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Water-Insoluble Polyacrylamide. II. Kinetics of Free-Radical Polymerization of o-N-Acryloylaminobenzoic Acid

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ABSTRACT

Synthesis of water-insoluble poly(o-N-acryloylaminobenzoic acid) was investigated by free radical polymerization. Kinetics of polymerization of o-N-acryloylaminobenzoic acid (OAB) initiated by 2,2'-azoisobutyronitrile (AIBN) in dioxane was studied at 78-100°C. The rate of polymerization was evaluated by varying the concentration of monomer and initiator. The rate of polymerization was found to increase steadily with increasing monomer concentration. The overall activation energy was found to be 9.8 kcal/mol. A suitable kinetic scheme is proposed, and a rate equation has been derived.

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INTRODUCTION

Several reports [1-4] have appeared on the mechanism and kinetics of vinyl polymerization initiated by a variety of initiators. Kinetic studies on aqueous polymerization of acrylamide have been reported [5-9]. However, reports concerning polyacrylamides with N-substituted carboxy phenyl residues are sparse. Only a small amount of information is available, mostly in patents [10-12]. The details of the synthesis of N-substituted acryloylbenzoic acids have been reported for the first time [13]. Part of the investigation of the polymerization and characterization of N-acryloylaminobenzoic acids has been communicated elsewhere [14]. It was considered worthwhile to study the present system in detail with regard to the kinetics of polymerization initiated by AIBN. The kinetic parameters in the nonaqueous medium dioxane at different concentrations of monomer and initiator were evaluated.

EXPERIMENTAL

Materials

Dioxane was distilled over sodium metal. 2,2'-Azoisobutyronitrile was recrystallized from methanol and dried in a desiccator. Other chemicals used were of analytical grade purity.

Monomer Synthesis

The amidification was performed under reflux with acryloyl chloride as described previously [14]. A suspension of anthranilic acid (0.1 mol), pyridine (0.02 mol), and hydroquinone (0.005 mol) in dry benzene (100 mL) was placed in a three-necked flask provided with stirrer, thermometer, and dropping funnel. It was cooled to 0°C and a solution of acryloyl chloride (0.1 mol) in dry benzene (100 mL) was added dropwise over 30 min. The reaction mixture was refluxed for 4 h. Upon cooling, the crude product was collected and washed with cold dilute hydrochloric acid (4 M) until unreacted anthranilic acid was removed. The crude product was crystallized from ethanol: mp 130-132°, yield 72%.

Polymerization Procedure

A typical polymerization experiment was as follows. Purified OAB, 0.262 mol/L in dioxane, and AIBN, 0.156×10^{-3} mol/L, were placed in a degassed glass tube which was constricted and sealed. The polymerization was carried out by placing the sealed tube in a thermostated oil bath at the required temperature. After polymerization for a given time, the content of the tube was poured into a large amount of petroleum ether (40-60°C) to isolate the polymer. The resulting polymer was washed with acetone-water (20:80 v/v) and boiling water, and then dried in vacuum at room temperature to constant weight. The rate of polymerization (R_p) was determined gravimetrically.

RESULTS AND DISCUSSION

The kinetics of radical polymerization of OAB initiated by AIBN was investigated in dioxane. Variables studied included monomer concentration, initiator concentration, and temperature.

Effect of Monomer Concentration

The effect of monomer concentration on the rate of polymerization was studied by varying concentration of OAB from 0.1561 to 0.2168 M. The rate of polymerization was found to increase linearly with increasing monomer concentration. Plots of R_p versus $[M]^2$ were linear, passing through the origin (Fig. 1), thus indicating that the order of reaction is 2 with respect to monomer concentration.

Effect of Initiator Concentration

The effect of initiator concentration on the rate of polymerization was studied by varying the concentration of the initiator, AIBN, from 0.156×10^{-3} to 9.186×10^{-3} M at a fixed monomer concentration. An increase in the rate of polymerization was observed with increasing AIBN concentration. Plots of R_p versus [I] were linear, passing through the origin (Fig. 2). This indicates that the order of reaction with respect to the initiator concentration was unity.

The polymerization was also carried out at 78 to 100°C, with the concentrations of all the reagents kept constant. The rate of polymerization was found to increase progressively with rising temperature (Fig. 2). This might be due to the following reasons: 1) the increase in the reaction rate at higher temperature, 2) the enhancement of the rate of diffusion of monomer into active sites with rising temperature, and 3) the increase in the rate of propagation of the polymer chain at higher temperature.

The Arrhenius plot (Fig. 3) gives an overall activation energy (E_a) of 9.8 kcal/mol.

