

NO₂-Initiated Polymerization of Acrylonitrile

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Synopsis

The polymerization of acrylonitrile initiated with NO₂ in dimethyl sulfoxide has been studied. The kinetics of polymerization was followed gravimetrically. The effect of monomer, initiator, and temperature on the rate of polymerization has been given. The overall activation energy was found to be 18.06 kcal·mol⁻¹. The polymerization with NO₂ appears to be initiated by a free-radical mechanism.

INTRODUCTION

It is recalled that the free radicals which are commonly used for initiation of polymerization are formed *in situ* by irradiation, electrochemical, or thermal decomposition (e.g., of peroxide), etc., reactions. However, it has been recently found that NO₂, a paramagnetic molecule, successfully initiates the polymerization of acrylamide and methylmethacrylate.¹⁻³ Preliminary investigation on NO₂-initiated polymerization of acrylonitrile (AN) in *N,N*-dimethylformamide (DMF) has been reported.⁴ The present paper describes the further study of NO₂-initiated polymerization of acrylonitrile (AN) in dimethyl sulfoxide (DMSO).

EXPERIMENTAL

Materials

Acrylonitrile (British Drug House Chemicals, Ltd. Poole, England) was washed with 5% NaOH followed by 5% phosphoric acid solutions and finally with de-ionized water. Acrylonitrile was then distilled under reduced pressure and stored at 0°C. Dimethyl sulfoxide (DMSO) and *N,N*-dimethylformamide (DMF) were fractionally distilled under reduced pressure at room temperature to get pure samples. Methanol was fractionally distilled, and only the middle fraction was collected. All other reagents were of analytical grade and were used without further purification. Pure and dry NO₂ was prepared by heating dried lead nitrate. Its concentration in DMSO was determined volumetrically by treating the solution with excess of sodium hydroxide solution and titrating the resulting solution with acidified KMnO₄ solution.⁵

Polymerization Method

Polymerization of acrylonitrile (AN) was carried out in glass vials which were tightly stoppered under inert atmosphere of nitrogen and thermostated. The

total volume of the reaction mixture was 5 mL. The kinetics of the polymerization was followed gravimetrically. After the measured period of time, the polymerizing mixture was poured into a large volume of ice-cold methanol to precipitate the polymer formed, filtered off, dried in an air oven, and weighed.

Viscosity measurements of polymers were carried out in DMF at 25°C by an Ostwald viscometer. The number-average molecular weight of polymer was obtained using the following relation⁶:

$$[\eta] = 3.93 \times 10^{-4} \bar{M}_n^{0.75}$$

RESULTS AND DISCUSSION

Bulk Polymerization

During the bulk polymerization of AN, with NO₂, the sudden appearance of a haze is thought to correspond to the onset of polymerization after an induction period; the polymer precipitates out and is insoluble in the monomer. The whole reaction mixture turns into a hard white solid mass. The insolubility of the polymer in DMF appears to be due to crosslinking. The results of bulk polymerization of AN have been shown in Table I.

Solution Polymerization

Effect of Monomer and Initiator

AN was polymerized with NO₂ in DMSO. It is noted that the reaction mixture becomes pale yellow, after an induction period. Since an induction period is usually associated with impurities in the monomer, efforts were made to obtain acrylonitrile (AN) of the highest purity by the above-mentioned method. Infrared and ultraviolet spectra did not disclose impurities that might influence rates. Attempts were made to eliminate the induction period by subjecting monomer to a more elaborate purification method, but the rate curves were not affected by these treatments. However, further study of the induction period was not carried out. The reaction mixture remains homogeneous during the course of reaction. The polymer was precipitated with methanol and filtered as a pale yellow powder. The polymer is soluble in H₂SO₄, DMF, DMSO, dimethylsulfone, and succinonitrile but insoluble in ethanol, benzene, and toluene.

