

NO₂-Initiated Polymerization of Acrylamide in Dimethylsulfoxide

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Synopsis

NO₂-initiated polymerization of acrylamide in dimethylsulfoxide was carried out. The dependence of monomer, initiator concentrations, and temperature on polymer yield and initial rate of polymerization was studied. The overall activation energy of polymerization was calculated to be about 15 kcal mol⁻¹. The copolymerization of acrylamide with methyl methacrylate was also studied. The kinetic mechanism of polymerization was proposed.

INTRODUCTION

Earlier acrylamide (AM) was polymerized with nitrogen dioxide (NO₂) in *N,N'*-dimethylformamide (DMF) and water.^{1,2} This dissertation describes the results of polymerization of AM with NO₂ in dimethylsulfoxide (DMSO). The copolymerization of AM with methylmethacrylate (MMA) in dilute solution of NO₂ in DMSO has also been carried out to support the proposed kinetics mechanism of polymerization.

EXPERIMENTAL

Materials

Acrylamide (AM) was recrystallized from methanol. Methyl methacrylate (MMA) was washed with 5 wt % caustic soda solution followed by distilled water and fractionally distilled in vacuum to get pure samples. Dimethylsulfoxide (DMSO) was fractionally distilled under reduced pressure at room temperature and only the middle fraction was collected. All other reagents were of analytical grade and were used without further purification. Dry and pure NO₂ was prepared by heating dried lead nitrate. The concentration of NO₂ in DMSO was determined volumetrically.³

Polymerization Method

AM was polymerized in separate glass vials which were tightly stoppered and thermostated. The total volume of the reaction mixture was 5 mL. The kinetics of polymerization was followed gravimetrically. The polymer as formed was precipitated by pouring the reaction mixture in ice-cold meth-

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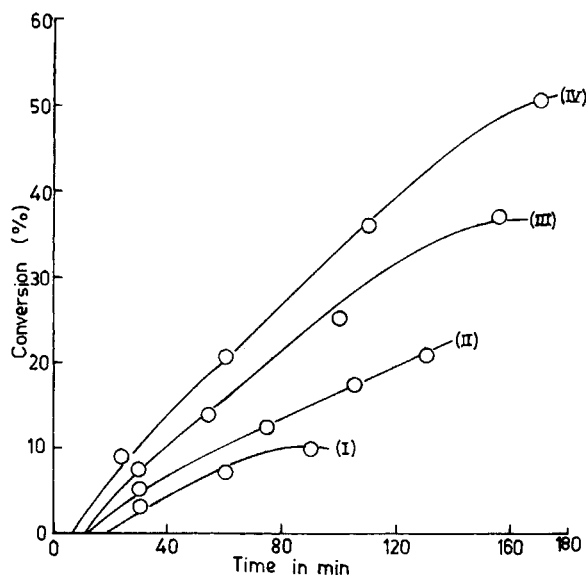


Fig. 1. Polymer conversion as a function of time and acrylamide (AM) concentration with a fixed concentration of NO_2 ($[\text{NO}_2] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$) in dimethylsulfoxide (DMSO) at 50°C . Concentration of AM: (I) 1.0 mol dm^{-3} ; (II) 2.0 mol dm^{-3} ; (III) 3.0 mol dm^{-3} ; (IV) 4.0 mol dm^{-3} .

anol. The polymer was filtered off, dried in an air oven, and weighed. The same procedure was followed for copolymerization.

The viscosity measurements of polymers were carried out in water at 30°C by an Ostwald viscometer. The average molecular weight of polymer was obtained using the following relationship⁴:

$$[\eta] = 3.73 \times 10^{-4} \bar{M}^{0.66} \quad \text{in water at } 30^\circ\text{C}.$$

RESULTS AND DISCUSSION

Dependence of Monomer and Initiator

During the polymerization of acrylamide (AM) with NO_2 in dimethylsulfoxide (DMSO), the polymer precipitates as white mass after some induction period as in DMF. In most solvent-initiator systems the precipitation limits the maximum molecular weight which can be achieved.⁵ We presume that the occurrence of the induction period is possibly due to residual oxygen and impurities present in the polymerizing mixture. Furthermore, it was found that induction period could not be eliminated even after use of inert atmosphere of nitrogen in the polymerization.² However, further detailed study in this regard has not been carried out.

