Radical polymerization and graft polymerization with ceric ion and 3-phenylmethyl-2,4-pentanedione system

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Summary

Radical polymerization of acrylamide (AAM) initiated with ceric ion /1, 3–diketone compound, i.e. 3–phenylmethyl-2,4-pentanedione system and grafting acrylamide polymerization onto macromolecules having 1,3–diketone pendant groups using ceric ion as an initiator have been studied. The initiation mechanism was proposed on the basis of EPR and kinetics studies. The formation of grafted copolymer was revealed by XPS spectra, FT-IR spectra and photomicrographs.

Introduction

Ceric ion coupled with aldehyde, ketone can form redox initiation systems for vinyl radical polymerization (1–4). It was reported in a patent (5) that ceric ion and 2,4-pentanedione(acetylacetone, AcAc) could initiate acrylamide(AAM) polymerization. In our laboratory, we have studied the polymerization kinetics and initiation mechanism of this redox initiation system by means of radical trapping technique and electron paramagnetic resonance (EPR) spectroscopy(6). Graft copolymerization of vinyl monomers onto macromolecules having active pendant groups such as 3,4-dihydroxycyclohexyl ester group, 4-methylphenylaminocarbonyl(p-tolylcarbamoyl) group using ceric ion as an initiator was investigated by Butler et al (7) and Qiu et al (8, 9) respectively. In this paper we would like to report some results on polymerization of acrylamide initiated by ceric ion/3-phenylmethyl-2,4-pentanedione(3-benzyl-2, 4-pentanedione, BzyAcAc) system and on grafting acrylamide polymerization onto macromolecule having 1, 3-diketone pendant group, such as poly[3-(4-vinylphenylmethyl)-2,4-pentanedione] [P(St–CH₂–AcAc)], initiated by ceric ion, and the characterization of grafted copolymer.

Experimental

Materials: Acrylamide(AAM), 2,4-pentanedione(AcAc), phenylmethyl chloride (benzyl chloride), metal sodium and organic solvents are all commercial chemical reagents and were purified by common methods. Ceric ammonium nitrate (CAN) was got as analytic grade reagent and used directly. Chloromethylated polystyrene [P(St–CH₂Cl)] beads were obtained from Chemical Factory of Nankai University. 2-Methyl-2-nitroso-propane(MNP) was purchased from Aldrich Chemical Company and was used without further purification. 1-Phenyl-1,3-butanedione(benzoylacetone, BzAc) was got from Aldrich Chemical Company and recrystallized three times with ethanol.

Preparation of 3-phenylmethyl-2,4-pentanedione(BzyAcAc):

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BzyAcAc was prepared from the reaction of benzyl chloride with sodium salt of 2,4-pentanedione (NaAcAc) according to the reference(10), b.p 117–119℃/133.3 Pa.
Preparation of poly[3-(4-vinylphenylmethyl)-2,4-pentanedione] [P(St–CH$_2$–AcAc)]:
P(St–CH$_2$Cl) 5.0g(Cl content 0.031 mol), NaAcAc 2.5g(0.02mol), sodium iodide 0.2g were added to dry N,N-dimethylformamide (DMF) 30ml. The mixture was heated to 60℃ with magnetic stirring and the reaction was kept at this temperature for 12 hours. P(St–CH$_2$–AcAc) beads were obtained by filtration and the beads were washed with DMF several times, then with water and ethanol twice respectively. Dried and stored for grafting reaction.

Polymerization and graft copolymerization:

(i) Polymerization: The rate of AAM polymerization initiated with ceric ion (CAN) alone and ceric ion/BzyAcAc system in H$_2$O–CH$_3$CN(v/v=3:1) mixed solvent was determined by dilatometric method. The molecular weight of PAAM was determined from the intrinsic viscosity of the polymer solution according to the reference (11).

(ii) Graft copolymerization: P(St–CH$_2$–AcAc) beads 0.2g were immersed with acetonitrile (5ml) overnight, to this mixture AAM 5.0g and H$_2$O 15ml were added then bubbled with nitrogen gas through the liquid phase and 0.0548g CAN was added. The graft copolymerization was carried out for 2–3 hours under nitrogen atmosphere at 45 ℃. The grafted copolymer P[(St–CH$_2$–AcAc)–g–AAM] was treated with boiling water many times, filtered, dried and weighed. The grafting percentage (G%) was calculated according to the following equation:

$$G(\%) = \frac{W-W_o}{W_o} \times 100$$

Where W is the weight of polymer beads after graft copolymerization and W$_o$ is the weight of polymer beads before the reaction. The water absorption percentage of polymer beads(including grafted and ungrafted beads) was determined as follows:

$$\text{Water absorption}(\%) = \frac{W_w-W_d}{W_d} \times 100$$

Where W$_w$ is the weight of wet polymer beads, which stand for the polymer beads after being immersed in water at ambient temperature for 12 hours, filtered, and then blotted softly with filter paper; W$_d$ is the weight of dry polymer beads.

