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Graft Polymerization of 1-[4-(2-Methyl-1-oxo-2-propenyl)amino]-phenyl-1,3-butanedione Polymers via Redox Initiation of Active Pendant Group with Ceric Ion

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GRAFT POLYMERIZATION OF 1-[4-(2-METHYL-1-OXO-2-PROPENYL)AMINO]-PHENYL-1,3-BUTANEDIONE POLYMERS VIA REDOX INITIATION OF ACTIVE PENDANT GROUP WITH CERIC ION

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Key Words: Vinyl monomer having β-diketone group; Graft polymerization; Redox initiation of β-diketone pendant group with ceric ion

ABSTRACT

1-[4-(2-Methyl-1-oxo-2-propenyl)amino]phenyl-1,3-butanedione (MPAPB), a vinyl monomer with a β-diketone group, was synthesized. The reaction of MPAPB with ceric ion was studied by the radical trapping technique and EPR spectrum. The homopolymer P(MPAPB) and the copolymers with methyl methacrylate (MMA), P(MPAPB-*co*-MMA), were prepared by a photoinitiated process using benzophenone (BP) and *N,N*-dimethyl-4-toluidine (DMT) as photoinitiators. The graft polymerization of acrylamide onto P(MPAPB) and P(MPAPB-*co*-MMA) films initiated by ceric ion was also investigated. The formation of the grafted copolymers was revealed by grafting percentage, water absorption, XPS spectra, and scanning electron photomicrographs. To determine the exact grafting site, the effect of two model compounds as well as MPAPB on the polymerization rate of acrylamide initiated by ceric ion was studied. Based on the EPR spectrum and the kinetic study, a mechanism of the grafting reaction was proposed.

INTRODUCTION

Ceric ion alone and redox initiating systems consisting of ceric ion and alcohol, aldehyde, ketone, amine, or carboxylic acid as well as amide have been widely used as initiators for vinyl radical polymerization [1–5]. Graft polymerization of vinyl monomers onto polymer substrates using ceric ion redox systems as initiators has also been reported and reviewed [6, 7]. Grafting polymerization is a very useful method to modify the surface of a polymer without affecting the bulk properties. Many properties of the polymer, e.g., adhesion, printability, dyeability, coating, antistatic behavior, and biocompatibility, are not related to the bulk of the material but to the surface layer. The introduction of polar substituents, e.g., as grafted chains onto a hydrophobic polymer surface, is expected to improve the above-mentioned properties of the polymer. This paper describes studies on the graft polymerization of vinyl monomer onto a polymer substrate having a special active pendant group by using ceric ion as initiator.

In our laboratory we found that β-dicarbonyl compounds, such as acetylacetone (AcAc), ethyl acetoacetate (EAcAc) [8], benzoylacetone (BzAc), and 3-benzyl-2,4-pentanedione (BzyAcAc) [9], coupled with ceric ion, can form highly active redox initiating system. We also found that the graft polymerization of vinyl monomer onto polymer substrates having β-dicarbonyl groups can take place smoothly by using ceric ion as initiator [9]. The polymer substrates used were β-dicarbonyl groups functionalized polystyrene beads were synthesized by means of alkylation of the chloromethylated polystyrene with sodium salts of β-dicarbonyl compounds. For this article we introduced the β-dicarbonyl groups to the polymers in another way. The β-dicarbonyl group functionalized polymer substrates were synthesized through homo- and copolymerization of 1-[4-(2-methyl-1-oxo-2-propenyl)amino]-phenyl-1,3-butanedione (MPAPB), a vinyl monomer with the β-diketone group. The graft polymerization of acrylamide (AAM) onto films of the homo- and copolymers of MPAPB were also investigated, and the grafted polymers were characterized by means of grafting percentage, water absorption, XPS spectra, and scanning electron photomicrographs.

