

# Graft Copolymerization of Methyl Acrylate onto Poly(vinyl alcohol) Initiated by Potassium Diperoxonickelate(IV)

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**ABSTRACT:** The graft copolymerization of methyl acrylate onto poly(vinyl alcohol) (PVA) with a potassium diperoxonickelate(IV) [Ni(IV)]–PVA redox system as an initiator was investigated in an alkaline medium. The grafting parameters were determined as functions of the temperature and the concentrations of the monomer and initiator. The structures of the graft copolymers were confirmed by Fourier transform infrared spectroscopy, scanning electron microscopy, X-ray diffraction, differential scanning calorimetry, and thermogravimetric analysis. The Ni(IV)–PVA sys-

tem was found to be an efficient redox initiator for this graft copolymerization. A single-electron-transfer mechanism was proposed for the formation of radicals and the initiation. Other acrylate monomers, such as methyl methacrylate, ethyl acrylate, *n*-butyl acrylate, and *n*-butyl methacrylate, were used as reductants for graft copolymerization. These reactions definitely occurred to some degree. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 529–534, 2003

**Key words:** graft copolymers; initiators; monomers

## INTRODUCTION

Poly(vinyl alcohol) (PVA) has many hydroxyl groups, which are responsible for its high solubility and also reflect on its poor resistance to water and poor mechanical properties. Because modified PVA possesses great potential as a unique polymeric material, attempts have been made to modify PVA through the grafting of a variety of vinyl monomers with chemical and radiation methods. Most of the grafting reactions have been implemented in aqueous media, and they are initiated by ceric ammonium nitrate,<sup>1–4</sup> ammonium persulfate,<sup>5</sup> potassium persulfate,<sup>6–8</sup> ferric ion/hydrogen peroxide,<sup>9</sup> copper(II),<sup>10–15</sup> or  $\gamma$  rays.<sup>16</sup> Of these methods, the chain-transfer reaction is the most common process for producing graft copolymers. As a rule, the grafting efficiencies of these initiators are very low. Although ceric ammonium nitrate is superior in its efficiency, it is expensive, and the copolymerizations initiated by it must be carried out in an acidic medium. There is no report on the graft copolymerization of a vinyl monomer onto PVA with a potassium diperoxonickelate(IV) [Ni(IV)]–PVA redox system as an initiator in an alkaline medium. It is generally believed that the mechanism of oxidation of Ni(IV) is a two-electron-transfer process without radicals and that Ni(IV) cannot initiate the polymerization of a vinyl monomer.<sup>17–24</sup> However, under our experi-

mental conditions, results have shown that the radical polymerization of some vinyl monomers can be initiated by a Ni(IV) redox system. A two-step single-electron-transfer mechanism has been proposed to explain the production of radicals and the initiation.<sup>25–29</sup>

In this study, Ni(IV) was used as an oxidant and PVA was used as a reductant to produce a redox system for initiating the grafting copolymerization of methyl acrylate (MA) onto the PVA backbone. Grafting parameters, such as the conversion of monomers (*C*%), the percentage of grafting (*P*%), and the efficiency of grafting (*E*%), were studied, and they varied with the temperature, monomer concentration, and initiator concentration. The structure and properties of the graft copolymer were characterized by IR, scanning electron microscopy (SEM), X-ray diffraction, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). Other acrylate monomers, including methyl methacrylate, ethyl acrylate, *n*-butyl acrylate, and *n*-butyl methacrylate, were successfully used to accomplish graft copolymerization as well.

## EXPERIMENTAL

### Materials

PVA, a product of the reagent factory of the Beijing Chemical Reagent Stocking and Providing Station (Beijing, China; degree of polymerization =  $1750 \pm 50$ , degree of saponification = 99%), was used as received. MA was washed successively with aqueous sodium hydroxide and distilled water for the removal of the inhibitor, and then it was dried over anhydrous sodium sulfate and distilled in vacuo. The other acrylate monomers were handled as previously described.

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Ni(IV) was synthesized and measured according to a reported procedure.<sup>30</sup> All the other solvents were analytical-grade and were used without any further purification.