EPR study: The active intermediates of AcAc, BzyAcAc and BzAc species were investigated by spin trapping technique and EPR. EPR spectra were recorded on a Bruker ER200D–SRC Electron Spin Resonance Spectrometer (12).

Characterization of grafted polymer: The FT–IR spectra, XPS spectra and photomicrographs were taken on NICOLET-7199B FT–IR spectrometer, VG–ESCA LAB5 electron spectrometer(Al K α X-ray) and Leitz Laborlux 12 Pol microscope respectively.

Results and discussion

1. Effects of 1,3-diketones on polymerization of acrylamide

The effects of 1,3-diketones such as AcAc, BzyAcAc and BzAc on the

polymerization of AAM in H_2O-CH_3CN(v/v = 3:1) mixed solvent initiated by ceric ion (CAN) were investigated and the data were compiled in Table 1. It shows that 1,3-diketone compounds have high promoting effect on the polymerization of AAM initiated by CAN. The values of overall activation energy of AAM polymerization in the presence of 1,3-diketones are always lower than that of CAN alone. Obviously, the CAN/AcAc, CAN/BzAc and CAN/BzyAcAc belong to redox initiation systems.

Table 1 Effects of 1,3-diketones on AAM polymerization(40.0 ℃)

Initiation System	1,3-Diketone	Induction period(min)	$Rp \times 10^4$ (mol/L.s)	MW $(\times 10^4)$	Ea (KJ/mol)
CAN	none	17.5	1.20	/	41.2
CAN/AcAc	AcAc	0.5	9.43	32.0	24.7
CAN/BzyAcAc	BzyAcAc	0.5	9.08	39.0	12.7
CAN/BzAc	BzAc	0.5	9.98	32.3	23.9

[CAN]= 2.5×10^{-3} mol/L, [Diketone]= 1.0×10^{-3} mol/L, [AAM] =1.0 mol/L, Mixture solvent: H_2O-CH_3CN (v/v = 3:1)

2. Preparation and characterization of P(St–CH$_2$–AcAc) and P(St–CH$_2$–BzAc) beads

P(St–CH$_2$–AcAc), P(St–CH$_2$–BzAc) beads were prepared from the reactions of chloromethylated polystyrene [P(St–CH$_2$Cl)] beads with sodium salt of 2,4-pentanedione (NaAcAc) and sodium salt of 1–phenyl–1,3–butanedione (NaBzAc) in DMF medium respectively. Table 2 shows the functionalized bead contains lower chlorine percentage than the unfunctionalized one. The chlorine content of P(St–CH$_2$Cl) is 20.0% and the functionalized beads such as P(St–CH$_2$–AcAc) and P(St–CH$_2$–BzAc) are 6.72%and 6.81% respectively. In FT–IR spectra of P(St–CH$_2$–AcAc) and P(St–CH$_2$–BzAc) new characteristic carbonyl absorption bands at 1698cm^{-1}, 1720cm^{-1} and at 1675 cm^{-1}, 1718 cm^{-1} were observed respectively.

Table 2 1,3–Diketones functionalized polystyrene beads

Polymer beads	Cl(%)	Characteristic absorption(carbonyl)(cm^{-1})
P(St–CH$_2$–AcAc)	6.72	1698, 1720(two –CO–CH$_3$)
P(St–CH$_2$–BzAc)	6.81	1675(–CO–C$_6$H$_5$), 1718(–CO–CH$_3$)

3. EPR studies on the intermediates of 1,3–diketones reacting with ceric ion and end group analysis

The active intermediates of AcAc, BzyAcAc, BzAc species formed during the initiation reactions were investigated by radical trapping technique and EPR spectra. 2–Methyl–2–nitroso–propane(MNP) was used as spin trapping agent, and the reactions of radicals with MNP were shown as follows:

R· + O=N–C(CH$_3$)$_3$ → R–N–C(CH$_3$)$_3$ Radical(R·)   R$_1$COCR$_2$COCH$_3$
$$\qquad\qquad\qquad\qquad \overset{|}{\underset{\cdot}{O}}$$

I   R$_1$= CH$_3$,   R$_2$= H;