EXPERIMENTAL

Materials

Acrylamide, methyl methacrylate (MMA), tetrahydrofuran (THF), and acetonitrile were purified by common methods. Ceric ammonium nitrate (CAN) was of analytic grade and used directly. 2-Methyl-2-nitrosopropane (MNP), which was used as a spin trapping agent, was purchased from Aldrich Company.

4-Acetylacetanilide (AAA) was prepared by the reaction of 4-acetylaniline with acetic anhydride and recrystallized three times in a water–ethanol mixture solvent: mp 175–177°C [10].

Synthesis of MPAPB Monomer

p-(Methacryloylamino)benzoyl chloride (MABC): *p*-(Methacryloylamino)-benzoic acid (MABA) or sodium *p*-(methacryloylamino)benzoate (NaMABA) was prepared by the Shotten–Bauman reaction [11]. MABC was prepared by the reac-

tion of NaMABA with thionyl chloride at the boiling temperature. The preparation process of MABC was as follows: 20 g NaMABA, 50 mL freshly redistilled $SOCl_2$, and 180 mL chloroform were refluxed about 4 hours until the NaMABA solid was thoroughly dissolved. After any NaCl formed is filtered, solvent and the excessive $SOCl_2$ in the filtrate were removed by rotatory evaporation under reduced pressure. A light yellow solid MABC was obtained, mp 119–121°C. MABC was dissolved in THF and used in the next reaction step.

MPAPB: Following the method of Viscontini and Merckling [12], ethoxymagnesium acetylacetonate was prepared from 12.2 g (0.12 mol) acetylacetone in THF. The MABC solution prepared above was dropped into the reaction vessel at 0–3°C during 2–3 hours. After overnight stirring, the mixture was decomposed by 400 ml 1:10 HCl and extracted with ether. The ethereal solution was washed with water, sodium bicarbonate aqueous solution, water, and dried. The solvent was removed by rotatory evaporation, and the solid product obtained was recrystallized with ethyl acetate. 13.5 g MPAPB was obtained from 20 g NaMABA, 62.5% yield, mp 145–147°C. MPAPB was characterized by ^1H NMR, FT-IR spectrum, and elemental analysis.

^1H NMR (CD_3COCD_3, ppm): δ = 2.06 (s, 3H, $=C-CH_3$); 2.17 (s, 3H, $-CO-CH_3$); 5.54 and 5.87 (d, 2H, $CH_2=$); 6.42 (s, 1H, $-CO-CH=C(OH)-$); 7.90 and 7.96 (m, 4H, $-C_6H_4-$); 9.38 (s, 1H, $-NH-$); 16.52 (s, 1H, $=C(OH)-$).

FT-IR (KBr, cm^{-1}): 3392 (N—H), 1677 ($-CONH-$), 1628 ($CH_2=C(CH_3)-$, double bond), 1603 ($-CO-CH_3$, enol form of β-diketone).

Analysis, Calculated for $C_{14}H_{15}NO_3$ (245): C, 68.57; H, 6.12; N, 5.71%. Found: C, 68.45; H, 6.19; N, 5.75.

EPR Study

The reaction of MPAPB with CAN was investigated by the spin trapping technique and EPR spectrum. In a small test tube, 0.3 mL MNP solution in acetonitrile, 0.3 mL MPAPB solution in acetonitrile, and 0.3 mL CAN aqueous solution were mixed and bubbled with N_2 for 2 minutes. The mixture solution was transferred into a small flat quartz cell, and the EPR spectrum was recorded at room temperature on a Bruker ER200D-SRC electron spin resonance spectrometer using the TM cavity at X-band, microwave power 19.9 mW and modulation frequency 100 kHz.

Kinetic Study

The polymerization rates of AAM initiated by CAN alone, AAA/CAN, BzAc/CAN, and MPAPB/CAN systems were determined by a dilatometric method [8].

