

Studies on the initiation mechanism of persulfate/aliphatic secondary amine system in vinyl polymerization

X. D. Feng*, X. Q. Guo, and K. Y. Qiu

Department of Chemistry, Peking University, Beijing, China

Abstract

Persulfate/aliphatic secondary amine initiation systems were studied. Secondary amines were discovered to be excellent accelerators for the polymerization of acrylic monomers in aqueous solution initiated by persulfate. The rate of acrylamide polymerization and the overall activation energies were determined respectively. The active intermediates of the secondary amine species formed during the initiation reaction were detected by ESR technique to be dialkylamino radicals (R_2N^\bullet). From the results the initiation mechanism was proposed.

Introduction

Organic peroxide coupled with tertiary amines is a well known organic redox initiation system⁽¹⁾, while the primary and secondary amines would inhibit or retard radical polymerization^(2,3). We^(4,5) have reported previously that persulfate coupled with cyclic secondary amines such as morpholine (MP) or piperidine (PD) could initiate the polymerization of acrylic monomers in aqueous solution. In this paper, we report some recent results on the persulfate/aliphatic secondary amine initiation system in vinyl polymerization.

Experimental

Materials: Acrylamide (AAM), persulfate, aliphatic secondary amines and polyethylenepolyamines are all commercial available chemical reagents and were purified by common methods. The spin trap 2-methyl-2-nitroso propane (MNP) was synthesized according to the reference⁽⁶⁾, and the 5,5-dimethyl pyrroline N-oxide (DMPN) was kindly offered by Dr. & Prof. Philip J. Barker.

* To whom offprint requests should be sent

Polymerization: The rate of AAM polymerization was determined by dilatometric method with the initiator concentration both persulfate and secondary amine in 1.00×10^{-3} mol/L and monomer concentration in 1.00 mol/L. The molecular weights of the polymer were determined from the intrinsic viscosity of the polymer solution according to the reference⁽⁷⁾.



ESR study: The active intermediates of amine species were studied by spin trapping technique and ESR spectrum. ESR spectra were detected on Bruker ER200D-SRC Electron Spin Resonance Spectrometer using TM cavity at X band in the conditions of modulation frequency 100 KHz, microwave power 19.9 mW, the Gain and Field modulation intensity were adjusted to suitable values.

Results and Discussion

1. Effects of Aliphatic Secondary Amines on the Polymerization of Acrylamide(AAM)

The effects of aliphatic secondary amines on the polymerization of AAM in aqueous solution initiated by ammonium persulfate (APS) were studied and the data were compiled in Table 1.

Table 1 Effects of secondary amines on AAM polymn. (45°C)

Initiation systems	Secondary amines	Induction period(min.)	$R_p \times 10^4$ (mol/L.s)	R_T
APS	No amine	11	2.33	1.00
APS/DPA	$(CH_3CH_2CH_2)_2NH$	4	6.25	2.68
APS/DBA	$[CH_3(CH_2)_3]_2NH$	4	6.49	2.78
KPS *	No amine	30	2.52	1.00
KPS/MP *	 N-H	32	4.22	1.63
KPS/PD *	 N-H	32	3.94	1.56

* Reference(5), KPS = potassium persulfate

Obviously, the data in the Table 1 show that the secondary amines have high promoting effects on the polymerization of AAM initiated by persulfate. These initiation systems may also initiate the polymerization of other acrylic monomers in aqueous solution or in water containing solutions.

2. Effects of Polyethylenepolyamines on AAM Polymerization

Polyethylenepolyamines $H_2N(CH_2CH_2NH)_nH$, $n = 2, 3, 4$, etc., i.e. diethylenetriamine(DETA), triethylenetetraamine(TETA), and tetraethylenepentamine(TEPA), exhibit high promoting effects on the copolymerization of butadiene and styrene in emulsion system using cumene hydroperoxide as initiator^(8,9,10). But it was reported that they inhibited the polymerization of methyl methacrylate(MMA) in bulk initiated by benzoyl peroxide(BPO)⁽²⁾. We have studied the behaviour of these polyethylenepolyamines in the polymerization of AAM using ammonium persulfate(APS) as initiator in aqueous solution and found that they were all effective accelerators in the polymerization. The rate of AAM polymerization increase about two to five times compared with that of using APS only. The experimental data were compiled in Table 2.

