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Graft Copolymerization of Methyl Acrylate onto Poly(Vinyl Alcohol) Initiated by Potassium Diperiodatocuprate(III)

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ABSTRACT

A novel redox system, potassium diperiodatocuprate(III) [Cu (III)]-poly(vinyl alcohol) (PVA) redox system, was employed to initiate the graft copolymerization of methyl acrylate (MA) onto PVA in alkaline medium. The grafting parameters varied with concentrations of monomer, initiator, macromolecular backbone ($DP = 1750$, $M = 80\,000$) and temperature. The formation of the graft copolymer was confirmed by Fourier transfer infrared spectroscopy (IR), scanning electron microscope (SEM), X-ray diffraction and thermogravimetric analysis (TGA). It was found that [Cu (III)]-PVA system is an efficient redox initiator for this graft copolymerization. A mechanism is introduced to explain the formation of radicals and the initiation. At the same time, the other acrylate monomers, such as methyl methacrylate, ethyl acrylate and n-butyl acrylate, were used as reductant to produce graft copolymerization. It was definitely observed that these reactions could occur in some degree. Thermal stabilities were checked by TGA and this indicated that graft copolymer was resistant to moisture absorption.

Key Words: Potassium diperiodatocuprate [Cu (III)]; Graft copolymerization; Poly(vinyl alcohol); Methyl acrylate; Initiation.

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INTRODUCTION

Nowadays, supernormal valence transition-metals have recently received considerable attention and the feasibility of their applications to radical polymerization appeals to more and more researchers. During the recent years, we have obtained some achievements on the polymerization and graft copolymerization of vinyl monomer initiated by supernormal valence transition-metals, such as Cu (III),[1−3] Ag (III)[4,5] and Ni (IV).[6−9] It has been demonstrated that Cu (III) is an efficient and cheap initiator for grafting methyl acrylate (MA) or methyl methacrylate (MMA) onto macromolecular, such as poly(acrylamide), nylon 1010[2], starch[3], and chitosan.

There are a large amount of hydroxyl groups on the PVA macromolecular backbone, which lead to its high hydrophilicity. This also reflects on its poor resistance to water and adverse mechanical properties. Due to the fact that modified PVA possesses great potential as a unique polymeric material, many works have been done in this field. Most of the grafting reactions were carried out in aqueous solution and initiated with ceric ammonium nitrate,[10−15] potassium persulfate,[16−19] ammonium persulfate, ferric ion-hydrogen peroxide,[20] copper(II)[21] and gamma rays.[22,23] Of these methods, the chain transfer reaction is the most ordinary process for engendering graft polymers. Generally speaking, grafting efficiency of these initiators is very low. Though that of ceric ammonium nitrate is excellent, it is expensive and the copolymerizations, which it initiated, must be implemented in acid solution medium. Grafting copolymerization of vinyl monomer onto PVA with Cu (III)-PVA redox system as initiator in alkaline medium has not been systematically studied and reported so far. The amphiphilic graft copolymer, which is prepared using PVA as hydrophilic backbone and PMA, PMMA, PBA etc., as hydrophobic branched chains, can serve as a compatibilizer between hydrophobic polymer and hydrophilic polymer in our future work.

In this paper, Cu (III) was used as oxidant and PVA as reductant to make up the redox system to initiate the grafting copolymerization of MA on PVA backbone. The effects of various factors on grafting parameters, such as conversion of monomers (C%), percentage of grafting (P%) and efficiency of grafting (E%), have also been studied. The structure and properties of graft copolymer were characterized by IR, SEM, X-ray diffraction and TGA. The other acrylate monomers, for example, methyl methacrylate, ethyl acrylate and n-butyl acrylate, have been successfully used to effect graft copolymerization as well.

EXPERIMENTAL

Materials

PVA, a product of reagent factory of Beijing chemical reagent stocking and providing station, with an average degree of polymerization 1750 ± 50 and degree of saponification of 99%, was used as received. MA was washed successively with sodium hydroxide aqueous and distilled water in order to get rid of the inhibitor, and then dried over anhydrous sodium sulfate and, finally distilled under vacuum. The other acrylate monomers were treated as above.

Cu (III) was synthesized and measured according to the reported procedure.[24] The other solvents were of analytical reagent and used as such.

