

Studies on the Polymerization of Acrolein Oxime. XIII. Initial Processes of the Radiation-Induced Polymerization

Tadatoshi OTA,* Yoshikazu MORI,* Masami TANAKA,**
Harumi TAMAI,* and Seizo MASUDA*

*Department of Applied Chemistry, Faculty of Engineering, Tokushima University,
Tokushima 770, Japan.

**Faculty of Pharmaceutical Science, Tokushima University of Arts and Science,
Tokushima 770, Japan.

(Received February 29, 1980)

ABSTRACT: The radiation-induced polymerization of acrolein oxime was carried out at temperatures ranging from room temperature to -78°C , and the resulting low molecular products were analyzed by gas chromatography-mass spectrometry. Acetaldoxime, propionaldoxime, propenylhydroxylamines, dioximes etc. were obtained. Initial processes of the polymerization are discussed on the basis of these reaction products. The present work offers further corroborating evidence for the already-described postulation that an anionic mechanism is operative above room temperature, and a cationic mechanism is predominant below -23°C .

KEY WORDS Acrolein Oxime / O-Substituted Acrolein Oximes / N-Substituted Hydroxylamines / Dioximes / Radiation-Induced Polymerization / Gas Chromatography-Mass Spectrometry Analysis /

In our previous paper,¹ it was concluded that, on the basis of temperature dependence of the polymerization rate and the results of the copolymerization with acrylonitrile, the radiation-induced polymerization of acrolein oxime (AOM) proceeds by two mechanism, irrespective of the dryness of the sample or the kind of solvent used. An anionic mechanism is operative above room temperature, and a cationic mechanism is predominant below -23°C . The reaction in the intermediate temperature range proceeds by a competitive mechanism, and the rate of the anionic and cationic becomes equal at a temperature near -5°C . The object of this report is to clarify the initiation processes of the radiation-induced polymerization of AOM by determining or making an inference on the structure of the resulting products by means of gas chromatography-mass spectrometer.

EXPERIMENTAL

AOM was prepared and purified according to the method described previously.² The polymerization

was carried out at room temperature, 0°C (in NaCl-ice bath) and -78°C (in CO_2 -methanol bath) in sealed tubes. After a definite time of irradiation (40—50 h at $6 \times 10^5 \text{ r h}^{-1}$), the reaction mixture, in certain cases after the polymer was precipitated by pouring the contents into a large amount of ether and then removed by filtration, was concentrated, and then the residue was subjected to gas chromatography-mass spectrometry (GC-MS) measurements.

Gas chromatograms were obtained with a Shimadzu GC-7A under following experimental conditions: stationary phase, PEG-6000 (25%) supported on Cellite 545 or Silicon OV-17 (5%) supported on Gaschrom Q; programming rate, $5^{\circ}\text{C min}^{-1}$; programming column temperature, $50-200^{\circ}\text{C}$; carrier gas, N_2 , 50 ml min^{-1} .

GC-MS spectra were determined with a Shimadzu LKB-9000 mass spectrometer, equipped with a gas chromatographic inlet system. The ionizing potential was 70 eV and the ionizing current was $60 \mu\text{A}$.

Characterization of poly(acrolein oxime) (PAOM) was determined as described previously.³

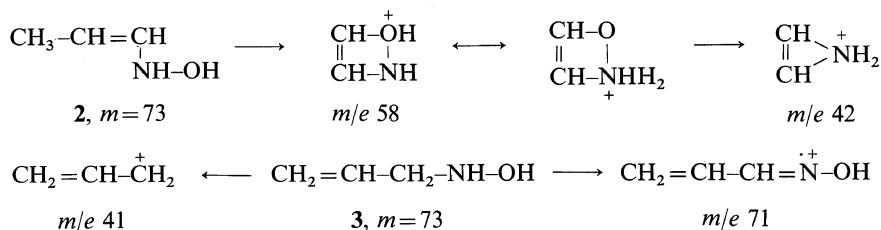
RESULTS AND DISCUSSION

When the radiation-induced polymerization of AOM at dose rate of $6 \times 10^5 \text{ r h}^{-1}$ was carried out at temperatures ranging from room temperature to -78°C for 20–40 h, several products, besides the polymer, having low molecular weight were formed. In order to clarify the initial processes of the polymerization by γ -irradiation, the structural determination of the products was carried out by GC-MS.