II   CH$_3$,   CH$_2$C$_6$H$_5$;
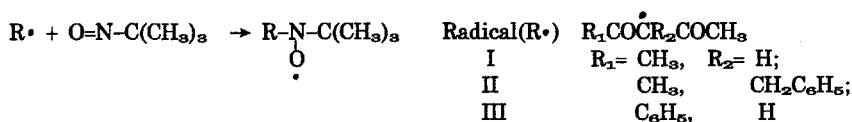
III   C$_6$H$_5$,   H

Fig.1 is the EPR spectrum obtained from CAN/BzyAcAc/MNP in $H_2O–CH_3CN$ mixture solution, it shows the hyperfine splitting by one α–^{14}N nucleus to form a three–line spectrum with equal intensity and the coupling constant a^{N}_{α} =1.36mT. The spectrum confirms the formation of radical II trapped by MNP. In CAN/AcAc /MNP and CAN/BzAc/MNP systems the adducts of radical I and III trapped by MNP were also detected. The data of hyperfine splitting constants are compiled in Table 3.

Table 3 Hyperfine splitting constants of spin adducts

System	Radical trapped by MNP	Hyperfine splitting constant(mT) a^{N}_{α}	a^{H}_{β}
CAN/AcAc/MNP	I	1.36	0.36
CAN/BzyAcAc/MNP	II	1.44	/
CAN/BzAc/MNP	III	1.41	0.46

From the FT–IR spectrum end group analysis of polyacrylonitrile (PAN) prepared by the polymerization of AN initiated with CAN/BzyAcAc system, the monitoring of characteristic absorption bands of 1,3–diketone group at 1698cm^{-1}, 1713 cm^{-1}(Fig.2) reveals the presence of BzyAcAc moiety as an end group in the PAN.
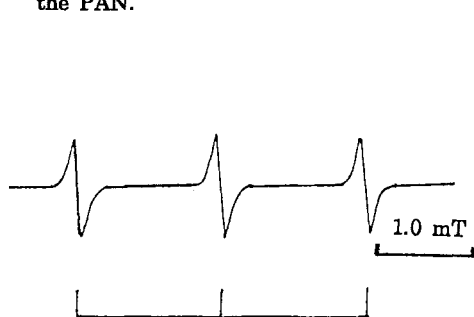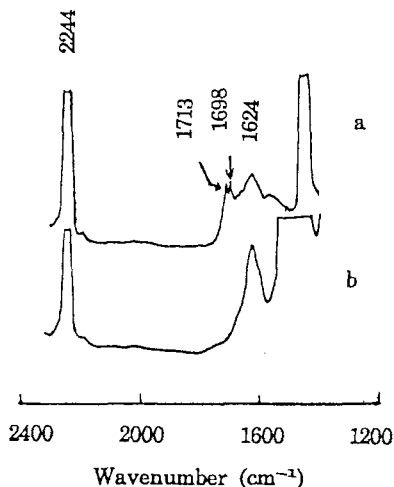

Fig.1 EPR spectrum of
CAN/BzyAcAc/MNP system

Fig.2 FT–IR spectra of PAN (a)
by CAN/BzyAcAc and (b) by CAN

4. Initiation mechanism of CAN/1,3–diketone systems

Based on the evidences mentioned above, it shows the polymerization of AAM initiated with CAN/1,3–diketone systems belongs to redox polymerization. The initiation mechanism of CAN/BzyAcAc and CAN/BzAc systems is proposed similarly to the CAN/AcAc system as discribed in our previous paper(4, 6)

5. Graft copolymerization of 1,3–diketone functionalized polystyrene initiated with ceric ion

In our previous work we reported that ceric ion can be used as an initiator either for grafting reaction of poly(ether–urethane)(13, 14) or grafting reaction of copolymers having 4-methylphenylaminocarbonyl active pendant group(8, 9). As mentioned above, AcAc, BzyAcAc and BzAc coupled with ceric ion can form effective redox initiation systems, therefore in the presence of ceric ion the 1,3–diketone pendant groups of macromolecules through the abstraction of hydrogen can form radicals and initiate AAM copolymerization. The results of graft copolymerization of AAM onto 1,3–diketones functionalized polystyrene beads such as P(St–CH$_2$–AcAc) and P(St–CH$_2$–BzAc) in H$_2$O–CH$_3$CN mixture solvent using CAN as an initiator are compiled in Table 4.

