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Initiation Mechanism of Radical Polymerization Using Ammonium Persulfate and Polymerizable Amine Redox Initiators

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INITIATION MECHANISM OF RADICAL POLYMERIZATION USING AMMONIUM PERSULFATE AND POLYMERIZABLE AMINE REDOX INITIATORS

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ABSTRACT

A redox initiation system consisting of a polymerizable amine such as N-[(3-dimethylamino)-propyl] acrylamide(DMAPAA) or N-[(3-dimethylamino)-propyl] methacrylamide(DMAPMA) and ammonium persulfate(APS) used for aqueous polymerization of acrylamide(AAM) has been studied. It has been found that the rate equation of AAM polymerization is in good agreement with the redox initiated polymerization rate equation, and the overall activation energies of the polymerization obtained are 35.04 and 40.96 kJ/mol for APS/DMAPAA and APS/DMAPMA systems, respectively. Accordingly, the systems belong to redox ones. The initiation mechanism of the polymerizable redox systems has been investigated by means of electron paramagnetic resonance(EPR), Fourier-transform infrared(FT-IR) and ultra violet(UV) spectroscopies. Two kinds of radicals, alkylamino methyl radical and monomeric propagating radical have been detected by EPR spectroscopy. Based on experimental results the initiation mechanism of ammonium persulfate/polymerizable amine system is proposed.

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INTRODUCTION

Persulfate(or peroxydisulfate) such as ammonium persulfate (APS), potasium persulfate(KPS) is a water soluble initiator. Persulfate in conjunction with aliphatic amine, polyamine can be used as redox initiator in aqueous solution polymerization of vinyl monomers[1-4]. Guo et al[4] reported the effect of various amine on acrylamide(AAM) aqueous solution polymerization and investigated the initiation mechanism of persulfate/amine systems by means of end group analysis and EPR spectroscopy[4-6]. Recently, functional monomer containing amino group, so-called polymerizable amine, such as N-(dimethylaminomethyl) methacrylamide (DMAMMA)[7], N-(dimethylaminomethyl) acrylamide (DMAMAA)[8] can couple with persulfate to initiate AAM polymerization. It was found that the presence of polymerizable amine can promote the rate of polymerization and enchance the molecular weight of PAAM obtained. The present paper reports the results of AAM polymerization using persulfate and polymerizable amine N-[(3-dimethylamino)-propyl] acrylamide (DMAPAA) or N-[(3-dimethylamino)-propyl] methacrylamide (DMAPMA) as redox initiator, including polymerization kinetics, EPR, FT-IR and UV spectra studies on the initiation mechanism of persulfate/polymerizable amine systems.

EXPERIMENTAL

Material: Acrylamide, methyl methacrylate(MMA), acrylonitrile(AN) and ammonium persulfate were of chemical reagent grade and purified by the common methods. Spin trapping agent 2-methyl-2-nitrosopropane (MNP) and tetracyano ethylene (TCNE) were purchased from Aldrich Chem. Co. and Tokyo Chem. Inds., respectively, and used without further purification. N-[(3-dimethylamino)-propyl] acrylamide (DMAPAA), N-[(3-dimethylamino)-propyl] methacrylamide (DMAPMA) and N-[(3-dimethylamino)-propyl] propionamide(DMAPPA) were synthesized by the reactions of 3-dimethylaminopropylamine (DMAPA) with acryloyl, methacryloyl and propionyl chloride, respectively. The fractions of DMAPAA, DMAPMA and DMAPPA were collected at 112-113°C/133.3Pa, 108-110°C/133.3Pa and 105-107°C/133.3Pa respectively. The purified products were characterized by elemental analysis, the data were listed as follows: DMAPAA, cacld: C, 61.51% H, 10.32% N, 17.93%, found: C, 61.88% H, 10.57% N, 17.16%. DMAPMA, cacld: C, 63.49% H, 10.66% N, 16.45%, found: C, 62.95% H, 10.57% N, 16.32%; DMAPPA, cacld: C, 60.67% H, 11.38% N, 17.70%; found: C, 60.62% H, 11.73% N, 17.88%. DMAPAA, DMAPMA and DMAPPA were further characterized by ^{1}H-NMR and FT-IR respectively.