Gas chromatogram of the reaction mixture is shown in Figure 1(1), where the products having a higher retention temperature than unreacted AOM are omitted; PEG-6000 was used as the stationary phase. Similar chromatographic diagrams were obtained, irrespective of reaction conditions except for a weak GC-peak C of the products obtained at room temperature. Figures 1(2)–(4) show the gas

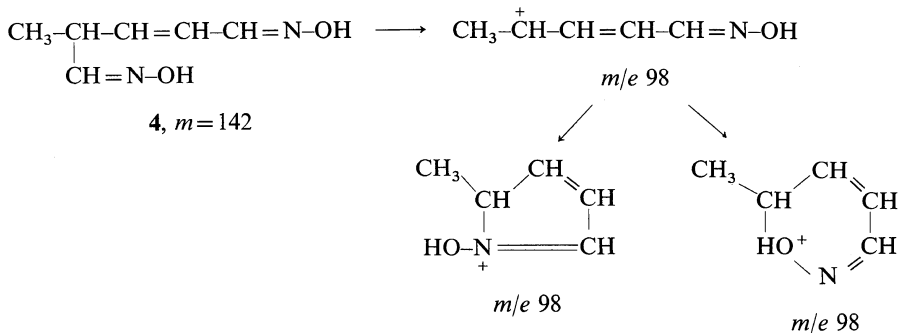
chromatograms (FID trace) of the products having a higher retention temperature than that of AOM, and Silicon OV-17 was used as the stationary phase. For simplification, the products corresponding to the respective peaks are given by the symbols A, B, C.

Compounds G and H gave mass fragmentations similar to each other and to AOM; that is, both are isomeric AOM, and the former is the *syn* form and the latter the *anti*. The mass spectra of compounds C, D, and E are shown in Figure 2, in which these compounds have molecular ion peaks at m/e 73. Compound D was identified as propionaldoxime (1) by comparing the spectrum with that of a previously obtained authentic sample. It is suggested that the spectra of compounds C and E correspond to *N*-1-propenylhydroxylamine (2) and *N*-2-propenylhydroxylamine (3), respectively. The fragmentation patterns may be represented as follows.



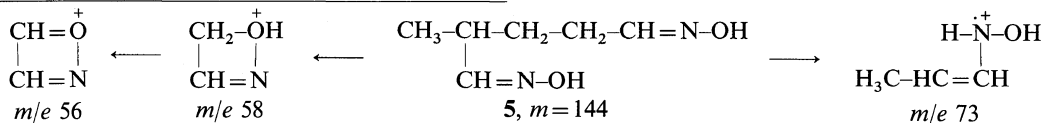
As shown in Figure 3, the spectra of compounds I and J, whose fragmentations are similar to each other, are characterized by the appearance of the

weak molecular ion peak m/e 142 and the base ion peak m/e 98; these compounds seem to be the *cis-trans* isomers of dioxime (4).



GC-peak K appears as a shoulder and is indistinguishable from GC-peak J (Figure 1). When dioxime (5) is assumed to be compound K, the mass

spectrum, shown in Figure 4(1), can be satisfactorily explained on the basis of the following fragmentation pattern.



