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Trushar Desai^a; Kishore Patel^a; Bhikhu Suthar^a

^a Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar, Gujarat State, India

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NOTE

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TRUSHAR DESAI, KISHORE PATEL, and BHIKHU SUTHAR*

Department of Chemistry
Sardar Patel University
Vallabh Vidyanagar 388120, Gujarat State, India

ABSTRACT

The synthesis of water-insoluble poly(N-acryloyl-m-aminobenzoic acid) was investigated for free-radical polymerization. The kinetics of polymerization of N-acryloyl-m-aminobenzoic acid initiated by AIBN in dioxane at 80-100°C were studied. The rate of polymerization was found for various concentrations of monomer and initiator. The overall activation energy was found to be 27.2 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, mostly in patents [6-8]. The synthesis of N-substituted acryloylaminobenzoic acids has been reported [9], and some studies on

*To whom correspondence should be addressed.

the polymerization and characterization of their polymers have been published [10, 11]. It was considered worthwhile to study in detail the kinetics of the polymerization of N-acryloyl-m-aminobenzoic acid (NAABA) initiated by AIBN.

EXPERIMENTAL

Materials

Dioxane was distilled over sodium metal. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized 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 [10]. A suspension of m-aminobenzoic acid (0.1 mol), pyridine (0.02 mol) and hydroquinone (0.005 mol) in dry benzene (100 mL) was placed in a flask provided with a 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 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 m-aminobenzoic acid had been removed. The crude product was crystallized from ethanol; mp 230-232°C, yield 78%.

Polymerization Procedure

A typical polymerization is described below. Purified NAABA (0.16 mol/L) in dioxane and AIBN (3.66 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 into 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 polymerization (R_p) after 100 min and at 40% conversion was determined gravimetrically.

RESULTS AND DISCUSSION

Effect of Monomer Concentration

The monomer concentration was varied from 0.11 to 0.18 mol/L. The plot of $\log R_p$ versus $\log [M]$ was linear. The order of reaction with respect to the monomer for the polymerization of MAB was found to be 2.06 (Fig. 1).

Effect of Initiator Concentration

The initiator concentration was varied from 1.22 to 3.65 mmol/L at a fixed monomer concentration. The plot of $\log R_p$ versus $\log [I]$ indicated the order of reaction with respect to initiator for the polymerization to be unity (Fig. 2).

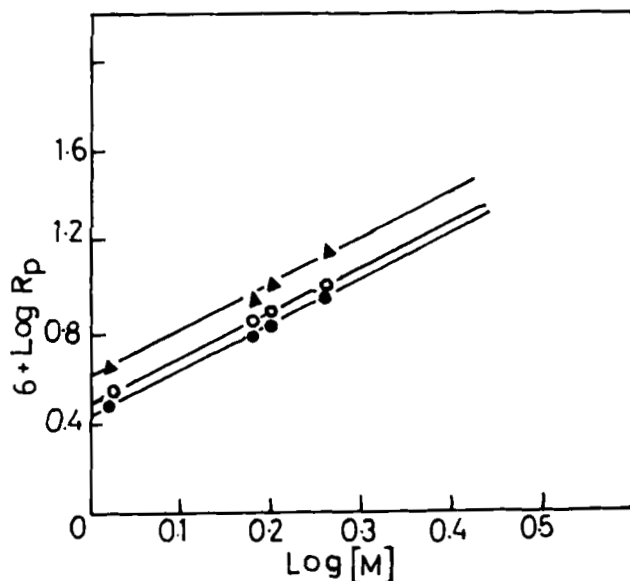


FIG. 1. Plot of $\log R_p$ versus $\log [M]$. Medium: Dioxane. Time: 100 min. $[I]$: 3.65 mmol/L. °C: (▲) 100, (○) 90, (●) 80.

