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## Free-Radical Polymerization of Acrylic Acid in Benzene

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### ABSTRACT

The polymerization of acrylic acid with  $\text{NO}_2$  in benzene was carried out. The initial rate of polymerization shows first-order dependence on the monomer concentration and half-power dependence on the initiator concentration. The molecular weight of polymers also shows dependence on monomer and initiator concentrations. The overall activation energy of polymerization was found to be about 22.7 kcal/mol. The kinetic mechanism of polymerization is discussed.

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## INTRODUCTION

Recent work on  $\text{NO}_2$ -initiated polymerization of acrylic acid gave evidence that a high molecular weight polymer can be achieved [1]. The investigations carried out in previous work were limited to tetrahydrofuran (THF) and 1,4-dioxane. The aim of this article is to establish the kinetic mechanism of polymerization. The present work is concerned with the polymerization of AA with  $\text{NO}_2$  in benzene.

## EXPERIMENTAL

Materials

Acrylic acid (AA), washed with 5 wt% sodium hydroxide solution followed by distilled water, was fractionally distilled in vacuum. Benzene and 1,4-dioxane (analytical reagent grade) were purified by standard methods. Dry and pure  $\text{NO}_2$  was prepared by heating dried lead nitrate. The concentration of  $\text{NO}_2$  in benzene was determined volumetrically, as described in Ref. [1].

Polymerization Procedure

Acrylic acid (AA) was subjected to polymerization in separate glass vials which were tightly stoppered and thermostated. The polymers so formed were precipitated by pouring the reaction mixture in the fresh ice-cooled benzene and redissolved in 1,4-dioxane to get a flaky white solid, recovered by reprecipitation with benzene, filtered, and dried.

The viscosity measurements of polymers were carried out in 1,4-dioxane at  $30^\circ\text{C}$  with an Ostwald viscometer. The average molecular weight of polymer was obtained using the relationship [2]

$$[\eta] = 8.5 \times 10^{-4} \bar{M}^{0.50}$$

## RESULTS AND DISCUSSION

Unlike the  $\text{NO}_2$ -initiated polymerization of acrylic acid (AA) in tetrahydrofuran (THF) and 1,4-dioxane, where the reaction mixture remains homogeneous, the polymerization of AA in benzene proceeds heterogeneously and the polymer is precipitated out after an induction period during the course of reaction. The polymer so obtained was soluble in THF and 1,4-dioxane.

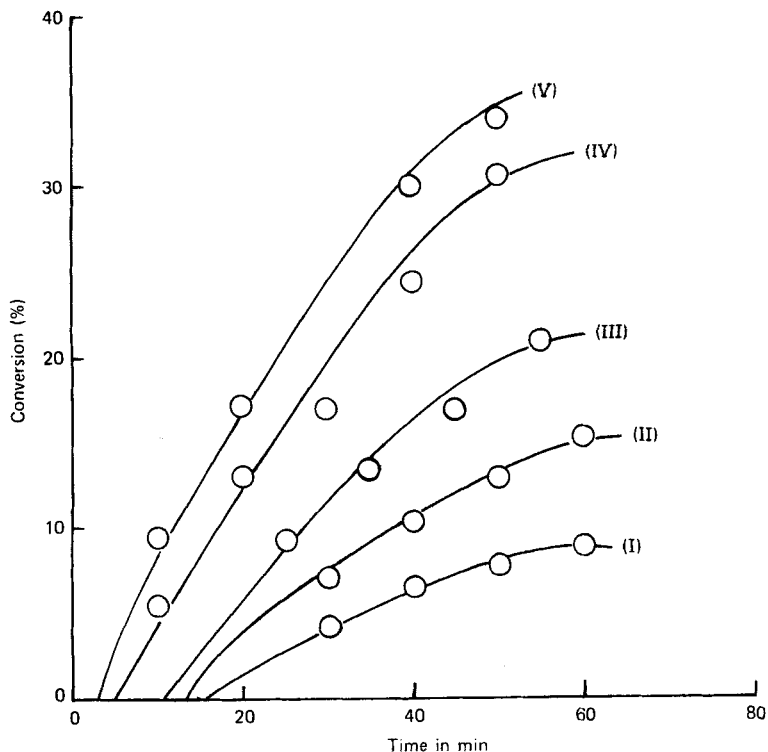


FIG. 1. Polymer conversion as a function of time and AA concentration with a fixed concentration of  $\text{NO}_2$  in benzene ( $[\text{NO}_2] = 1.0 \times 10^{-1} \text{ mol/dm}^3$ ) at  $50^\circ\text{C}$ . (I),  $5.79 \text{ mol/dm}^3$ ; (II),  $7.24 \text{ mol/dm}^3$ ; (III),  $8.69 \text{ mol/dm}^3$ ; (IV),  $10.14 \text{ mol/dm}^3$ ; (V),  $11.59 \text{ mol/dm}^3$  of AA.