Initial Processes of AOM Polymerization by γ -Ray

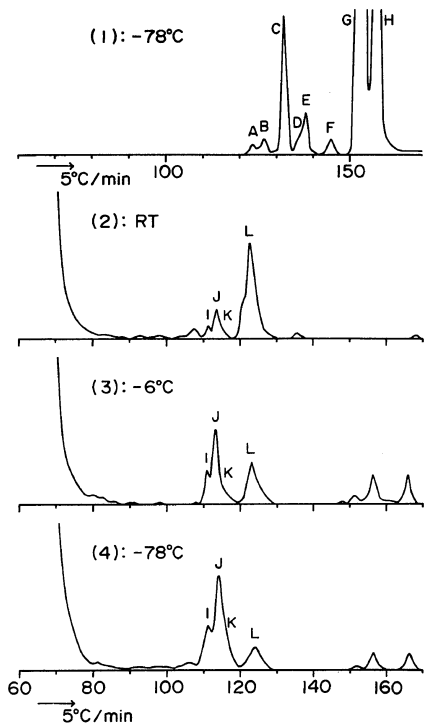


Figure 1. Gas chromatograms of reaction mixture. AOM was irradiated at dose rate of $6 \times 10^5 \text{ r h}^{-1}$ for 20–40 h in sealed tubes. (1) products having lower retention temperature than has unreacted AOM, (2)~(4) products having higher retention temperature than has unreacted AOM.

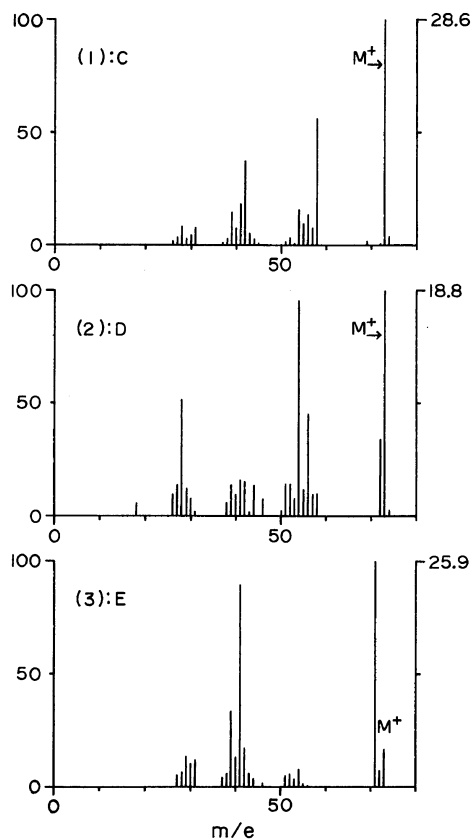


Figure 2. Mass spectra: (1), compound C; (2), compound D; (3), compound E.

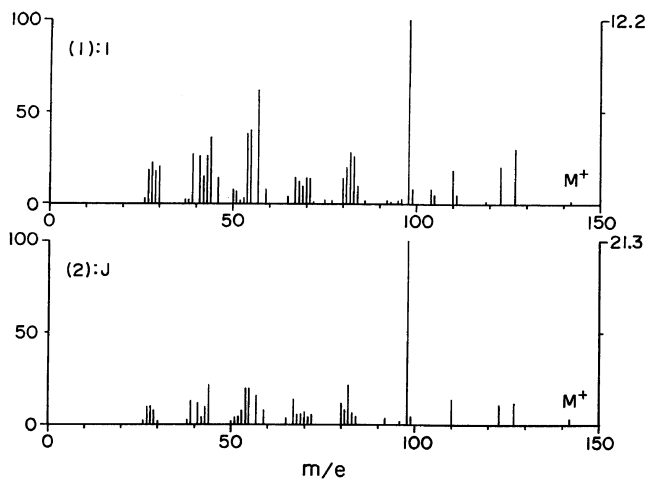


Figure 3. Mass spectra: (1), compound I; (2) compound J.

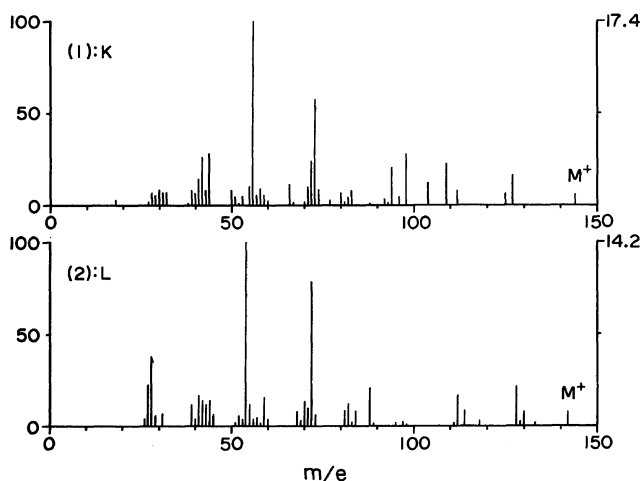
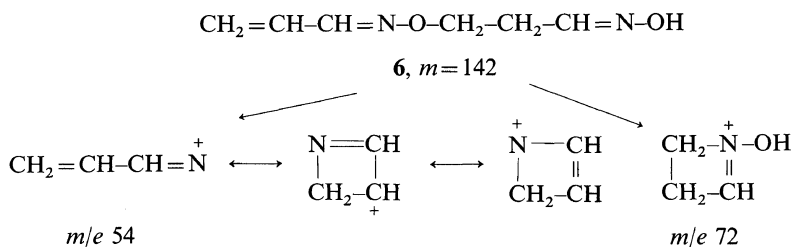


