

VINYL RADICAL POLYMERIZATION INITIATED WITH CERIC ION AND ETHYL N, N-DIETHYLDITHIOCARBAMYL ACETATE SYSTEM

XU Shoujun (许守军) and QIU Kunyuan (丘坤元)*

(Department of Polymer Science and Engineering, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871)

ABSTRACT

Acrylamide polymerization initiated with a redox initiation system consisting of ceric ion and ethyl N, N-diethyldithiocarbamyl acetate (EDCA) has been studied. It was found that the polymerization rate equation is in good agreement with that of a redox initiated polymerization, and the overall activation energy of the polymerization was determined to be $25.2 \text{ kJ} \cdot \text{mol}^{-1}$. Accordingly, the system belongs to a redox initiator. The initiation mechanism was proposed based on the end group analysis using FT-IR, UV spectroscopies. Analysis results revealed that the N, N-diethyldithiocarbamyl radical produced from the redox reaction of EDCA with ceric ion can initiate acrylonitrile (AN) polymerization and form the end group on PAN. The resulting PAN was photopolymerized with butyl acrylate (BA) to form PAN-b-PBA block copolymer.

INTRODUCTION

Redox initiation systems consisting of ceric ion and reductants such as alcohol, aldehyde, ketone, hydroxycarboxylic acid, etc., are used for vinyl radical polymerization in aqueous medium^[1-4]. Recently, in our laboratory some new redox initiation systems, such as Ce(IV) ion/acetanilide, Ce(IV) ion/acylacetanilide^[5-9], and Ce(IV) ion/1,3-diketone compounds^[10-12] have been investigated in acrylamide (AAM) polymerization.

However, much less attention has been paid on the Ce(IV) ion in conjunction with sulfur compounds. Although a few papers^[13-15] reported that Ce(IV) ion in conjunction with thiourea or mercaptoacetic acid, thioacetamide systems could initiate

The Project 29234093 was supported by the National Natural Science Foundation of China

* To whom correspondence should be addressed

Received September 3, 1996

vinyl monomers radical polymerization, yet there is still lack of works on the initiation mechanism and kinetics studies. Recently, alkyl 2-(N, N-diethyldithiocarbamyl) isobutyrate, n-butyl 2-(N, N-diethyldithiocarbamyl) propionate and ethyl N, N-diethyl dithiocarbamylacetate (EDCA) reported by Otsu^[6], Dikamanga^[17] and Yang, et al.^[18] could serve as photoinitiator for radical polymerization of several monomers. This paper describes the kinetics and initiation mechanism of AAM polymerization initiated by a novel Ce(IV) ion and EDCA system.

EXPERIMENTAL

Materials: Acrylamide, acrylonitrile (AN) and butyl acrylate (BA) were chemical reagent grade and purified by common methods. Ceric ammonium nitrate (CAN) was analytically pure grade used as received. Acetonitrile, N, N-dimethylformamide (DMF), dimethylsulfoxide (DMSO) were purified by distillation and deionized water was used for polymerization medium.

EDCA was synthesized from chloroacetyl chloride via two-steps reaction with anhydrous ethanol and sodium N, N-diethyldithiocarbamate. The purified EDCA was a white needle crystal with m.p: 51—52.5°C (yield: 74%). ¹H-NMR of EDCA (δ , in CDCl₃ 400 MHz): 1.27—1.33 [9H, CH₃CH₂OOC and (CH₃CH₂)₂N], 3.77 [2H, (CH₃CH₂)₂N], 4.02 [2H, (CH₃CH₂)₂N], 4.16 [2H, OOCCH₂—SSC], 4.23 [2H, CH₃—CH₂OOC]. Elemental analysis for C₉H₁₇NO₂S₂:

	C	H	N	S
Calculated%	45.92	7.29	5.95	27.24
Found%	45.81	7.31	5.37	27.37

Polymerization: The AAM polymerization was carried out in a mixed solution of acetonitrile and water (v/v=1:2) using CAN/EDCA as an initiator. The rate of polymerization (R_p) was determined by dilatometric method^[19]. The samples of polyacrylonitrile (PAN) were prepared by the polymerization of 3 ml AN in 42 ml mixed solution of acetonitrile and water (v/v=1:2) initiated by CAN/EDCA system (with equal concentration of 1.5×10^{-2} mol·L⁻¹) and CAN alone, respectively. The resulting polymers were washed with acetonitrile and dried under vacuum.

Photopolymerization of BA with the resulting PAN: Butyl acrylate was photopolymerized with the above resulting PAN in DMSO. The polymer obtained was extracted by acetone for 48 h and washed thoroughly by ethanol until there is no absorption of acetone appeared in the FT-IR spectrum of the washed ethanol.