Photoinitiated Polymerization of MPAPB

The photoinitiated homopolymerization of 1.0 g MPAPB was carried out in 5 mL THF in a degassed sealed tube for a few days at room temperature under UV irradiation of a 80 W high-pressure mercury lamp with a 20 cm irradiating distance. Benzophenone (BP, 2%) and *N,N*-dimethyl-4-toluidine (DMT, 4%) were used as

photoinitiators. The resulting polymer was isolated by pouring the polymerization mixture into a large amount of methanol. The polymer was filtrated, dried in vacuum, and weighed. The copolymerization of MPAPB with MMA was performed in a similar way. The intrinsic viscosities of the polymers were determined viscometrically in DMF at 25°C.

The ^{1}H NMR characterization of the homopolymer P(MPAPB) was as follows: ^{1}H NMR (6d-DMSO, ppm): δ = 1.09 (s, 2H, $-CH_2-$); 2.11 (s, 3H, $-C-CH_3$); 3.39 (s, 3H, $=C(OH)-CH_3$); 6.37 (s, 1H, $-CO-CH=C(OH)-$); 7.61 and 7.77 (d, 4H, $-C_6H_4-$); 9.32 (s, 1H, $-NH-$); 16.43 (s, 1H, $=C(OH)-$).

Graft Polymerization

P(MPAPB) and P(MPAPB-*co*-MMA) films used in the grafting reaction were cast in a polytetrafluoroethylene mold by evaporation of 2% DMF solution at 60°C under reduced pressure. The thickness of the films was about 0.2–0.5 mm. In a 100-mL 3-neck flask, 0.03 g polymer film, 2.84 g AAM, 20 mL deionized water were placed. After the AAM was thoroughly dissolved, the solution was bubbled with N_2 and 0.0548 g CAN was added. The mixture was slightly stirred at 40°C for 2 hours. By this process, graft polymerization always took place prior to AAM homopolymerization. The homopolymerization could be observed by adding a few drops of the mixture solution to methanol, whereby the polyacrylamide (PAAM) precipitated at once. The grafted film was removed from the solution just before homopolymerization occurred. To avoid any possible PAAM homopolymer on the surface of the grafted film, it was washed with boiling water four times, dried in vacuum, and weighed. The grafting percentage (G%) was calculated according to

$$G\ (\%) = \frac{W - W_0}{W_0} \times 100$$

where W is the weight of the grafted film and W_0 is the weight of the ungrafted film. The water absorption percentage was determined as follows:

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

where W_w is the weight of the wet film (which was immersed in water at ambient temperature for 12 hours after which the free water on the surface was softly blotted with filter paper) and W_d is the weight of the dry film.

Measurements

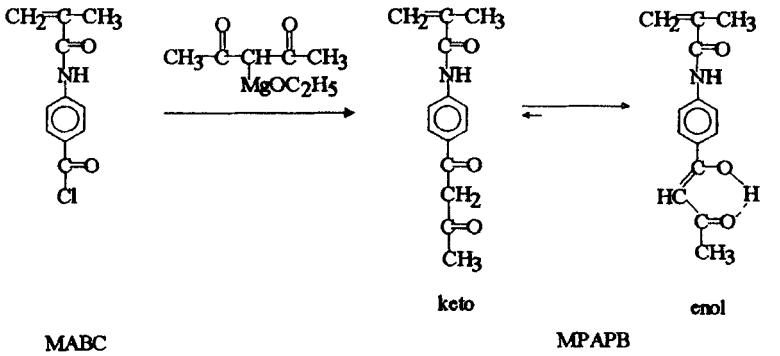
^{1}H-NMR, FT-IR, and XPS spectra and scanning electron photomicrographs were recorded on a Bruker ARX400 spectrometer, a Nicolet Magana-IR 750 spectrometer, a VG-ESCA LAB5 electron spectrometer (AlKα x-ray), and a KYKY 1000B scanning electron microscope, respectively.