Figure 4. Mass spectra: (1), compound K; (2), compound L.

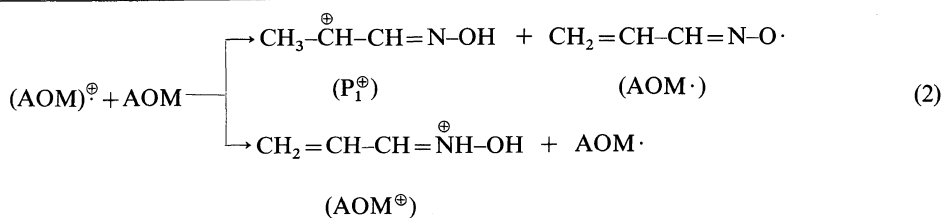
As reported previously,^{4,5} the thermal polymerization of AOM is initiated by an anion, $\text{CH}_2=\text{CH}-\text{CH}=\text{N}-\text{O}^-$, which arises from the dissociation of the molecular aggregates of the oxime. Thus, the oligomer obtained by thermal polymerization seems

to contain the AOM unit as its ending. Compound L agrees with one of the oligomers obtained thermally in the fragmentation of the mass spectrum, *i.e.*; this compound may be O-substituted AOM (6).



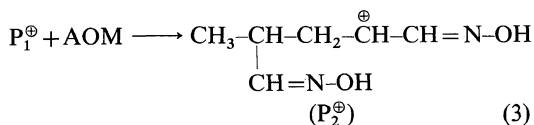
On the basis of the above-described six products (1–6), the initial processes of the radiation-induced polymerization are presented as follows.

For the cationic polymerization

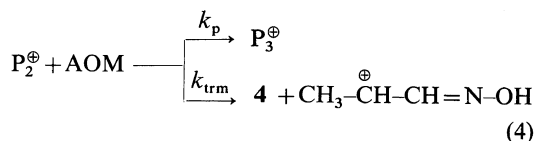


The resulting carbonium ion is able to initiate the polymerization, but the N^\oplus -type ion of AOM does not seem to participate in the propagation but only in the termination. The growing cation undergoes a chain-transfer reaction to give dioxime 4, and this is

the oligomer of the polymerization degree of 2.

