

Kinetics of Polymerization of Acrylamide with Nitrogen Dioxide

INTRODUCTION

Nitrogen dioxide (NO_2) initiates the polymerization of acrylamide (AM) in *N,N*-dimethylformamide (DMF), dimethyl sulfoxide and aliphatic (C_1 - C_5) alcohols¹⁻⁴ via free radical mechanism. In order to get polymers of higher conversions and molecular weights, we explored this matter by polymerization of AM in tetrahydrofuran (THF). Kinetics of polymerization has been also studied in brief.

EXPERIMENTAL

Materials: Acrylamide (AM) was purified by recrystallization with ethanol and subsequent drying under vacuum. Tetrahydrofuran (THF) was purified by the usual procedures. Pure and dry NO_2 was prepared by heating lead nitrate. Its concentration in THF was determined volumetrically by treating the solution with excess of NaOH solution and titrating the nitric solution with acidic potassium permagnate solution.⁵

Polymerization Technique: AM was polymerized by previously described method.^{3,4}

The viscosity of polyacrylamide was determined in water by an Ostwald viscometer emerged in a constant temperature bath at $30 \pm 0.1^\circ\text{C}$. The limiting viscosity number was converted into average molecular weight by using the following relation⁶:

$$[\eta] = 3.73 \times 10^{-4} \bar{M}^{0.66} \text{ dL g}^{-1}$$

RESULTS AND DISCUSSION

During the NO_2 -initiated polymerization of AM in THF, the polymerization occurred after an induction period, which was possibly due to residual impurities and also oxygen present in the reaction mixture. The polymer precipitates out from the polymerizing solution during the course of reaction as white mass. A profile of polymer conversion as a function of polymerization time at different concentrations of NO_2 with a fixed concentration of AM is shown in Figure 1, which shows a systematic increase of polymer conversion with time and initiator concentration. The initial rate of polymerization, R_{in} (extrapolated from conversion time curves), increases linearly with square root of the initiator concentration as shown in Figure 2. Figure 3 shows polymer conversion-time curves obtained for different concentrations of the monomer with a fixed concentration of NO_2 at 40°C . Here we find a systematic increase of polymer yield with time and monomer concentration.

The order dependence with respect to the monomer and initiator may also be examined by integrated first order expression as follows:

$$-\frac{d[M]}{dt} = k_p[M][I]^n \quad (1)$$

where $[M]$ and $[I]$ are the monomer and initiator concentrations, respectively.

When the initiator concentration is constant, on integration of the above expression, and putting $[M]_t = [M]_0$, when $t = 0$, we get

$$\log_{10}[M]_t = -k_p t + \log_{10}[M]_0 \quad (2)$$

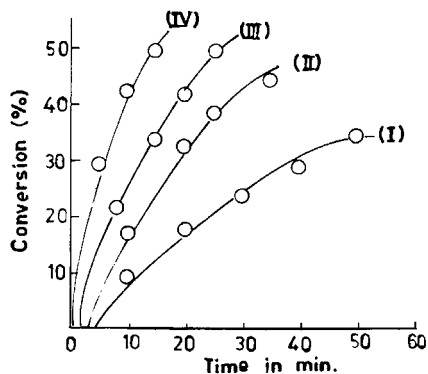


Fig. 1. Time vs. conversion curves for the polymerization of acrylamide (AM) (concn 4.0 mol/L) with varying concentration of NO_2 in tetrahydrofuran (THF) at 40°C ; (i) 1.0×10^{-2} mol/L; (ii) 2.0×10^{-2} mol/L; (iii) 3.0×10^{-2} mol/L; (iv) 4.0×10^{-2} mol/L.

or

$$\log_{10} \frac{[M]_0}{[M]_t} = k_p t \quad (3)$$

where k_p is the rate constant. This is simple first-order kinetics.

The plot of $\log_{10} ([M]_0/[M]_t)$ vs. polymerization time with variation of initiator concentration is linear as expected for the first order rate expression and is shown in Figure 4.