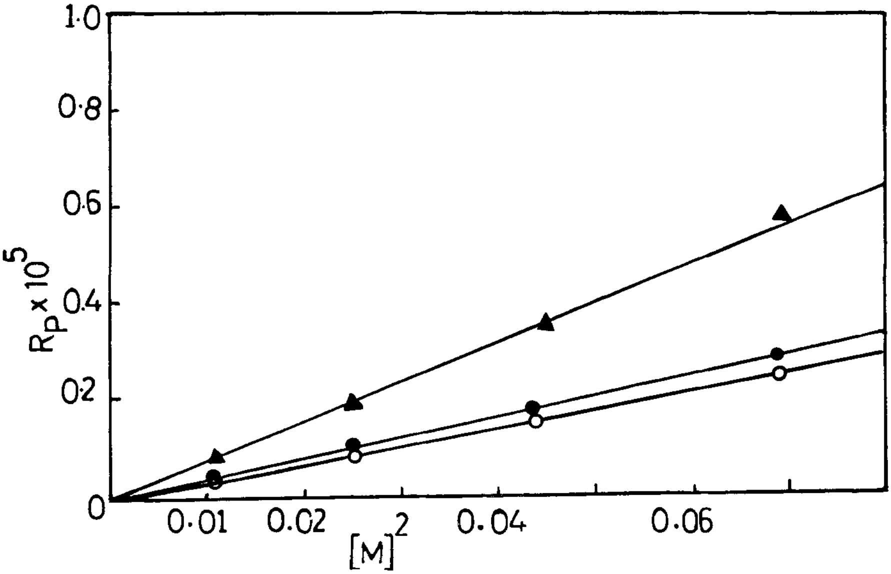


FIG. 1. Effect of monomer concentration on the rate of polymerization (R_p). Medium: Dioxane. Time: 100 min. [I]: 4.567 mol/L. (▲) 100°C, (●) 90°C, (○) 78°C.

Relation between Conversion and Reaction Time

Monomer OAB was polymerized in dioxane at 78 to 100°C with AIBN as the initiator. The time-conversion curves in Fig. 4 indicate that limiting conversion is attained within 20 min. The conversion increases with the monomer as well as the initiator concentrations (Figs. 5 and 6).

The order of reaction for initiation was determined graphically from a double logarithmic plot of R_i versus [I] (Fig. 7).

PROPOSED KINETIC SCHEME AND RATE EXPRESSION

The following mechanism is suggested for the polymerization of o-N-acryloylaminobenzoic acid initiated by AIBN in dioxane.

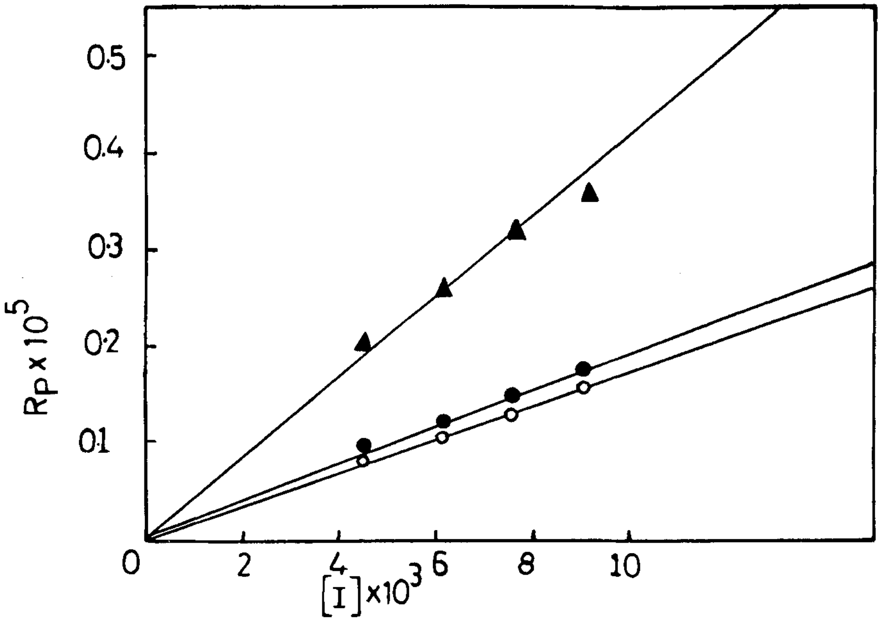
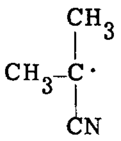


FIG. 2. Effect of initiator concentration on the rate of polymerization (R_p). Medium: Dioxane. Time: 100 min. [M]: 0.1571 mol/L. (▲) 100°C, (●) 90°C, (○) 78°C.