Graft Copolymerization and Treatment of Copolymer

The graft reactions were carried out in a 50 ml four-necked flask equipped with thermometer, condenser, stirrer, and gas inlet. In a typical experiment, a known amount of PVA was dissolved in 10 ml distilled water and constantly stirred under nitrogen. The required amount of monomer was added, followed by Cu (III) aqueous solution and the total volume was made up to 15 ml with distilled water. After the reaction completion, the reactant was cooled and neutralized by an aqueous hydrochloric acid solution. It was poured into excessive methanol and the precipitated product was filtered through a weighted sintered glass funnel. Then, the crude graft copolymer was dried to a constant weight under vacuum at 50°C. The homopolymer was removed from the crude graft copolymer by exhaustive Soxhlet extraction with acetone for 48 h. The final graft copolymer was dried at 50°C to a constant weight under vacuum. The above process was repeated for the different ratio of monomer/PVA, initiator concentration, PVA concentration, and temperature.

All the graft copolymerizations of the other acrylate monomers, such as methyl methacrylate, ethyl acrylate and n-butyl acrylate, were also accomplished in accord with the above procedure.

Determination of the Grafting Parameters

The grafting parameters were defined and calculated in the following manner:

$$C\% = (\text{total weight of PMA}/\text{weight of MA charged}) \times 100\%$$

$$P\% = (\text{weight of PMA grafted}/\text{weight of copolymer}) \times 100\%$$

$$E\% = (\text{weight of PMA grafted}/\text{total weight of PMA}) \times 100\%$$

Measurements

PVA-g-PMA was characterized after exhaustive Soxhlet extraction to remove homo-PMA by IR analysis using an FTS-40 spectrophotometer in the potassium bromide medium. X-ray diffraction of the graft copolymer was carried out with Yaa 900 X-ray diffraction. A scanning electron microscope, AMKAY-1000B, was used to observe the morphologies of pure PVA and graft copolymer. The TGA of PVA (4.1 mg) and the copolymers (5.65 mg) were completed on a Shimadzu apparatus DGC-40 DTA-TG in atmospheric oxygen at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Evidence of Grafting

Gravimetric Estimation

The graft polymerization was followed gravimetrically. It is known that PVA is soluble in hot water and homo-PMA is soluble in acetone. When a crude product was extracted by means of a Soxhlet extractor with a mixture of distilled water and acetone, alternately, to remove the ungrafted PVA and the homo-PMA, the insoluble solid, PVA-g-PMA, still remained, and was obviously heavier than the original PVA. The PMA grafted onto the PVA backbone resulted in the gained weight.

Effect of Different Factors on Grafting Parameters

Initiator Concentration

As shown in Fig. 1, C%, P% and E% went up with an increase in initiator concentration and then leveled off, when the total volume, the ratio of monomer/PVA and reaction temperature was kept invariably. It is probable that Cu (III) attacks the characteristic group (—OH) of PVA backbone directly and increasing macroradicals could be originated to initiate the graft polymerization of MA. As a result, C% and P% grew sharply. However, an excess of the Cu (III) concentration accelerated the oxidation of Cu (III) to radicals, which terminated the chain propagation reaction. In addition, the chance of the transfer reaction to monomer was enhanced, and the homopolymerization of MA was raised with a further increase of Cu (III) concentration. All these led to the decline of grafting parameters accordingly.

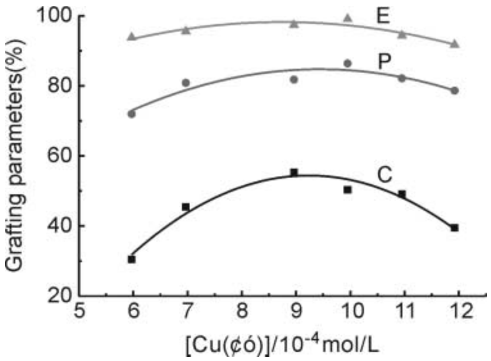


Figure 1. Effect of [Cu (III)] on grafting parameters MA/PVA = 9.54 (weight), 35°C, 1 h.

The Ratio of Monomer/PVA

Figure 2 exhibits that an increase in the ratio of monomer/PVA improved the grafting parameters of C%, P% and E%, and then they all dropped. This may be due to the fact that [Cu (III)] in an aqueous phase relatively increases with the amount of MA increased when the total volume was fixed. Cu (III) not only reacts with reductant to produce radicals initiating graft polymerization of monomer, but also reacts with radicals terminating polymerization. Though the total weight of PMA enhanced, related to the weight of MA added, it decreased. The result is the reduction of C%. As a result, P% decreases. In addition, the more MA charged, the more chance of the chain transfer reaction to monomer. The increase of homopolymerization causes the decrease of P% and E%.