Measurements: UV spectrum was recorded using a Shimatsu 250 UV spectrometer in DMF solution. FT-IR spectrum of the sample in KBr was taken on a Nicolet 750 Magna-IR 750 spectrometer. $^1\text{H-NMR}$ spectrum was recorded on a Bruker ARX-400 spectrometer in CDCl_3 solution using tetramethylsilane as internal reference.

RESULTS AND DISCUSSION

1. Kinetics of AAM polymerization

The rate of polymerization (R_p) of AAM was determined by dilatometric method and the double logarithmic plots of R_p versus concentrations of EDCA, CAN and AAM are shown in Figs. 1 and 2, respectively. From which the following rate equation is obtained:

$$R_p = K [\text{CAN}]^{0.47} \cdot [\text{EDCA}]^{0.58} [\text{AAM}]^{0.88}$$

This equation is in agreement with a redox initiated rate equation, which is

$$R_p = K [\text{Oxidant}]^{0.5} \cdot [\text{Reductant}]^{0.5} [\text{Monomer}]^{1.0}$$

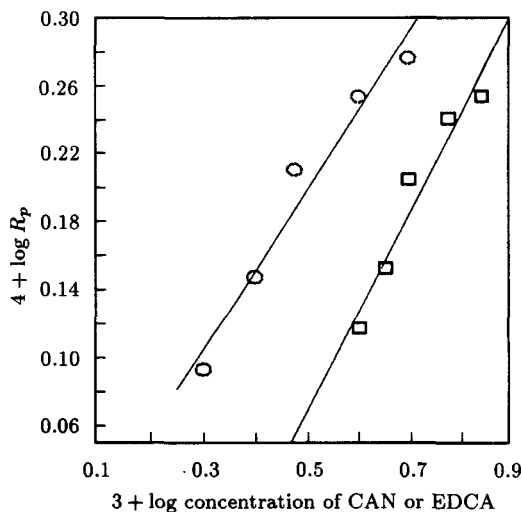


Fig. 1 Double logarithmic plots of $\log R_p$ of AAM versus (○) $\log [\text{CAN}]$ and (□) $\log [\text{EDCA}]$

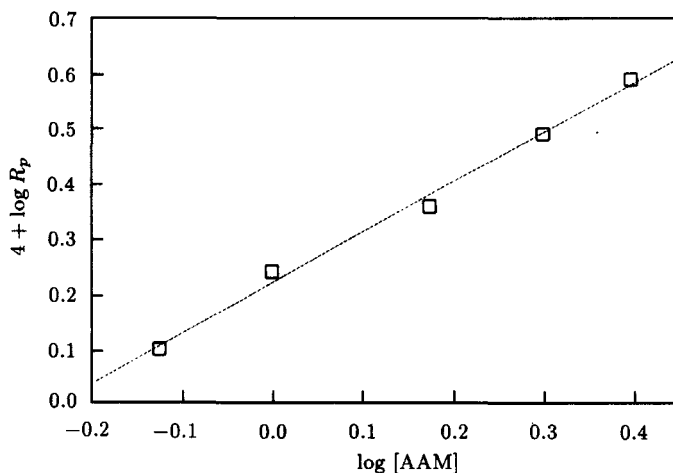


Fig. 2 Double logarithmic plot of $\log R_p$ versus $\log [\text{AAM}]$

When the concentrations of CAN, EDCA, AAM were fixed at 4.0×10^{-3} , 6.0×10^{-3} and $1.0 \text{ mol} \cdot \text{L}^{-1}$, respectively, the polymerization was carried out at different temperatures in the range of $25\text{--}44^\circ\text{C}$, the values of R_p were determined. From the Arrhenius plot, i.e., $\ln R_p$ versus $1/T$ as shown in Fig. 3, the value of overall activation energy (E_a) for AAM polymerization initiated with CAN/EDCA system was calculated to be $25.2 \text{ kJ} \cdot \text{mol}^{-1}$. It is much lower than the value of E_a initiated by CAN alone. ($E_a = 48.0 \text{ kJ} \cdot \text{mol}^{-1}$). Accordingly, the CAN/EDCA system belongs to a redox initiation system.