Polymerization: The kinetics of AAM polymerization in aqueous solution was determined by dilatometric method.

FT-IR mesurements: The PANs prepared from the polymerization of AN using APS/amine systems as initiators were used as samples for FT-IR measurement. The molecular weights of resulting PAN are 2.95×10^4, 2.82×10^4 for APS/DMAPA and APS/DMAPPA initiation systems, respectively. The FT-IR measurement was recorded by a Nicolet 750 Magna-IR spectrometer.

UV-VIS measurement: The PMMA samples were prepared from the polymerization of MMA initiated with APS/DMAPPA and APS/DMAPA, respectively. A solution of resulting PMMA dissolved in CH_2Cl_2, was mixed with a solution of TCNE in CH_2Cl_2. The charge transfer complex (CTC) spectrum of the mixed solution was recorded by a Shimatsu 250-UV spectrometer[4].

EPR measurement: The EPR spectra were recorded in the similar conditions with references[4-6]. MNP was used as a spin trap and acetonitrile/water mixed solvent was used for the reaction medium. The EPR spectra were mearsured at room temperature on a Brucker ER200D-SRC EPR spectrometer using a TM cavity at X-band, and a field modulation frequency of 100kHz.

RESULTS AND DISCUSSION

1. Kinetics of AAM polymerization initiated with redox initiator

The rate of AAM aqueous solution polymerization using APS/DMAPAA as initiator was determined by dilatometry and the following rate equation was obtained from the plot of $-\ln R_p$ versus $-\ln[\mathrm{APS}]$, $-\ln[\mathrm{DMAPAA}]$, $-\ln[\mathrm{AAM}]$, respectively as shown in Fig. 1.

$$R_p=k[\mathrm{APS}]^{0.40}[\mathrm{DMAPAA}]^{0.55}[\mathrm{AAM}]^{1.14}$$

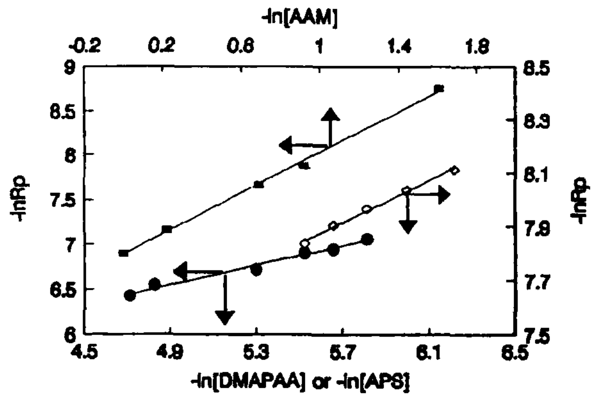


Fig.1. Plot of -lnRp versus -ln[DMAPAA], or -ln[APS], or -ln[AAM] for AAM aqueous solution polymerization at 25°C

The rate equation is in good agreement with the redox initiated polymerization rate equation, i.e., the polymerization rate is nearly proportional to the 0.50th power for the oxidant concentration, 0.5th power for the reductant concentration, and the 1th power for monomer concentration. Similar result was obtained for APS/DMAPMA system.

TABLE 1. Ea values for AAM polymerization

Initiation system	Ea (kJ/mol)	Reference
APS	69.19	This work
APS/DMAPAA	35.04	This work
APS/DMAPMA	40.96	This work
KPS/DMAMMA	36.40	[7]
KPS/DMAMAA	27.86	[8]

The values of overall activation energy of polymerization Ea for AAM polymerzation initiated with various initiators were evaluated by Arrhenius plot(Fig.2), and the data were listed in Table 1, along with the other systems reported in the literatures. The result reveals that APS/DMAPAA, APS/DMAPMA systems belong to redox initiation system.

