

"CAGE" VANADYL POLYCARBOXYLATE-THIOUREA COMPLEX FOR THE POLYMERIZATION OF ACRYLONITRILE*

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ABSTRACT

The polymerization of acrylonitrile (AN) in aqueous nitric acid initiated by "cage" vanadyl polycarboxylate (P=VO) — thiourea (TU) complex was investigated. The overall rate of polymerization is

$$R_p = 9.7 \times 10^5 e^{-10,500/RT} [\text{AN}] [\text{HNO}_3]^{1.5} [\text{P=VO}]^{0.50} [\text{TU}]^{0.76}$$

The relationship between the induction period (τ) and the temperature of polymerization as well as the concentrations of reactants can be expressed as follows:

$$\frac{1}{\tau} = 4.6 \times 10^{12} e^{-13,500/RT} [\text{HNO}_3]^3 [\text{P=VO}] [\text{TU}]^{3/2} = K_i R_i$$

The molecular weight of polyacrylonitrile ($\overline{M}_n$) increases with increasing monomer concentration and decreases with increasing temperature of polymerization and concentrations of vanadyl polycarboxylate and thiourea

$$\overline{M}_n = K_M \frac{1}{T} \cdot \frac{[\text{AN}]}{[\text{HNO}_3]^{3/2} [\text{P=VO}]^{1/2} [\text{TU}]^{3/4}} = K_M \cdot \frac{1}{T} \cdot R_p / R_i$$

The polymerization mechanism was proposed and discussed.

INTRODUCTION

It is found that the vanadyl sulfate (VOSO_4) coupled with a reductant such as thiourea does not initiate the polymerization of acrylonitrile^[1]. However, when the VO^{2+} ion is supported onto the "arbutus" polymers containing carboxyl groups, for example, the polypropylene-based polycarboxylate^[2], polypropylene-based polyimimidodiacetate^[3] or polypropylene-based poly(oxime-imimidodiacetate)^[4], respectively, it can be oxidized into a pentavalent vanadyl ion, VO_2^+ , by the synergy between two carboxyl groups bonding with VO^{2+} in acidic media. Afterwards, the thiourea coordinates and/or associates with it to produce an active species and initiate the polymerization of acrylonitrile.

The present paper deals with the polymerization of acrylonitrile in the presence of "cage" vanadyl polycarboxylate-thiourea complex (CVCT). We found that the decomposition of an active complex gives a primary radical rather than a monomeric radical, which is contrary to that of the "arbutus" vanadyl polycarboxylate-thiourea complex (AVCT). Moreover, the rate parameters of CVCT-AN system differ from those of AVCT-AN for the steric hindrance.

EXPERIMENTAL

Acrylonitrile (AR) was purified by distillation and stored in a refrigerator.

Received April 28, 1992

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

Thiourea (AR) and nitric acid (GR) were used as received. Dimethylformamide (AR) was distilled under vacuum before use. Deionized water was used as the solvent in all experiments.

"Cage" vanadyl polycarboxylate was prepared as follows: Polypropylene was grafted and crosslinked with methacrylic acid, acrylic acid, and bis-(3-methacryloyloxy-2-hydroxy propyl) ether of bisphenol A in aqueous solution. The product was extracted with xylene to remove the ungrafted polypropylene inside the particles. The hollow "cage" resin obtained was neutralized with 10% sodium hydroxide solution, washed repeatedly with water and then immersed into a 0.2 mol/dm³ vanadyl sulfate solution for 24 hours, filtered, washed, and dried. The vanadium-content of the "cage" catalyst was determined by combustion analysis.

Thiourea solution was prepared before use and determined iodometrically.

Polymerization was carried out in a ground-glass stoppered flask. The acrylonitrile-nitric acid mixture prepared freshly was charged into the flask and kept in a thermostat for 30 minutes, the "cage" vanadyl polycarboxylate and thiourea solution were then added successively. After polymerization for a given time, the polymer obtained was filtered through a previously weighed sintered glass crucible, washed thoroughly with water and dried in a vacuum oven at 50 °C. to a constant weight. The conversion was estimated gravimetrically.

