

DEPENDENCE OF ACRYLONITRILE POLYMERIZATION KINETICS ON THE COMPOSITION OF POLYAMID- OXIME-THIOUREA SYSTEM

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ABSTRACT

The polymerization of acrylonitrile (AN) initiated by polypropylene based-polyamidoxime (PPAO)-thiourea (TU) system was investigated at $[TU]/[PPAO] > 0.5$ molar ratio. It shows that the variation of the concentrations of PPAO, thiourea and nitric acid does not exert an observable influence on the reaction rate. The overall rate of polymerization (R_p) is

$$R_p = 2.07e^{-7.800/RT} [AN]^{2.0}$$

The zero order dependence on PPAO and thiourea concentrations and the lowest value of the collision frequency factor were considered to be a feature of the primary radical termination.

INTRODUCTION

The activity of a complex catalyst, composed of a central compound and some ligands, is frequently governed by the molar ratio of both components. It is known that the mechanism of coordination polymerization^[1] and radical polymerization^[2] will be controlled by the composition of the complex catalysts. In vinyl polymerization, the uncoordinated central compounds and/or ligands as well as the complexes all are possible to act as a terminator. This brings about a great change on the mechanism of polymerization, which is bound to give expression in the rate parameters of kinetics^[3].

We have studied on the polymerization of acrylonitrile in aqueous nitric acid initiated by PPAO-thiourea system at $[TU]/[PPAO] < 0.5$ molar ratio^[4], in which a "coordination-proton transfer" mechanism has been proposed and a pattern of the active complex is given.

This article deals with the polymerization of acrylonitrile at $[TU]/[PPAO] > 0.5$ molar ratio. In the polymerization system, a great number of primary radicals generate and accumulate within the domains of the polymeric complex. Each of them stands a good chance of coupling with a growing chain to form a dead polymer. As a result, the value of collision frequency factor was very low and the reaction order with respect to the concentration of every component of the initiating system was found to be zero. The latter has been explained by assuming exclusive termination of polymer radicals by the primary radicals^[5,6]. This assumption was demonstrated further by the relationship between the molecular weight of

* Received April 20, 1992

This project is supported by the National Natural Science Foundation of China.

the polymer and the concentration of the reactants in the present paper.

EXPERIMENTAL

Materials

Acrylonitrile (AR) was distilled and stored in a refrigerator. Dimethylformamide (AR) was purified by distillation under reduced pressure before use. Thiourea (AR) and nitric acid (GR) were used without further purification. Water distilled and deionized by passing through a column of the mixed bed of resins.

Preparation of polyamidoxime

Granular polypropylene was grafted heterogeneously with acrylonitrile and then amidoximation in water-methyl alcohol mixture with hydroxylamine hydrochloride. The content of the amidoxime group in polymer matrix was determined by usual method.

Polymerization procedure

To a 60 mL vessel a mixture of acrylonitrile and aqueous nitric acid was introduced and kept in a thermostat bath for 30 minutes, the PPAO and thiourea solution were then added successively with stirring by a magnetic stirrer. Polymerization was carried out at a given temperature without stirring. At a definite interval, the reaction was arrested by adding a known excess of ethyl alcohol. The precipitated polymer was filtered, washed with water, and dried to constant weight. The conversion was determined by gravimetry.

Molecular weight determination

The intrinsic viscosity of the polymer in dimethylformamide was measured by an Ubbelohde viscometer at 25.0 °C. The number-average molecular weight ($\overline{M}_n$) was calculated using the Mark-Houwink equation given by Onyon^[7].

RESULTS AND DISCUSSION

Rate of polymerization

PPAO The rate of polymerization is independent of PPAO concentration within the range from 1.48×10^{-3} to 7.40×10^{-3} mol/L ($[TU]/[PPAO] = 2.60 \sim 0.52$ molar ratios) (Fig.1).

Thiourea Thiourea is subjected to protonation in acidic media to give an isothiurea cation, which reacts with PPAO to compose an active complex for the initiation of vinyl polymerization. In general, the variation of thiourea concentration will affect the generation of the primary radical in amount and follow by the initial rate of polymerization. It seems surprising that the rate of polymerization is unvaried while the molar ratio of thiourea to PPAO is over 0.5 (Fig. 2). We consider that the isothiurea plays the role either as an initiator, a terminator, or a transfer agent during the polymerization. However, it is not the same as the so called "Iniferter" in nature.