Table 2 Effects of the polyamines on AAM polymn.(45°C)

Initiation systems	Polyethylene-polyamines	$R_p \times 10^4$ (mol/L.S)	R_r	MW ($\times 10^{-6}$)	E_a (KJ/mol)
APS	No amine	2.33	1.00	1.96	62.0
APS/sym-DMEDA	$CH_3NHCH_2CH_2NHCH_3$	11.16	4.79	0.96	24.9
APS/DETA	$H_2N(CH_2CH_2NH)_2H$	6.07	2.61	2.03	32.9
APS/TETA	$H_2N(CH_2CH_2NH)_3H$	8.13	3.49	1.56	31.9
APS/TEPA	$H_2N(CH_2CH_2NH)_4H$	10.97	4.70	1.11	21.8
APS/EDA	$H_2N-CH_2CH_2-NH_2$	4.01	1.76	1.09	36.9

Fig.1 shows experimental results under the same equivalent concentration of amino group of the polyamines with the other conditions the same. The rate of AAM polymerization varies remarkably as the the structure of the polyamines changes.

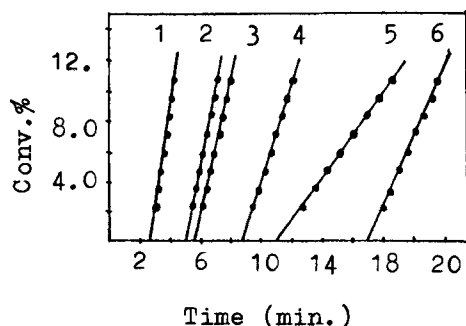


Fig.1 The plot of Conv.% vs. T
 $[AAM] = 1.00 \text{ mol/L}$; $T = 45^\circ\text{C}$;
 $[APS] = 1.00 \times 10^{-3} \text{ mol/L}$;
 $[Polyamine] = 2.00 \times 10^{-3} \text{ N/L}$.
 The curves($R_p \times 10^4 \text{ mol/L}\cdot\text{s}$):
 1. sym-DMEDA(11.16);
 2. TEPA(8.68); 3. TETA(7.96);
 4. DETA(5.41); 5. APS only
 6. EDA (4.01). (2.33);

The promoting activities of the polyamines are in the following decreasing order:



Although the primary amines such as EDA(ethylenediamine) may accelerate the polymerization of AAM, the secondary amines have much higher promoting effect for the polymerization of AAM.

3. ESR Studies on the Intermediates of the Secondary Amine Reacting with Persulfate

The active intermediates of secondary amine species formed during the initiation reaction were studied by ESR technique using 2-methyl-2-nitroso propane(MNP) and 5,5-dimethyl pyrroline N-oxide(DMPN) as free radical traps. Fig.2 shows the ESR spectrum obtained from APS/MP/MNP system in methanol-water mixture solution. The spectrum indicates the formation of the morpholino radical trapped by MNP. In APS/PD/MNP system the similar ESR spectrum was obtained as the APS/MP/MNP system. The ESR data are listed in Table 3.

