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WATER-INSOLUBLE POLYACRYLAMIDES - KINETICS OF FREE-RADICAL POLYMERIZATION OF N-ACRYLOYL-p-AMINOBENZOIC ACID

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ABSTRACT

The synthesis of water-insoluble poly(N-acryloyl-p-aminobenzoic acid) was investigated for free radical polymerization. The kinetics of polymerization of N-acryloyl-p-aminobenzoic acid initiated by AIBN in dioxane at 60-100°C were studied. The rate of polymerization was determined at various concentrations of monomer and initiator. The overall activation energy was found to be 16.2 KJ/mol.

INTRODUCTION

A number of kinetic studies of the aqueous polymerization of acrylamide have been reported [1-5], but there are few reports on polyacrylamides with N-substituted carboxyphenyl residues, and little information is available [6-9]. The synthesis of N-substituted acryloyl aminobenzoic acids [10], and some studies on the polymeriation and characterization of their polymers have been published [11,13]. It was considered worthwhile to study in detail the kinetics of the polymerization of N-acryloyl-p-aminobenzoic acid (PAB) initiated by AIBN.

EXPERIMENTAL

Materials

Dioxane was distilled over sodium metal. 2,2'--azobisisobutyronitrile (AIBN) was recrystallised from methanol and stored in a desiccator. Other chemicals were of analytical grade purity.

Monomer Synthesis

The amidation was performed under reflux with acryloyl chloride as described previously [11]. A suspension of p-aminobenzoic acid (0.1 mol), pyridine (0.02 mol) and hydoroquinone (0.005 mol) in dry benzene (100 mL) was placed in a flask provided with a stirrer, thermometer, and dropping funnel. It was cooled at 0°C, and a solution of acryloyl chloride (0.1 mol) in dry benzene (100 mL) was added dropwise over a period of 30 min. The reaction mixture was refluxed for 4 h. After cooling, the product was collected and washed with cold dilute HCl (4 M) until unreacted p-aminobenzoic acid had been removed. The crude product was crystallized from ethanol; m.p. 218°C, yield 70%.

Polymerization Procedure

A typical polymerization is described below. Purified PAB (0.1047 mol/L) in dioxane and AIBN (1.2195 mmol/L) were placed in a glass tube, degassed and sealed. The sealed tube was placed in an oil bath at the required temperature. After a given time the contents of the tube were poured in to a large volume of petroleum ether (60-80°C). The precipitated polymer was washed well with an acetone water mixture (20-80 V/V) and dried in vacuum at room temperature to constant weight. The rate of polymeriation (R_p) after 100 min and at 30 % conversion was determined gravimetrically.

RESULTS AND DISCUSSION

Effect of Monomer Concentration

The monomer concentration was varied from 0.1047 to 0.3141 mol/L. The plot of log versus log [M] was

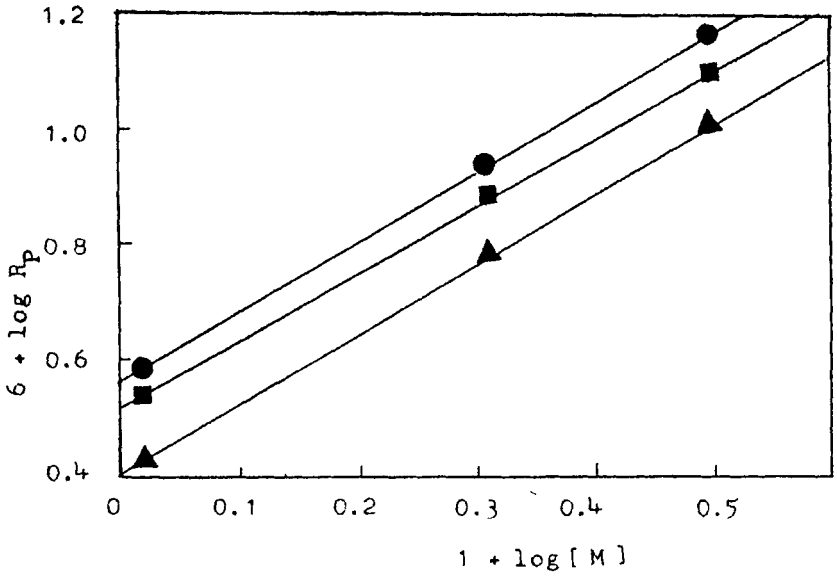

FIG. 1 Double logarithmic plot of rate of polymerization versus monomer concentration : Time - 100 minutes; [I] = 2.439 m.mol./L; Medium - Dioxane plots - (●) 100°C; (■) 80°C; (▲) 60°C.