Temperature

The relationship between temperature and grafting parameters has been investigated and is shown in Fig. 3. Corresponding with the general law of radical polymerization, E% boosted and then leveled off slightly. It is perhaps because the advance of temperature quickened the chain transfer reaction to monomer. However, P% and C % show the tendency of ascending quickly, first with the increasing temperature, and then falling gradually. There are two reasons which account for this result. In the first place, the chain transfer reaction sped up with the increase of temperature, which results in the reinforcement of homopolymerization of MA. In the next place, the extortionate temperature made Cu (III) oxidize radicals more easily. The optimum temperature for affording maximum grafting is suggested to be 35°C.

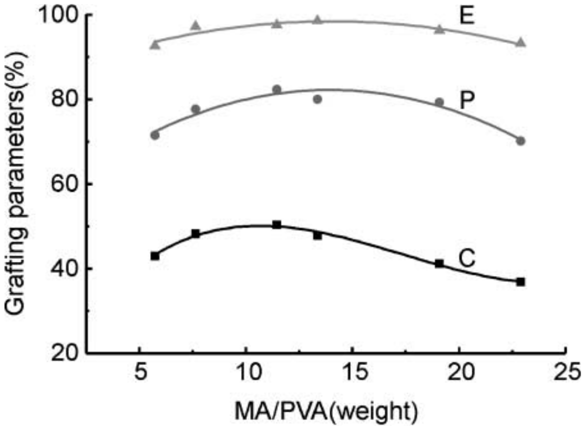


Figure 2. Effect of MA/PVA on grafting parameters [Cu (III)] = 9.95×10^{-4} mol/L, 35°C, 1 h.

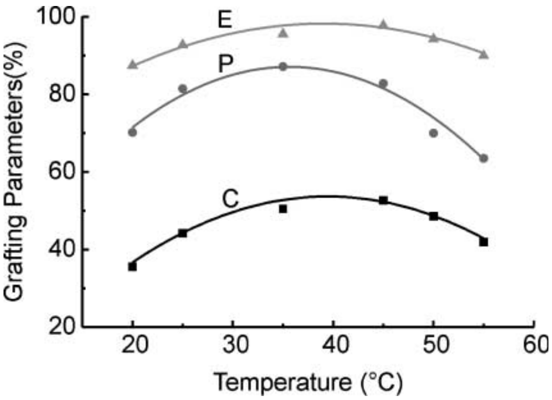


Figure 3. Effect of temperature on grafting parameters MA/PVA = 9.54, [Cu (III)] = 9.95×10^{-4} mol/L, 1 h.

Backbone Concentration

The effect of backbone concentration on grafting parameters is shown in Fig. 4. It is seen that an increase in backbone concentration made more monomers and initiators easily approachable to the surface of PVA and produced a larger number of grafting sites, which provided graft copolymer giving rise to an increase in grafting parameters. With a further increase of backbone concentration, the higher viscosity of the reaction solution medium made the diffusion of monomer more difficult, and the PVA main chain became coiled so that PVA macroradicals interacted with each other to terminate the chain propagation reaction. Consequently, this led to a decrease in grafting parameters.

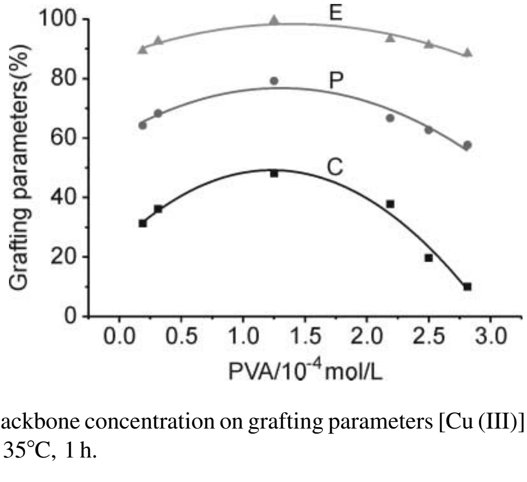


Figure 4. Effect of backbone concentration on grafting parameters [Cu (III)] = 9.95×10^{-4} mol/L, [MA] = 0.739 mol/L, 35°C, 1 h.

Table 1. Effect of different acrylate monomers on grafting parameters.

Monomer	C%	P%	E%
Methyl acrylate	70.73	84.44	80.39
Methyl methacrylate	13.99	51.34	67.98
Ethyl acrylate	27.13	64.55	90.73
n-Butyl acrylate	—[a]	—[a]	—[a]

Condition: [Cu (III)], 9.95×10^{-4} mol/L; [monomer], 0.739 mol/L; [PVA], 8.33×10^{-5} mol/L; 35°C; 1 h.

