Free-Radical Polymerization of Acrylic Acid in Benzene

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ABSTRACT

The polymerization of acrylic acid with 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 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 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 NO_2 was prepared by heating dried lead nitrate. The concentration of 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°C with an Ostwald viscometer. The average molecular weight of polymer was obtained using the relationship [2]

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

RESULTS AND DISCUSSION

Unlike the 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.
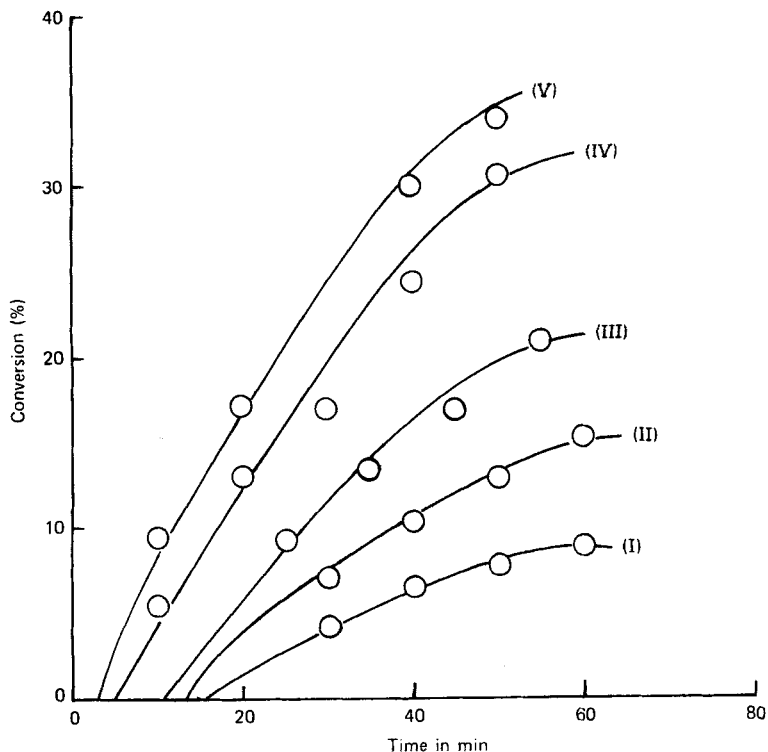
FIG. 1. Polymer conversion as a function of time and AA concentration with a fixed concentration of NO_2 in benzene ($[NO_2]$ = 1.0 × 10^{-1} mol/dm^3) at 50°C. (I), 5.79 mol/dm^3; (II), 7.24 mol/dm^3; (III), 8.69 mol/dm^3; (IV), 10.14 mol/dm; (V), 11.59 mol/dm^3 of AA.

The polymer conversion increases with an increase in the initial monomer concentration as shown in Fig. 1. The initial rate of polymerization, R_{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_{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
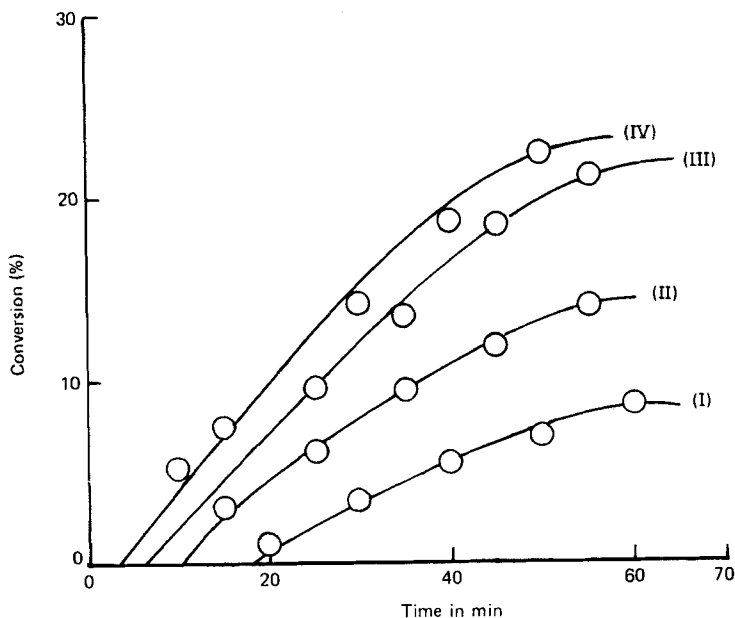
FIG. 2. Polymer conversion as a function of time and NO_2 con-
centration with a fixed concentration of AA ([AA] = 8.69 mol/dm^3) in
benzene at 50°C. (I), 0.6×10^{-1} mol/dm^3; (II), 0.8×10^{-1} mol/dm^3;
(III), 1.0×10^{-1} mol/dm^3; (IV), 1.2×10^{-1} mol/dm^3 of NO_2.

molecular weight polymers, whereas an increase in the initiator con-
centration increases the growing chain population, which in turn en-
hances the polymerization rate and simultaneously lowers the molecu-
lar weights of the polymers so formed. This is further added to by an
increase in termination.