TABLE I
Bulk Polymerization of AN (concn: 15.09 mol·dm⁻³) with NO₂ (concn: 10.0 × 10⁻² mol·dm⁻³)
at Room Temperature

Time (day)	Polymer conversion		Solubility of polymer in DMF
	<i>g</i>	(%)	
1	0.07	1.74	Soluble
2	0.26	6.5	Soluble
3	0.35	9.0	Soluble
4	0.52	13.0	Sparingly soluble
5	0.70	17.4	Insoluble

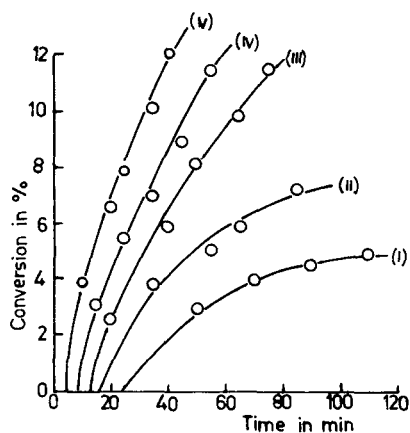


Fig. 1. Conversions in the solution polymerization of AN with NO₂ (concn: $10.0 \times 10^{-2} \text{ mol-dm}^{-3}$) at 50°C in DMSO as function of time at different [AN]: (I) 6.03 mol-dm^{-3} ; (II) 7.54 mol-dm^{-3} ; (III) 9.05 mol-dm^{-3} ; (IV) $10.05 \text{ mol-dm}^{-3}$; (V) $12.07 \text{ mol-dm}^{-3}$.

The reaction profiles as a function of the monomer and initiator concentrations are presented in Figure 1 and 2, which shows that polymer conversion increases with the increase of the concentration of monomer and initiator. The initial rate of polymerization, R_{in} [extrapolated from conversion (%)–time curves], increases linearly with the first power of the monomer concentration and the square root of the initiator concentration, as shown in Figures 3 and 4, respectively. Figure 3 indicates that R_{in} is zero when the monomer concentration is below 5.25 mol-dm^{-3} . It was experimentally observed that the polymer formation was negligible and a very long induction period appeared when either the monomer or initiator concentration were less than 5.25 mol-dm^{-3} or $7.0 \times 10^{-2} \text{ mol-dm}^{-3}$, respectively. Therefore, within the experimental range of monomer and initiator concentration employed here, the initial rate of polymerization may be roughly given by the following rate expression:

$$R_{in} = K[M][I]^{1/2}$$

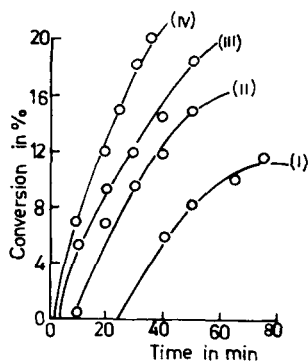


Fig. 2. Time-conversion curves for the polymerization of AN (concn: 9.05 mol-dm^{-3}) with different concentrations of NO₂ in DMSO at 50°C: (I) $10.0 \times 10^{-2} \text{ mol-dm}^{-3}$; (II) $20.0 \times 10^{-2} \text{ mol-dm}^{-3}$; (III) $30.0 \times 10^{-2} \text{ mol-dm}^{-3}$; (IV) $40.0 \times 10^{-2} \text{ mol-dm}^{-3}$.

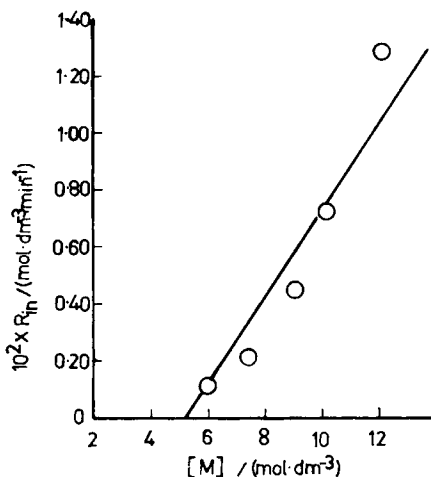


Fig. 3. Influence of the concentration of AN on initial rate of polymerization (R_{in}) with NO_2 (concn: $10.0 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$) at 50°C in DMSO.

It has been reported that the free-radical polymerization also exhibits such first-order dependence on the monomer and half-order dependence on the initiator concentrations.⁷ The dependence of the rate of polymerization (R_{in}) on the square root of the initiator concentration indicates that the termination reaction may take place by a bimolecular mechanism.