The time-conversion curves for different initial monomer concentrations and a fixed initiator concentration at 50°C are shown in Figure 1. The initial rate of polymerization, R_{in} (extrapolated from time-conversion curve), increases linearly with first power of monomer concentration, as shown in Figure 2. A reaction profile of conversion to polymer as a function of po-

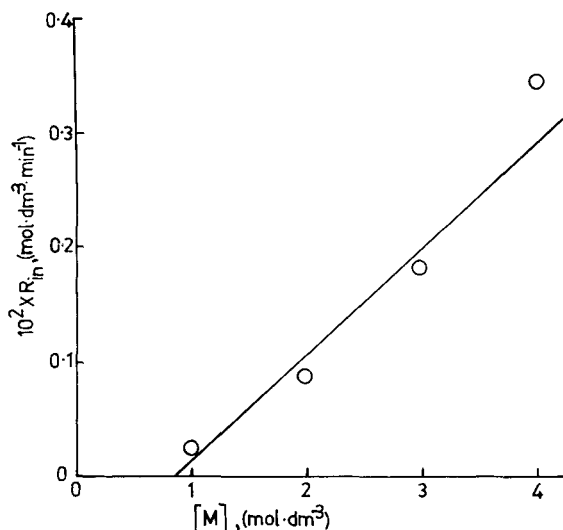


Fig. 2. Dependence of the initial rate of polymerization (R_{in}) on monomer concentration AM in DMSO at 50°C, $[NO_2] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$.

lymerization time at different concentrations of NO₂ and a fixed concentration of AM was given in Figure 3, which shows an increase of conversion to polymer with time and the initiator concentration. The R_{in} increases linearly with the square root of the initiator concentration as shown in Figure 4. 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.

The kinetic mechanism of polymerization was proposed as follows: NO₂ is a gaseous free radical, which initiates successfully the polymerization of acrylamide (AM), a plausible mechanism may be put forward to explain the experimental facts:

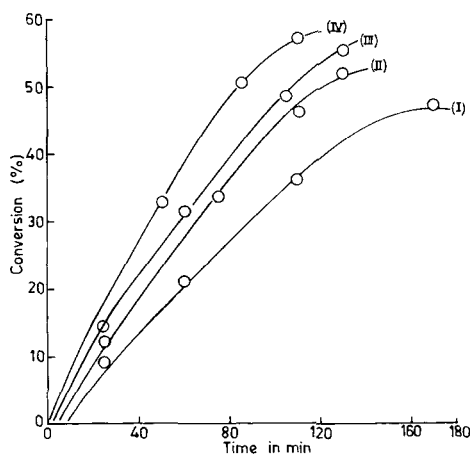


Fig. 3. Polymer conversion versus time curves with variation of NO₂ concentration at constant acrylamide concn ($[AM] = 4.0 \text{ mol dm}^{-3}$) in DMSO at 50°C: (I) $5.0 \times 10^{-2} \text{ mol dm}^{-3}$; (II) $6.0 \times 10^{-2} \text{ mol dm}^{-3}$; (III) $7.0 \times 10^{-2} \text{ mol dm}^{-3}$; (IV) $8.0 \times 10^{-2} \text{ mol dm}^{-3}$ of NO₂.

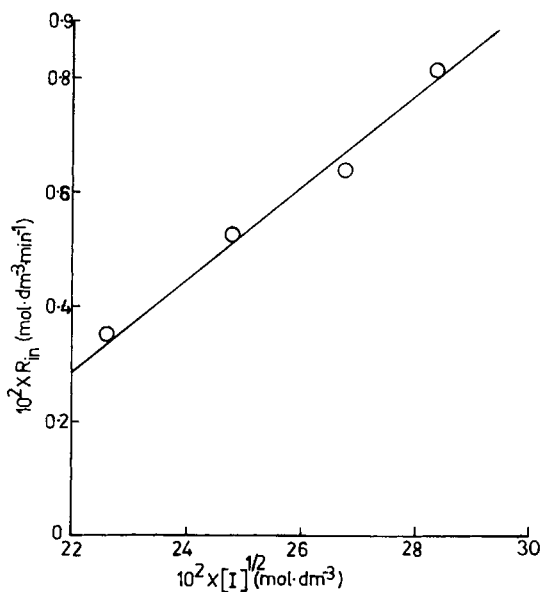
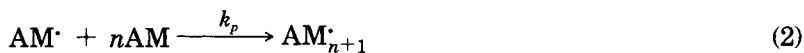