2. EPR studies on the initial free radical

Radical trapping and EPR spectrum as well as end group analysis are very useful techniques for clarifying and revealing the initiation mechanism of persulfate/amine

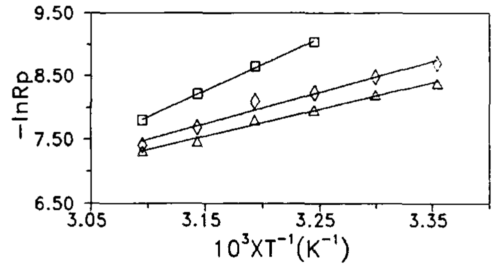


Fig.2. Plot of -lnRp versus 1/T for AAM aqueous solution polymerization by various initiators
[AAM]=1.00 mol/l, [APS]=[DMAPAA]=[DMAPMA]=1.00x10^{-3}mol/l.
(□)APS (△)DMAPAA/APS (◇)DMAPMA/APS

systems in vinyl polymerization[4-6]. The EPR spectrum of APS/DMAPPA system using MNP as trapping agent is shown in Fig.3. It shows the hyperfine splitting by one α-^{14}N nucleus, two β-protons, and one β-^{14}N nucleus to form the 3X3X3 type spetrum with the coupling constant a_α^N=15.72G, a_β^H=8.51G, a_β^N=2.81G (1G=0.1mT). The theoretic stick lines are given at the bottom of Fig.3. This result reveals the formation of alkylaminomethyl radical **1**.

EPR spectra of APS/DMAPAA/MNP system are shown in Fig.4. The formation of alkylaminomethyl radical **2** consisting of 27 lines spectrum is observed in Fig. 4a. The other lines labled with "T" are due to the spin adduct of the tertiary butyl radical ($\dot{C}(CH_3)_3$), resulting from the decomposition of MNP itself, with MNP. However, in the lower concentration of MNP, the other radical **4** resulting from the addition of vinyl group of polymerizable amine is detected as shown in Fig.4b. Similarly, radical **3** and radical **5** are also detected in APS/DMAPMA/MNP system as shown in Fig.5. The hyperfine splitting constants of spin adducts obtained from various APS/amine/MNP systems are compiled in Table 2.

The results reveal again that the tertiary amine having methyl group attached to nitrogen atom will form alkyamino methyl free radical preferably in the persulfate/aliphatic amine systems[4-6]. In the polymerizable amine, the monomeric propagating radical formed by the addition reaction of monomer's double bond with radical was observed as well. Accordingly, the reactions are shown as follows:

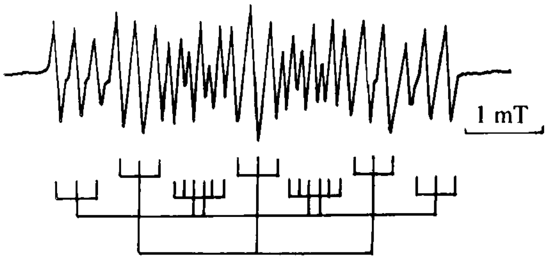


Fig.3. EPR Spectrum of DMAPPA/APS/MNP system in H_2O/CH_3CN solvent.
[DMAPPA]=9.04x10^{-2}mol/l [APS]=7.10x10^{-2}mol/l [MNP]=2.87x10^{-2}mol/l.
Macrowave Frequency: 9.778GHz Gain: 1.25x10^5
Field modulation intensity:1.6Gpp Microwave power: 1.00mW