The molecular weight of the polyacrylonitrile formed was measured by viscometry and calculated by using the Mark-Houwink equation as given by Onyon^[9].

RESULTS AND DISCUSSION

Rate of polymerization

The rate of polymerization increases with increasing P=VO concentration in the range from 5.88×10^{-4} to 2.94×10^{-3} mol/dm³. The order of the reaction with respect to P=VO concentration was found to be 0.50 (Fig.1). A half-order dependence of the rate on [P=VO] was found repeatedly to exist in acrylonitrile polymerization with an "arbutus" polymer supported vanadyl (IV)-thiourea complex^[2-4]. We considered that it is a feature of the chain termination by bimolecular reaction.

The rate of polymerization increases with increasing thiourea concentration in the range from 4.00×10^{-3} to 7.00×10^{-3} mol/dm³. The order of the reaction with respect to the thiourea concentration was found to be 0.76 (Fig.2). It shows that the average of thiourea molecule coordinated with P=VO is one and half.

The rate of polymerization increases with increasing monomer concentration within the range from 0.57 to 1.43 mol/dm³. The order of the reaction with respect to the monomer concentration was found to be unity (Fig.3). It suggests that acrylonitrile is impossible to participate in the composition of an active species because an AN-HNO₃ complex diffuses hardly into the network of cage matrix.

Nitric acid plays an important role in the initiation process. It controls the activation of an initiating system including both the "oxidant" P=VO and the

reductant thiourea. Under the same experimental conditions, no polymerization was observed within 60 minutes when the concentration of nitric acid is lower than 1.5 mol/dm^3 . While $[\text{HNO}_3] > 1.5 \text{ mol/dm}^3$, the polymerization takes place and the conversion increases rapidly (Fig. 4). The order of the reaction with respect to nitric acid concentration was found to be 1.5 in the range from 2.21 to 3.31 mol/dm^3 (Fig. 5).

The rate of polymerization increases regularly with increasing temperature from 22.5 to 40.5°C . From the Arrhenius' plot of $\log R_p$ vs. $1/T$, the overall activation energy (E_0) was calculated to be 10.5 kcal/mol (44.0 kJ/mol) (Fig. 6).

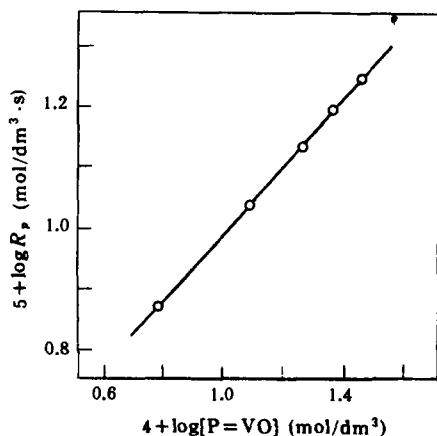


Fig.1 Effect of P=VO concentration on polymerization rate.

[AN]: 1.43 mol/dm^3 ; $[\text{HNO}_3]$: 3.31 mol/dm^3 ;
[TU]: $5.00 \times 10^{-3} \text{ mol/dm}^3$; Temp.: 25.0°C

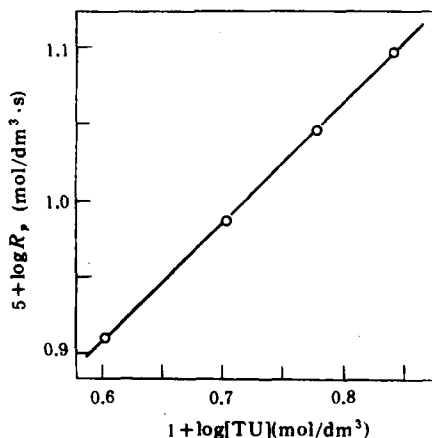


Fig.2 Effect of thiourea concentration on polymerization rate.

[AN]: 1.43 mol/dm^3 ; $[\text{HNO}_3]$: 3.31 mol/dm^3 ;
[P=VO]: $1.18 \times 10^{-3} \text{ mol/dm}^3$; Temp.: 25.0°C .