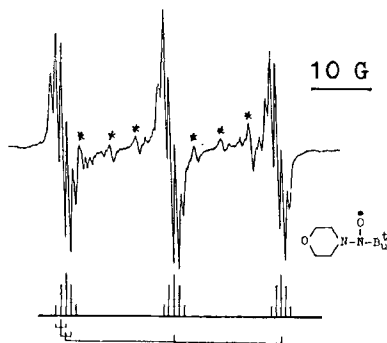


Fig.2 ESR spectrum of the APS/MP/MNP system
* HOCH₂• trapped by MNP

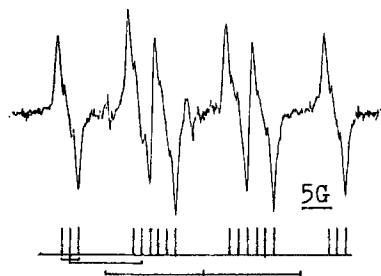


Fig.3 ESR spectrum of the APS/DPA/DMPN system

On the other hand, the dialkylamino radicals, i.e. (CH₃CH₂)₂N• (CH₃CH₂CH₂)₂N• etc., could not easily be trapped by MNP but they could be trapped by DMPN as illustrated in Fig.3.

When the free radical trap MNP was added to the APS/DETA, APS/TETA and APS/TEPA reaction systems, another kind of ESR signal was recorded as shown in Fig.4. The ESR spectrum results from

hyperfine coupling to the nitrogen nucleus to give three lines of equal intensity with secondary splitting on the β -nitrogen atom. This ESR spectrum indicates the formation of dialkylamino radical ($R_2N\cdot$) which is then trapped by MNP. The relative ESR data are compiled in Table 4.

Table 3 ESR data of the trapped dialkylamino radicals



System	Radical trapped	Coupling constant (G)				g
		a_{α}^N	a_{β}^H	a_{β}^N	a_{γ}^H	
APS/MP/MNP	 N \cdot	18.72	/	0.88	0.88	2.0055
APS/PD/MNP	 N \cdot	18.61	/	0.93	0.93	2.0057
APS/DEA/DMPN	$(CH_3CH_2)_2N\cdot$	13.73	9.87	1.31	/	2.0058
APS/DPA/DMPN	$(CH_3CH_2CH_2)_2N\cdot$	13.65	9.92	1.17	/	2.0068

Table 4 ESR data of APS/Polyamine/MNP systems

Reaction systems	Radicals trapped	Coupling constant (G)	
		a_{α}^N	a_{β}^N
APS/DETA/MNP	$(H_2NCH_2CH_2)_2N\cdot$	14.93	2.13
APS/TETA/MNP	$R_1R_2N\cdot$	14.96	2.16
APS/TEPA/MNP	$R_1R_2N\cdot$	14.93	2.16

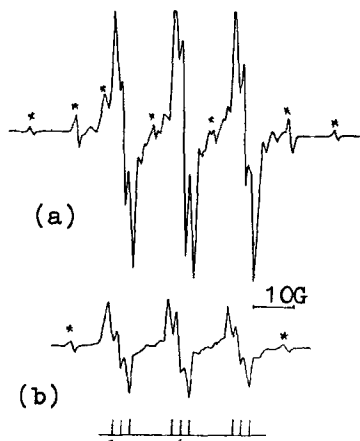
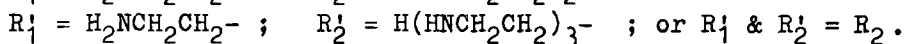
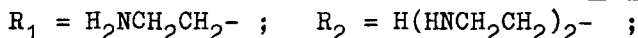
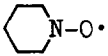
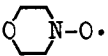


Fig. 4 ESR spectrum of the APS/TETA/MNP system

- (a) Spectrum was recorded at beginning; (* $R_1R_2N\cdot$)
 (b) Spectrum was obtained at latter, showing the formation of adduct of $R_1R_2N\cdot$ radical with MNP.

