

GRAFT POLYMERIZATION OF ACRYLAMIDE ONTO HOMOPOLYMER OF 5-METHYL-5-HEXEN-2, 4-DIONE INITIATED BY CERIC ION*

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ABSTRACT

The homopolymerization of 5-methyl-5-hexen-2,4-dione (methacryloylacetone, MAA), a vinyl monomer having β -diketone group, was carried out in the presence of benzophenone (BP)/N N-dimethyl-4-toluidine (DMT) system. Graft polymerization of acrylamide initiated by ceric ion onto the homopolymer film was investigated and the mechanism of the grafting reaction was proposed on the basis of ESR study. The grafted copolymer was characterized by means of grafting percentage, water absorption, XPS spectra and scanning electron photomicrographs.

INTRODUCTION

5-Methyl-5-hexen-2, 4-dione (methacryloylacetone, MAA), a vinyl monomer having β diketone group, was synthesized a few decades ago^[1]. Its polymer was mainly used as polymer chelates^[2] due to the affinity of the β -diketone group to metal ions. In our previous work, we have found that the β -dicarbonyl compounds such as acetylacetone (AcAc), ethyl acetoacetate (EAcAc)^[3], benzoylacetone (BzAc), 3-benzyl-2,4-pentanedione (BzyAcAc)^[4] coupled with ceric ion can form highly active redox systems. We also investigated the graft polymerization of vinyl monomer onto polymer substrates having β -dicarbonyl groups, i.e. β -dicarbonyl groups functionalized polystyrene beads, initiated by ceric ion^[4]. The functionalized beads were synthesized by means of alkylation of the chloromethylated polystyrene with sodium salts of β -dicarbonyl compounds. The forms of the polymer substrates were restricted by their especially spheric shapes because of their cross-linked state.

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In this article, we synthesized MAA from Claisen condensation reaction of methyl methacrylate (MMA) with acetone in presence of sodium ethoxide and polymerized it in bulk by photoinitiation in the presence of benzophenone (BP)/N, N-dimethyl-4-toluidine (DMT) system. The linear polymer poly(methacryloylacetone) (PMAA) obtained can be moulded into different shapes desired and was used as polymer substrate. We investigated the graft polymerization of acrylamide (AAM) onto the PMAA film using ceric ion as an initiator. The grafted polymer was characterized by means of grafting percentage, water absorption percentage, XPS spectra and scanning electron photomicrographs.

EXPERIMENTAL

Materials

Acrylamide and acetonitrile were purified by conventional methods. Methyl methacrylate and acetone were of commercial grade and dried by anhydrous sodium sulphate before used. Ceric ammonium nitrate (CAN) was of analytical grade and used directly. 2-Methyl-2-nitrosopropane (MNP) which was used as spin trapping agent was obtained from Aldrich Co.. MAA was synthesized from Claisen condensation reaction of MMA with acetone in the presence of NaOC_2H_5 and purified via copper chelate^[1]. The yield is low, b.p. 51—52°/666.5Pa.

MAA($\text{C}_7\text{H}_{10}\text{O}_2$):	Calcd.	C%, 66.67;	H%, 7.93
	Found	C%, 66.07;	H%, 7.91

ESR study

The reaction of MAA with CAN was investigated by spin trapping technique and ESR spectroscopy^[3]. The ESR spectrum was recorded on a Bruker ER200D-SRC electron spin resonance spectrometer.

Photoinitiated homopolymerization of MAA

The photoinitiated homopolymerization of MAA was carried out in bulk in a degassed sealed tube for 48 h at room temperature under irradiation of 80w high pressure mercury lamp with 20 cm irradiating distance. 2 wt% benzophenone (BP) and 4 wt% N,N-dimethyl-4-toluidine (DMT) 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 under reduced pressure and weighed. The intrinsic viscosity of the polymer was determined viscometrically in DMF at 25°C.