(i) Generation of free radical:

$$\text{AIBN} \xrightarrow{k_d} 2\text{I}\cdot + \text{N}_2,$$

where I· is



$$\text{CH}_3-\overset{\overset{\text{CH}_3}{|}}{\underset{\underset{\text{CN}}{|}}{\text{C}}}\cdot$$

(ii) Initiation:

$$\text{I}\cdot + \text{M} \xrightarrow{k_i} \text{M}\cdot,$$

where M is the monomer.

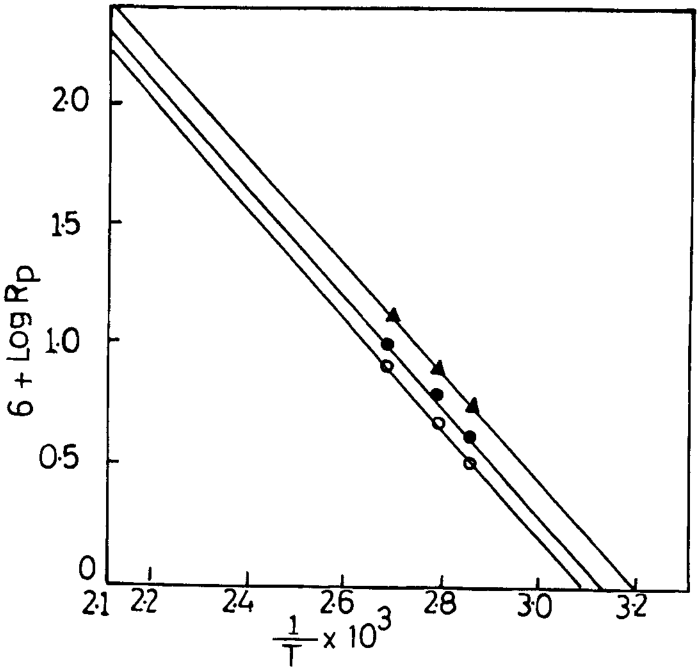


FIG. 3. Arrhenius plot of log R_p versus 1/T. Medium: Dioxane. Time: 100 min. [I]: 9.1350×10^{-3} mol/L. (○) M = 0.1571 mol/L, (●) M = 0.2094 mol/L, (▲) M = 0.2618 mol/L.

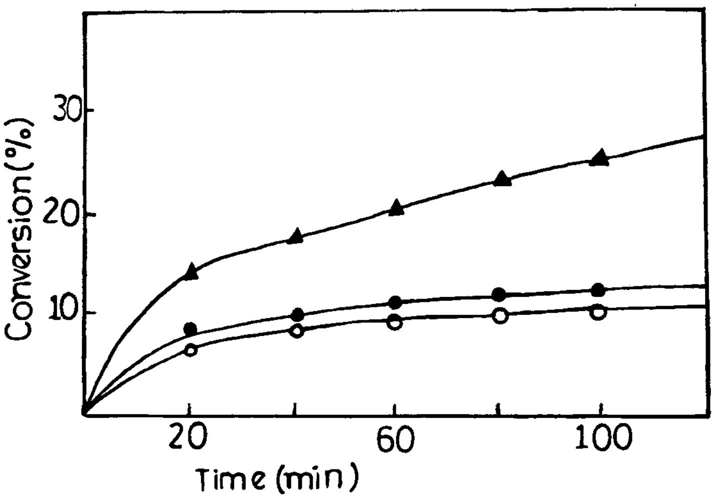


FIG. 4. Plot of percent conversion versus time (min) at different temperatures. Medium: Dioxane. [I]: 9.135×10^{-3} mol/L. [M]: 0.2618 mol/L. (▲) 100°C, (●) 90°C, (○) 78°C.

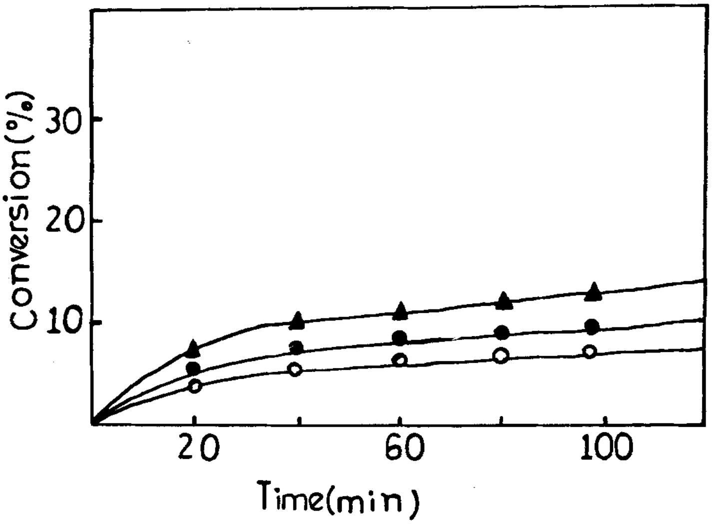


FIG. 5. Plot of percent conversion versus time at different monomer concentrations. Medium: Dioxane. 100°C. [I]: 4.5673 × 10^{-3} mol/L. (○) [M] = 0.1571 mol/L, (●) [M] = 0.2094 mol/L, (▲) [M] = 0.2618 mol/L.