A similar and more stringent corroboration of the first-order dependence in the monomer is shown in Figure 5. Here the results are collected from various initial monomer concentrations at a fixed concentration of NO_2 . The rate constants determined from the slopes of the curve $\log_{10} ([M]_0/[M]_t)$ vs. time, increases linearly with the first power of the monomer concentration, as can be seen from Figure 5. It is expected for the first-order decay in the monomer. Therefore, the results cited above unambiguously show that the rate of polymerization is first order in the monomer and half order with respect to the initiator. The polymerization of AM initiated with azocatalyst in aqueous solution also exhibits such first-order dependence on the monomer and half-order dependence on the initiator concentrations.⁷

The polymerization of AM in THF is dependent on the reaction temperature (Figure 6). An Arrhenius plot is presented in Figure 7. The overall activation energy of the polymerization was found to be about 11.5 kcal/mol. The value of activation energy for the polymerization of AM with NO_2 in DMF, DMSO, methyl alcohol, ethyl alcohol, isopropyl alcohol, *tert*-butyl

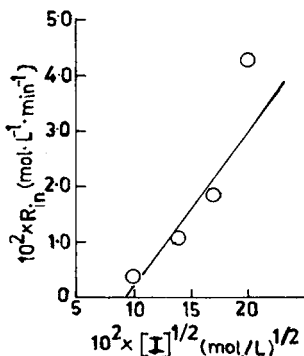


Fig. 2. Dependence of the initial rate of polymerization (R_{in}) on the square root of NO_2 concentration at constant $[\text{AM}] = 4.0$ mol/L in THF at 40°C .

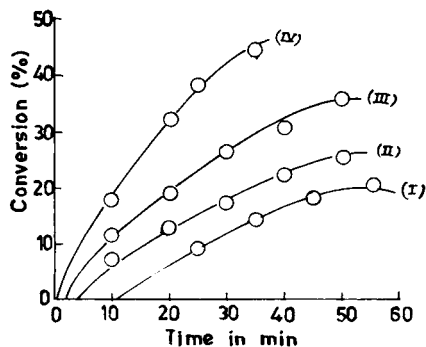


Fig. 3. Polymer conversion as a function of time and acrylamide (AM) concentration with a fixed concentration of NO_2 ($[\text{NO}_2] = 2.0 \times 10^{-2}$ mol/L) THF at 40°C : (i) 1.0 mol/L; (ii) 2.0 mol/L; (iii) 3.0 mol/L; (iv) 4.0 mol/L.

alcohol and *tert*-amyl alcohol has been reported to be 20, 15.0, 15.3, 16.8, 18.4, and 20.5, respectively.¹⁻⁴ The lower value of activation energy in THF reflect the higher polymerization rate. In fact, the polymerization rate has been found to be higher in THF than the above solvents. Thus energy of activation depends on the nature of the solvents.

It is seen from Table I that polymers formed in THF from NO_2 initiation have fairly high molecular weights, which increase with the monomer concentration and decrease with the increase of initiator concentration. This is expected since the increase in the initiator concentration increases the growing chain population, which, in turn, enhances the polymerization rate and simultaneously lowers the molecular weights of the polymer formed. This is further added by an increase in termination. However, when the monomer concentration is increased, propagating polymer chains add more monomer units, yielding higher polymers.

The polymerization of AM with NO_2 in THF completely stopped by *p*-benzoquinone, which was used as a free-radical scavenger. This suggests the free-radical polymerization of AM with NO_2 .

