermal polymerization of acrolein oxime are investigated. The reaction order with respect to the concentration of the oxime is 2.3-2.6 in benzene and in several other solvents; 3.5 in acetone and tetrahydrofuran, and 3.8 in dimethylformamide. These facts are quantitatively explained on the basis of the following assumptions. The oxime in solution is in aggregate form, mainly that of the dimer and the trimer forms. The quantity of the aggregate varies according to the solvent, but the initiating species, an anion of the oxime, is always produced from these aggregates, irrespective of the quantity in solution, through thermal and ionic dissociation.

KEY WORDS Acrolein Oxime / Thermal Polymerization / Reaction Order / Solvent Effect /

In our preceding paper,¹ the following was suggested on the thermal polymerization of acrolein oxime (AOM): (1) The reaction follows an anionic mechanism. (2) The initiating species is an anion, $\text{CH}_2=\text{CH}-\text{CH}=\text{N}-\text{O}^\ominus$, produced by the ionic dissociation of the molecular aggregates of AOM.

The present investigation was undertaken in order to establish the detailed kinetics for the thermal polymerization of AOM.

EXPERIMENTAL

AOM was prepared by oximation of acrolein as described previously;² bp 44°C (14 mm). All solvents used were purified by the usual methods.

The rate of thermal polymerization was measured by dilatometry at 60°C. The molecular weight of poly(acrolein oxime) (PAOM) was measured in dimethylformamide (DMF) at 70°C by means of a vapor pressure osmometer (Hitachi Perkin-Elmer, model 115).

RESULTS AND DISCUSSION

The temperature dependence of the rate of bulk polymerization of AOM without addition

of any initiating substance is shown in Figure 1; the overall activation energy was thus found to be 21.5 kcal/mol in the temperature range 30-60°C. The same value was also found for

Figure 1. Arrhenius plot for thermal polymerization of AOM.

the overall activation energy when AOM was polymerized in acetone or carbon tetrachloride in the absence of any initiator of external origin. Though these thermal polymerizations were

shown in the preceding paper¹ to proceed by an anionic mechanism, the value of the activation energy is relatively high compared with that obtained for the usual anionic polymerization.

Figure 2 shows the effects of solvents and AOM concentration on the overall rate of the AOM polymerization at 60°C. As can be seen in Table I, the experimental value of the reaction order with respect to the AOM concentration changes considerably, depending on the kind of solvent. The solvents used fall into two groups: (A) Those in which the polymerization rate, R_p , is proportional to the 2nd up to 3rd power of the AOM concentration. (B) Those in which R_p is proportional to 3rd power or above of the concentration.

Figure 2. Dependence of rate on AOM concentration. Solvent: ○, benzene; ●, nitrobenzene; ◐, carbon tetrachloride; ◑, dichloromethane; ◒, chlorobenzene; △, acetone; ▲, THF; □, DMF.

Table I. Solvent effect on reaction order with respect to AOM concentration

Solvent	Reaction order
Benzene	2.3
Nitrobenzene	2.3
Carbon tetrachloride	2.3
Dichloromethane	2.4
Chlorobenzene	2.6
Acetone	3.5
Tetrahydrofuran	3.5
Dimethylformamide	3.8

Figure 3. *Syn-anti* isomerization reaction of AOM in various solvents at 60°C. Solvents: ●, none; ○, nitrobenzene; ◐, carbon tetrachloride; ◑, acetone; ◒, DMF.

The steps of initiation and termination generally determine the reaction order of a thermal polymerization. As can be seen in Figure 3, the rate of the isomerization is the same in all the solvents of group (A) as well as in bulk, but it considerably decreases in the solvents of group (B) such as acetone and DMF. These facts seem to indicate that the ionic dissociation step determines the reaction order in the thermal polymerization of AOM.

A. Kinetics for AOM Polymerization in Group (A) Solvents

The reaction order observed was 2.3–2.6 in benzene, chlorobenzene, nitrobenzene, dichloromethane, or carbon tetrachloride. Though the evidence for and the important role of the association of AOM molecules were described in the preceding paper,¹ complementary data are shown in Table II. AOM seems to be present in benzene mainly as dimer and trimer. The aggregation factor tends to increase with the increasing concentration of AOM.

On the basis of the qualitative investigation described in the preceding paper,¹ the kinetic scheme can be written as follows.

ionic dissociation

initiation

propagation

chain transfer to monomer

termination

k_i , k_p , k_{trm} , and k_t are the rate constants for the corresponding reactions, respectively, and K is the equilibrium constant for reaction (1). P_n^* and P_n represent the growing chain and the stable polymer, respectively, both having the polymerization degree of n . $(AOM)_1$ and $(AOM)_{2-3}$ denote the free AOM and the AOM aggregate with the aggregation factor of 2–3, respectively. $AOM^{\ominus}$ and $AOM^{\oplus}$ represent the following structural formulae.

Introducing the usual steady-state approximation with respect to P_n^* , we obtain

$$\begin{aligned} k_i[M^*][(AOM)_{2-3}] \\ = k_t[P_n^*] + k_{trm}[P_n^*][(AOM)_{2-3}] \quad (7) \end{aligned}$$

Therefore

$$[P_n^*] = \frac{k_i[M^*][(AOM)_{2-3}]}{k_t + k_{trm}[(AOM)_{2-3}]} \quad (8)$$

The overall rate, R_p , is

$$\begin{aligned} R_p &= k_p[P_n^*][(AOM)_{2-3}] \\ &= \frac{k_p k_i [M^*] [(AOM)_{2-3}]^2}{k_t + k_{trm} [(AOM)_{2-3}]} \quad (9) \end{aligned}$$