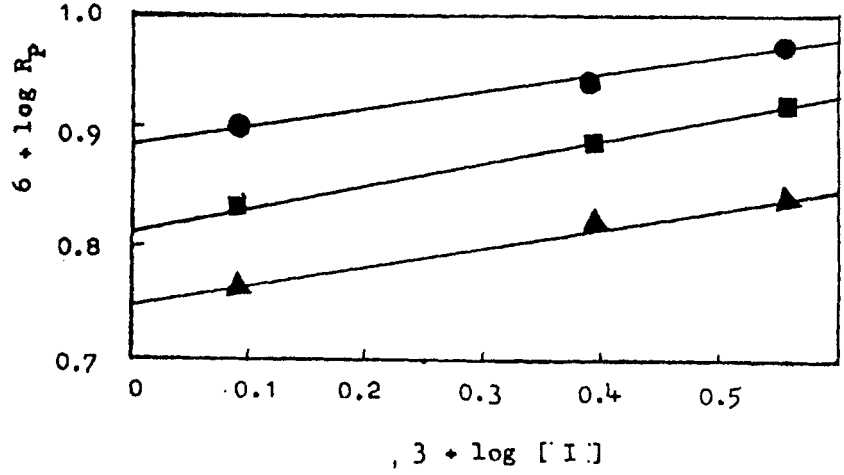

FIG. 2. Double logarithmic plot of rate of polymerization versus concentration of initiator Time - 100 minutes; [M] = 0.2097 mol./L; Plots - (●) 100°C; (■) 80°C; (▲) 60°C.

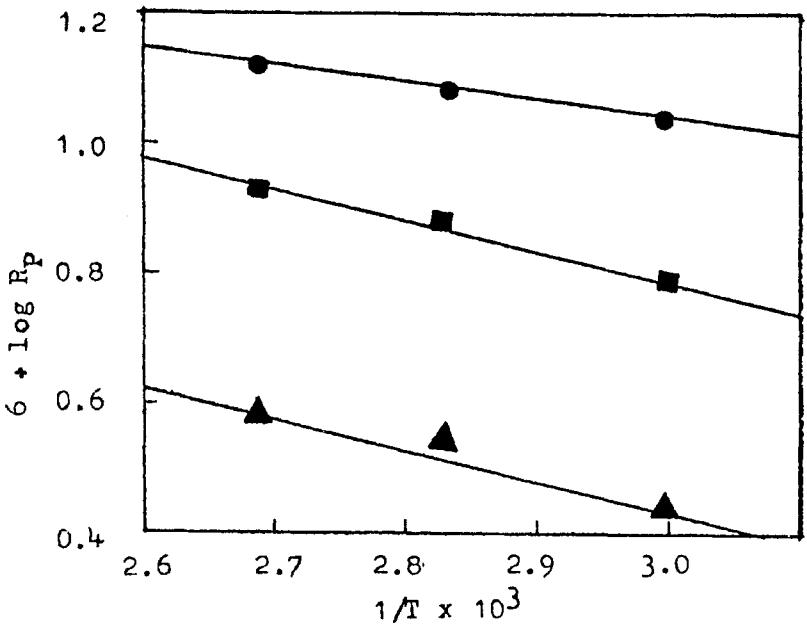

FIG. 3. Arrhenius plot of log R_p versus 1/T. Time - 100 minutes; Medium - Dioxane [I] = 2.439 mol./ L. [M] = (●) = 0.3141 mol./L; (■) 0.2097 mol./L; (▲) 0.1047 mol./L.

linear. The order of reaction with respect to the monomer for the polymeriation of PAB was found to be 1.30 (Fig. 1.).

Effect of Inifiator Concentration

The initiator concentration was varied from 1.1295 to 3.6585 m mol/L at a fixed monomer concentration. The plot of log Rp versus log [I] indicated the order of reaction with respect to initiator for the polymerization to be 0.25 (Fig. 2).

Effect of Temperature

The polymerization was caried out at 60-100°C, keeping the concentration of all reagents fixed. From