Nitric acid The polymer precipitate does not appear in polymerization system within 240 minutes if the nitric acid concentration is lower than 2.0 mol/L

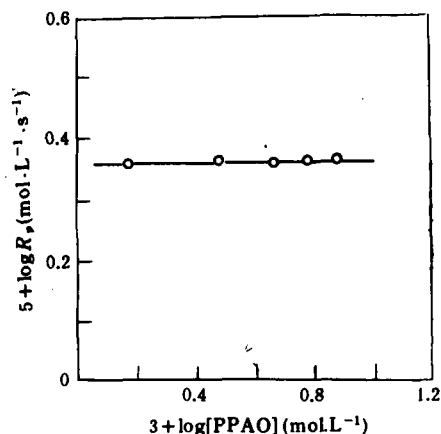


Fig. 1 Effect of PPAO concentration on the rate of polymerization at 35.0 °C
 [AN]: 1.78 mol/L; [HNO₃]: 3.26 mol/L;
 [TU]: 3.85×10^{-3} mol/L; [PPAO]: 1.48×10^{-3} ~ 7.40×10^{-3} mol/L.

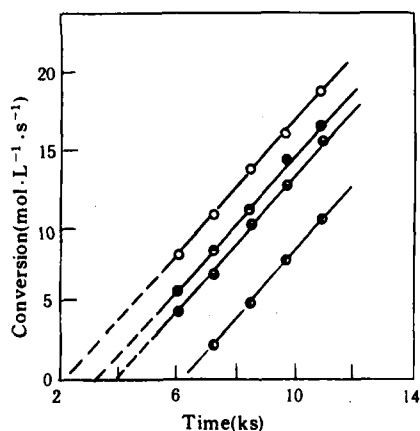


Fig. 2 Effect of TU concentration on time-conversion curves at 35.0 °C
 [AN]: 1.78 mol/L; [HNO₃]: 3.19 mol/L;
 [PPAO]: 4.44×10^{-3} mol/L; [TU] (mol/L):
 (○) 4.62; (◐) 5.38; (●) 6.15;
 (◑) 7.69.

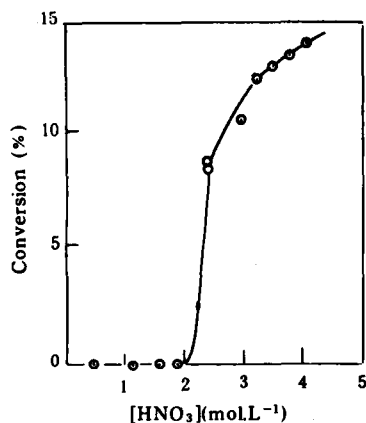


Fig. 3 Relationship between conversion and nitric acid concentration at 35.0 °C for 240 min
 [AN]: 1.44 mol/L; [HNO₃]: 0.54 ~ 4.06 mol/L;
 [PPAO]: 4.44×10^{-3} mol/L; [TU]: 3.85×10^{-3} mol/L.

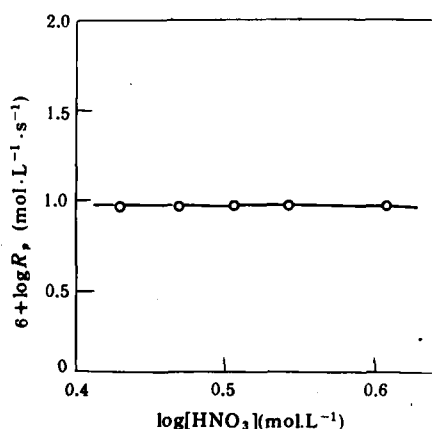


Fig. 4 Dependence of polymerization rate on nitric acid concentration at 35.0 °C
 [AN]: 1.15 mol/L; [HNO₃]: 2.67 ~ 4.01 mol/L;
 [PPAO]: 4.44×10^{-3} mol/L; [TU]: 3.85×10^{-3} mol/L.

(Fig. 3). The rate of polymerization remains constant on varying the nitric acid concentration from 2.67 to 4.01 mol/L (Fig. 4).

Monomer The rate of polymerization increases with increasing monomer concentration within the range from 0.87 to 1.75 mol/L. The order of the reaction with respect to the monomer concentration was found to be 2.0 (Fig. 5).

Temperature With increasing temperature in the region of 35.0 to 55.0 °C, the rate of polymerization increases as illustrated in Fig. 6. From the Arrhenius plot of $\text{Log } R_p$ vs $1/T$, the overall activation energy (E_0) was calculated to be 7.8 kcal/mol (32.6 kJ/mol).