If the value of K is relatively small, the concentration of the activated AOM species $[M^*]$ is approximately represented by the equation

$$[M^*] = K[(AOM)_{2-3}] \quad (10)$$

This is because the free AOM produced by ionic dissociation (eq 1), in the case of trimer, can return immediately to its aggregated form. Substituting this value in eq 9, we obtain

$$R_p = \frac{k_p k_i K [(AOM)_{2-3}]^3}{k_t + k_{trm} [(AOM)_{2-3}]} \quad (11)$$

when $k_t \ll k_{trm}[(AOM)_{2-3}]$, we find $R_p \propto [(AOM)_{2-3}]^2$, and when $k_t \gg k_{trm}[(AOM)_{2-3}]$, we

Table II. Apparent molecular weight and aggregation factor obtained from cryoscopic measurements

Solvent	Concentration (molality)	Apparent molecular weight	Aggregation factor
Benzene	0.86	160	2.26
Benzene	1.80	183	2.57
Dioxane	0.85	77	1.08

Figure 4. Dependence of the degree of polymerization on AOM concentration.

find $R_p \propto [(AOM)_{2-3}]^3$. The experimental value was lying in the range from 2.3 to 2.6 when benzene and certain other solvents were used (Table I).

The degree of polymerization, $\bar{P}_n$, may be expressed as

$$\frac{1}{\bar{P}_n} = \frac{R_t + R_{trm}}{R_p} = \frac{k_t}{k_p[(AOM)_{2-3}]} + \frac{k_{trm}}{k_p} \quad (12)$$

Figure 4 shows a plot of $1/\bar{P}_n$ against $1/[(AOM)_{2-3}]$ in the AOM polymerization in carbon tetrachloride, from which the values of k_t/k_p and k_{trm}/k_p are determined to be 1.25×10^{-1} and 2.92×10^{-2} , respectively.

B. Kinetics for AOM Polymerization in Group (B) Solvents

At AOM concentrations above 7 mol/l, the overall reaction order with respect to the AOM concentration in acetone, tetrahydrofuran (THF), or DMF was found to be 3.5–3.8; these values are the slopes of the straight lines in Figure 2. But these linear relationships did not hold at a concentration range below 7 mol/l, though the data for this are not shown in Figure 2. Accordingly, the polymerization behavior of AOM in these three solvents seems to be different from that in the solvents of group (A). The infrared spectra of AOM in these solvents show an OH peak at 3400 cm^{-1} , indicating an infrequent occurrence of the aggregation. It is supported by the fact that the aggregation factor of AOM in dioxane is about 1. However, it

may be assumed that the AOM anion, the initiator, is still produced from small amounts of the aggregates. Thus, the polymerization scheme can be represented as follows.

ionic dissociation of dimer

ionic dissociation of trimer

initiation

propagation

chain transfer to monomer

termination

k_i' , k_p' , k_{trm}' , and k_t' are the rate constants for the corresponding reactions, respectively, and K_1 and K_2 are the equilibrium constants.

Introducing the usual steady-state approximation with respect to P_n^* , we obtain

$$k_i'[M^*][(AOM)_1] = k_t'[P_n^*] + k_{trm}'[P_n^*][(AOM)_1] \quad (19)$$

Therefore

$$[P_n^*] = \frac{k_i'[M^*][(AOM)_1]}{k_t' + k_{trm}'[(AOM)_1]} \quad (20)$$

The over-all rate, R_p' , is

$$R_p' = k_p'[P_n^*][(AOM)_1] = \frac{k_p'k_i'[M^*][(AOM)_1]^2}{k_t' + k_{trm}'[(AOM)_1]} \quad (21)$$

If K_1 and K_2 are relatively small, the concentration of the activated AOM species $[M^*]$ is in both cases of ionic dissociation

$$[M^*] = K_1 K_2 [(AOM)_1]^2 \quad (22)$$

Accordingly, from eq 21

$$R_p' = \frac{k_p' k_i' K_1 K_2 [(AOM)_1]^4}{k_t' + k_{trm}' [(AOM)_1]} \quad (23)$$

when $k_t' \ll k_{trm}' [(AOM)_1]$, we find $R_p' \propto [(AOM)_1]^4$, and when $k_t' \gg k_{trm}' [(AOM)_1]$, we find $R_p' \propto [(AOM)_1]^3$.

These results are concordant with the experimental values of the reaction order, 3.5 in acetone and THF, 3.8 in DHF.

The degree of polymerization, $\bar{P}_n$, may be represented as

$$\frac{1}{\bar{P}_n} = \frac{R_t' + R_{trm}'}{R_p'} = \frac{k_t'}{k_p' [(AOM)_1]} + \frac{k_{trm}'}{k_p'} \quad (24)$$

CONCLUSIONS

In the thermal polymerization of AOM, the apparent order of reaction with respect to the AOM concentration changes with the type of solvent used. The experimental value was 2.3–2.6 in benzene, nitrobenzene, carbon tetra-

chloride, dichloromethane, and chlorobenzene, and 3.5–3.8 in acetone, THF, and DMF. A consistent explanation for the polymerization behavior is as follows. Some of the AOM molecules in solution or in bulk associate with each other to form cyclic aggregates, mainly dimer and trimer, from which the initiating species is produced by their ionic dissociation. On the other hand, the kind of AOM species participate in the propagation process differs depending on the kind of solvent used. The AOM dimer and trimer participate in aggregate formation when benzene and other certain solvents are used; but free AOM plays this role in the case of acetone, THF, and DMF.

REFERENCES

1. S. Masuda and T. Ota, *Polym. J.*, **9**, 459 (1977).
2. S. Masuda, H. Kihara, and T. Ota, *Nippon Kagaku Kaishi (J. Chem. Soc. Jpn. J. Chem. Ind. Chem.)*, **1974**, 608.