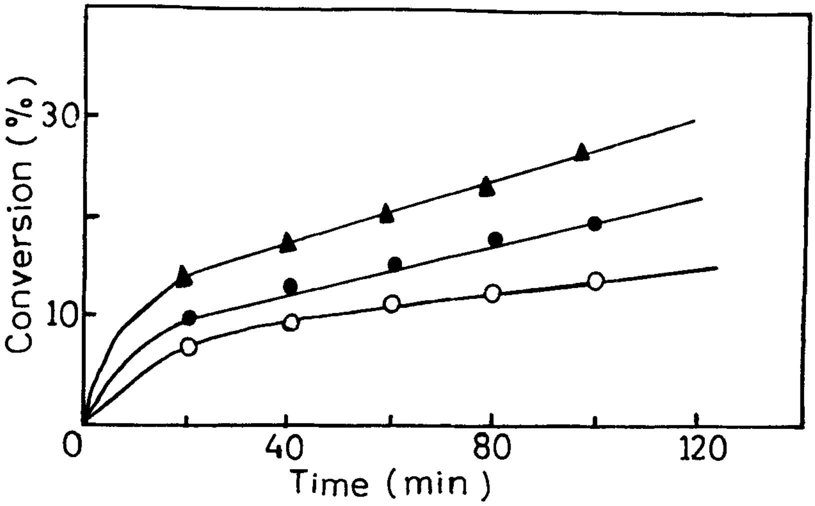


FIG. 6. Plot of percent conversion versus time at different initiator concentrations. Medium: Dioxane. 100°C. [M]: 0.2618 mol/L. (○) [I] = 9.135 × 10^{-3} mol/L, (●) [I] = 6.090 × 10^{-3} mol/L, (▲) [I] = 4.657 × 10^{-3} mol/L.

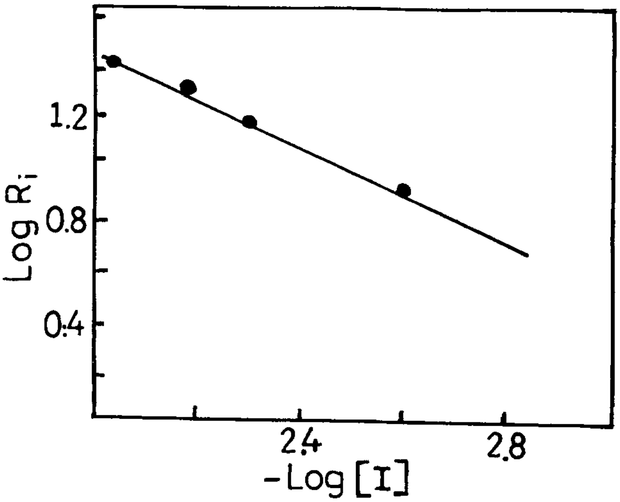


FIG. 7. Double logarithmic plot of rate of polymerization (R_i) (in percent conversion/min) versus amount of initiator (AIBN). Medium: Dioxane. [M]: 0.2618 mol/L. 100°C.

(iii) Propagation:

$$M\cdot + M \xrightarrow{k_p} M\cdot_2$$

$$\vdots$$

$$M_{n-1}\cdot + M \xrightarrow{k_p} M_n\cdot .$$

(iv) Termination

$$I \sim\sim M\cdot + SH \xrightarrow{k_t} I \sim\sim M + S\cdot ,$$

where SH is the solvent.

Assuming steady state for the free radicals, the rate laws can be derived for the case of termination by chain transfer through solvent:

$$R_i = k_i[I\cdot][M],$$

$$R_t = k_t[IM\cdot][SH].$$

Hence, assuming [SH] is constant:

$$k_t[IM\cdot] = k_i[I\cdot][M],$$

$$R_p = k_p[IM\cdot][M].$$

Hence,

$$R_p = k_p \frac{k_i}{k_t} [I\cdot][M]^2.$$

Plots of R_p versus $[M]^2$ (Fig. 1) and R_p versus $[I\cdot]$ (Figs. 2 and 7) are linear, passing through the origin in agreement with the above reaction scheme.

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