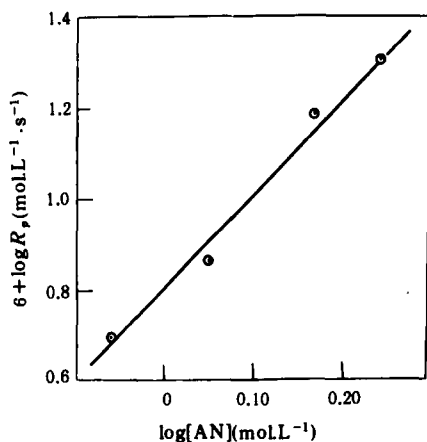


Fig. 5 Effect of monomer concentration on the rate of polymerization at 35.0 °C

[AN]: 0.87 ~ 1.75 mol/L; [HNO₃]: 3.18 mol/L;

[PPAO]: 4.44×10^{-3} mol/L; [TU]: 3.85×10^{-3} mol/L.

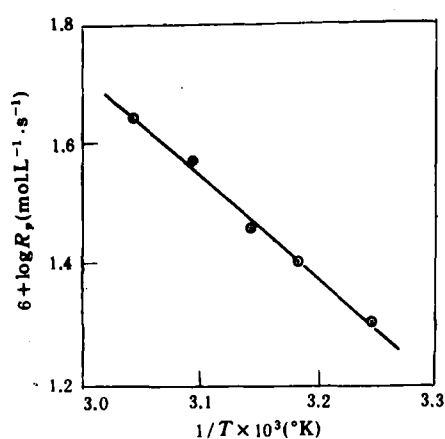


Fig. 6 Arrhenius plot

[AN]: 1.78 mol/L; [HNO₃]: 3.20 mol/L;

[PPAO]: 4.44×10^{-3} mol/L;

[TU]: 3.85×10^{-3} mol/L;

Temp.: 35.0 ~ 55.0 °C.

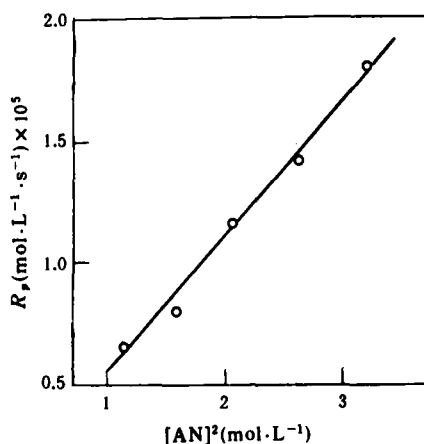


Fig. 7 Dependence of polymerization rate on reactants concentrations at fixed molar ratio

[AN](M)	[HNO ₃](M)	[PPAO] × 10 ³ (M)	[TU] × 10 ³ (M)
1.073	2.823	3.55	2.31
1.252	3.293	4.14	2.69
1.431	3.764	4.74	3.08
1.610	4.234	5.33	3.46
1.789	4.705	5.92	3.85
(1.00 : 2.63 : 3.31 × 10 ⁻³ : 2.15 × 10 ⁻³)			

The overall rate of polymerization obtained from the experimental results mentioned above is

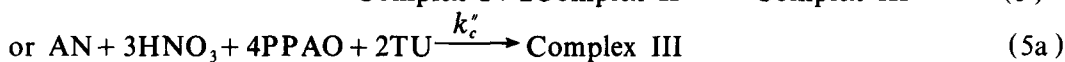
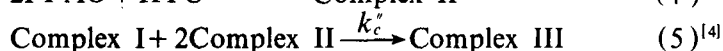
$$R_p = 2.07e^{-7.800/RT} [\text{AN}]^{2.0} \quad (1)$$

The lowest value of collision frequency factor A is reliable because we have also got $A' = 2.10$ from another run (Fig. 7). It is in agreement with the value

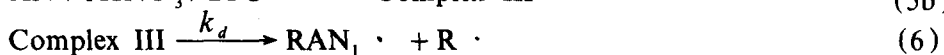
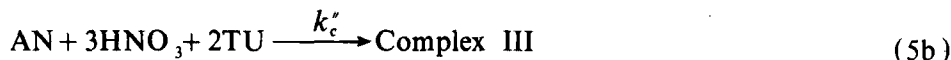
of A in Eq. (1).