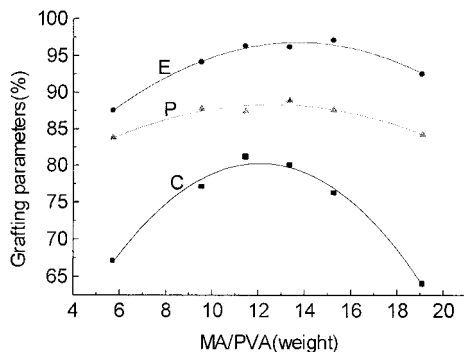
### Graft copolymerization and treatment of the copolymer

The graft reactions were carried out in a 50-mL, four-necked flask equipped with a thermometer, a condenser, a stirrer, and a gas inlet. In a typical experiment, a known amount of PVA was dissolved in 10 mL of distilled water and constantly stirred under nitrogen. The required amount of the monomer was added, followed by an aqueous Ni(IV) solution, and the total volume was raised to 15 mL with distilled water. The graft copolymerization was performed under the conditions of different monomer concentrations, initiator concentrations, and temperatures. After the completion of the reaction, the reactant was cooled and neutralized by an aqueous hydrochloric acid solution. It was poured into methanol, and the precipitated product was filtered through a weighted, sintered glass funnel and was washed several times with methanol. Then, the crude graft copolymer was dried to a constant weight in vacuo 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 in vacuo.

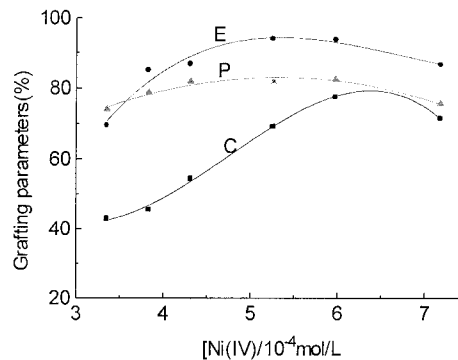
All the graft copolymerizations of the other acrylate monomers, including methyl methacrylate, ethyl acrylate, *n*-butyl acrylate, and *n*-butyl methacrylate, were handled with the aforementioned procedure.

### Determination of the grafting parameters

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



**Figure 1** Effect of the MA/PVA ratio on the grafting parameters.  $[\text{Ni(IV)}] = 4.43 \times 10^{-4}$  mol/L; temperature = 35°C; time = 1 h.



**Figure 2** Effect of the Ni(IV) concentration on the grafting parameters. MA/PVA = 9.54 (w/w); temperature = 35°C; time = 1 h.

$$C\% = \frac{\text{(Total weight of PMA)} \div \text{Weight of MA charged}}{\times 100\%}$$

$$P\% = \frac{\text{(Weight of PMA grafted)} \div \text{Weight of copolymer}}{\times 100\%}$$

$$E\% = \frac{\text{(Weight of PMA grafted)} \div \text{Total weight of PMA}}{\times 100\%}$$

where PMA is poly(methyl acrylate).

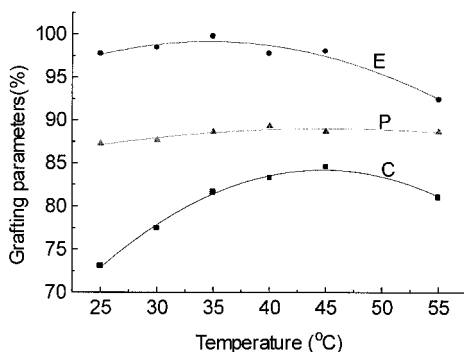
### Measurements

PVA-*g*-PMA was characterized after exhaustive Soxhlet extraction for the removal of homo-PMA by IR analysis with an FTS-40 spectrophotometer (BIO-RAD, USA) in a potassium bromide medium. The X-ray diffraction of the graft copolymer was carried out with a Yaa 900 X-ray diffraction instrument (Dandong Ray Apparatus Corp., China). A scanning electron microscope (Amkay 1000B, Scientific Apparatus Factory of the Chinese Academy of Sciences, China) was used to observe the morphologies of the pure PVA and graft copolymer. DSC was performed with a DuPont differential scanning calorimeter (Shimadzu, Japan) attached to a 9900 thermal analyzer, and the samples were scanned at 10°C/min under nitrogen. The TGAs of PVA (4.1 mg) and the copolymers (3.88 mg) were completed with a Shimadzu DGC-40 DTA-TG apparatus (Shimadzu, Japan) 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. PVA is soluble in hot water, and homo-PMA is soluble in acetone. When a crude product was ex-