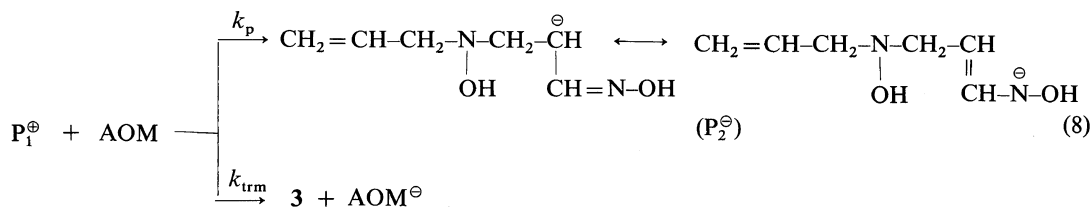
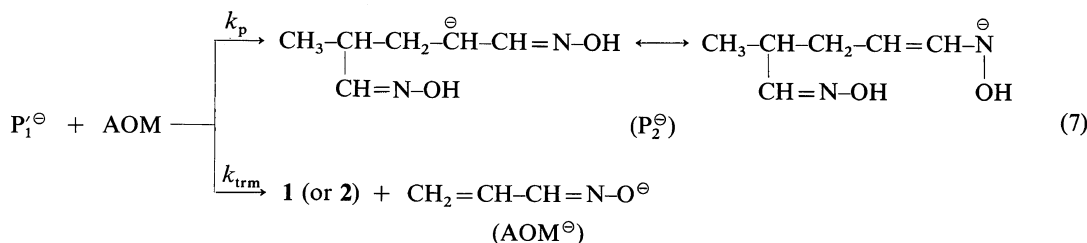
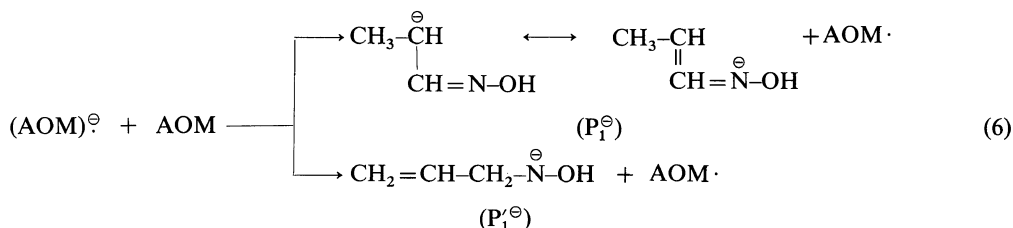
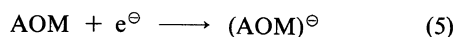


Initial Processes of AOM Polymerization by γ -Ray



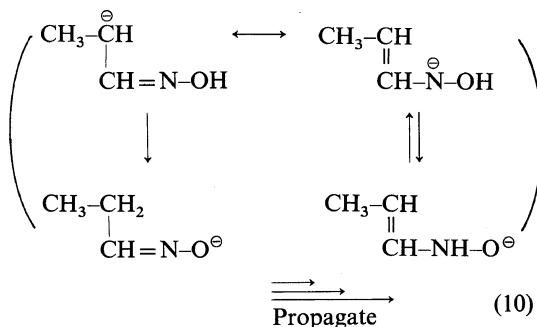
In our previous paper, we indicated that the chain-transfer reaction with a monomer is likely to take place in the polymerization by hydrochloric acid

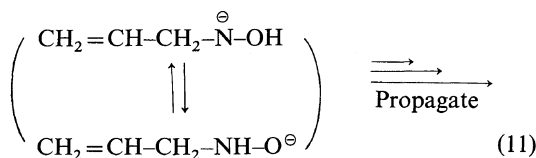
catalyst.⁶ The rate constants for the propagation and chain-transfer reactions were thus found to be 3.69×10^{-3} and $4.01 \times 10^{-4} \text{ mol}^{-1} \text{ s}^{-1}$, respectively. On the other hand, for the anionic polymerization,



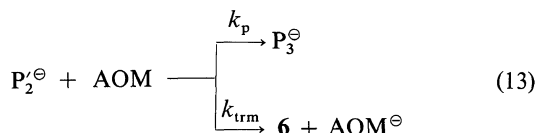
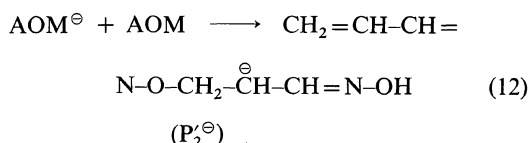
Because both P_1^\ominus and $P_1'^\ominus$, produced according to eq 6, are relatively stable, the anions are unlikely to propagate at low temperatures. Consequently, the cationic polymerization is predominant below -23°C . However, the anionic polymerization is by no means suppressed completely and the only carbanion-type species in P_1^\ominus seems to be anticipated in the propagation reaction at a low temperature. This assumption is supported by the fact that dioxime 5 (GC-peak K in Figure 1) is formed even by polymerization at -78°C . As the temperature increases, both P_1^\ominus and $P_1'^\ominus$ come to participate in the polymerization and the anionic mechanism is operative above room temperature. In the thermal

and catalyzed anionic polymerizations, hydrogen-transfer polymerization, in addition to vinyl polymerization, also occurs.³

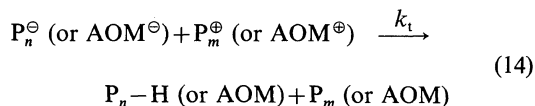




As described previously,^{4,5} the active species of the thermal and catalyzed anionic polymerizations is the AOM anion. The AOM anion, formed according to eq 7–9, is capable of initiating the polymerization and the resulting oligomer is O-substituted AOM **6**.