Fig. 4. Influence of square root of initiator concentration (NO_2) on the initial rate of polymerization (R_{in}) at constant monomer concentration ($[\text{AM}] = 4.0 \text{ mol dm}^{-3}$) at 50°C in DMSO.

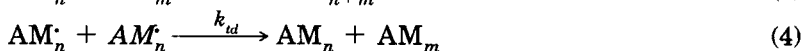
Initiation:



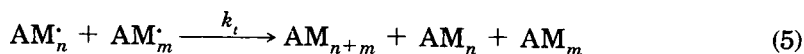
Propagation:



Termination:



The above symbols have their usual meanings. Equations (3) and (4) correspond to chain termination by radical combination and disproportionation, respectively. In the relative importance of two processes, disproportionation reactions generally are of lesser importance than combination reactions. However, for kinetic purposes the two are equivalent, and it is convenient to combine them as⁶



with $k_t = k_{tc} + k_{td}$

Considering the steady-state principle for NO₂ and AM_n, the rate of polymerization was derived to be

$$R_{in} = -\frac{d[AM]}{dt} = k_p \left(\frac{f_i^k}{2k_t} \right)^{1/2} [NO_2]^{1/2} [AM] \quad (6)$$

Equation (6) may be roughly written as follows:

$$R_{in} = -\frac{d[AM]}{dt} = k_p [NO_2]^{1/2} [AM] \quad (7)$$

The plots of R_{in} vs. $[AM]$, i.e., $[M]$ (Fig. 2) and $[NO_2]^{1/2}$, i.e., $[I]^{1/2}$ (Fig. 4) supports the above-proposed schemes. This is in accordance with the kinetics of a free radical polymerization.⁶

Dependence of Temperature

The increase of temperature enhances the conversion to polymer and the rate of polymerization. The overall activation energy of polymerization was calculated to be about 15.0 kcal mol⁻¹ from Figure 5.

Molecular Weight of Polymers

The molecular weight of polyacrylamide increases with the increase of initial monomer concentration and decreases with the increase of initial initiator concentration as shown in Table I. This is expected since increase in the initiator concentration increases the growing chain population, which in turn enhances the polymerization rate and simultaneously lowers the

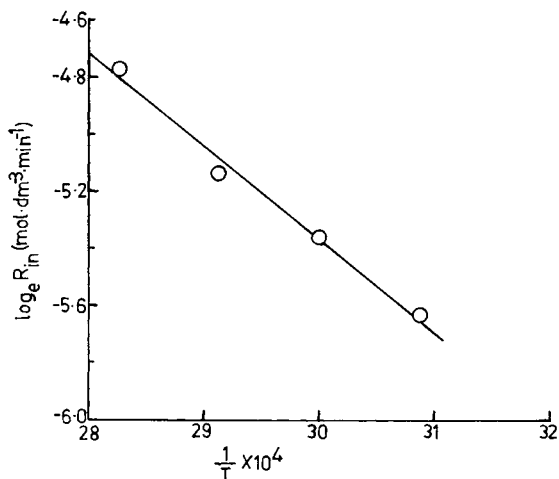


Fig. 5. Dependence of initial rate of polymerization (R_{in}) on the reciprocal absolute temperature of AM polymerization: $[AM] = 4.0 \text{ mol dm}^{-3}$; $[NO_2] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$ in DMSO.

