

Polymerization of Acrylonitrile with DMSO—H₂O₂—Fe³⁺ System

Hiroshi MINATO* and Hiroshi FURUE

*Department of Chemistry, International Christian University,
Mitaka, Tokyo 181, Japan.*

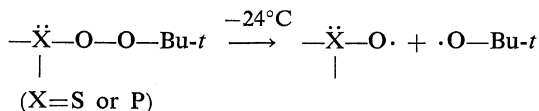
(Received November 15, 1973)

KEY WORDS Acrylonitrile / Dimethyl Sulfoxide / Hydrogen Peroxide / Ferric Chloride / Radical Polymerization /

Methods for generation of free radicals at low temperatures in homogeneous media have been investigated in our laboratories.¹⁻³ Such mixtures as 1) CISO₂Me + *t*-BuOOH, 2) MeOSOMe + *t*-BuOOH + HCl, and 3) PCl₃ + *t*-



BuOOH were found to be effective for initiating the polymerization of vinyl chloride,² styrene, vinyl acetate, or methyl methacrylate³ at -24°C. Plausible intermediates which are very unstable even at -24°C may be the ones possessing the following structures.



As an extension of these studies, the use of dimethyl sulfoxide (DMSO) in place of dimethyl sulfide was examined, but free radical polymerization was not initiated.

However, when a small amount of FeCl₃ was added to a DMSO—H₂O₂—acrylonitrile mixture, rapid polymerization took place. Therefore, the initiating systems consisting of DMSO, a hydroperoxide, and a metal ion have been investigated; the results are described in this paper.

The rate of polymerization was found to be greatly increased by the addition of a small amount of water. Therefore, the effect of water concentration was studied. The results are shown in Table I. Since a 30-% aqueous H₂O₂ solution was used, the system contained 5.27-mmol H₂O per 100-mmol AN or DMSO, even

when no additional water was added. The rate of polymerization rapidly increases when water is added, and is highest when 170 mmol of water is present in a mixture of 100 mmol of AN and 100 mmol of DMSO. The role of water for this rate enhancement cannot be easily explained.

The effect of the amount of FeCl₃·6H₂O on the rate of polymerization was also studied. The results are shown in Table II. When no FeCl₃ was added, no polymerization occurred. The rate of polymerization increased with the FeCl₃ concentration, but use of too much FeCl₃ is not desirable for practical purposes, since use of 0.168-mmol FeCl₃ per 100-mmol AN resulted in the formation of a slightly brownish polymer.

Table I. Effect of amounts of water on the rates of polymerization of acrylonitrile^a

| | | | | | | |
|-----------------------|------|------|------|-----|-----|-----|
| Water, mmol | 5.27 | 49.1 | 89.2 | 170 | 290 | 411 |
| Conversion in 1 hr, % | 10 | 13 | 30 | 78 | 72 | 56 |

^a Reaction mixture: Acrylonitrile, 100mmol; DMSO, 100 mmol; H₂O₂, 1.2 mmol; FeCl₃·6H₂O, 0.080 mmol; water. The mixture was allowed to polymerize for 60 min at 30°C.

Table II. Effect of amounts of FeCl₃·6H₂O on the rates of polymerization of acrylonitrile^a

| | | | | | | | |
|--|---|-------|-------|-------|-------|-------|-------|
| FeCl ₃ ·6H ₂ O, mmol | 0 | 0.013 | 0.019 | 0.035 | 0.056 | 0.080 | 0.168 |
| Conversion in 1 hr, % | 0 | 11 | 31 | 46 | 63 | 79 | 85 |

^a Reaction mixture: Acrylonitrile, 100mmol; DMSO, 100 mmol; H₂O₂, 2.0 mmol; H₂O, 170 mmol; FeCl₃·6H₂O. The mixture was allowed to polymerize for 60 min at 30°C.

* Present address: Department of Chemistry, Tokyo Metropolitan University, Setagaya, Tokyo 158, Japan.

Table III. Effect of amounts of H₂O₂ on the rates of polymerization of acrylonitrile^a

| | | | | | | |
|--------------------------------------|---|-----|-----|-----|-----|-----|
| H ₂ O ₂ , mmol | 0 | 0.4 | 0.8 | 1.2 | 1.6 | 2.0 |
| Conversion in 1 hr, % | 0 | 36 | 65 | 78 | 78 | 79 |

^a Reaction mixture: Acrylonitrile, 100mmol; DMSO, 100 mmol; H₂O, 170 mmol; FeCl₃·6H₂O, 0.080 mmol; H₂O₂. The mixture was allowed to polymerize for 60 min at 30°C.

The effect of the amount of H₂O₂ on the polymerization rate was studied, and the results are shown in Table III. When 1.2-mmol H₂O₂ was present per 100-mmol AN or DMSO, the polymerization was 78% complete in 1 hr, and the use of greater amounts of H₂O₂ did not result in any significant increase in conversion.

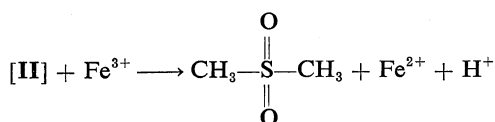
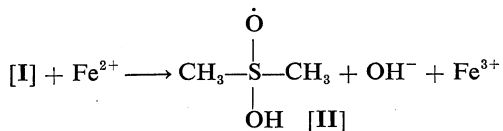
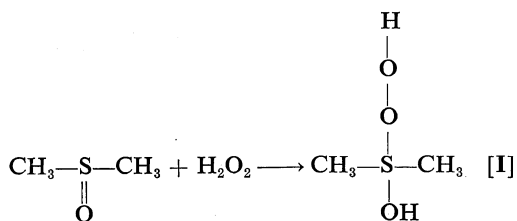
In order to study the effect of changes of temperature on the rate of polymerization, the following composition (concn in mmol) was chosen: AN, 100; DMSO, 100; H₂O₂, 1.2; FeCl₃·6H₂O, 0.03; H₂O, 170. The initial rates of polymerization (soon after the beginning of polymerization) were 0.12%/min at 20°C, 0.34%/min at 30°C, and 1.20%/min at 40°C. The apparent activation energy calculated was 20.8 kcal/mol.