Table 4 Graft copolymerization of AAM onto 1,3–diketones functionalized polystyrene beads

Polymer beads	Reaction time(h)	Grafting percentage(%)	N Content (%)	Water absorption(%)	
				Grafted	Ungrafted
P(St–CH$_2$–AcAc)[1]	1.5	156.2	12.65	399	5.0
P(St–CH$_2$–BzAc)[2]	3.0	40.3	7.51	365.2	4.7

T = 45 ℃, Mixture solvent: H$_2$O–CH$_3$CN (v/v=3:1).
1. [AAM] = 3.5 mol/L, [CAN]= 5.0×10^{-3}mol/L;
2. [AAM] = 4.0 mol/L, [CAN]= 7.5×10^{-3}mol/L

It shows that the water absorption of virgin beads(ungrafted polymer) is about 5%, that of the grafted copolymer beads, however, is much higher, about 400%. This is due to the contribution of the grafted PAAM macromolecular chains, which have higher water absorbability.

When the graft copolymerization was carried out at fixed [CAN]=5.0×10^{-3}mol/L and P(St–CH$_2$–AcAc) weight= 0.2g in H$_2$O–CH$_3$CN(v/v=3:1) mixture solvent at 45℃, the grafting percentage increased with increasing concentration of AAM. The data are compiled as follows:

[AAM] (mol/L)	2.0	2.5	3.0	3.5
Reaction time (h)	4.0	2.5	2.0	1.5
Grafting percentage(%)	2.35	73.1	110.2	156.2

6. Characterization of grafted copolymer

Besides the increasing of water absorption percentage of grafted copolymer, P[(St–CH$_2$–AcAc)–g-AAM],two new characteristic bands at 3195cm^{-1} and 3341cm^{-1} (N–H stretching vibration of primary amide) and a band at 1667cm^{-1} (carbonyl stretching vibration of amide) for the grafted copolymer were monitored by FT-IR spectrum(Fig. 3b).

Photomicrography: When the photomicrograph of the grafted beads(Fig.4b) is compared with that of virgin ones(Fig. 4a), it is showed that the virgin uniform spheric beads change to nonuniform beads, revealing the grafting reaction on the surface of the beads. In Fig.4b, it is also observed that some particle sizes of the grafted copolymer are smaller than that of the virgin ones. It is due to the break of the particles during grafting reaction and extraction process with boiling water under vigorous stirring.
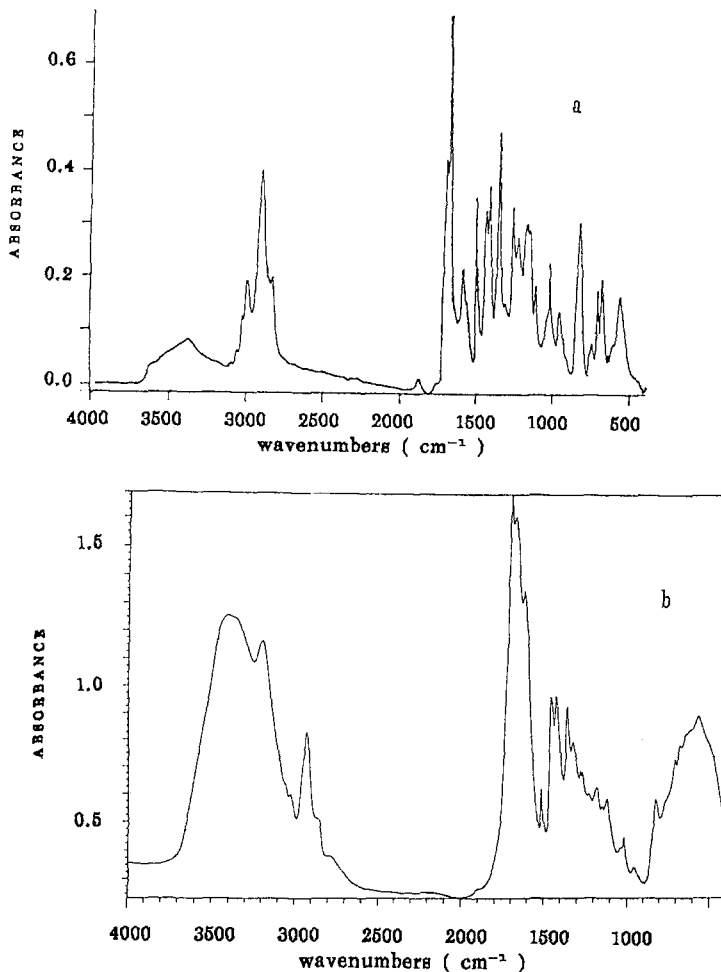
Fig.3 FT–IR spectra of P(St–CH₂–AcAc)(a) and P[(St–CH₂–AcAc)-g-AAM](b)