**Figure 3** Effect of the temperature on the grafting parameters. MA/PVA = 9.54;  $[\text{Ni(IV)}] = 4.43 \times 10^{-4} \text{ mol/L}$ ; time = 1 h.

tracted with a Soxhlet extractor with a mixture of distilled water and acetone to remove the ungrafted PVA and homo-PMA, respectively, the insoluble solid, PVA-g-PMA, still remained and was obviously heavier than the original PVA. The PMA grafted onto the PVA backbone led to the increased weight.

#### Effect of the different factors on the grafting parameters

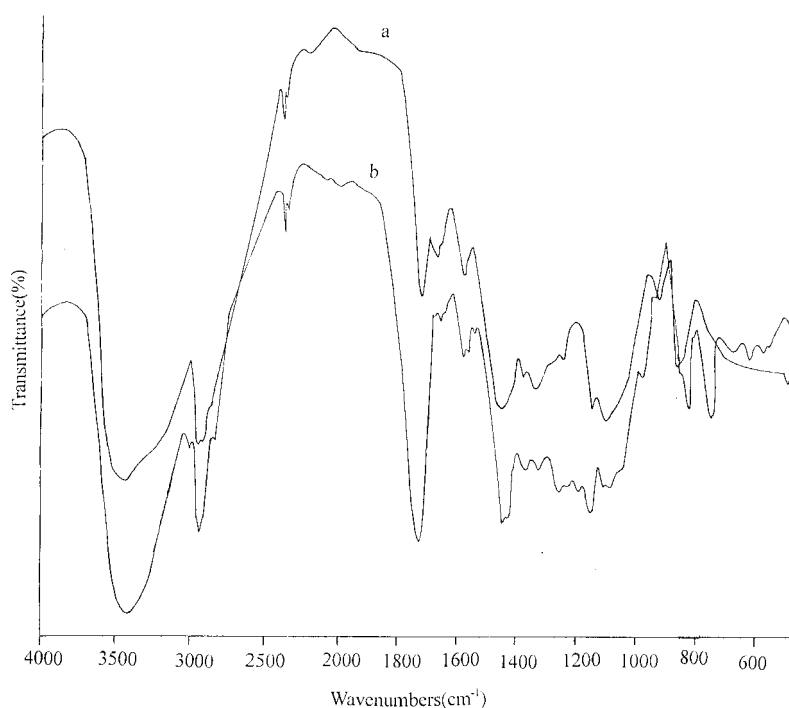
##### Monomer/PVA ratio

As shown in Figure 1,  $C\%$ ,  $P\%$ , and  $E\%$  went up with an increase in the monomer/PVA ratio and then leveled off when the total volume, the weight of PVA, the concentration of the initiator, and the reaction temperature were

kept unchanged. This may be due to the fact that the number of radical sites produced by Ni(IV) and PVA remained constant, so each site averaged a greater availability of monomer molecules in close vicinity to PVA macroradicals with the increasing MA concentration. With a further increase in the MA concentration, the monomers that graft-copolymerized onto PVA were inclined to saturation, which resulted in the reduction of  $P\%$  and  $E\%$ . In addition, the conversion rate of MA was relatively slower than the charged monomer amount. As a result,  $C\%$  decreased.

##### Initiator concentration

The effect of the initiator concentration on the grafting parameters is shown in Figure 2. An increase in the Ni(IV) concentration improved  $C\%$ ,  $P\%$ , and  $E\%$ , and then they all dropped. This happened because Ni(IV) attacked the characteristic group ( $-\text{OH}$ ) of the PVA backbone directly, and an increasing number of macroradicals initiated the graft copolymerization between PVA and MA. As a result,  $C\%$  and  $P\%$  grew. However, an excess of Ni(IV) accelerated the oxidation of Ni(IV) to radicals, which terminated the chain propagation reaction. At the same time, the chance of a transfer reaction to the monomer was enhanced, and the homopolymerization of MA was increased with a further increase in the Ni(IV) concentration. All this resulted in a decrease in the grafting parameters accordingly.