[a] Denoting the reaction did not take place.

The Different Acrylate Monomers

The grafting parameters of graft reactions of the different acrylate monomers have been investigated and listed in Table 1. The value of grafting parameters, C% and P%, was found to be methyl acrylate > ethyl acrylate > methyl methacrylate > n-butyl acrylate. It is obvious that the reactive degree of methyl acrylate is superior. This is probably due to the fact that the solubility of methyl acrylate ranked first among these acrylate monomers and the touching opportunity between MA and PVA macroradicals had the advantage of others. But, E% of methyl acrylate was lower in contrast with that of ethyl acrylate. The reason is that the preferable solubility of MA also augmented the chain transfer reaction to monomer.

Characterization of Graft Copolymer

IR Spectroscopy

The IR spectra of grafted copolymer PVA-g-PMA (b), along with pure PVA (a), is shown in Fig. 5. The weakened and narrowed characteristic absorption band at 3410 cm^{-1} is due to the hydroxyl group (ν_{O-H}) in PVA in the copolymer, and a stronger characteristic absorption band at 1730 cm^{-1} ($\nu_{C=O}$), an added absorption band at 1150 cm^{-1} (ν_{C-O-C}), 1190 cm^{-1} (ν_{C-O-C}), 1240 cm^{-1} (ν_{C-O-C}), and 1268 cm^{-1} (ν_{C-O-C}) are due to the characteristic groups in PMA in the copolymer, confirmed the formation of PVA-g-PMA.

Scanning Electron Microscope

The SEM micrographs of PVA (a) and PVA-g-PMA (b) were measured and shown in Fig. 6. It is clear that the surface of ungrafted PVA is very rough and not smooth, whereas the surface of the MA-grafted PVA tends to be smoother and has almost turned whole. It is no doubt that the graft reaction brings these alterations.

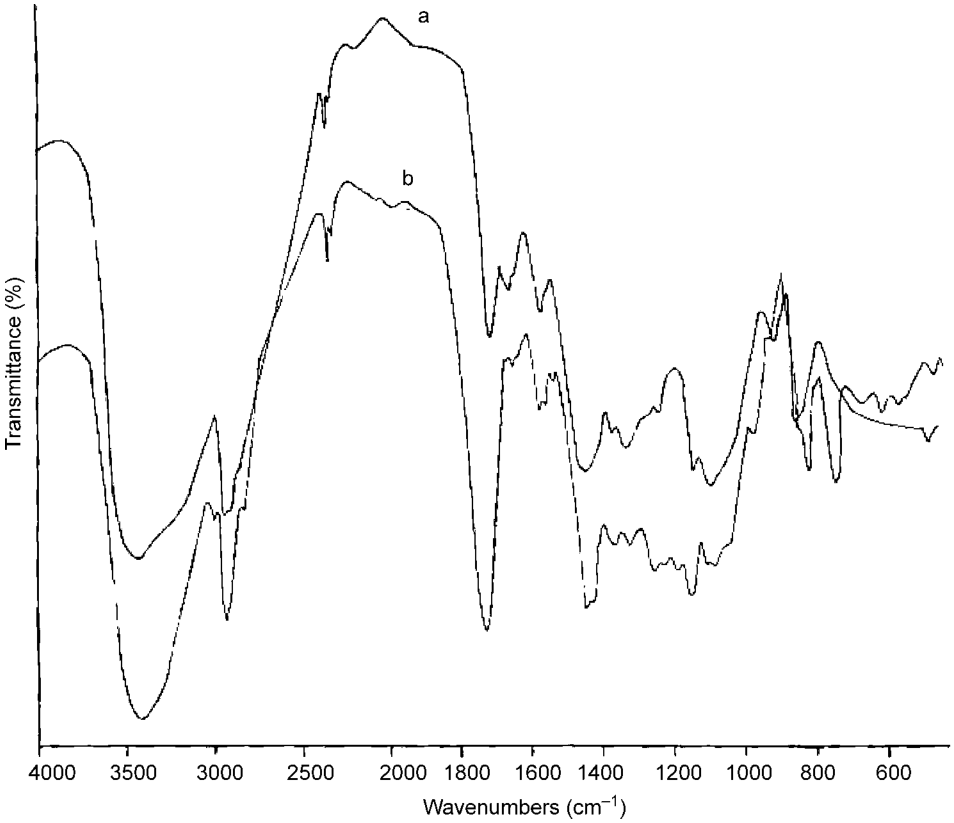


Figure 5. IR spectras of PVA and PVA-g-PMA.