The polymer conversion increases with an increase in the initial monomer concentration as shown in Fig. 1. The initial rate of polymerization,  $R_{\text{in}}$  (extrapolated from conversion-time curves), increases linearly with the first power of the monomer concentration (Fig. 2). The increase in initial initiator concentration increases the rate of polymer conversion (Fig. 3). The  $R_{\text{in}}$  increases linearly with the square root of the initiator concentration (Fig. 4). A bimolecular mechanism of termination was thus indicated.

The molecular weight of the polymers increases with an increase in the initial monomer concentration while it decreases with an increase in the initial initiator concentration as shown in Table 1. The reason for this is that when the monomer concentration is increased, the growing polymer chains add more monomeric units, yielding high

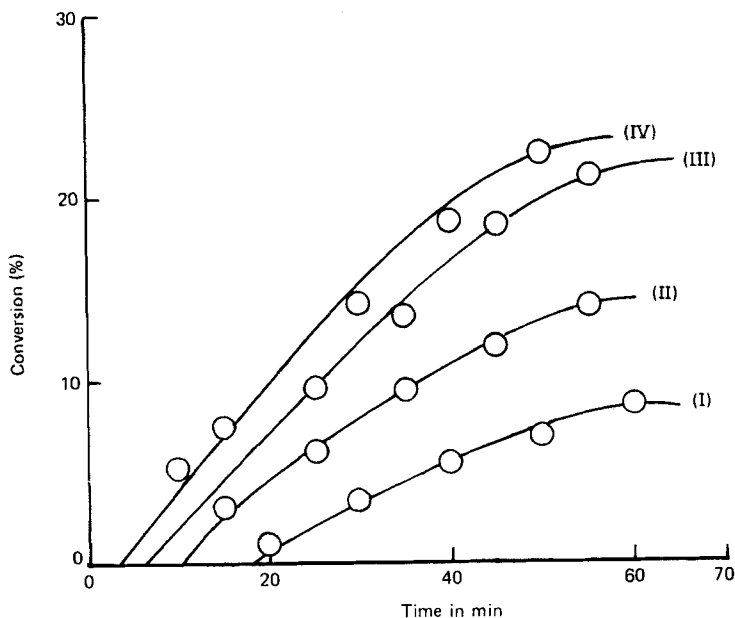


FIG. 2. Polymer conversion as a function of time and  $\text{NO}_2$  concentration with a fixed concentration of AA ( $[\text{AA}] = 8.69 \text{ mol/dm}^3$ ) in benzene at  $50^\circ\text{C}$ . (I),  $0.6 \times 10^{-1} \text{ mol/dm}^3$ ; (II),  $0.8 \times 10^{-1} \text{ mol/dm}^3$ ; (III),  $1.0 \times 10^{-1} \text{ mol/dm}^3$ ; (IV),  $1.2 \times 10^{-1} \text{ mol/dm}^3$  of  $\text{NO}_2$ .

molecular weight polymers, whereas an 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 polymers so formed. This is further added to by an increase in termination.

With an increase in reaction temperature, polymer conversion increases. From the data presented in an Arrhenius plot as shown in Fig. 5, the overall activation energy of polymerization of AA in benzene was found to be 22.7 kcal/mol, which is in good agreement with the reported value [3]. The overall activation energies of polymerization of AA in THF and 1,4-dioxane were 16.3 and 15.5 kcal/mol, respectively [1].

The polymerization of AA in benzene with  $\text{NO}_2$  is inhibited by *p*-benzoquinone, indicating that the polymerization proceeds by a free-radical initiation process.