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

    The polymerization of AA in benzene with 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 pro-
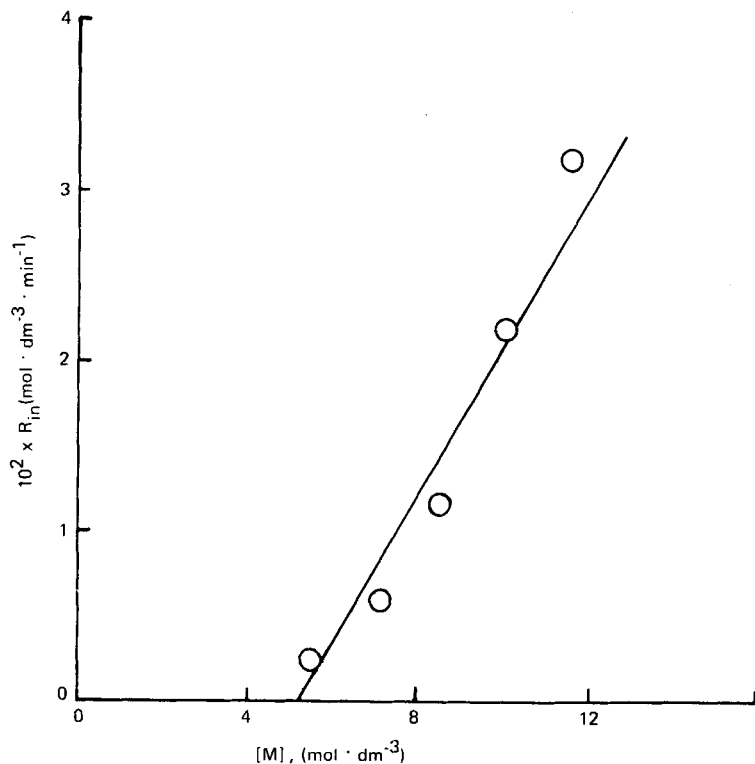posed. NO_2 is a gaseous free-radical which initiates the polymeriza-

FIG. 3. Influence of the monomer concentration on the initial rate of polymerization (R_{in}) of AA in benzene at $50°C$. $[NO_2]$ = 1.0×10^{-1} mol/dm^3.

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

Initiation:

$$NO_2^{\cdot} + M \xrightarrow{k_i} M^{\cdot} \tag{1}$$

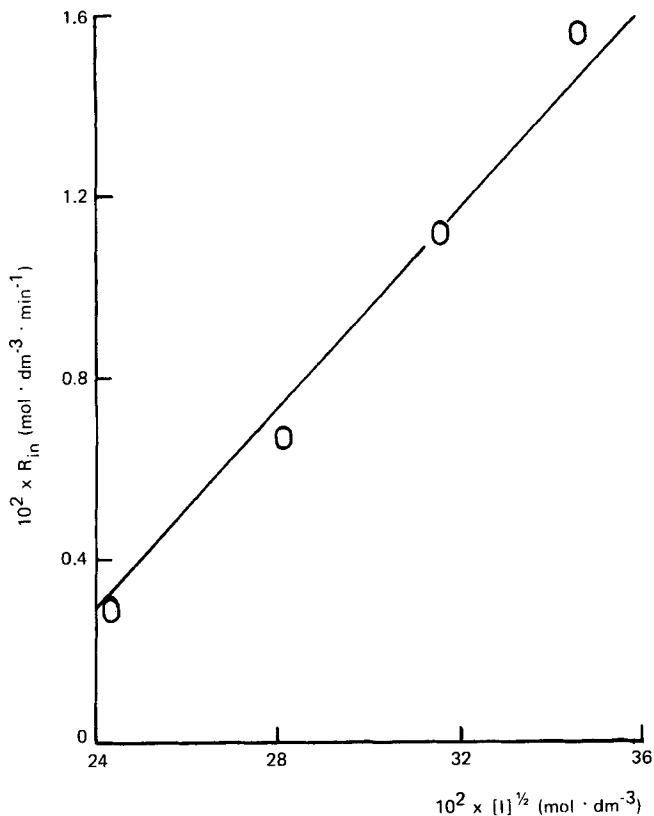Propagation:

$$M^{\cdot} + M \xrightarrow{k_p} M_{n+1}^{\cdot} \tag{2}$$

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 mol/dm³ in benzene.