X-Ray Diffraction

Figure 7 illustrates the X-ray diffraction patterns of pure PVA and PVA-g-PMA. It is clear that PVA has a strong peak at 19.08, indicating high crystallinity. The X-ray diffraction pattern of PVA-g-PMA exhibits a weakened peak at 20.07, indicating decreased crystallinity, and three added peaks at 26.56, 30.13, and 31.12. These indicate that the incorporation of MA changes the crystal structure of PVA.

Thermogravimetric Analysis

The thermograms from TGA are shown in Fig. 8. In the TG curve of pure PVA, an inflexion due to absorbed moisture lies between 85.6°C–150°C. No such inflexions are observed in the TG curve of PVA-g-PMA. This reveals that graft copolymer is resistant to moisture absorption. In addition, the TG curve of PVA shows two stages of decomposition marked at 313.3°C, but the copolymer only shows one stage. They also show that PVA with a crystallinity peak at 218.5°C has more oxidation peaks. This is

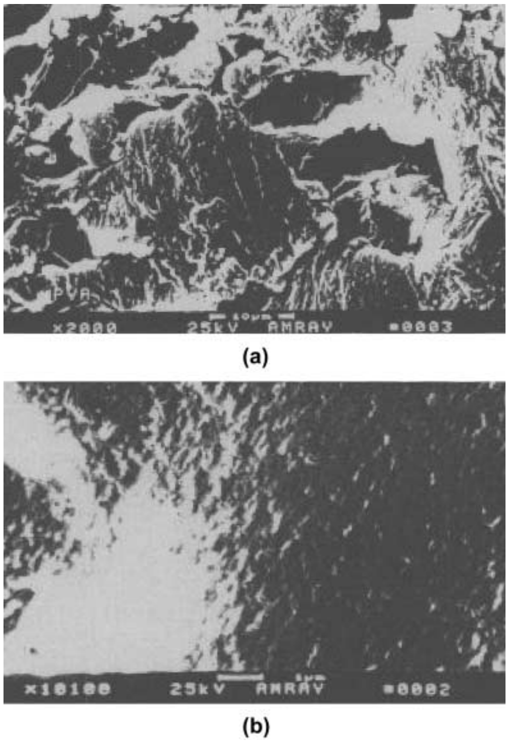


Figure 6. SEM micrographs of PVA and PVA-g-PMA.

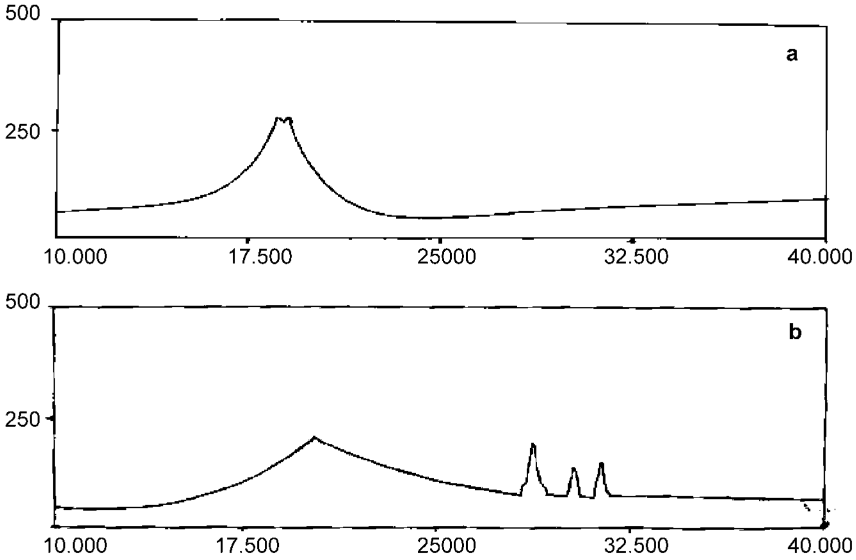


Figure 7. X-ray diffraction patterns of PVA and PVA-g-PMA.