The following kinetic mechanism of polymerization has been proposed.  $\text{NO}_2$  is a gaseous free-radical which initiates the polymeriza-

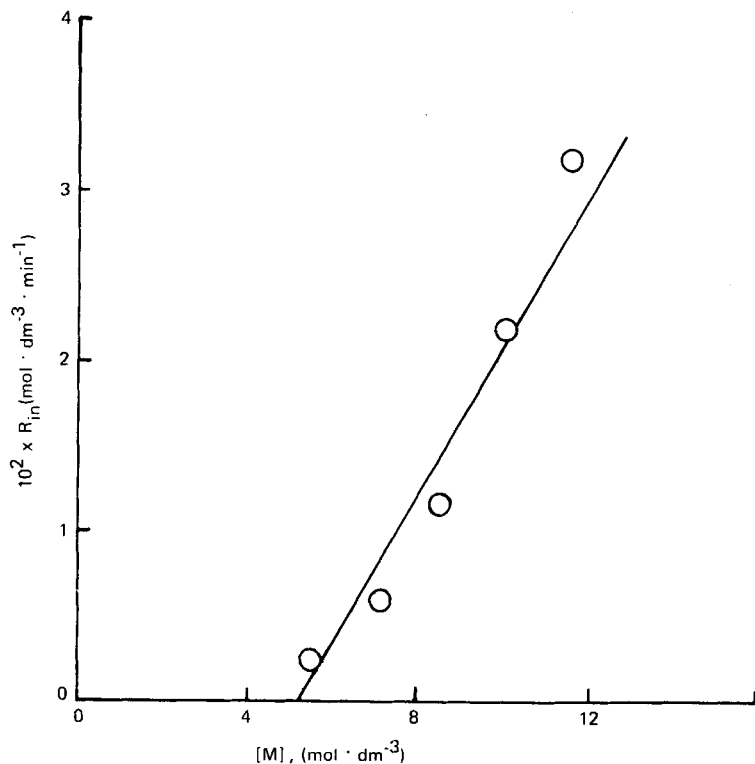


FIG. 3. Influence of the monomer concentration on the initial rate of polymerization ( $R_{in}$ ) of AA in benzene at  $50^\circ\text{C}$ .  $[\text{NO}_2] = 1.0 \times 10^{-1} \text{ mol/dm}^3$ .

tion of AA in benzene; thus a plausible mechanism may be given to explain the experimental results.

Initiation:



Propagation:



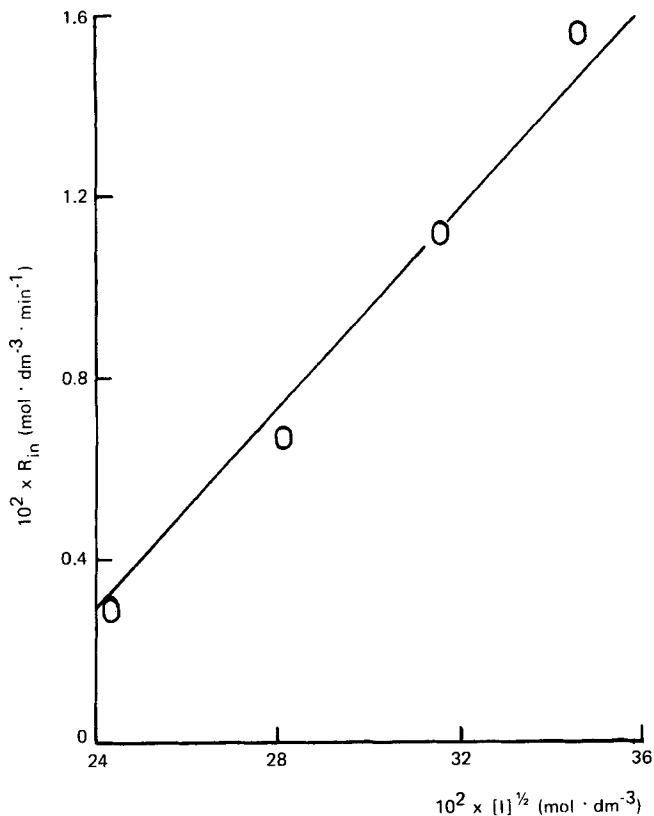


FIG. 4. Influence of the initiator concentration on the initial rate of polymerization ( $R_{in}$ ) of AA in benzene at 50°C.  $[AA] = 8.69 \text{ mol/dm}^3$  in benzene.