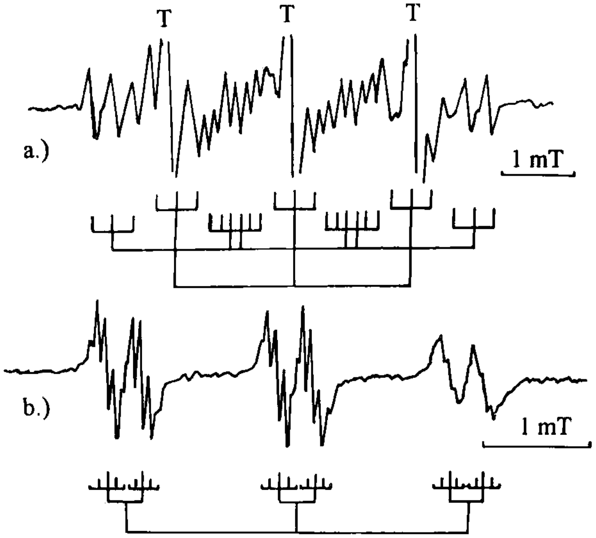


Fig.4. EPR Spectra of DMAPAA/APS/MNP system in H_2O/CH_3CN solvent.
"T": Spin adduct of $\dot{C}(CH_3)_3$ and MNP
a.) [DMAPAA]=4.57x10^{-2}mol/l [APS]=1.00x10^{-1}mol/l [MNP]=1.00x10^{-1}mol/l.
Macrowave Frequency: 9.774GHz Gain: 8.0x10^5
Field modulation intensity: 0.08Gpp Microwave power: 1.57mW
b.) [DMAPAA]=4.57x10^{-2}mol/l [APS]=1.43x10^{-1}mol/l [MNP]=2.87x10^{-2}mol/l.
Macrowave Frequency: 9.775GHz Gain: 2.0x10^5
Field modulation intensity: 0.16Gpp Microwave power: 1.00mW

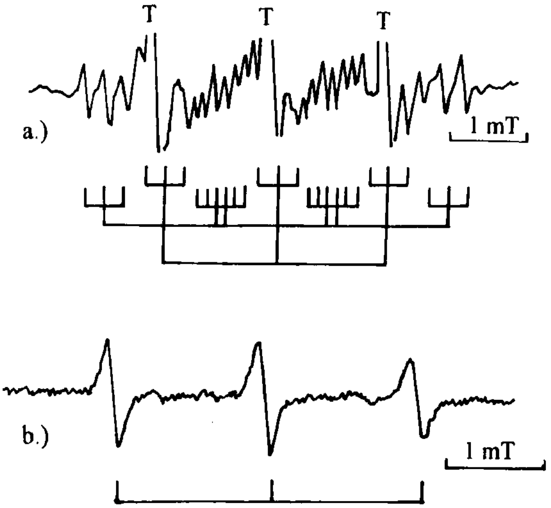


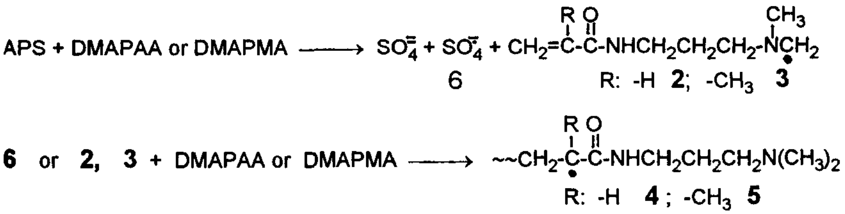
Fig.5. EPR Spectra of DMAPMA/APS/MNP system in H_2O/CH_3CN solvent.
"T": Spin adduct of $\dot{C}(CH_3)_3$ and MNP

a.) [DMAPMA]=2.20×10^{-2}mol/l [APS]=1.00×10^{-1}mol/l [MNP]=1.00×10^{-1}mol/l.
Macrowave Frequency: 9.770GHz Gain: 8.0×10^5
Field modulation intensity: 0.125Gpp Microwave power: 1.57mW

b.) [DMAPMA]=4.13×10^{-2}mol/l [APS]=1.43×10^{-1}mol/l [MNP]=2.87×10^{-2}mol/l.
Macrowave Frequency: 9.778GHz Gain: 2.5×10^5
Field modulation intensity: 0.08Gpp Microwave power: 1.00mW

TABLE 2. Hyperfine splitting constants of spin adducts obtained from APS/Amine/MNP systems