Termination:

$$M_n{}^{\cdot} + M_m{}^{\cdot} \xrightarrow{\ k_t\ } \text{polymer} \tag{3}$$

Here all the terms have their usual meanings. Considering the steady-state principle for $NO_2{}^{\cdot}$ and $M^{\cdot}$, the rate of polymerization was derived to be

$$-d[M]/dt = R_{in} = k_p(fk_i/2k_t)^{1/2}[NO_2]^{1/2}[M] \tag{4}$$

TABLE 1. Average Molecular Weights of Polyacrylic Acid Formed by Polymerization of Acrylic Acid (AA) with NO_2 at 50°C in Benzene

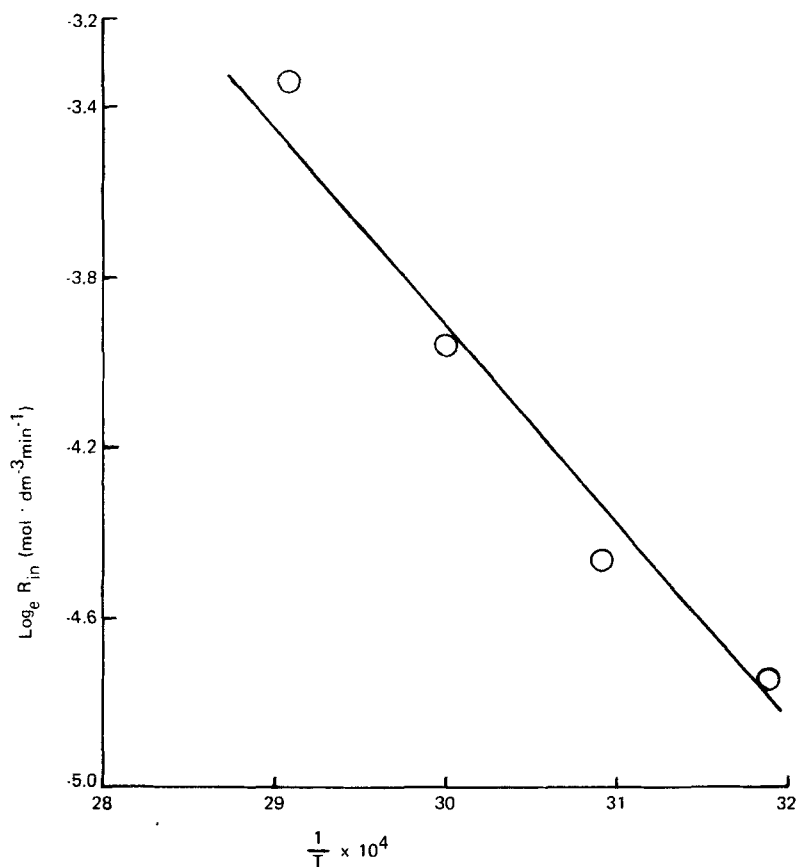| [AA] (mol/dm^3)	$10 \times [NO_2]$ mol/dm^3	Conversion (%)	$[\bar{\eta}]$ (dL/g)	$\bar{M} \times 10^{-5}$
7.24	1.0	15.34	0.05	0.0346
8.69	1.0	21.23	0.22	0.6699
10.14	1.0	30.43	0.37	1.8940
11.59	1.0	33.55	0.59	4.8170
8.69	0.6	8.89	0.35	1.6970
8.69	0.8	14.09	0.25	0.8630
8.69	1.2	22.65	0.19	0.4996

FIG. 5. Dependence of the initial rate of polymerization (R_{in}) on the reciprocal absolute temperature of AA polymerization, [AA] = 8.69 mol/dm^3, $[NO_2]$ = 1.0×10^{-1} mol/dm^3 in benzene.

Equation (4) may be roughly written as

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

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.

REFERENCES

[1]   M. K. Mishra and S. N. Bhadani, Makromol. Chem., 184, 955 (1983).
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