The polyacrylonitrile obtained at 20°C and 30°C was dissolved in *N,N*-dimethylformamide, and the viscosity of the solution was determined at 25.0°C. From η_{sp}/C and η_{inh} , the intrinsic viscosity was obtained; for the PAN obtained at 20°C, the intrinsic viscosity $[\eta]=5.6$ and the average molecular weight is 30400, and for the PAN obtained at 30.0°C, $[\eta]=5.0$ and the average molecular weight is 26200.

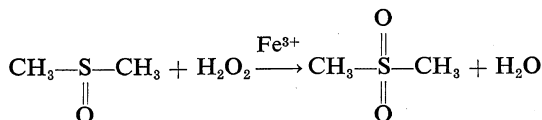
When 30-% H₂O₂ was mixed with DMSO containing a small amount of FeCl₃·6H₂O, considerable heat was evolved. From the DMSO solution colorless needles were obtained, which melted at 109°C; these were identified as dimethyl sulfone.

No reaction took place between H₂O₂ and DMSO, DMSO and Fe³⁺, or Fe³⁺ and H₂O₂. Polymerization is initiated only when all three components are present. Since termolecular collisions are less probable, it is likely that two components form a complex, which then reacts with the third component.

A plausible mechanism of the reaction in the DMSO—H₂O₂—Fe³⁺ system is the following.



Overall reaction should be the following.



Just like a hydrated formaldehyde molecule formed in an aqueous formaldehyde solution, a DMSO—H₂O₂ adduct may be formed by the nucleophilic attack of the oxygen atom of H₂O₂ to the positively charged sulfur atom of DMSO. The O—O bond of the adduct [I] may be more readily cleaved than that of hydrogen peroxide itself due to the resonance stabilization of the radical [II] by the lone pair on the sulfur atom of [II] (see the introduction, and also ref 2).

Another possibility is the formation of a complex from Fe³⁺, DMSO, and H₂O₂, the latter two being the ligands in a manner analogous to the formation of a Fe³⁺—polyamine complex.^{1(a)}

The literature notes that alkyl sulfoxides are not oxidized with neutral hydrogen peroxide, although alkyl sulfides are oxidized with this agent to alkyl sulfoxides.⁴ However, it is now clear that dimethyl sulfoxide can be oxidized with neutral hydrogen peroxide if a small amount of Fe³⁺ is present, and the oxidation involves some free-radical intermediates which initiate free-radical polymerization.

This initiating system is quite unique in that the solvent (DMSO) is the reducing agent. Thus, when a monomer is dissolved in a solvent

(DMSO) containing a small amount of FeCl₃·6H₂O and some H₂O₂ is added, free-radical polymerization starts as if H₂O₂ spontaneously decomposed in the presence of Fe³⁺.

Use of other metal salts and hydroperoxides was examined. As for the metal salts, FeCl₃ and FeCl₂ were equally effective, CuSO₄ was somewhat less, and CoCl₂ was not effective. When 0.080 mmol of FeCl₃, FeCl₂, CuSO₄ or CoCl₂ was added to a mixture of AN (100 mmol), DMSO (100 mmol), H₂O (170 mmol), and H₂O₂ (1.2 mmol), the conversion in 1 hr at 30°C was 78, 75, 30, and 0%, respectively.

As for the hydroperoxides, hydrogen peroxide was most effective, *t*-butyl hydroperoxide was somewhat less, and cumyl hydroperoxide was much less effective. When 1.2 mmol of hydrogen peroxide, *t*-butyl hydroperoxide, or cumyl hydroperoxide was added to a mixture of AN (100 mmol), DMSO (100), H₂O (170), and FeCl₃ (0.080), the conversion in 1 hr at 30°C was 78, 40, and 5%, respectively.

EXPERIMENTAL

Dimethyl sulfoxide was purified by distillation. Acrylonitrile was passed through a silica gel column in order to remove inhibitors. Commercial hydrogen peroxide (30%) was used without further purification.

A glass tube containing a mixture of DMSO,

acrylonitrile and FeCl₃·6H₂O under nitrogen was placed in a constant temperature bath. When hydrogen peroxide was added and the solution was mixed, polymerization started. Polymerization was stopped by the addition of water containing hydroquinone; the precipitated polymer was washed with methanol and then dried in an evacuated desiccator.

For the determinations of the molecular weights of the polymer, polyacrylonitrile was dissolved in *N,N*-dimethylformamide, and the viscosity of the solutions obtained was measured at 25.0°C.

Acknowledgment. Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

REFERENCES

1. (a) H. Minato and R. Hisada, *J. Polym. Sci., Part A-1*, **7**, 735 (1969); (b) H. Minato, M. Oku, and N. Higosaki, *Bull. Chem. Soc. Japan*, **43**, 500 (1970); (c) H. Minato and M. Iwakawa, *Polymer J.*, **6**, 234 (1974).
2. H. Minato, H. Iwai, K. Hashimoto, and T. Yasui, *J. Polym. Sci., Part C*, **23**, 761 (1968).
3. H. Minato and H. Ohta, *Polymer J.*, **5**, 181 (1973).
4. L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," John Wiley & Sons, Inc., New York, N.Y., 1967, p 471.