Free radical trapped by MNP	No.	Hyperfine splitting constants (0.1mT) a_α^N	a_β^H	a_β^N	a_γ^H / a_γ^N
$CH_3CH_2CONHCH_2CH_2CH_2(CH_3)N\text{-}\dot{C}H_2$	1	15.72	8.57	2.81	
$CH_2{=}CHCONHCH_2CH_2CH_2(CH_3)N\text{-}\dot{C}H_2$	2	15.53	8.16	2.94	
$CH_2{=}C(CH_3)CONHCH_2CH_2CH_2(CH_3)N\text{-}\dot{C}H_2$	3	15.79	8.03	3.01	
$\sim\sim CH_2\text{-}\dot{C}HCONHCH_2CH_2CH_2\text{-}N(CH_3)_2$	4	15.26	3.19		0.55 / 0.55
$\sim\sim CH_2\text{-}\dot{C}(CH_3)CONHCH_2CH_2CH_2\text{-}N(CH_3)_2$	5	15.60			



$$\text{APS} + \text{DMAPAA or DMAPMA} \longrightarrow \underset{6}{SO_4^{=}} + SO_4^{\overset{-}{\bullet}} + CH_2{=}\overset{R}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-NHCH_2CH_2CH_2-\overset{CH_3}{\overset{|}{N}}\underset{\bullet}{C}H_2 \quad R:\ -H\ \mathbf{2};\ -CH_3\ \mathbf{3}$$

$$\mathbf{6}\ \text{or}\ \mathbf{2},\ \mathbf{3} + \text{DMAPAA or DMAPMA} \longrightarrow \sim\sim CH_2-\underset{\bullet}{\overset{R}{\overset{|}{C}}}-\overset{O}{\overset{\|}{C}}-NHCH_2CH_2CH_2N(CH_3)_2 \quad R:\ -H\ \mathbf{4};\ -CH_3\ \mathbf{5}$$

3. End group analysis

Two end group analysis methods are performed. One is FT-IR spectrum end group analysis. As mentioned above the vinyl group of polymerizable amine can undergo addition reaction with radical. According, in order to avoid the disturbance of copolymerization of polymerizable amine in end group analysis of polymer obtained, a saturate amine, such as DMAPA and a saturate amide containing amino group, i.e. DMAPPA were chosen as reductant. Fig.6 shows the FT-IR spectra of PAN initiated with APS/amine systems. PAN2 is obtained by APS/DMAPPA system and PAN1 by using APS/DMAPA as initaitor. It can be seen from the substration spectrum (curve C) that the absorption peak of amide group at 1694.3cm^{-1} is observed. The result implies the presence of saturate amide moiety containing amine group in the polymer formed.

The other one is CTC spectrum method by means of UV-VIS spectrometer. In previous paper[4] we have found that TCNE could react with aliphatic amine to form the CTC which exhibited a characteristic absorption at UV or visible band. It can be seen from the UV spectrum of DMAPPA with TCNE in CH_2Cl_2 solution (Fig.7 curve a) that a CTC characteristic absorption bands of a tertiary amine with TCNE two peaks at 398 and 418nm are determined. Curve b is the UV spectrum of PMMA(initiated by APS/DMAPPA system) with TCNE in CH_2Cl_2 solution which also shows the similar two peaks of CTC characteristic absorption bands. It reveals the presence of tertiary amine moiety in the end group of PMMA obtained. However, in the curve c, only one peak at 325nm(a characteristic absorption bands of TCNE with primary amine) is detected. It implies the primary amino group of DMAPA is more reactive than tertiary amine group toward TCNE.

4. Initiation mechanism

Based on the EPR studies and end group analysis metioned above, the initiation mechanism of APS/DMAPAA and APS/DMAPMA systems is proposed to be

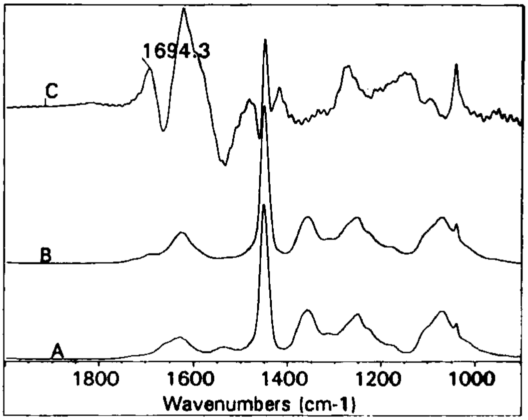
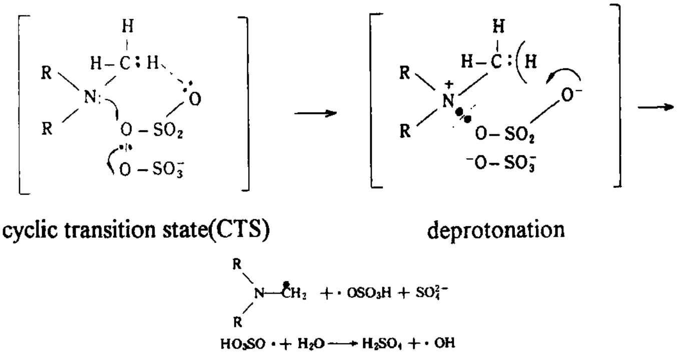