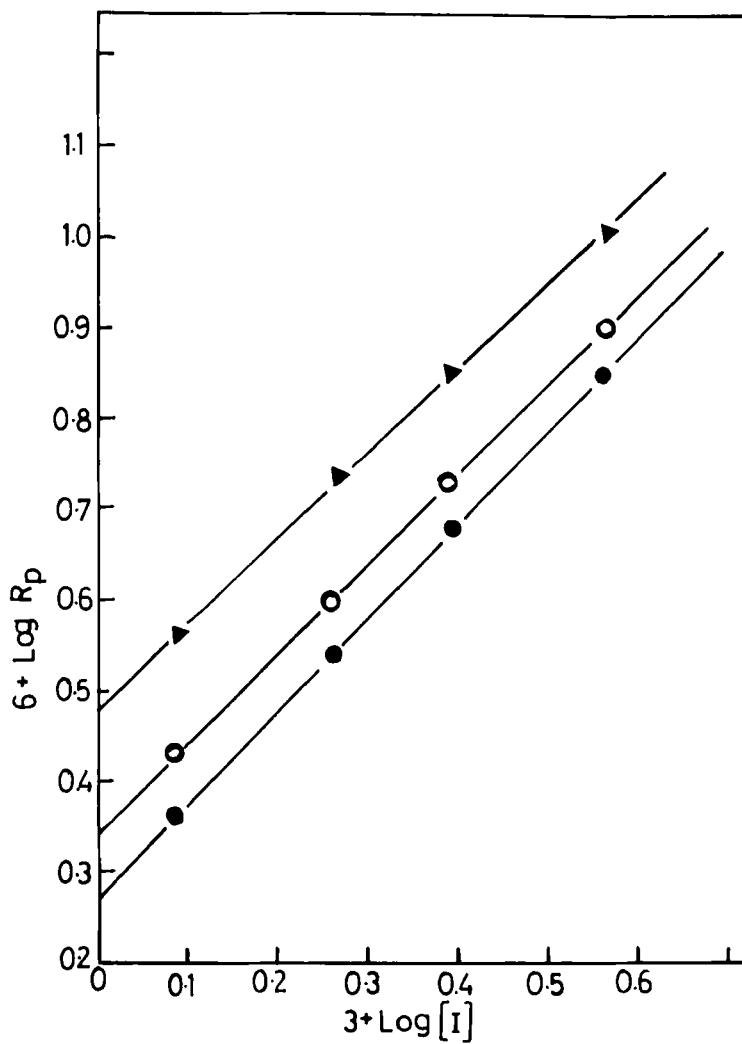


FIG. 2. Plot of $\log R_p$ versus $\log [I]$. Medium: Dioxane. Time: 100 min. $[M]$: 0.16 mol/L. $^{\circ}\text{C}$: (▲) 100, (○) 90, (●) 80.

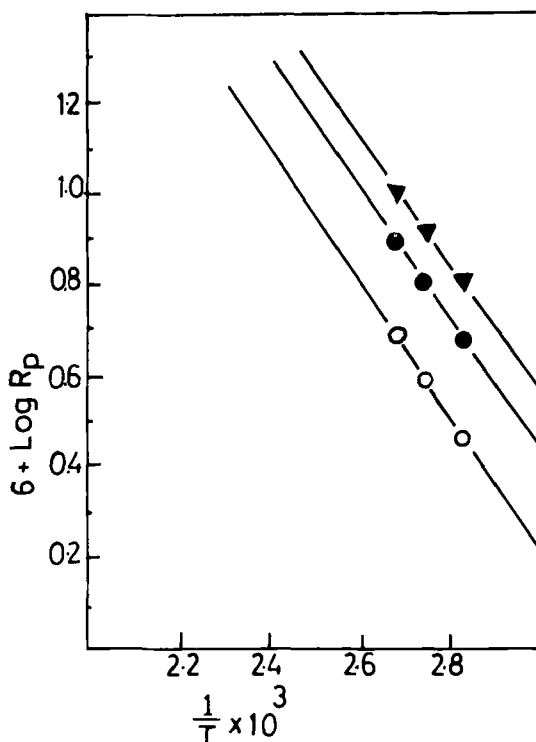


FIG. 3. Arrhenius plot of $\log R_p$ versus $1/T$. Medium: Dioxane. Time: 100 min. $[I]$: 3.65 mmol/L. $[M]$: (\circ) 0.11 mol/L, (\bullet) 0.13 mol/L, (\blacktriangle) 0.16 mol/L.