REACTION MECHANISM AND RATE EXPRESSION

In the previous paper, we have reported the polymerization of acrylonitrile initiated by PPAO-thiourea system at $[TU]/[PPAO] < 0.5$ molar ratio. We consider that the active complexes are formed rapidly by coordination of PPAO, thiourea, acrylonitrile and the ion-pair of nitric acid in aqueous solution, and then it decomposes to give a monomeric radical and/or a primary radical. The latter induces the polymerization of acrylonitrile^[4]. The pathway of initiation may be written as follows:



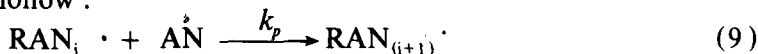
PPAO is not consumed during polymerization, that Eq. (5b) may be derived.



From Eqs. (2)–(7), the rate of initiation (R_i) is given by

$$R_i = k_c k_d k_i [AN]^2 [HNO_3]^3 [TU]^2 \quad (8)$$

The propagation is as follow:



$$R_p = k_p [RAN \cdot] [AN] \quad (10)$$

In the case of $[TU]/[PPAO] > 0.5$ molar ratio, a great number of primary radicals generate by decomposing of complex III, they accumulate surrounding the graft chains of polymer supporter and become to be the main substrate for termination. If the growing chains couple with the primary radicals predominately, the rate of termination (R_t) may be expressed as

$$R_t = k_{prt} [RAN \cdot] [R \cdot] \quad (11)$$

Applying the steady-state approximation for the radical $RAN \cdot$

$$\frac{d[RAN \cdot]}{dt} = k_i [R \cdot] [AN] - k_{prt} [RAN \cdot] [R \cdot] = 0 \quad (12)$$

$$[RAN \cdot] = \frac{k_i}{k_{prt}} [AN] \quad (13)$$

Substituting the value of $[RAN \cdot]$ in Eq. (10), the rate of polymerization may be written as follows.

$$R_p = k_p \cdot \frac{k_i}{k_{prt}} [AN]^2 \quad (14)$$

Eq.(14) is in fine agreement with the experimental results as shown in Eq.(1).

In this research, the primary radical termination is proved further according to the relationship between the degree of polymerization and the speed of reactions.

$$\frac{1}{\bar{P}_n} = \frac{R_{prt} + \Sigma R_{tr}}{R_p} \quad (15)$$

Fixed the molar ratio of all the reactant concentrations in a series of polymerization runs as shown under Fig. 7, Eq. (15) will be reduced to

$$\frac{1}{\bar{P}_n} = \frac{R_{prt}}{R_p} + K \quad (16)$$

$$= \frac{k_{prt} [R \cdot]}{k_p [AN]} \quad (17)$$

From Eq. (8), we obtained

$$R_i = k_d [R \cdot] [AN] = k_c' k_d k_i [AN]^2 [HNO_3]^3 [TU]^2 \quad (18)$$

$$[R \cdot] = k_c' k_d [AN] [HNO_3]^3 [TU]^2 \quad (19)$$

Substituting the value of $[R \cdot]$ in Eq. (17), we obtained

$$\frac{1}{\bar{P}_n} = \frac{k_c' k_d k_{prt}}{k_p} [HNO_3]^3 [TU]^2 \quad (20)$$

The linear dependence of $1/\bar{P}_n$ on $[HNO_3]^3 [TU]^2$ is shown in Fig. 8. It indicates that the reaction $R_{prt} = k_{prt} [RAN \cdot] [R \cdot]$ is reliable.

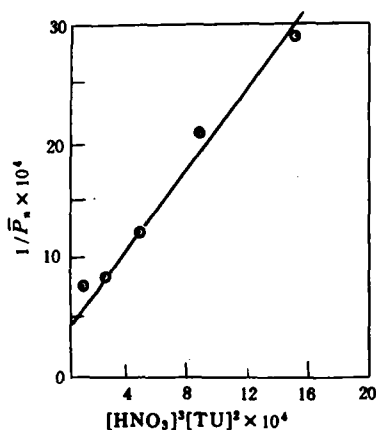


Fig. 8 Relationship between $1/\bar{P}_n$ and $[R \cdot] [AN]$ (cf. the footnote of Fig. 7)

The primary radical acted as either an initiator or a terminator is governed by the relative concentration of the substrates, namely, the composition of the complex III to a considerable extent. As we know, the rate of polymerization and the mechanism of reaction are almost dependent upon the initiator concentration used for radical polymerization.

Keywords:

Acrylonitrile; Polymerization; Kinetics, Polyamidoxime-thiourea system.

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