Fig.6. FT-IR Spectra of PAN samples and their substraction
A.) PAN1 initiated by DMAPA/APS system
B.) PAN2 initiated by DAMPPA/APS system
C.) substraction result of PAN2-PAN1 based on the 1453.99 cm^{-1} peak

similar to the initiation reaction of aliphatic tertiary amine with persulfate as described in our previous papers[4,6].



$$R_2N\text{—}\dot{C}H_2 + \cdot OSO_3H + SO_4^{2-}$$

$$HO_3SO\cdot + H_2O \longrightarrow H_2SO_4 + \cdot OH$$

The primary radicals both the alkylaminomethyl radical and the sulfate radical can initiate monomer to polymerize.

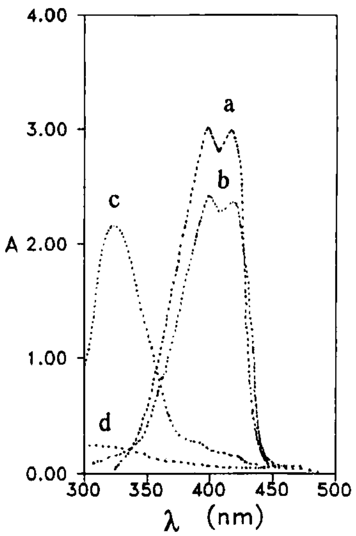


Fig.7. The UV spectra of PMMA samples combined with TCNE in CH_2Cl_2 solution

a).DMAPPA/TCNE dilute solution in CH_2Cl_2

b).PMMA initiated by DMAPPA/APS system

c).PMMA initiated by DMAPA/APS system

d).PMMA initiated by AIBN

CONCLUSIONS

The kinetic studies on the AAM polymerization using APS/polymerizable amine(DMAPAA, DMAPMA) as initiator revealed that the systems belong to redox ones. Two kinds of carbon center radicals are detected in the redox reaction of DMAPAA, DMAPMA with APS by EPR spectrocopy. The initial radicals alkylaminomethyl radical derived from amine component as well as sulfate radical derived from peroxydisulfate component are responsible for initiation of vinyl polymerization and exsiting as end groups in the resulting polymers. The structure of initial radical and end group moiety have been confirmed by EPR spectrocopy, FT-IR and UV spectra analysis.

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REFERENCES

[1] *U. S.* 4,189,370 (1980), Societe Sebia, inv.: E. Boschetti; Chem. Abstr. **93**, 41046h (1980)

[2] T. Tanaka, *Sci. Am.* **244**(1), 110 (1981)

[3] M. K. Gupta, R. Bansil, *Polym. Prepr.(Am. Chem. Soc. Div. Polym. Chem.)* **22**(2), 375 (1981)

[4] X. Q. Guo, K. Y. Qiu, X. D. Feng, *Sci. Sin.* **B30**(9), 897 (1987)

[5] X. D. Feng, X. Q. Guo, K. Y. Qiu, *Makromol. Chem.* **189**, 77 (1988)

[6] X. Q. Guo, K. Y. Qiu, X. D. Feng, *Makromol. Chem.* **191**, 577 (1990)

[7] Z. Y. Zhang, C. X. Zu, L. Y. Qiao, F. M. Li, *Acta Polymerica Sinica,* (5), 623 (1990)

[8] S. H. Pan, K. T. Tang, Z. Wang, Z. Z. Wang, *Acta Polymerica Sinica,* (1), 99 (1994)