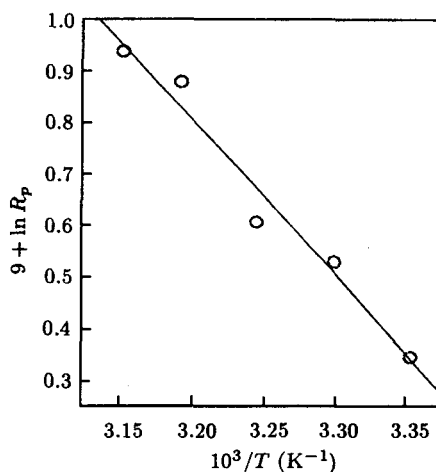


Fig. 3 Correlation between $\ln R_p$ and $1/T$

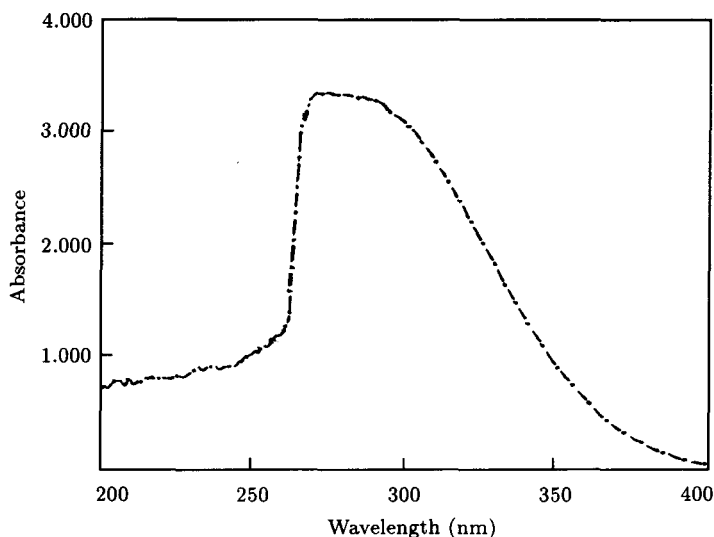


Fig. 4 UV spectrum of PAN initiated with CAN/EDCA system

2. End group analysis and photolytic reaction of resulting PAN

In order to clarify the initiation mechanism it is necessary to determine the radical species formed from the reaction of the oxidant and reductant. However, it is difficult to determine the radical species from the CAN and EDCA using radical trapping agent and electron paramagnetic resonance (EPR) technique. The end group analysis and photolytic reaction of resulting PAN from the polymerization of

AN using CAN/EDCA system were investigated carefully and some valuable results were obtained.

Fig. 4 is the UV spectrum of PAN. From which it can be seen that a broad absorption peak at 270–290 nm is the characteristic band of diethyldithiocarbamyl group ($\text{Et}_2\text{NSCS—}$, $\lambda_{\text{max}} = 278 \text{ nm}$ for EDCA in THF), indicating the presence of this group as the end group of PAN. This can be further confirmed by the FT-IR spectrum of PAN initiated by CAN/EDCA as shown in Fig. 5b. In comparison with Fig. 5a (PAN initiated with CAN alone), it shows that besides the characteristic absorption of CN group at 2243 cm^{-1} , new absorption at 1033 , 1291 and 1510 cm^{-1} are present, these bands are characteristics of SCSNR_2 group^[20]. However, there is no absorption at 1730 cm^{-1} (carbonyl of ester group). The results indicate the presence of diethyldithiocarbamyl moiety end group in the PAN obtained with CAN/EDCA system as initiator.

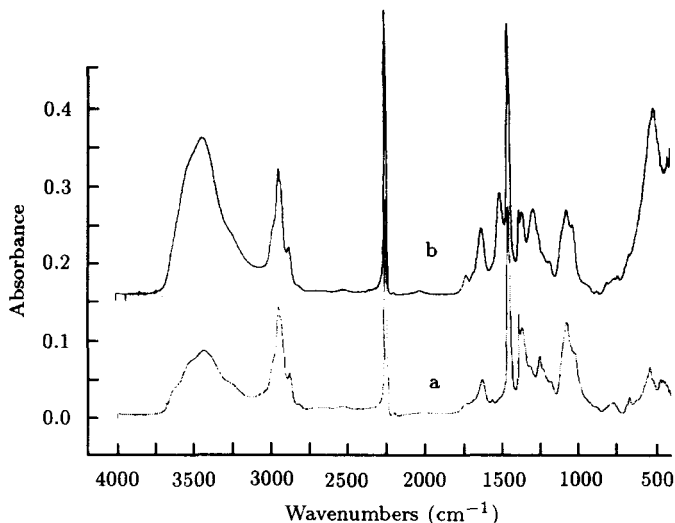
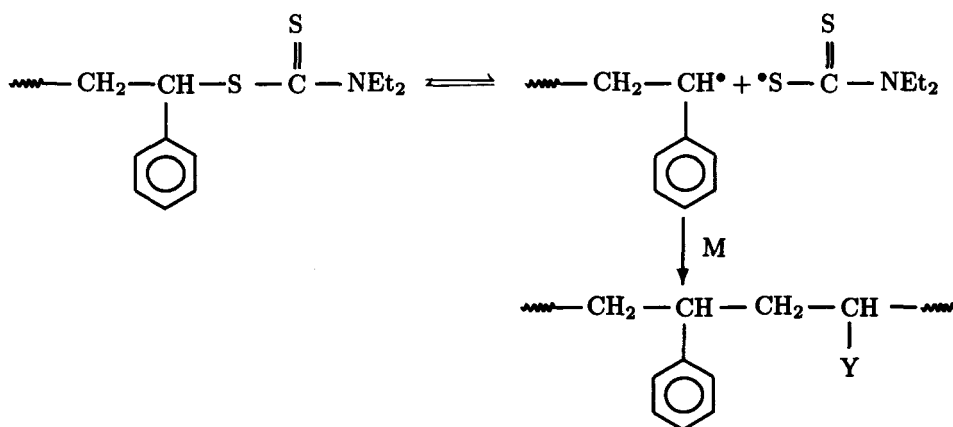