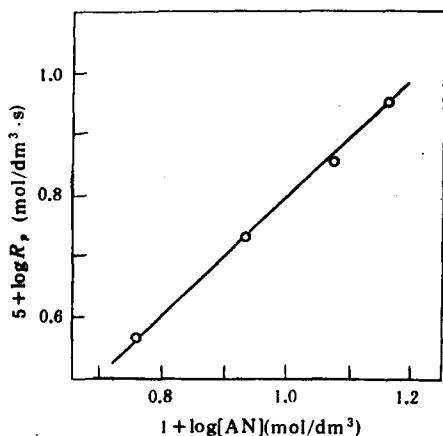


Fig.3 Effect of monomer concentration on polymerization rate.

$[\text{HNO}_3]$: 3.31 mol/dm^3 ;
[P=VO]: $1.18 \times 10^{-3} \text{ mol/dm}^3$;
[TU]: $5.00 \times 10^{-3} \text{ mol/dm}^3$;
Temp.: 25.0°C

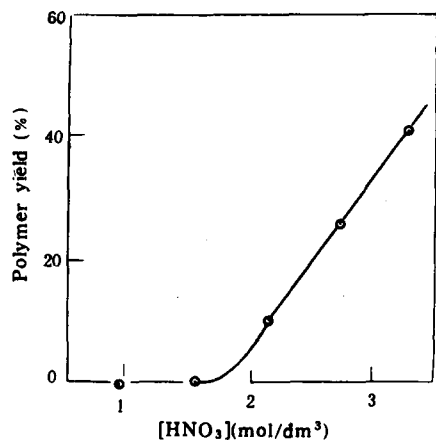


Fig.4 Effect of nitric acid concentration on conversion.

[AN]: 1.51 mol/dm^3 ; $[\text{HNO}_3]$: $0.97 - 3.29 \text{ mol/dm}^3$;
[P=VO]: $9.40 \times 10^{-4} \text{ mol/dm}^3$;
[TU]: $5.00 \times 10^{-3} \text{ mol/dm}^3$;
Temp.: 30.0°C . Time: 60 min.

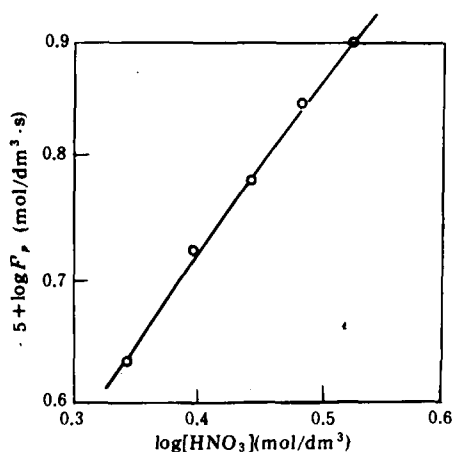


Fig.5 Effect of nitric acid concentration on polymerization rate .

[AN] : 1.43 mol/dm^3 ; [P = VO] : $1.18 \times 10^{-3} \text{ mol/dm}^3$;
[TU] : $5.00 \times 10^{-3} \text{ mol/dm}^3$; Temp. : 25.0°C .

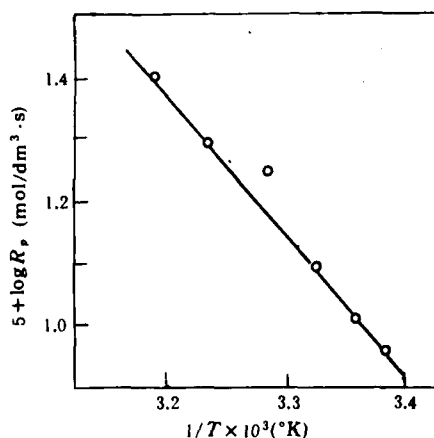


Fig.6 Effect of temperature on polymerization rate .

[AN] : 1.43 mol/dm^3 ; [HNO₃] : 3.31 mol/dm^3 ;
[P = VO] : $1.18 \times 10^{-3} \text{ mol/dm}^3$;
[TU] : $5.00 \times 10^{-3} \text{ mol/dm}^3$.