Graft polymerization

PMAA film used in grafting reaction was casted in a polytetrafluoroethylene mould by evaporation of a 2% DMF solution at 60°C under reduced pressure. In a 100ml 3-necked flask, 0.03 g polymer film, 2.84 g AAM, 20ml deionized water were added. After AAM was thoroughly dissolved, the solution was bubbled with N₂ and 0.0548 g CAN was added. The mixture was slightly stirred at 40°C for 2h. Since the graft polymerization takes place prior to AAM homopolymerization, the homopolymerization scarcely occurs during the circumstances of the grafting reaction. After the solution was decanted, the film was washed with boiling water four times, dried in vacuum and weighed. The grafting and water absorption percentage were calculated in a similar way as described in our previous work^[4].

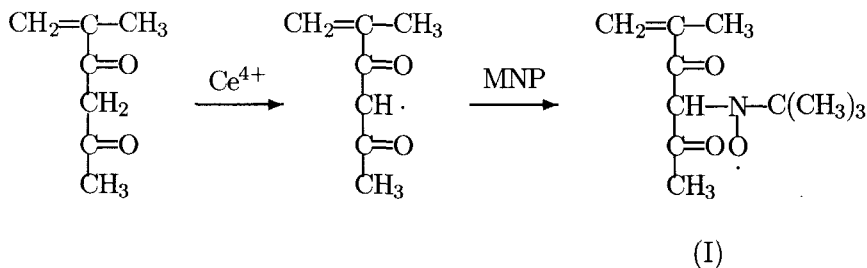
Measurement

XPS spectra and scanning electron photomicrographs were recorded on VG-ESCA LA B5 electron spectrometer (AlK α X-ray) and KYKY 1000B scanning electron microscope.

RESULTS AND DISCUSSION

ESR study

The radical formed from the reaction of MAA with CAN can be captured by 2-methyl-2-nitrosopropane. ESR spectrum of MAA/CAN/MNP system shows the hyperfine splitting of one α -¹⁴N nucleus and a β -proton to form a 6-line spectrum (Fig.1). The hyperfine splitting constants calculated from ESR spectrum are $a_{\alpha}^N = 1.40\text{mT}$, $a_{\beta}^H = 0.48\text{mT}$. It reveals that MAA reacts with ceric ion to form a radical at methene carbon of β -diketone group. This radical is captured by MNP and forms the radical (I). The process is demonstrated as follows:



Photoinitiated polymerization of MAA

Homo- and co-polymerization of MAA initiated by azobisisobutyronitrile (AIBN) were thoroughly investigated by Masuda^[5]. Even though MAA can slowly polymer-

ized when stored at room temperature, it has lower polymerization rate than that of the conventional monomers such as methyl methacrylate, styrene, etc.. This is due to the high chain transfer tendency of the enol form of the β -diketone group and the low activity of the enolic radical by comparison with the propagating chain radical. In order to depress the chain transfer reaction, the homopolymerization of MAA was carried out in a photoinitiated process at room temperature using BP

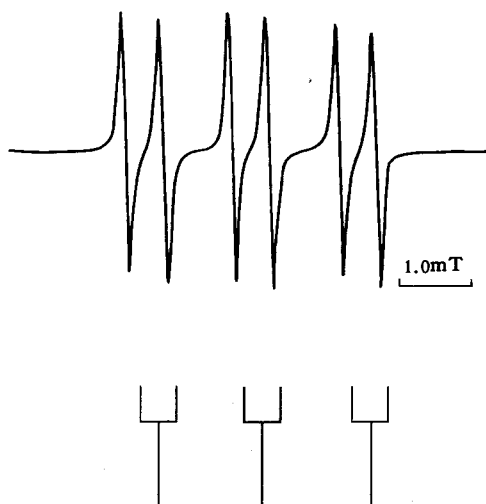


Fig.1 ESR spectrum of MAA/CAN/MNP system

Table 1 Polymerization of MAA and UV light

Initiator	BP+DMT	BP	DMT	Without initiator	No irradiation*
Conversion (%)	12.32	5.53	13.90	5.0	4.0
$[\eta]$ (ml/g)	37.5	33.0	25.0	48.6	71.4