RESULTS AND DISCUSSION

Synthesis and Characterization of MPAPB

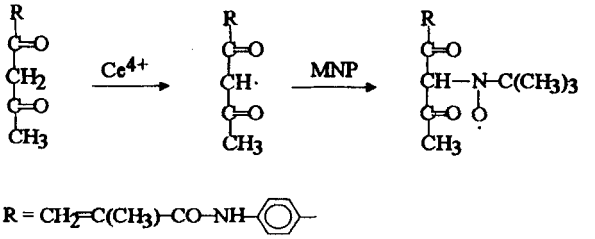
MABA or NaMABA was synthesized by the reaction of 4-aminobenzoic acid with methacryloyl chloride in a weakly basic medium as described by Sueling et al. [11]. NaMABA reacts much more smoothly with thionyl chloride than does MABA

and is completely transformed into MABC. Usually, β-triketones such as benzoyldiacetylmethane and tribenzoylmethane [13] were obtained from the reaction of acyl chlorides with ethoxymagnesium acetylacetonate. However, in the reaction of MABC with ethoxymagnesium acetylacetonate, an unusual deacetylating product, MPAPB, a vinyl monomer with the β-diketone group, is obtained. This may be due to the unstability of the usual β-triketone product, 3-[4-(2-methyl-1-oxo-2-propenyl)amino]benzoyl-2,4-pentanedione (MPABP), which deacetylates during the synthesis reaction and forms MPAPB in high yield (62.5%). MPAPB was characterized by ^{1}H-NMR and FT-IR spectra and elemental analysis. The chemical shift at δ 16.52 ppm in ^{1}H-NMR spectrum and the absorption band at 1603 cm^{-1} in IR spectrum reveal that the β-diketone group in MPAPB is mainly in the enol form.



EPR Study

The resulting radical from the reaction of MPAPB with CAN can be captured by 2-methyl-2-nitroso-propane. The EPR spectrum of the MPAPB/CAN/MNP system shows hyperfine splitting by one α-^{14}N nucleus and a β-H to form a 6-line spectrum (Fig. 1). The hyperfine splitting constants calculated from the EPR spectrum are a_α^N = 1.39 mT and a_β^H = 0.47 mT. This reveals that MPAPB reacts with ceric ion, forming the radical at the methene carbon of the β-diketone group. The process of radical formation was demonstrated as follows:



Photoinitiated Polymerization of MPAPB

Vinyl monomers containing β-diketone groups have lower polymerization rates [14–16] than monomers such as MMA, St, etc. This is due to the high chain-transfer tendency of the enol forms of their β-diketone groups and the low activity of the enolic radicals by comparison with propagating chain radicals. To depress the

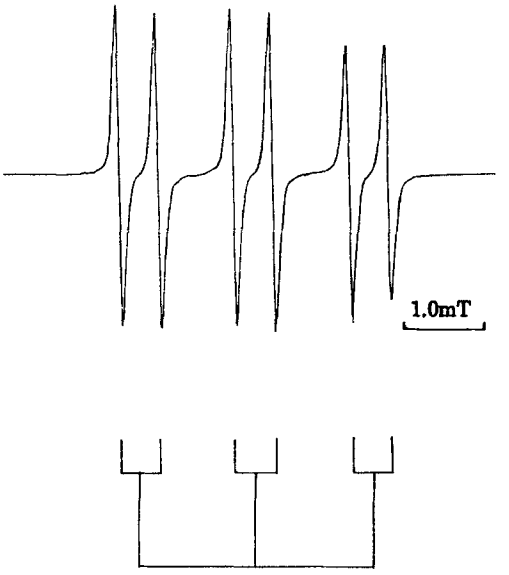


FIG. 1. EPR spectrum of MPAPB/CAN/MNP system. [MNP] = [MPAPB] = 0.033 mol·dm^{-1}, [CAN] = 0.027 mol·dm^{-1}, H_2O:CH_3CN = 1:2 (v/v). Room temperature.

chain-transfer reaction, the homo- and copolymerization of MPAPB were carried out by a photoinitiated process at room temperature using BP and DMT as photoinitiators. Table 1 shows that in the homopolymerization of MPAPB, the polymer yields increase with increasing polymerization time, but the molecular weights of polymers are little affected by the irradiation time. The homopolymer P(MPAPB) and copolymer P(MPAPB-*co*-MMA) obtained in this way were used as polymer substrates for the graft polymerization. The chemical shift at δ 16.43 ppm in the ^{1}H-NMR spectrum of the homopolymer and the absorption at 1603 cm^{-1} in the FT-IR spectra of homo- and copolymers verified that the β-diketone group in homo- and copolymers is mainly in the enol form.