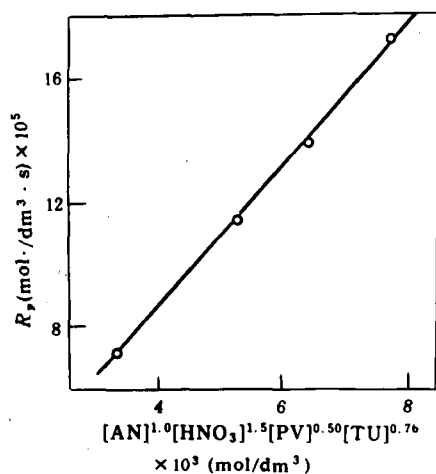


Fig.7 Plot of R_p vs. $[\text{AN}]^{1.0} [\text{HNO}_3]^{1.5} [\text{P}=\text{VO}]^{0.50} [\text{TU}]^{0.76}$.

Runs	[AN] (mol/dm ³)	[HNO ₃] (mol/dm ³)	[P = VO] × 10 ³ (mol/dm ³)	[TU] × 10 ³ (mol/dm ³)
1	1.15	2.82	1.79	3.81
2	1.29	3.17	2.01	4.29
3	1.36	3.35	2.13	4.52
4	1.44	3.53	2.24	4.76

Temp. = 25.0°C

From the experimental results mentioned above, the overall rate of polymerization may be written as

$$R_p = 9.7 \times 10^5 e^{-10,500/RT} [\text{AN}]^{1.0} [\text{HNO}_3]^{1.5} [\text{P}=\text{VO}]^{0.50} [\text{TU}]^{0.76} \quad (1)$$

Fixing the molar ratios of [AN] : [HNO₃] : [P = VO] : [TU] into 1.00 : 2.45 : 1.56×10^{-3} : 3.32×10^{-3} and varying the concentrations of these reactants simultaneously, a straight line was obtained from the plot of R_p vs. $[\text{AN}]^{1.0} [\text{HNO}_3]^{1.5} [\text{P}=\text{VO}]^{0.50} [\text{TU}]^{0.76}$. The value of the parameter K given by the slope is 2.16×10^{-2} at 25.0°C . (Fig.7).

The collision frequency factor A' calculated according to $K = A' e^{-E/RT}$ was found to be 10.7×10^5 . The value A' is in excellent agreement with the value A in Eq.(1). It confirms the authenticity of our kinetic data.

Induction period

The length of the induction period is independent of the variation of monomer concentration, but it reduces with increasing concentrations of nitric acid, P = VO and thiourea as well as the temperature of polymerization as shown in Fig.8.

The relationship between the induction period and the temperature of polymerization as well as the concentrations of reactants can be written as follows :

$$\frac{1}{\tau} = 4.6 \times 10^{12} e^{-13,500/RT} [\text{HNO}_3]^3 [\text{P}=\text{VO}] [\text{TU}]^{3/2} \quad (2)$$

From Eq.(1) and Eq. $R_p = k_p [\text{AN}] [\text{RAN} \cdot]$, we obtained

$$\frac{1}{\tau} = K [\text{RAN} \cdot]^2 \quad (2a)$$

If the growing chains are terminated by bimolecular mechanism, the Eq.(2a) may be derived as