* Kept at room temperature for 10 days

and DMT as photoinitiators. Table 1 shows that whether the photoinitiators present or not, the polymerization rates of MAA under UV light are much higher than that of without irradiation. It was also found that different photoinitiators have different initiating efficiency. The polymerization initiated by DMT or DMT coupled with BP has much higher polymerization rate than that by BP alone, while the polymerization rate initiated by BP alone is almost the same as that of no photoinitiator present. In view of the electron-deficient feature of MAA and the electro-rich feature of DMT, as well as the fact that the mixture turns yellow when DMT is mixed with

MAA, the high initiating efficiency of DMT is attributed to the formation of charge-transfer complex, which initiates the homopolymerization of MAA under UV light. The homopolymer PMAA was used as polymer substrates for graft polymerization. The IR characterization of PMAA shows that the β -diketone group is mainly in enol form as described by Teyssie^[1].

Graft polymerization

Graft polymerization of AAM onto PMAA films can smoothly proceed at 30–40°C when CAN is used as initiator. Table 2 shows that the grafting percentages are high, and the measured value of water absorption of the grafted film (117.0%) is much higher than that of the ungrafted film (1.2%), due to the high water affinity of the grafted polyacrylamide (PAAM) chains.

Table 2 Graft polymerization of AAM onto PMAA films

Substrate	Grafting percentage (%)
PMAA ¹⁾	87.5
PMAA ¹⁾	83.2
PMAA ²⁾	103

[CAN] = 5.0×10^{-3} mol/L, [AAM] = 2.0 mol/L

1) $T = 40.0^\circ\text{C}$, $t = 2.0\text{h}$; 2) $T = 30.0^\circ\text{C}$, $t = 3.0\text{h}$

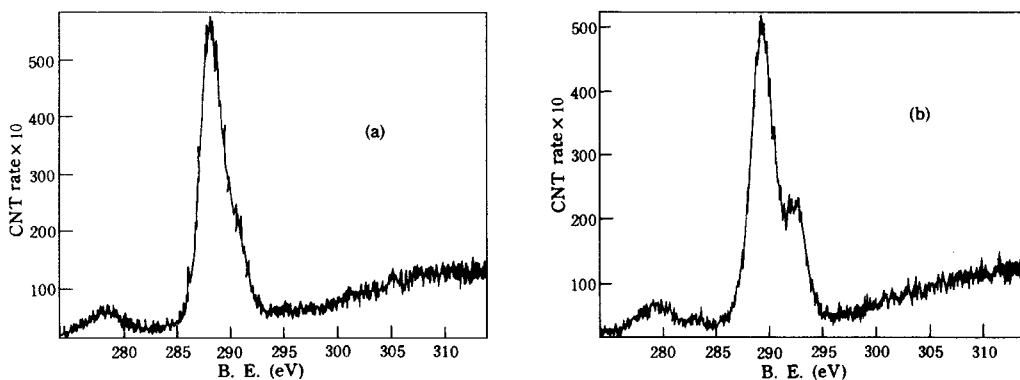


Fig.2 XPS (C_{1s}) spectra of (a) PMAA and (b) P(MAA-g-AAM)

The graft polymers were also characterized by XPS spectra and scanning electron photomicrographs. XPS characterization shows that on the surface of the grafted film, the C/N value is 2.56, while on the surface of the ungrafted film no nitrogen element is detected. XPS(C_{1s}) spectra reveal from another evidence that a shoulder peak at higher binding energy region (293.2 eV) emerges after the grafting reaction compared to the single peak at 289.0 eV for the ungrafted film (Fig.2(a), (b)), that carbon atoms having different environments were introduced. These facts clarified that PAAM chains were introduced onto the PMAA films through the grafting

reaction. Fig.3(a) and Fig.3(b) are the scanning electron photomicrographs of the ungrafted and grafted film of PMAA. It seems that the surface of the grafted film becomes cotton-like and is different from that of the ungrafted film which is smooth in appearance, because the PMAA chains on the grafted film take a different shape from the ungrafted film under the scanning electron microscope.