XPS spectra: The surface composition of the beads was measured by XPS spectra. Since P(St–CH₂–AcAc) consists of C, H, O elements and PAAM in addition to these three elements it also consists of N. In the XPS spectrum of P[(St–CH₂–AcAc)-g-AAM] a new peak for N1s (binding energy of 402.5eV) was detected. The formation grafts of PAAM will increase the content of N and O, the ratio of C/N and C/O on the surface of grafted beads will become smaller than that of the virgin one. The data are compiled as follows:

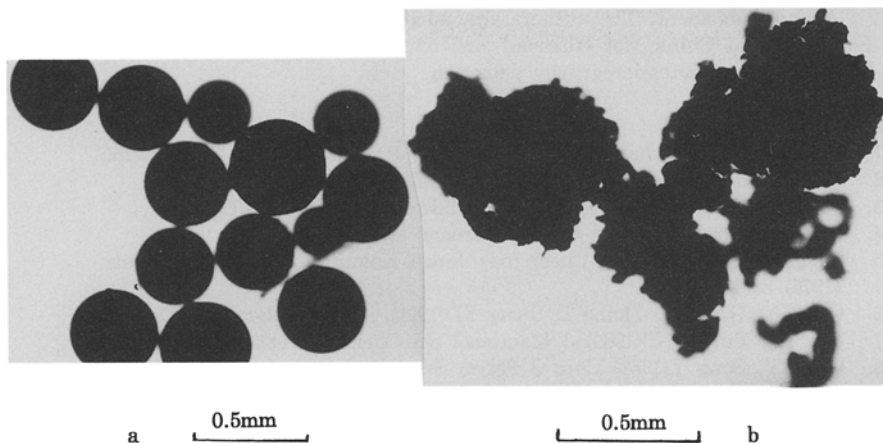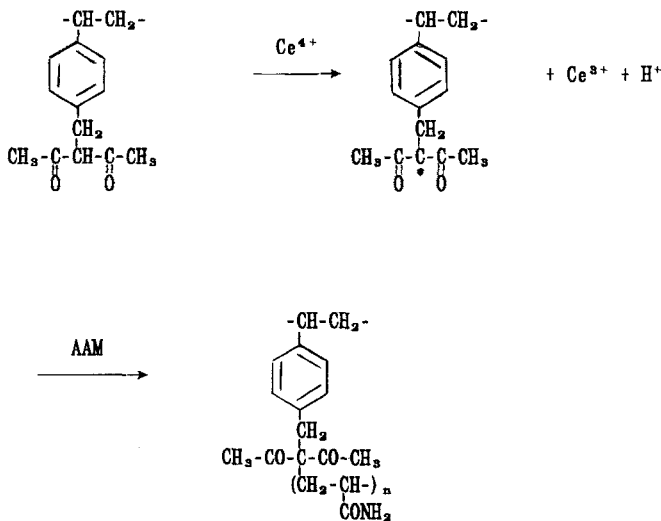| Polymeric beads	C/O value	C/N value	C1s Binding energy(eV)
P(St–CH₂–AcAc)	4.26	/	288.9
P[(St–CH₂–AcAc)-g-AAM]	2.60	3.69	289.3, 292.3(shoulder)

a   0.5mm   0.5mm   b

Fig.4 Photomicrographs of P(St–CH$_2$–AcAc) (a) and P[(St–CH$_2$–AcAc)–g–AAM](b)

7. Mechanism of graft copolymerization

From the results mentioned above, AAM graft copolymerization onto poly-styrene beads having 1,3–diketone pendant groups will take place using ceric ion as an initiator. The grafted copolymer has been verified by FT–IR, photomicrography and XPS. The grafting reaction takes place on the methenyl carbon of 1,3–diketone via the abstraction of hydrogen by ceric ion to form radical and then initiate monomer graft copolymerization. The initiation mechanism of graft copolymerization is proposed as follows:

$$-\text{CH}-\text{CH}_2- \quad \xrightarrow{\text{Ce}^{4+}} \quad -\text{CH}-\text{CH}_2- \quad + \text{Ce}^{3+} + \text{H}^+$$

-CH-CH$_2$-

|
CH$_2$
|
CH$_3$-C-CH-C-CH$_3$
‖   ‖
O   O

-CH-CH$_2$-

|
CH$_2$
|
CH$_3$-C-C-C-CH$_3$
‖ • ‖
O   O

$$\xrightarrow{\text{AAM}}$$

-CH-CH$_2$-

|
CH$_2$
|
CH$_3$-CO-C-CO-CH$_3$
|
(CH$_2$-CH-)$_n$
|
CONH$_2$

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