$$\frac{1}{\tau} = k_t \cdot R_i \quad (2b)$$

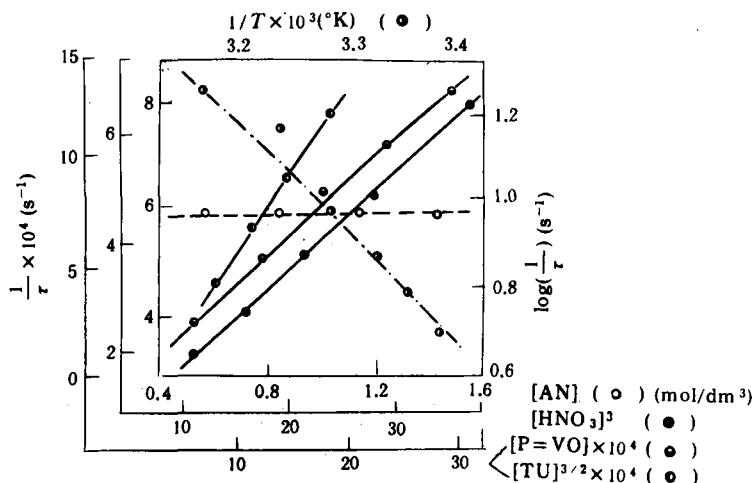


Fig.8 Effect of the concentrations of monomer, nitric acid, P=VO, thiourea, and temperature on the induction period

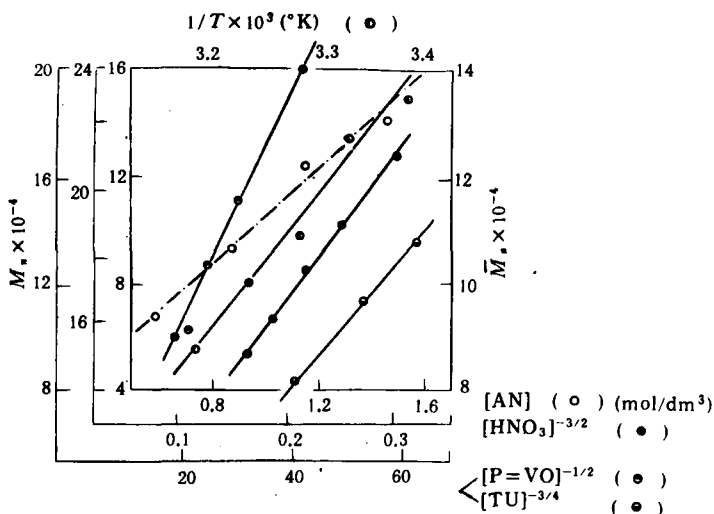


Fig.9 Effect of the concentrations of monomer, nitric acid, P=VO, thiourea, and temperature on the molecular weight of PA

Molecular weight

The molecular weight of polymer decreases with the elevation in temperature of polymerization and increases with the increase in monomer concentration. In addition, it is inversely proportional to the 1/2th power of $P=VO$ concentration, 3/4th power of thiourea concentration and 3/2th power of nitric acid concentration (Fig. 9). The relationship between the molecular weight of polymer and the concentration of reactants as well as the temperature of polymerization may be expressed as

$$\overline{M}_n = K \cdot \frac{1}{T} \cdot \frac{[AN]}{[P=VO]^{1/2} [TU]^{3/4} [HNO_3]^{3/2}} \quad (3)$$

Applying the bimolecular termination and the steady-state assumptions, thus

$$\overline{M}_n = K' \cdot \frac{1}{T} \cdot \frac{[AN]}{[RAN \cdot]} \quad (3a)$$

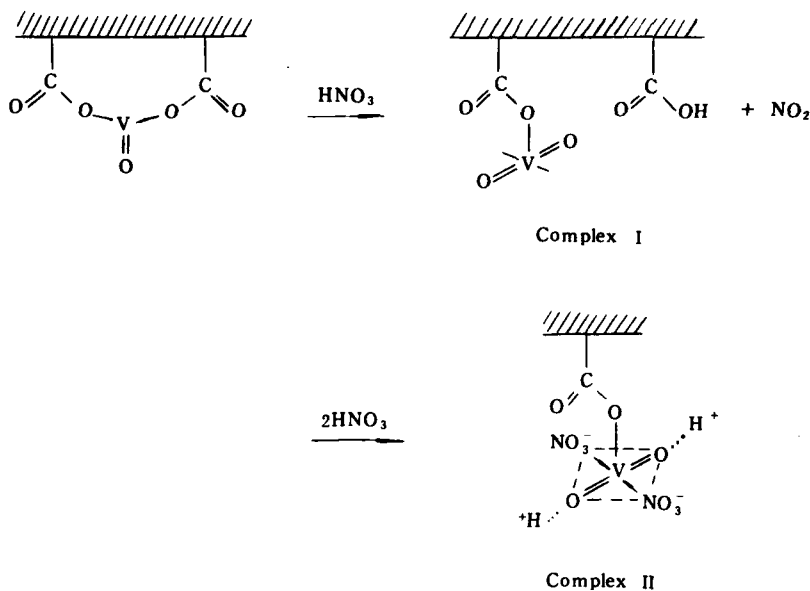
$$= K_M \cdot \frac{1}{T} \cdot \frac{R_p}{R_t} \quad (3b)$$