The rate of the reaction in eq 12 largely depends on temperature because **6** (GC-peak L) is subject to formation at elevated temperatures as can be seen from Figure 1. As reported previously,¹ the rate of the radiation-induced polymerization of AOM is proportional to the square-root of the dose rate. This means bimolecular termination by the transfer of a proton from the free cations to the free anions.



The resulting PAOM is soluble in dimethylformamide and partly soluble in water and tetrahydrofuran. Table I shows the characteristics of PAOM. It can be seen from the table that the molecular weight of PAOM decreases with a decrease in temperature. However, the temperature dependence of the molecular weight is not clear. On the other hand, as for the catalyst dependence, the molecular weights of PAOM prepared in the presence of certain catalysts were compared with each other.^{2–6} When PAOM obtained by γ -irradiation are compared with those obtained either thermally or catalytically and Table I illustrates that the characteristics of PAOM prepared at room temperature are similar to those of the polymer obtained anionically and that the characteristics of PAOM prepared at -78°C similar to those of the polymer obtained cationically. These findings are evidence that the anionic mechanism is predominant above the room temperature and that the cationic mechanism is operative below -23°C .

Since AOM is not polymerized radically but rather serves as an inhibitor for the radical polymerization of vinyl compounds,⁷ and since the radiation-induced polymerization of styrene or acrylonitrile is also inhibited in the presence of a small amount of AOM,¹ the AOM radical formed by an ion radical-molecule reaction (eq 2 and 6) and various other radicals by decomposition of excited molecules are incapable of initiating the AOM polymerization. However, these radicals can react with each other and with the AOM molecule to give inactive products having low molecular weight. The GC-MS technique may be capable of revealing the

Table I. Characteristics of PAOM

Polymerization conditions	Molecular weight	C=C bond content	Oxime group content	Ref
		% ^a	% ^b	
[HCl], 0.116 mol l ⁻¹ , in DCE, at 0°C	560	14.6	73.8	6
[BuLi], 0.452 mol l ⁻¹ , in DCE, at 30°C	660	48.4	44.8	3
No catalyst, in bulk, at 60°C	2100	42.0	46.0	4
γ -Irradiation, at room temperature	920	47.5	36.2	This work
γ -Irradiation, at -5°C	840	40.8	40.3	This work
γ -Irradiation, at -78°C	620	19.4	50.8	This work

^a % of structural units having a carbon-carbon double bonds per unit.

^b % of structural units having a pendant oxime group per unit.

presence of these radicals.

Compounds **A** and **B** were identified as the *syn* and *anti* forms of acetaldoxime by comparing their mass spectra with that of a previously obtained authentic sample. Because there was no resistance to γ -ray, **1** may possibly undergo radicalolysis according to eq 15. The resulting radical reacts with AOM to give acetaldoxime,

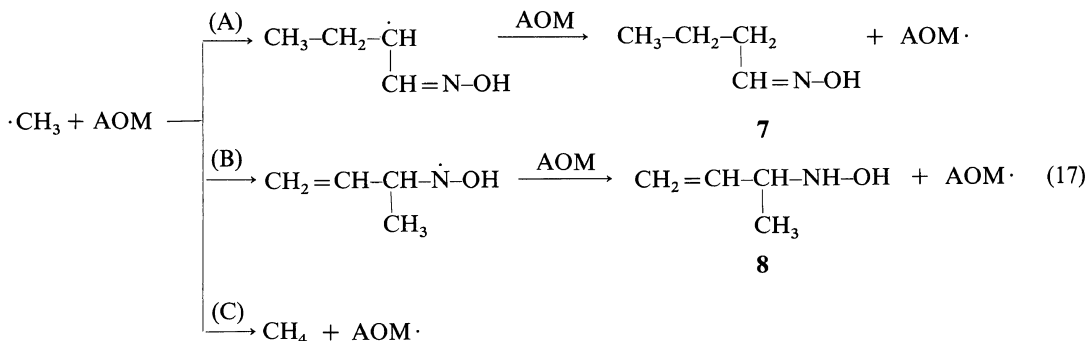
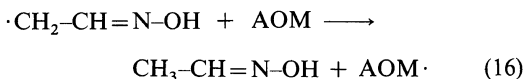
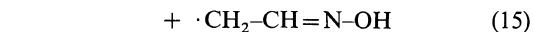