Thus we found that the rate of polymerization of AM and molecular weights of polymers was higher in THF than in DMF,^{1,2} DMSO,³ and aliphatic alcohols.⁴ The variation in the reactivity of AM in its free-radical polymerization in above solvents may be due to an interaction between the molecules of the solvent and the monomer or the radical which affects the propagation and termination reactions. In solid state, AM exists as dimers, which when dissolved in solvents capable of forming hydrogen bonds, may dissociate to single molecules. It is reported in the literature that AM dimerized to some extent in DMF, DMSO, and alcohols.^{7,8} We assume that, as the individual monomer molecules probably take part in the transition state of propagation, additional energy is needed for breaking of the dimer bond in AM. This increases the activation energy of chain propagation. On the basis of this assumption, the activation energy of chain propagation should have its least value in THF, and thus a high rate of polymerisation is observed in THF. In DMF, DMSO, and alcohols, where molecules of AM interact through H-bonds, activation energy of chain propagation is sub-

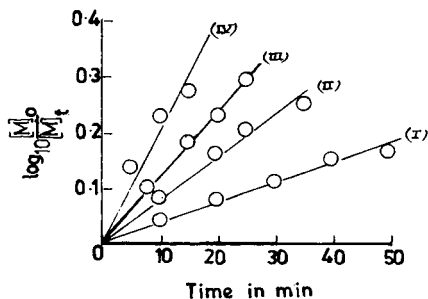


Fig. 4. First order plot of conversion curves of the Figure 2.

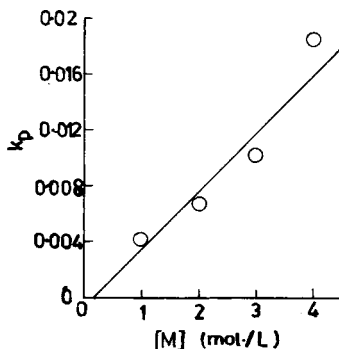


Fig. 5. Influence of the monomer concentration on the rate constant (k_p) of acrylamide (Am) in THF at 40°C, $[\text{NO}_2] = 2.0 \times 10^{-2}$ mol/L.

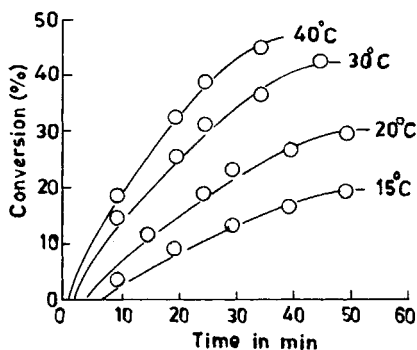


Fig. 6. The effect of the reaction temperature on the polymerization of acrylamide (conc 4.0 mol/L) initiated by NO_2 (conc 2.0×10^{-2} mol/L) in THF.

TABLE I
Influence of Monomer (AM) and Initiator (NO_2) Concentration on Molecular Weights of Polymers Formed in THF at 40°C

[AM] (mol/L)	$10^2 \times [\text{NO}_2]$ (mol/L)	Polymerization time (min)	$[\eta]$ (dL g ⁻¹)	$\bar{M} \times 10^{-4}$
1.0	2.0	35	0.04	0.1192
2.0	2.0	20	0.07	0.2783
3.0	2.0	20	0.10	0.4777
4.0	2.0	25	0.25	1.9190
4.0	1.0	30	0.30	2.5242
4.0	3.0	25	0.21	1.4700
4.0	4.0	15	0.18	1.1640

stantially greater, and, ultimately lowering the rate of polymerization in this case, the energy comprises that for breaking of intermolecular H-bonds in AM dimer. Gromov et al.⁷ confirmed by PMR spectroscopy the different degree of interaction of AM with THF, DMF, DMSO, and alcohols and concluded that there is an unequal interaction of solvent with the C=O group of AM because of hydrogen bonds.

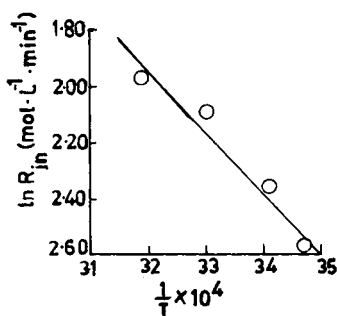


Fig. 7. Arrhenius plot showing the dependence of the initial rate of polymerization, R_{in} , on the reciprocal temperature of acrylamide (AM) polymerization: $[AM] = 4.0 \text{ mol/L}$, $[NO_2] = 2.0 \times 10^{-2} \text{ mol/L}$ in THF.

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