Reaction mechanism and rate expression

The following mechanism was suggested for the heterogeneous polymerization of acrylonitrile initiated by "cage" vanadyl polycarboxylate-thiourea complex in aqueous nitric acid.

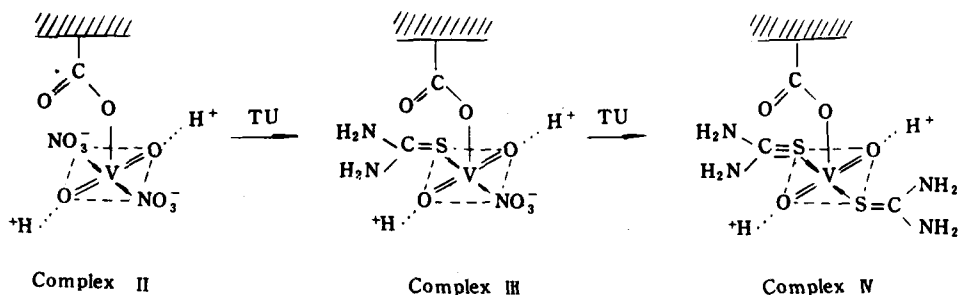
Production of primary radical:

While a $P=VO$ particle swelling in aqueous nitric acid, $=VO$ is oxidized into pentavalent $-VO_2$ by means of the synergy of the two bonding carboxyl groups. The oxidation product (complex I) couples immediately with the ion pairs of nitric acid to give the complex II by metal-ligand bonds (Scheme 1).



Scheme 1 Formation of complexes I and II.

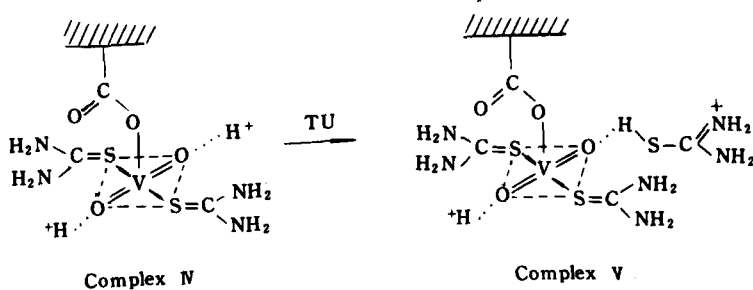
Thiourea is a Lewis base. Its basic constant is larger than that of nitrate. The formation of 2:1 complex of thiourea and VO_2^+ has been confirmed by Amjad and McAuley^[6]. When the thiourea solution is introduced to the complex (II)-containing system, the substitution reaction will take place as presented in Scheme 2.



Scheme 2

Scheme 2 Coordination between vanadium (V) complexes and thiourea.

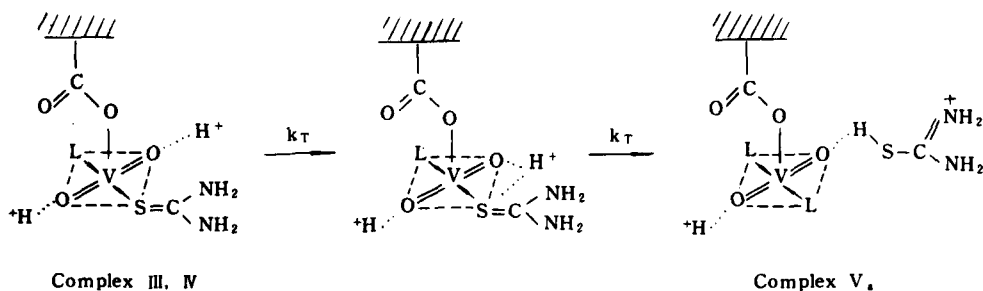
Under the conditions of a higher thiourea concentration and a lower mass transfer resistance, the formation of a complex V by Scheme 3 is unavoidable as reported in our earlier paper⁽¹⁾.