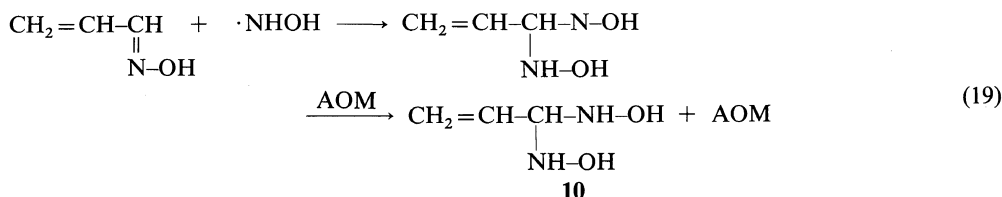
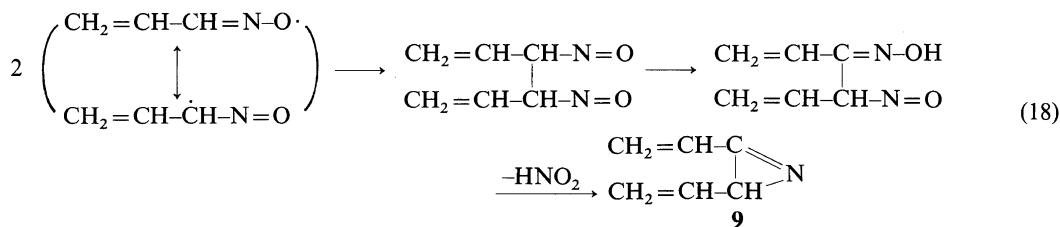
Figure 5(3) has a strong molecular ion peak m/e 87 and a base ion peak m/e 42. Thus, compound **F** was assumed to be *N*-1-methyl-2-propenylhydroxylamine **8**, since butylaldoxime **7** must have a strong peak m/e 59 corresponding to the McLafferty rearrangement.

Several peaks appear in the intermediate region between peaks **H** and **I** in Figure 1. The structure of two of these products could be determined by GC-MS analysis. The mass spectrum shown in Figure 6(1) suggests compound **9**, which is characterized by the appearance of a strong molecular ion peak m/e 93, and peaks m/e 66 and 39 corresponding to the lost of one or two vinyl fragments. Compound **9**



On the other hand, when the resulting methyl radical reacts with AOM, there are three possible paths (for the reaction to take),

may possibly be formed by the recombination of AOM radicals (eq 18). When *N*-1-hydroxylamino-2-propenylhydroxylamine **10** is assumed, the mass spectrum shown in Figure 6(2) can be satisfactorily explained. This demonstrates that the molecular ion m/e 104 is lost as a vinyl fragment in the formation of mass 77. Compound **10** may be produced according to eq 19. The formation of compound **10** suggests that *N*-substituted hydroxylamine, formed in the initial stage of the anionic polymerization, undergoes radiolysis to give $\text{R}\cdot$ and $\cdot\text{NHOH}$ radicals. However, the presence of these products, related to the $\text{R}\cdot$ radical, could not be detected by GC-MS measurements.