Effect of Temperature

The effect of temperature on the PAN formation was also investigated. Typical conversion (%)–time curves are shown in Figure 5. There is only 22.82% conversion after 35 min of reaction time at 70°C . The overall activation energy of the polymerization was found to be $18.06 \text{ kcal}\cdot\text{mol}^{-1}$, which is in the same order, as obtained in other free-radical polymerization systems of AN.⁸

Proof for Free-Radical Mechanism

It was found that the polymer formation decreases drastically in the presence of *p*-benzoquinone, a free-radical inhibitor. When its concentration was made

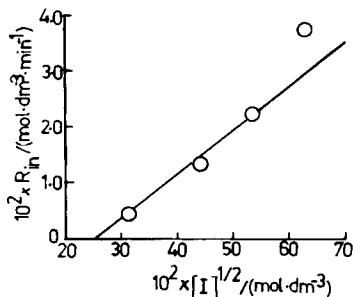


Fig. 4. Influence of the $[\text{NO}_2]$ on the initial rate of the polymerization of AN (concn: $9.05 \text{ mol}\cdot\text{dm}^{-3}$) at 50°C in DMSO.

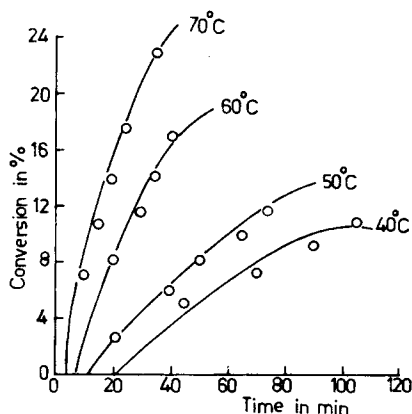


Fig. 5. The effect of the reaction temperature on the polymerization of AN (concn.: 9.05 mol-dm^{-3}) at 50°C in DMSO, $[\text{NO}_2] = 10.0 \times 10^{-2} \text{ mol-dm}^{-3}$.

equal to that of NO₂, the polymerization was totally inhibited, as is evident from the data shown in Table II. Therefore, it appears that the polymerization may occur via a free-radical mechanism.

Molecular Weight of Polymers

The molecular weight (\bar{M}_n) of the polymers increase with increasing initial monomer concentration, while they decrease with the increase in the initiator concentration. This is in accordance with expectation for a free-radical propagation mechanism with bimolecular termination between growing chains. However, the molecular weights are independent of the polymer conversion, as is seen from Table III.

Color of Polymer

In the course of the bulk polymerization of AN, we have observed that the polymers are a white powdery mass whereas, in the solution polymerization, the color of polymer is yellow. At a lower temperature (40°C), light-colored polymers were obtained. However, it has been found that when polymer formed in DMSO was precipitated with methanol and dissolved in DMF and was washed with H₂SO₄ and reprecipitated with methanol, the color of polymer changes from yellow to white.

TABLE II
Effect of *p*-Benzoquinone on NO₂-Initiated Polymerization of AN^a

[<i>p</i> -Benzoquinone] $\times 10^2 \text{ (mol-dm}^{-3}\text{)}$	0	2.5	5.0	10.0
Polymer conversion (%)	11.52	1.26	0.35	Nil

^a Conditions: $[\text{AN}] = 9.05 \text{ mol-dm}^{-3}$; $[\text{NO}_2] = 10.0 \times 10^{-2} \text{ mol-dm}^{-3}$ in DMSO. Time of polymerization: 75 min at 50°C .

TABLE III
Molecular Weights of Polymers Obtained from NO₂-Initiated Polymerization of AN in DMSO at 50°C

[AN] (mol-dm ⁻³)	10 ⁻² × [NO ₂] (mol-dm ⁻³)	Polymer conversion (%)	[η] (dL-g ⁻¹)	$\bar{M}_n \times 10^{-4}$
6.03	10.0	5.67	0.03	0.0323
7.54	10.0	7.41	0.11	0.1831
9.05	10.0	11.52	0.20	0.4062
10.05	10.0	11.44	0.29	0.8240
12.07	10.0	12.14	0.44	1.1620
9.05	20.0	15.02	0.17	0.3271
9.05	30.0	18.76	0.12	0.2056
9.05	40.0	20.10	0.08	0.1198

CONCLUSION

These results indicate that NO₂ is an excellent initiator for the polymerization of AN. Copolymerization of AN with acrylamide initiated by NO₂ in DMSO has also been carried out, to gain a thorough understanding of polymerization, and will be published elsewhere.

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