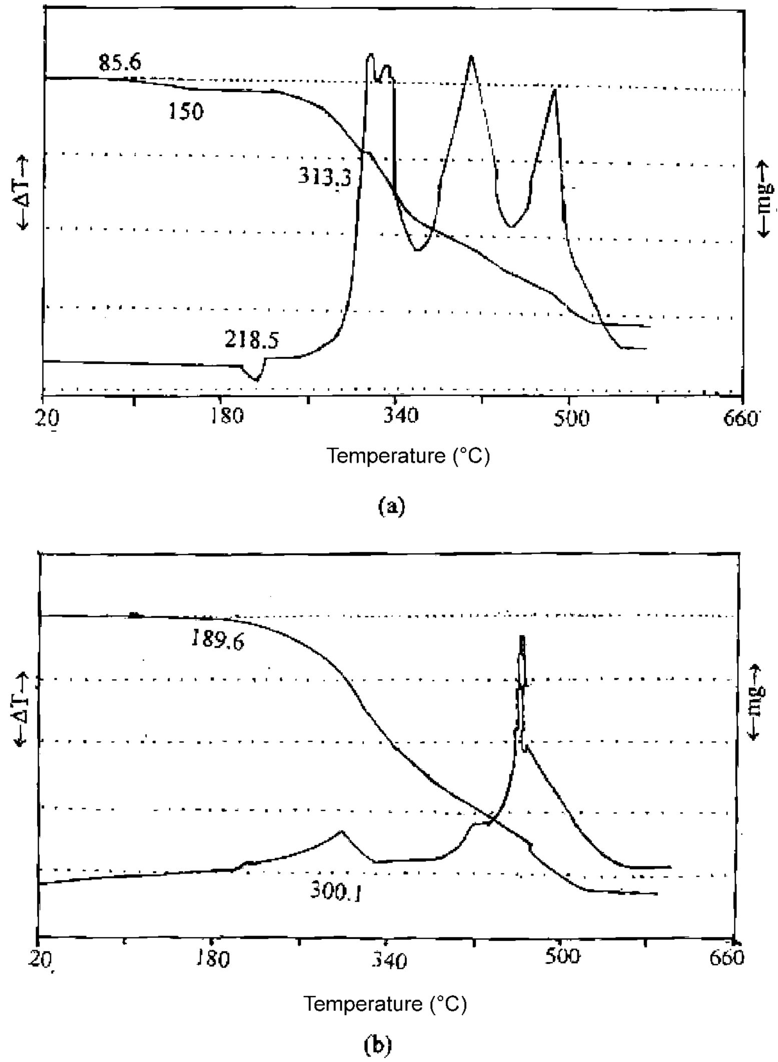
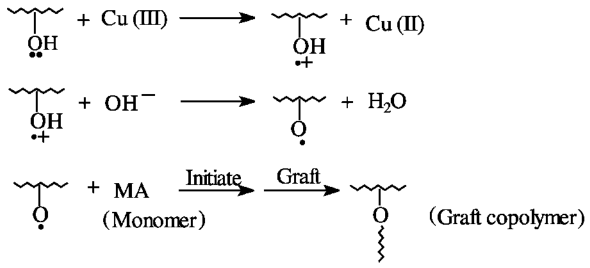


Figure 8. TGA curves of PVA and PVA-g-PMA.

probably because that pure PVA holds more tiny groups and hydrogen bonds than graft copolymer.

The Initiation Mechanism of Grafting Reaction

IR spectra has confirmed that MA has been grafted onto PVA. Thus, it can be concluded the single electron in the process of Cu (III) → Cu (II) is able to initiate PVA to graft MA. The initiation mechanism may be shown as follows:



CONCLUSION

It has been shown that the characteristic group (—OH) in PVA macromolecular backbone was directly used as a reductant and Cu (III) as oxidant to constitute the redox system to initiate grafting copolymerization successfully. Gravimetric estimation, IR, SEM, X-ray diffraction and TGA demonstrated the formation of graft copolymer. Compared with pure PVA, the crystallinity of PVA-g-PMA levels off greatly due to the presence of PMA. Moreover, TGA indicates that the grafted product shows enhanced resistance to water, which differs from that of unmodified PVA.

During this research work, graft polymer with high graft efficiency and grafting percentage has been obtained. Cu (III)–PVA system is found to be an efficient redox initiator for this graft copolymerization. At the same time, Cu (III) obtained from $CuSO_4 \cdot 5H_2O$ is cheaper than other initiators, which makes it favorable to facilitate its application. Furthermore, the graft reaction is able to be achieved at a mild temperature of 35°C and in alkali aqueous medium, which is superior to other initiators. Thus, the Cu (III)–PVA redox system is considered to be a practical initiator and has a good foreground. Further work is being carried out.

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