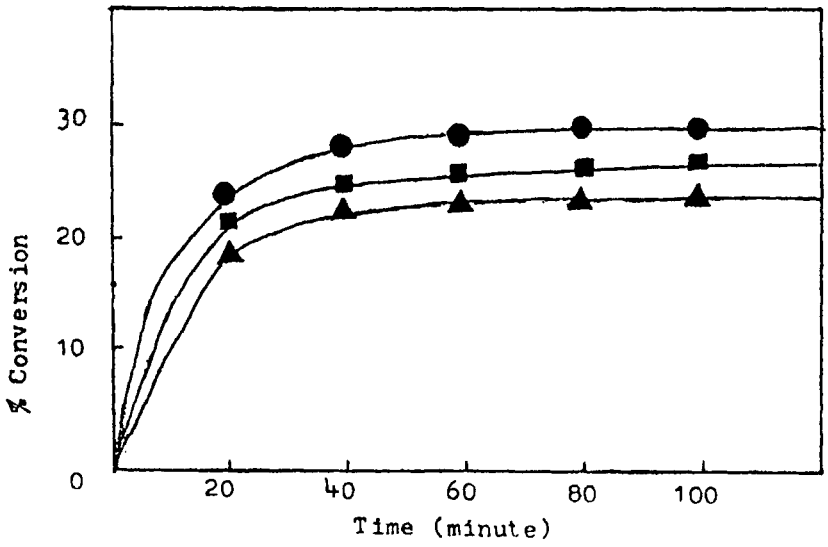

FIG. 4. Plot of % conversion versus time (minute) at different temperatures. Medium - Dioxane; [I] = 3.6585 m.mol./L; [M] = 0.3141 mol./L; plots - (●) 100°C; (■) 80°C; (▲) 60°C.

the Arrhenius plot of log Rp versus 1/T (Fig. 3), the overall activation energy (Ea) was found to be 16.2 KJ/mol.

Relation between Conversion and Reaction time

Time conversion curves at three temperature are shown in Fig. 4. As mentioned in the experimental section, the rate of polymerization (R_p) was measured for 100 min. duration at 30% conversion of the monomer. A plot of Rp versus time is shown in Fig. 5.

On the basis of the standard free radical polymerization scheme and the derivation of the kinetic equation suggested in the literature [12], the rate expression is derived :

$$R_p = K_p \cdot \frac{2K_d}{K_t} \cdot [M]^2 [I]$$

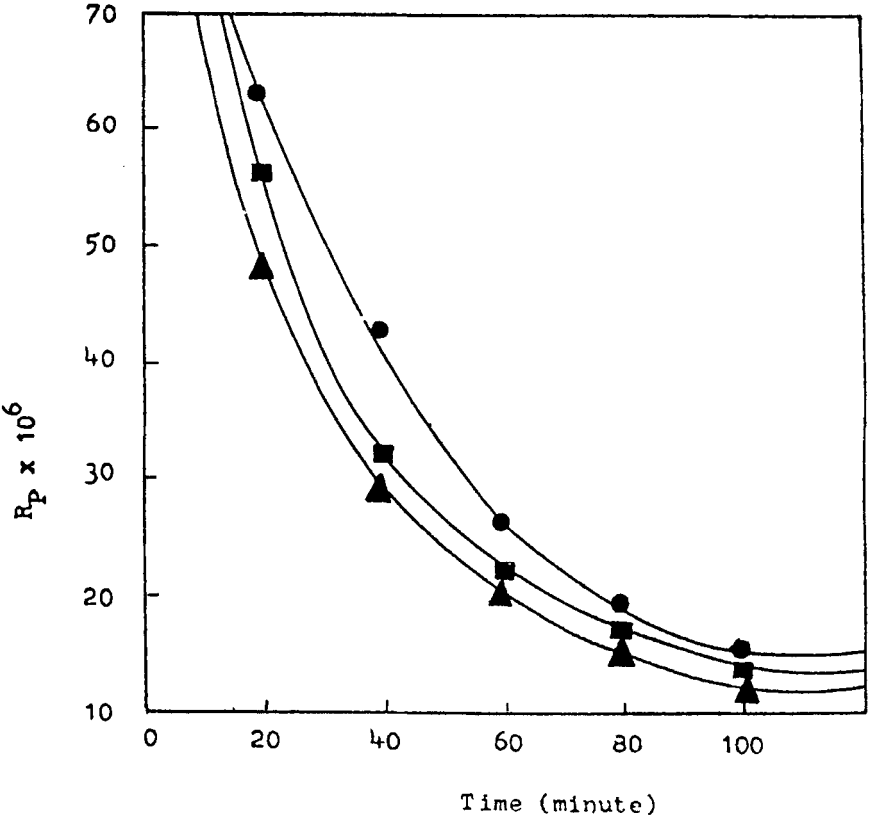

FIG. 5. Plot of R_p versus time (minute) at different temperatures
Medium - Dioxane; [I] = 3.6585 m.mol./L;
[M] = 0.3141 mol./L;
Plots (●) 100°C; (■) 80°C; (▲) 60°c.

This rate expression satisfactorily explains all the kinetic results obtained. These results of the present study are in agreement with those reported by Suthar et al. [11,12].

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