Termination:



Here all the terms have their usual meanings. Considering the steady-state principle for  $\text{NO}_2^{\cdot}$  and  $M^{\cdot}$ , the rate of polymerization was derived to be

$$-d[M]/dt = R_{in} = k_p (fk_i/2k_t)^{1/2} [\text{NO}_2]^{1/2} [M] \quad (4)$$

TABLE 1. Average Molecular Weights of Polyacrylic Acid Formed by Polymerization of Acrylic Acid (AA) with  $\text{NO}_2$  at  $50^\circ\text{C}$  in Benzene

[AA] (mol/dm <sup>3</sup> )	$10 \times [\text{NO}_2]$ mol/dm <sup>3</sup>	Conversion (%)	$[\bar{\eta}]$ (dL/g)	$\bar{M} \times 10^{-5}$
7.24	1.0	15.34	0.05	0.0346
8.69	1.0	21.23	0.22	0.6699
10.14	1.0	30.43	0.37	1.8940
11.59	1.0	33.55	0.59	4.8170
8.69	0.6	8.89	0.35	1.6970
8.69	0.8	14.09	0.25	0.8630
8.69	1.2	22.65	0.19	0.4996

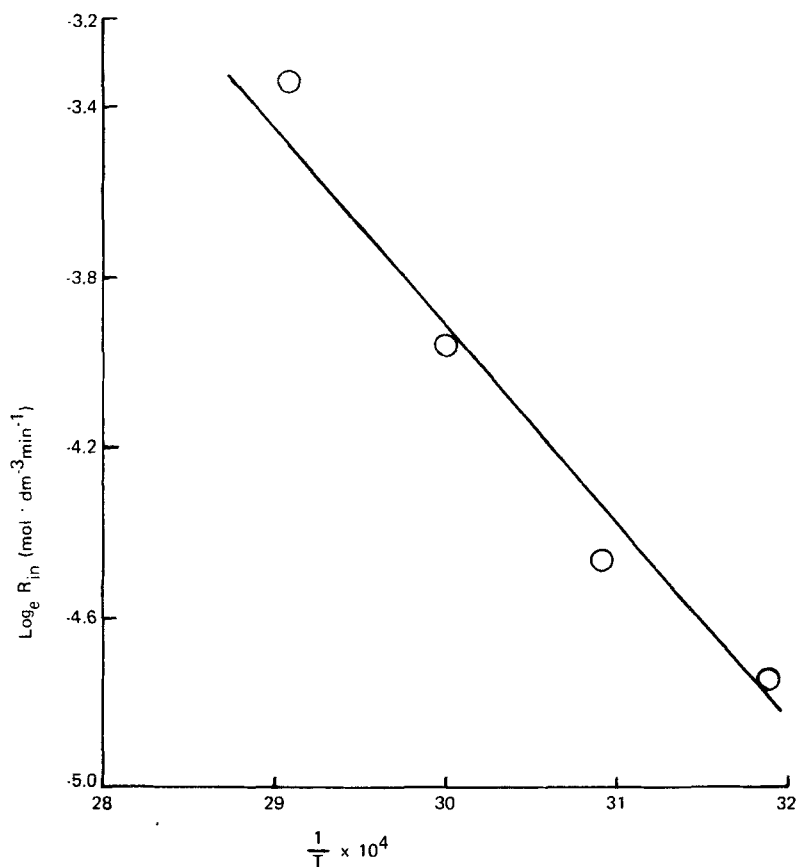


FIG. 5. Dependence of the initial rate of polymerization ( $R_{in}$ ) on the reciprocal absolute temperature of AA polymerization,  $[\text{AA}] = 8.69$  mol/dm<sup>3</sup>,  $[\text{NO}_2] = 1.0 \times 10^{-1}$  mol/dm<sup>3</sup> in benzene.



Equation (4) may be roughly written as

$$-d[M]/dt = R_{in} = k_p[NO_2]^{1/2} [M] \quad (5)$$

The results suggest that within the studied experimental ranges, Eq. (5) is valid. This appears compatible with the kinetics of a free-radical polymerization [4].

In conclusion, it was found that the yield of polymers was higher in benzene than in THF or 1,4-dioxane, but the molecular weight of the polymers was lower in benzene. This may be attributed to the heterogeneous nature of polymerization in benzene.

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