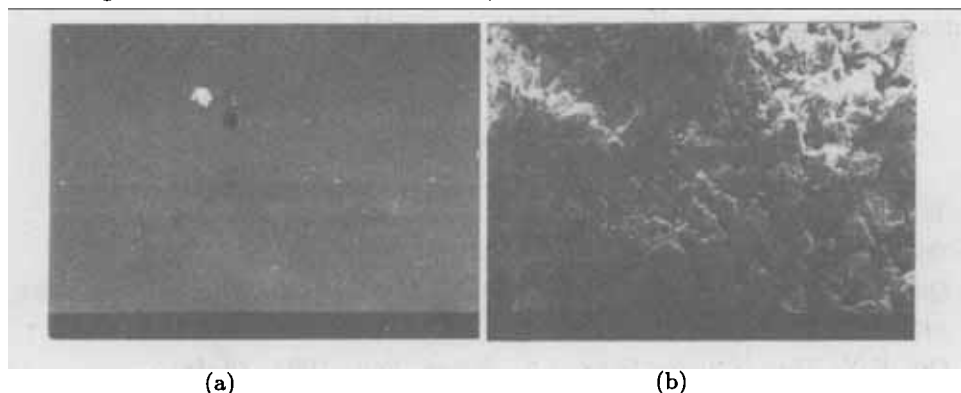
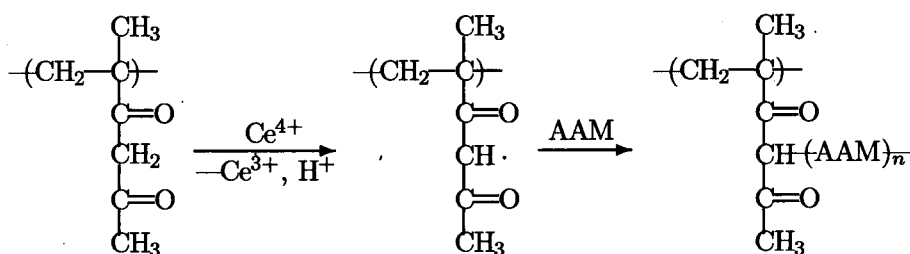


Fig.3 Scanning electron photomicrographs of (a) PMAA ($\times 108$) (b) P(MAA-g-AAM) ($\times 71.0$)

Mechanism of the graft polymerization

In our previous work, we have thoroughly investigated the polymerization of vinyl monomers initiated by AcAc, a model compound of the homopolymer PMAA, coupled with ceric ion, by means of kinetic study, FTIR spectrum, end group analysis and ESR spectrum^[3]. Based on the result as well as the ESR study of MAA/CAN/MNP system mentioned above, it was identified that the methene carbon of the β -diketone group is the active center whereat the radical can form. Even though the β -diketone group in PMAA is mainly in enol form in pure solid state, under the circumstances of the grafting reaction, the β -diketone group in keto form on the surface of PMAA films reasonably takes part in the initiating step of the graft polymerization, since the proportion of the enol form of β -diketone compound drops dramatically in water^[6]. So the mechanism of the grafting reaction is proposed as follows:



The graft polymerization takes place at the methene carbon of the β -diketone group via oxidative abstraction of hydrogen by ceric ion, to form radical and thus initiate the grafting reaction.

Keywords:

Poly(methacryloylacetone); Photoinitiated polymerization; Graft polymerization; Redox initiation of β -diketone pendant group with ceric ion

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