Effect of Temperature

The polymerization was carried out at 80–100°C, keeping the concentration of all reagents fixed. From the Arrhenius plot of $\log R_p$ versus $1/T$ (Fig. 3), the overall activation energy (E_a) was found to be 27.2 kJ/mol.

Relation between Conversion and Reaction Time

Time-conversion curves at three temperatures are shown in Fig. 4. As mentioned in the Experimental section, the rate of polymerization (R_p) was measured for 100 min duration at 40% conversion of the monomer. A plot of R_p versus time is shown in Fig. 5.

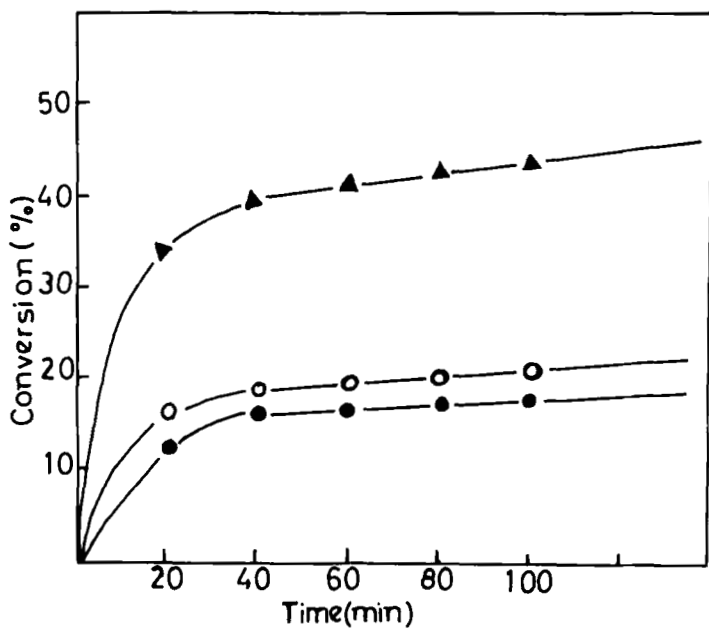


FIG. 4. Plot of % conversion versus time (min) at different temperatures. Medium: Dioxane. $[I]$: 5.4 mmol/L. $[M]$: 0.16 mol/L. °C: (▲) 100, (○) 90, (●) 80.

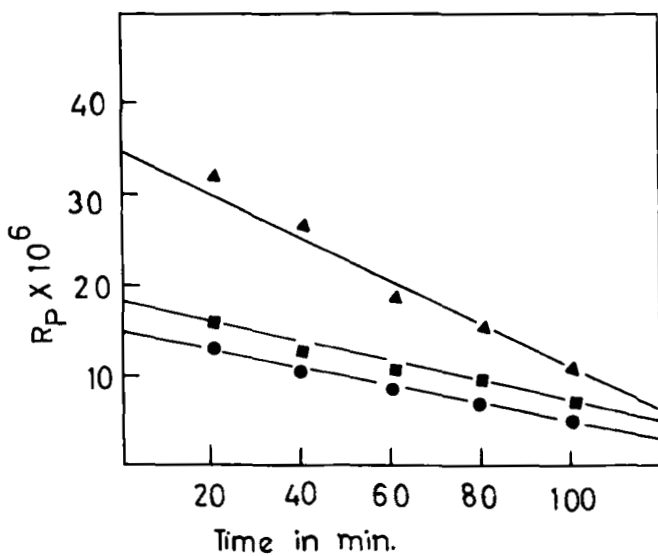


FIG. 5. Plot of R_p versus time (min) at different temperatures. Medium: Dioxane. $[I]$: 5.48 mmol/L. $[M]$: 0.06 mol/L. °C: (▲) 100, (■) 90, (●) 80.

On the basis of the standard free-radical polymerization scheme and the derivation of the kinetic equation suggested in the literature [11], the rate expression is derived:

$$R_p = k_p \frac{2K_d}{K_t} [M]^2 [I].$$

This rate expression satisfactorily explains all the kinetic results obtained.

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