TABLE 1. Photopolymerization of MPAPB Initiated by BP/DMT System[a]

					MPAPB: MMA (w/w)	
Monomer	MPAPB				1:1	1:2
Irradiation time, hours	20	40	62	80	80	80
Conversion, %	16.1	35.3	41.9	43.7	45.0	40.2
[η], mL/g	33.9	37.4	32.4	38.2	31.8	30.9

[a]BP, 2%; DMT, 4%; room temperature.

TABLE 2. Characterization of the Grafted Films

Substrate	MPAPB component, %[a]	Grafting percentage, %[b]	Water absorption, %	
			Ungrafted	Grafted
P(MPAPB)	100	898.7	2.5	385.5
P(MPAPB-*co*-MMA)	68.6	285.7	2.5	403.6
P(MPAPB-*co*-MMA)	59.5	79.9	4.2	286.7
P(MPAPB-*co*-MMA)	39.2	33.3	0.6	172.8
P(MPAPB-*co*-MMA)	20.6	6.9	4.0	42.4

[a]MPAPB component means the weight percent of the MPAPB unit in P(MPAPB-*co*-MMA).

[b]Grafting time, 2 hours; [CAN] = 5.0×10^{-3} mol·dm^{-3}; [AAM] = 2.0 mol·dm^{-3}; temperature 40.0°C.

Graft Polymerization

Graft polymerization of AAM onto P(MPAPB) and P(MPAPB-*co*-MMA) films can take place when CAN is used as initiator. Table 2 shows that the grafting percentages are high and the values of water absorption of the grafted films are much higher than those of the ungrafted films. The high water absorption is due to the high water affinity of the grafted PAAM chains. It also shows that the grafting percentages for the P(MPAPB-*co*-MMA) films decrease with decreasing MPAPB component in the copolymer substrates because of the lowering of the grafting sites.

The grafted polymer films were also characterized by XPS spectra and scanning electron photomicrographs. In Table 3 the decrease of C/N ratios and the shoulder peaks at higher binding energy (eV) are also evidence of the grafting reaction. The grafting reaction lowers the C/N and C/O ratios at the surface of the P(MPAPB) substrate because PAAM chains have lower C/N and C/O ratios than does the original film. The increase of C/O ratio after the grafting reaction of P(MPAPB-*co*-MMA) film is due to the lower C/O ratio of PMMA than of PAAM. The XPS(C_{1s}) spectra of P(MPAPB) and P[(MPAPB)-*graft*-AAM] (Fig. 2) are additional evidence that a shoulder peak in a higher binding energy region (292.5 eV) emerged after the grafting reaction compared to the single peak at 289.0 eV for

TABLE 3. XPS Data of the Ungrafted and Grafted Films

Film	Ungrafted			Grafted		
	C/N	C/O	C_{1s}(eV)	C/N	C/O	C_{1s}, eV[a] (shoulder)
P(MPAPB)	142	1.7	289.0	3.8	1.2	289.5 (292.5)
P(MPAPB-*co*-MMA)[b]	281	1.1	286.7	9.0	1.6	286.5 (288.7)

[a]Binding energy of C_{1s}.

[b]The weight percentage of MPAPB unit in P(MPAPB-*co*-MMA) is 39.2%.