TABLE I
Effect of Acrylamide and NO₂ Concentrations on the Average Molecular Weight of Polyacrylamide Formed in Dimethylsulfoxide at 50°C

[AM] (mol dm ⁻³)	10 ² × [NO ₂] (mol dm ⁻³)	Polymer conversion (%)	$[\bar{\eta}]$ (dL g ⁻¹)	$\bar{M} \times 10^{-4}$
1.0	5.0	13.95	0.06	0.2203
2.0	5.0	21.00	0.09	0.4071
3.0	5.0	37.93	0.15	0.8831
4.0	5.0	50.92	0.26	2.0320
4.0	6.0	52.13	0.21	1.4700
4.0	7.0	54.79	0.17	1.0680
4.0	8.0	56.35	0.13	0.7109

molecular weights of the polymer so formed. When the monomer concentration is increased, propagating polymer chains add more monomer units, yielding higher polymers.

Evidence for a Free-Radical Mechanism

Effect of Inhibitor. The conversion to polymer decreased drastically in the presence of hydroquinone, a free radical scavenger. When its concentration was made equal to that of NO₂ the polymerization was totally inhibited, as is clear from Table II. Therefore, it appears that the polymerization may occur via a free-radical mechanism.⁷

Copolymerization. In order to obtain a clear proof of a free-radical mechanism for the polymerization, the copolymerization of AM with methylmethacrylate (MMA) in the solution of NO₂ in DMSO was carried out with different monomer ratios in the feed (Table III). Unlike the homopolymerization of AM where the polymer precipitates as a white mass, the homopolymerization of MMA⁸ and the copolymerization of AM with MMA proceeds homogeneously. The copolymers were precipitated in acetone. The polyacrylamide and poly(methyl methacrylate) dissolve in water and acetone, respectively, whereas the copolymer is insoluble in both. This polymer solubility pattern indicates that AM copolymerizes with MMA. The composition of copolymer was not assayed. Table III shows the copolymer yield as a function of molar ratio of monomers. It is to be noted that the copolymerization superceded the homopolymerization when either monomer was greatly in excess. This was indicated by the polymerizing mixture remaining homogeneous. Furthermore, it appears from Table III that viscosity number increases with the increase of the AM concentration and

TABLE II
Influence of Hydroquinone on NO₂-Initiated Polymerization of Acrylamide in Dimethylsulfoxide^a

[Hydroquinone] × 10 ² (mol dm ⁻³)	0	0.1	2.0	5.0
Polymer conversion (%)	9.23	3.18	0.05	Nil

^a Conditions: [AM] = 4.0 mol · dm⁻³; [NO₂] = 5.0 × 10⁻² mol · dm⁻³, in DMSO, temperature 50°C, time of polymerization 25 min.

TABLE III
Copolymer Yields and Viscosities at Different Feed Ratios of Acrylamide (AM) and Methyl methacrylate (MMA) in DMSO^a

Feed composition					
Weight of AM (g)	Weight of MMA (g)	Amount of AM (mol %)	Copolymer yield (g)	$\bar{\eta}_{sp}/C^b$ (dL g ⁻¹)	
0.35	2.81	15.38	0.58	0.51	
0.71	1.01	50.00	0.86	2.22	
1.06	0.50	75.00	0.38	0.67	
0.35	1.87	26.95	0.22	1.01	
0.71	0.50	66.66	0.46	1.60	
1.42	1.01	66.00	0.69	1.63	

^a Conditions: time of polymerization 2 h; polymerization temperature 50°C; volume of reaction mixture at 25°C, 5 mL; [NO₂] = 10 × 10⁻² mol dm⁻³.

^b Temperature: 30°C, C = 0.5 g/dL in DMF.

was found that the copolymer formed at 1:1 mole ratio of the monomers has the highest viscosity number.

In conclusion, the yield and molecular weight of polyacrylamide were found to be lower in DMSO than DMF.^{1,2} This may be due to the variation in the reactivity of AM in DMSO due to an interaction between the molecules of the solvent and the reacting monomer and radical particles. The free-radical polymerization of AM in DMSO is also reported in the literature.^{9,10} Gromov et al.⁹ have suggested that the change in the reactivity of AM in its radical polymerization in various solvents is due to the formation of complexes between the molecules of the solvent and the monomer and radical particles. DMSO shows the greatest ability to form complexes with growing polymer radicals, causing the lowest reactivity of radical in this solvent. Kurenkov and Myagchenkov¹⁰ have also reported that the AM radical is associated with the molecules of DMSO, resulting in the decrease of rate of polymerization.

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