Fig.5 shows the ESR spectrum obtained from APS/DPA system in the absence of spin trap in methanol/water mixture solution. The ESR spectrum results from hyperfine coupling to the ^{14}N nucleus to give three lines of equal intensity, and then each line is further splitting into a 1:4:6:4:1 quintet by the four equivalent β -H atoms. A total of 15 lines is expected, but only 13 lines are observed due to overlapping of some of the components. This result indicates that DPA is oxidized by persulfate to form the corresponding nitro-oxide compound ($\text{R}_2\text{N-O}\cdot$), i.e. $(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{N-O}\cdot$. The other secondary amines such as DEA, DBA, DIPA (diisopropylamine), PD etc., when they are reacted with persulfate in the absence of free radical trap, give the similar ESR spectra as shown in Fig.5. The hyperfine splitting constants and the g values of the ESR spectra of nitro-oxide radicals are collected in Table 5.

Table 5 Summary of ESR data of nitro-oxide radicals

Reaction systems	Nitro-oxide radicals	Splitting constant (G)		g
		a_{α}^{N}	a_{β}^{H}	
APS/DEA	$(\text{CH}_3\text{CH}_2)_2\text{N-O}\cdot$	16.27	11.04(4H)	2.0060
APS/DPA	$(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{N-O}\cdot$	15.73	10.56(4H)	2.0059
APS/DBA	$[\text{CH}_3(\text{CH}_2)_3]_2\text{N-O}\cdot$	15.57	10.61(4H)	2.0057
APS/DIPA	$[(\text{CH}_3)_2\text{CH-}]_2\text{N-O}\cdot$	16.00	4.69(2H)	2.0058
APS/PD	 $\text{N-O}\cdot$	17.60	11.73(4H)	2.0059
APS/MP	 $\text{N-O}\cdot$	17.49	$(a_{\beta}^{\text{Ha}} + a_{\beta}^{\text{He}})$ 23.47	2.0061

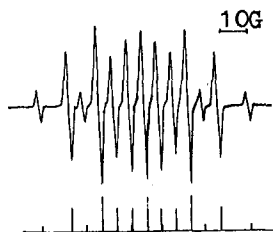


Fig.5 ESR spectrum of APS/DPA system

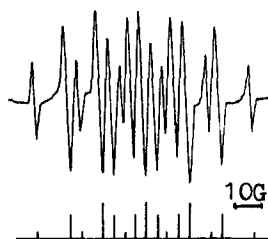


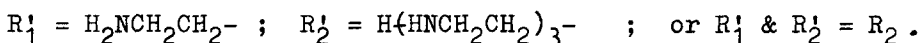
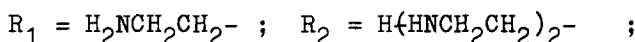
Fig.6 ESR spectrum of APS/TETA system

The same ESR spectra are obtained either in the APS/secondary amine reaction systems or by reacting the secondary amines with hydrogen peroxide in water as illustrated in Fig.5. There would be no such ESR signal of nitro-oxide to be detected if vinyl monomer such as acrylamide were present in the system. These results imply that the nitro-oxide compounds are probably formed through a secondary reaction step of the dialkylamino radicals in the solution.

Polyethylenepolyamines, i.e. sym-DMEDA, DETA, TETA, TEPA etc., reacting with persulfate, are also oxidized to form the corresponding nitro-oxide compounds as shown in Fig.6 and Fig.7. The summary of ESR data are compiled in Table 6.

Table 6 Summary of ESR data on APS/polyamine system

Reaction systems	Radicals formed	Coupling constant(G)		g
		a_{α}^N	a_{β}^H	
APS/sym-DMEDA	$\text{CH}_3\text{NHCH}_2\text{CH}_2\text{N}\cdot\text{O}$ CH_3	16.05	14.13(3H) 10.13(2H)	2.0060
APS/DETA	$(\text{H}_2\text{NCH}_2\text{CH}_2)_2\text{N}\cdot\text{O}$	14.93	11.36(4H)	2.0060
APS/TETA	$\text{R}_1\text{R}_2\text{N}\cdot\text{O}$	15.04	11.20(4H)	2.0061
APS/TEPA	$\text{R}'_1\text{R}'_2\text{N}\cdot\text{O}$	15.47	11.20(4H)	2.0061