Fig. 5 FT-IR spectra of PAN; (a) PAN initiated with CAN alone; (b) PAN initiated with CAN/EDCA system

Otsu et al.^[16,21] and the authors^[22] reported that in the styrene polymerization using diethyldithiocarbamyl-containing photoinitiator, the SCSNEt_2 end group of resulting polystyrene could photodissociate and initiate vinyl monomer block copolymerization as shown in Scheme 1. So we investigated the photolytic reaction of PAN prepared by CAN/EDCA redox system in the presence of BA monomer. A polymer was obtained by purification. After photolytic reaction the intrinsic viscosity of the polymer increased from $0.44 \text{ dl}\cdot\text{g}^{-1}$ to $0.66 \text{ dl}\cdot\text{g}^{-1}$ (in DMF at 30°C) and its weight increased from 0.029 g to 0.041 g. The polymer obtained was further characterized by FT-IR spectroscopy.

Fig. 6 is a FT-IR spectrum of the resulting polymer of photopolymerization of BA in the presence of PAN (initiated with CAN/EDCA system). It shows that besides the characteristic absorption of nitrile group at 2243 cm^{-1} , the characteristic absorption of ester group at 1735 cm^{-1} and 1166 cm^{-1} are also present. It is evident that PAN-b-PBA has been obtained and the end group of PAN must be diethyldithiocarbamyl group.



Scheme 1

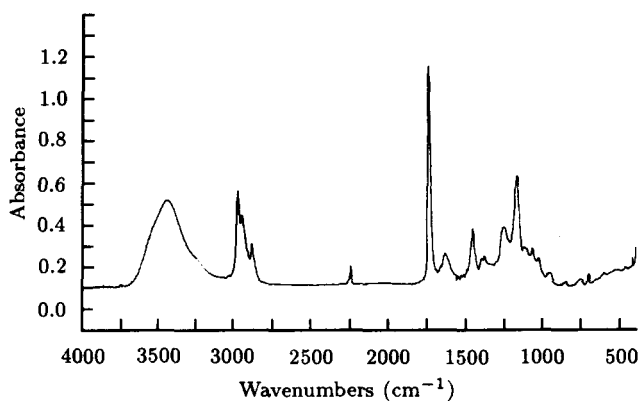


Fig. 6 FT-IR spectrum of P(AN-b-BA)

3. Initiation mechanism

Based on the above studies, the initiation mechanism of CAN/EDCA redox system is proposed as the following:



- [12] Zhao, J.B. and Qiu, K.Y., *Chem. J. Chinese Univ.* (in Chinese), **1996**, 17: 315.
- [13] Misra, G.S. and Bhattacharya, S.N., *J. Polym. Sci. Polym. Chem. Ed.*, **1982**, 20: 131.
- [14] Misra, G.S. and Dubey, G.P., *J. Macromol. Sci. Chem.*, **1981**, A16: 601.
- [15] Samal, R.K.; Nayak, M.C.; Parda, G. and Syryinarayana, G.V., *J. Polym. Sci. Polym. Chem. Ed.*, **1982**, 20: 53.
- [16] Otsu, T.; Matsunaga, T. and Doi, T., *Europ. Polym. J.*, **1995**, 31: 67.
- [17] Dikamanga, J.; Polto, A.; Tardi, M. and Sigwalt, P., *Macromol. Reports*, **1995**, A32: 695.
- [18] Yang, X.M. and Qiu, K.Y., *J. Macromol. Sci. Pure. Appl. Chem.*, **1997**, A34(2): 315—325.
- [19] Guo, X.Q.; Qiu, K.Y. and Feng, X.D., *Scientia Sinica, Ser B.*, **1987**, 30(9): 897.
- [20] Socrates, G., "Infrared Characteristic Group Frequencies", Chichester: John Wiley & Sons, **1980**, Chapter 16.
- [21] Otsu, T.; Yoshida, M. and Tazaki, T., *Macromol. Chem., Rapid Commun.*, **1982**, 3: 133.
- [22] Yang, X.M. and Qiu, K.Y., *J. Appl. Polym. Sci.*, **1996**, 61: 513.