Scheme 3

Scheme 3 Association of thiourea with complex IV.

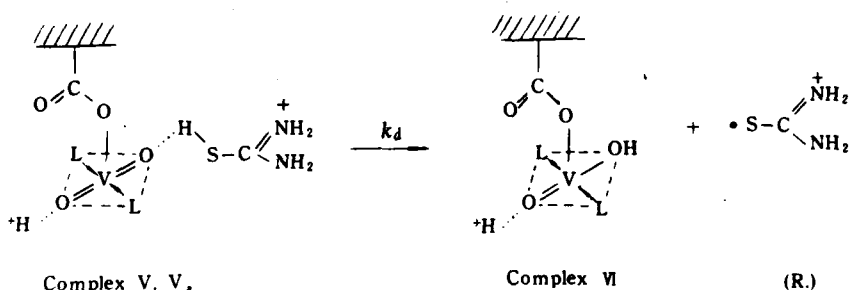
The steric hindrance of the "cage" polymer supporter, however, obstructs the further permeance of thiourea to coordinate with complex III and/or associate with complex IV, therefore, the formation of an isothiurea-bearing complex Va is mainly accomplished via the proton transfer within the complex III or IV (Scheme 4).



Scheme 4

Scheme 4 Formation of complex Va

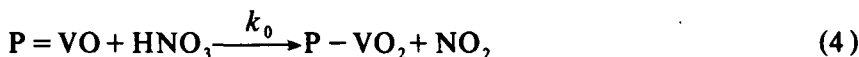
Complex V or Va is an active species, it decomposes to give a primary radical by Scheme 5.



Scheme 5

Schem 5 Formation of a primary radical

Accordingly, the production of a primary radical may be expressed as



Initiation :



Propagation :



Termination :

In this system, primary radical termination is of seldom occurrence because of the steric hindrance. It was confirmed by using the equation derived by Deb and Meyerhoff^[7] (Fig.10).

The relationship between the number-average degree of polymerization ($\bar{P}_n$) and the rate of reactions is :

$$\frac{1}{\bar{P}_n} = \frac{R_t + \sum R_{tr}}{R_p} \quad (9)$$

$$= \frac{2k_t}{k_p^2} \cdot \frac{R_p}{[AN]^2} + C_{AN} + C_{HNO_3} \frac{[HNO_3]}{[AN]} + C_{P=VO} \frac{[P=VO]}{[AN]} + C_{TU} \frac{[TU]}{[AN]} \quad (9a)$$

When a series of experiments were performed at fixing molar ratios of reactants as listed in the footnote under Fig.7, the values of $[HNO_3]/[AN]$, $[P=VO]/[AN]$, and $[TU]/[AN]$ were calculated to be 2.45, 1.56×10^{-3} , and 3.32×10^{-3} , respectively. Accordingly, Eq.(9a) can be written as follows :

$$\frac{1}{\bar{P}_n} = \frac{2k_t}{k_p^2} \cdot \frac{R_p}{[AN]^2} + k \quad (9b)$$

From the experimental data (Fig.11, 12), we obtained :

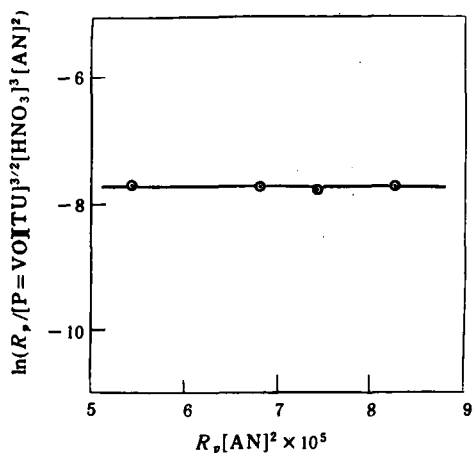


Fig.10 Plot of $\ln(R_p^2/[I][M]^2)$ vs. $R_p/[M]^2$.
(see foot-note below Fig.7).