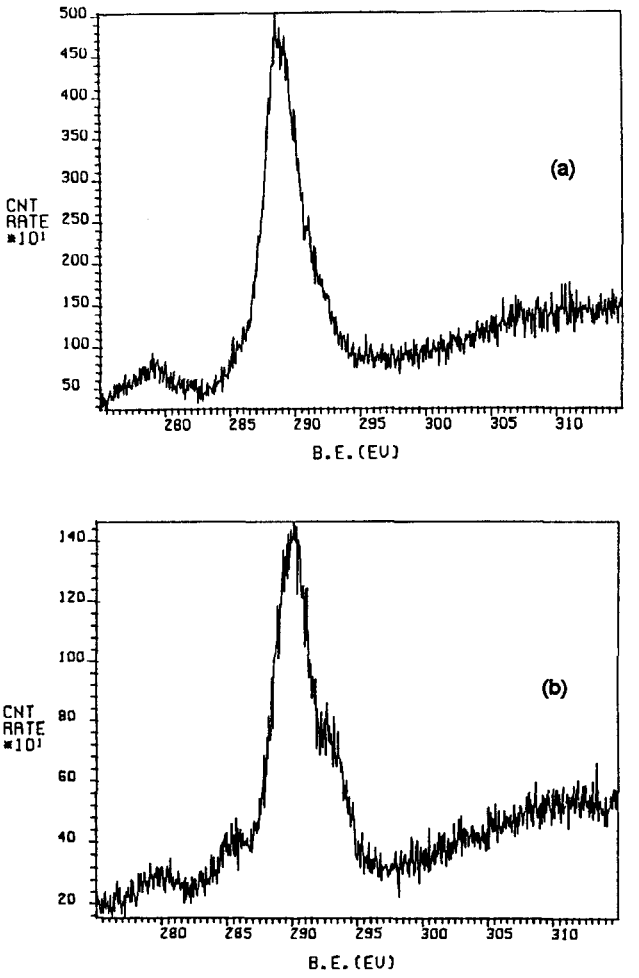


FIG. 2. XPS (C_{1s}) spectra of (a) P(MPAPB) and (b) P[(MPAPB)-graft-AAM].

the ungrafted film, and that carbon atoms having different environments were introduced. Figures 3(a) and 3(b) are scanning electron photomicrographs of the ungrafted and grafted film of P(MPAPB). In addition to some small dots on the surface of the photomicrographs, the ungrafted film is flat, but the grafted film seems cloudlike because the PAAM chains on the grafted film take a different shape. A similar result is observed in the P[(MPAPB-*co*-MMA)-*graft*-AAM] photomicrograph (see Fig. 3c).

Mechanism of Graft Polymerization

In previous work we found that besides β-dicarbonyl compounds, acetanilides having different substituents at the *p*- or *o*-position of the benzene ring can enhance the polymerization rate of AAM initiated by ceric ion to some extent. The promoting efficiencies of acetanilides having electron-donating substituents at the *p*-

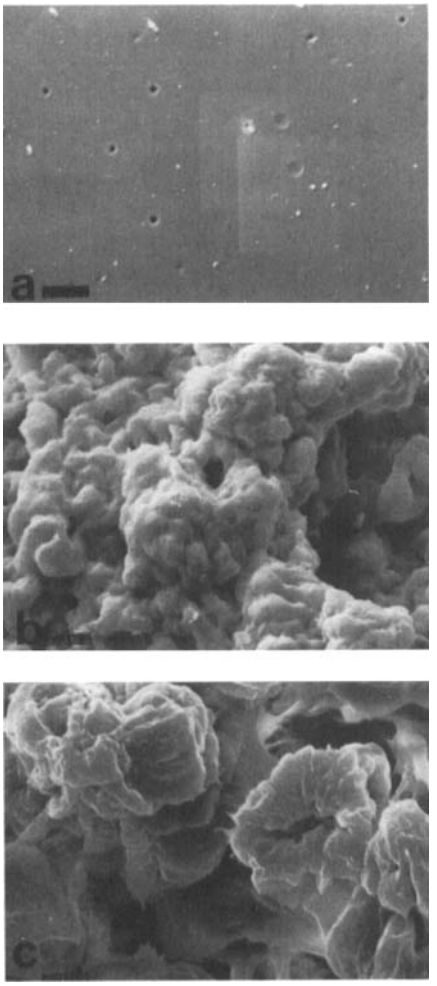


FIG. 3. Scanning electron photomicrographs of (a) P(MPAPB) (×2000), (b) P[(MPAPB)-*graft*-AAM] (×2020), and (c) P[(MPAPB)-*co*-MMA)-*graft*-AAM] (×2000).