4. The Initiation Mechanism of Persulfate/Aliphatic Secondary Amine System

According to the experimental results discussed above, we propose the initiation mechanism of the persulfate/aliphatic secondary amine system as the follows:

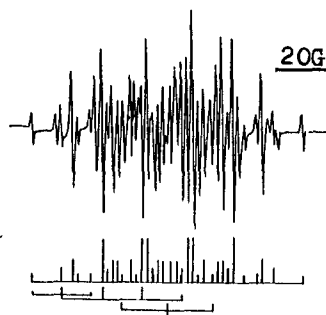
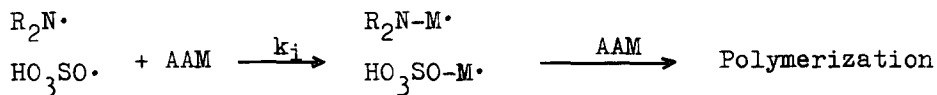
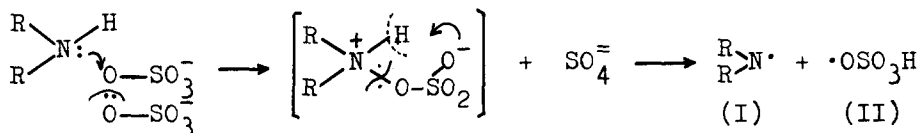
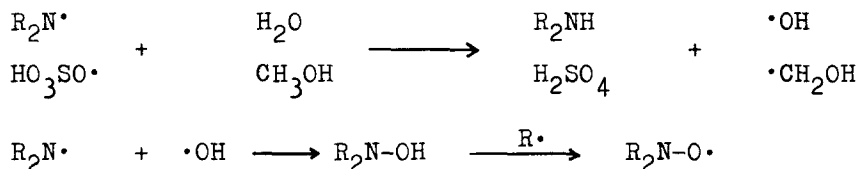


Fig.7 ESR spectrum of the APS/sym-DMEDA system



In the absence of monomer, the primary radical I and II would react with H_2O or CH_3OH to form $\cdot\text{OH}$ or $\cdot\text{CH}_2\text{OH}$ radicals, which then undergo secondary reaction to form the corresponding nitro-oxide compounds as follows:



$\text{R} \cdot$ may be any kind of free radicals present in the system.

ACKNOWLEDGEMENT The authors are indebted to the Science Fund of the Chinese Academy of Science for financial support of this work.

References

- ODIAN, G., "Principle of Polymerization", Chapt.3, 2nd Ed., John Wiley & Sons, New York (1981)
- LAL, J., GREEN, R., J. Polym. Sci., 17, 403(1955)
- ZHANG, J.Y., QIU, K.Y., FENG, X.D., Chem. J. Chinese Univ., 1(2), 114(1985); (Eng. Ed.)
- QIU, K.Y., GUO, X.Q., FENG, X.D., Kexue Tongbao, 31(11), 736(1986)(Eng. Ed.)
- GUO, X.Q., QIU, K.Y., FENG, X.D., Scientia Sinica, B(11), 1121(1986); (Chinese Ed.)
- CALDRE, A., FORREUSTER, A.R., HEPBURN, S.P., Org. Synth., 52, 77(1972)
- COLLINSON, E., DAINTON, F.S., MCNAUGHTON, G.S., Trans. Faraday Soc., 53, 489(1957)
- WHITBY, G.S., WELLMAN, N., et al., Ind. Eng. Chem., 42, 445; 452(1950)
- SPOLSKY, R., WILLIAM, H.L., Ind. Eng. Chem., 42, 1847(1950)
- EMBREE, W.H., SPOLSKY, R., WILLIAM, H.L., Ind. Eng. Chem., 43, 2553(1951)