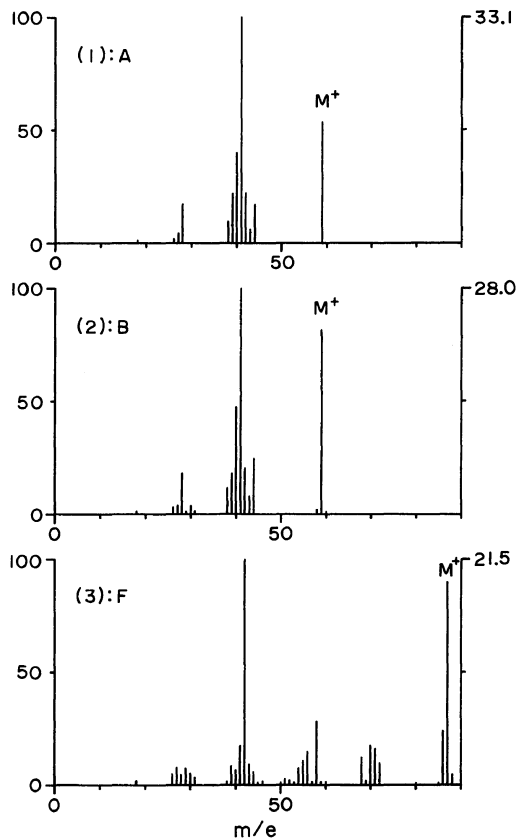
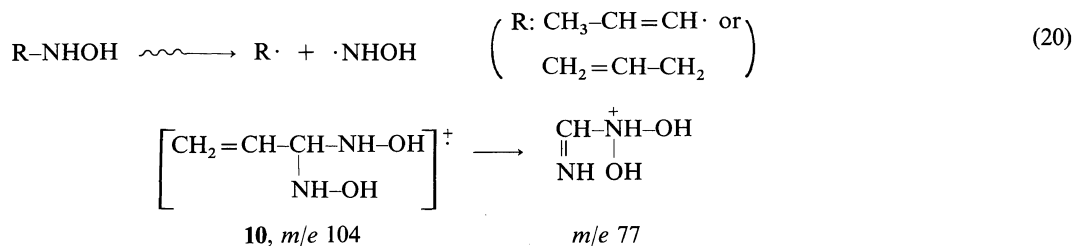


Figure 5. Mass spectra: (1), compound A; (2), compound B; (3), compound F.

In the case of the radicals-AOM molecular action, even though the transfer of a hydrogen radical from AOM to the radicals mainly occurs because of the stability of the resulting iminoxy-type radical of the oxime, the radicals seems to attack the oxime carbon rather than the vinyl carbon, of the oxime during process of the addition reaction.

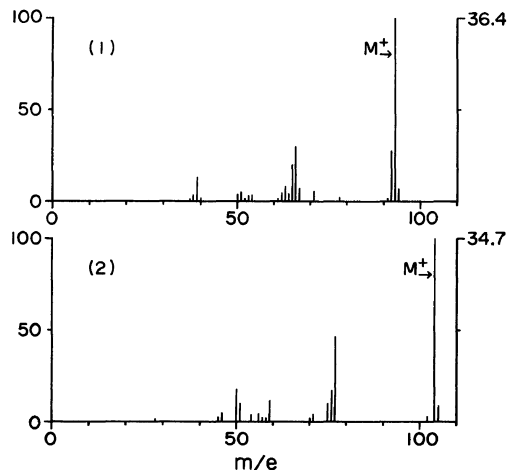


Figure 6. Mass spectra: (1), compound 9; (2), compound 10.

Acknowledgement. A part of this work has been carried out under the Visiting Researchers Program of Kyoto University Research Reactor Institute. The authors wish to thank Assistant Professor Hitoshi Yamaoka for his continuing interest and encouragement.

REFERENCES

1. S. Masuda, H. Tamai, M. Torii, M. Tanaka, and T. Ota, *Polym. J.*, **11**, 213 (1979).
2. S. Masuda, H. Kihara, and T. Ota, *Nippon Kagaku Kaishi*, 608 (1974).
3. S. Masuda, M. Tanaka, and T. Ota, *Polym. J.*, **10**, 387 (1978).
4. S. Masuda and T. Ota, *Polym. J.*, **9**, 459 (1977).
5. S. Masuda and T. Ota, *Polym. J.*, **9**, 465 (1977).
6. S. Masuda and T. Ota, *Polym. J.*, **10**, 397 (1978).
7. S. Masuda and T. Ota, *Kobunshi Ronbunshu*, **31**, 61 (1974).