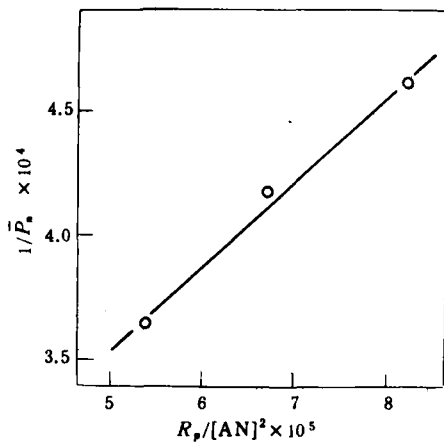


Fig.11 Plot of $1/\bar{P}_n$ vs. $R_p/[AN]^2$.

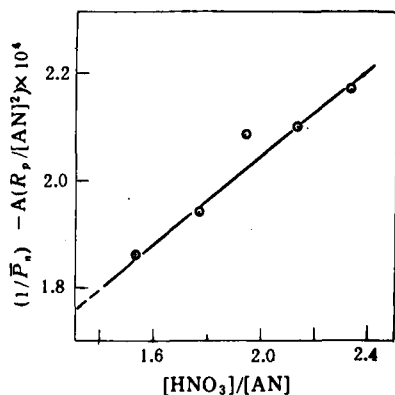
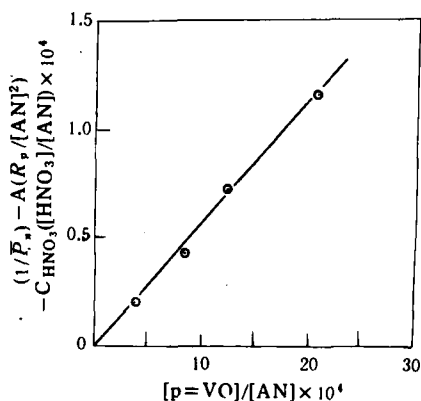
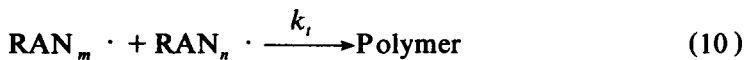


Fig.12 Chain transfer to nitric acid, P=VO, thiourea and monomer.



$$\frac{2k_t}{k_p^2} = 3.5, \quad C_{AN} = 0, \quad C_{HNO_3} = 5.0 \times 10^{-5}, \quad C_{P=VO} = 6.0 \times 10^{-2}, \quad C_{TU} = 0.$$

It shows that the chain radicals are terminated mainly by bimolecular mechanism.



Making the usual assumptions for the steady-state concentrations, the following expressions may be derived :

$$\frac{d[R \cdot]}{dt} = k_0 k_c k_d [P=VO][HNO_3]^3 [TU]^n - k_t [R \cdot][AN] = 0. \quad (11)$$

$$\frac{d[RAN \cdot]}{dt} = k_i [R \cdot][AN] - k_t [RAN \cdot]^2 = 0 \quad (12)$$

Eqs. (11) and (12) lead to

$$[RAN \cdot] = \left(\frac{k_0 k_c k_d}{k_t} \right)^{1/2} [HNO_3]^{3/2} [P=VO]^{1/2} [TU]^{n/2} \quad (13)$$

The rate of polymerization is given by

$$R_p = k_p \left(\frac{k_o k_c k_d}{k_t} \right)^{1/2} [\text{HNO}_3]^{3/2} [\text{P} = \text{VO}]^{1/2} [\text{TU}]^{n/2} \quad (14)$$

Make a comparison between the Eq.(14) and the experimental results (Eq.1), the order of the reaction with respect to the thiourea concentration was found to be 1.5 since $n/2=0.76$. This data shows that the opportunity of the formation of complex V_s from the complex IV is almost equal to that from the complex III.

Keywords :

Cage catalyst; Vanadyl polycarboxylate-thiourea complex; Polymerization; Acrylonitrile.

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