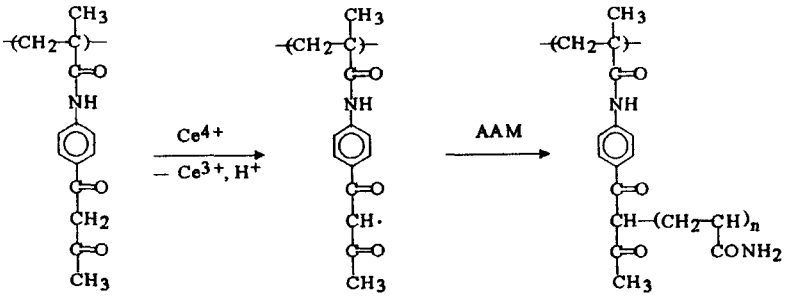
position of the benzene ring are much higher than those having electron-withdrawing substituents [5]. There are two types of functional groups in MPAPB units of homopolymer P(MPAPB) and copolymer P(MPAPB-*co*-MMA), a β-diketone group and an α-substituted acetanilide group with an electron-withdrawing group at the *p*-position of the benzene ring, which could potentially react with ceric ion to form radicals and initiate graft polymerization. In order to clarify the exact grafting reaction site, we utilized BzAc and AAA as model compounds of the β-diketone group and the α-substituted acetanilide group, respectively, and determined the polymerization rates of AAM initiated by BzAc/CAN, AAA/CAN, and MPAPB/CAN systems and CAN alone. Table 4 shows that the polymerization rate of AAM initiated by the BzAc/CAN or MPAPB/CAN system is much higher than that by the AAA/CAN system or CAN alone.

TABLE 4. The Polymerization of AAM Initiated by Redox System[a]

Reducer	Induction period, minutes	R_p ($\times 10^4$), $mol \cdot dm^{-3} \cdot s^{-1}$	Relative rate
–	4.0	6.7	1.0
AAA	4.0	7.9	1.2
BzAc	0.4	69.4	10.3
MPAPB	0.5	66.7	10.0

[a][Reducer] = 2.0×10^{-4} $mol \cdot dm^{-3}$; [CAN] = 1.0×10^{-3} $mol \cdot dm^{-3}$; temperature, 40.0°C; Solvent, H_2O: CH_3CN = 3:1 (v/v).

The β-diketone group in the MPAPB unit will be the first to react with CAN and initiate the grafting reaction. Because the proportion of the enol form of β-diketone drops dramatically in water [17], the keto form of MPAPB unit will reasonably react with ceric ion in the initiating process of graft polymerization. Based on the kinetic data and the EPR study of the MPAPB/CAN/MNP system, we propose the following mechanism.



CONCLUSIONS

There are some valuable results from the above investigations.

MPAPB, a vinyl monomer with a β-diketone group, unlike the normal monomer MPABP, a vinyl monomer with a β-triketone group, was synthesized by the reaction of MABC with ethoxymagnesium acetylacetonate in a relatively high yield.

The homo- and copolymerization of MPAPB can be smoothly carried out by a photoinitiated process.

Graft polymerization of AAM onto P(MPAPB) and P(MPAPB-*co*-MMA) can take place using ceric ion as initiator. The formation of the grafted copolymers was characterized by grafting percentage, water absorption, XPS spectra, and scanning electron photomicrographs. The grafting site is at the methene carbon of the β-diketone group in the MPAPB unit.

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