**Figure 4** IR spectra of (a) PVA and (b) PVA-g-PMA.

**TABLE I**  
Effect of Different Acrylate Monomers  
on Grafting Parameters

| Monomer                      | C%             | P%             | E%             |
|------------------------------|----------------|----------------|----------------|
| MA                           | 56.16          | 85.30          | 82.05          |
| Methyl methacrylate          | 41.07          | 82.33          | 78.91          |
| Ethyl acrylate               | 37.05          | 70.24          | 74.21          |
| <i>n</i> -Butyl acrylate     | 1.17           | 41.56          | 6.21           |
| <i>n</i> -Butyl methacrylate | — <sup>a</sup> | — <sup>a</sup> | — <sup>a</sup> |

Conditions: [monomer] = 1.11 mol/L, [PVA] =  $1.25 \times 10^{-4}$ ; [Ni(IV)] =  $5.21 \times 10^{-4}$  mol/L, 35°C, 1 h.

<sup>a</sup> Denotes that the reaction did not take place.

### Temperature

At fixed concentrations of MA and Ni(IV) and at a fixed amount of PVA, the relationship between the temperature and grafting parameters was investigated, and it is shown in Figure 3. The temperature influenced *E*% a little at the beginning and later reduced it. This occurred because the rise in temperature quickened the chain-transfer reaction to the monomer. However, the grafting parameters *P*% and *C*% showed a tendency of ascending first with increasing temperature, which conforms to the general principle of radical polymerization, and then falling gradually. This outcome resulted for two reasons. On the one hand, the chance of a chain-transfer reaction increased with an increase in the temperature, and this led to the intensification of the homopolymerization of MA. On the other hand, the mixture became viscous and congealed quickly when the temperature was higher, and it was difficult for the grafting reaction to be carried out. The optimum temperature for maximum grafting was suggested to be 35°C.

### Different acrylate monomers

The grafting parameters of the graft reactions of the different acrylate monomers were determined and are listed in Table I. The order of the grafting parameters (*C*%, *P*%, and *E*%) was found to be MA > methyl methacrylate > ethyl acrylate > *n*-butyl acrylate > *n*-butyl methacrylate. This was perhaps due to the fact that the solubility of MA ranked first among these acrylate monomers and that the opportunity for contact between MA and PVA macroradicals excelled that of the others.

### Characterization of the graft copolymer

#### IR spectroscopy

The IR spectra of pure PVA and PVA-g-PMA purified by thorough Soxhlet extraction are shown in Figure 4. Compared with pure PVA, the final product had a weakened and narrowed absorption band at 3410

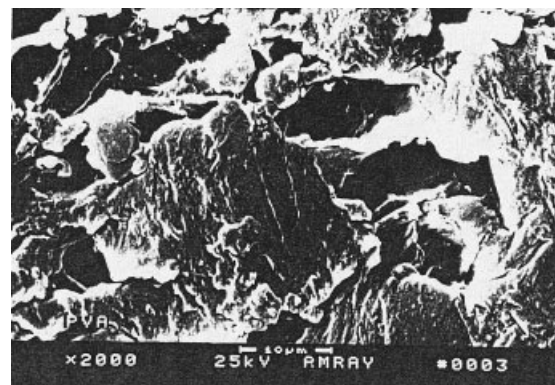
$\text{cm}^{-1}$  ( $\nu_{\text{O-H}}$ ), which is characteristic of PVA, and also had a stronger absorption band at  $1730 \text{ cm}^{-1}$  ( $\nu_{\text{C=O}}$ ) and added absorption bands at  $1150$  ( $\nu_{\text{C-O-C}}$ ) and  $1268 \text{ cm}^{-1}$  ( $\nu_{\text{C-O-C}}$ ), which are characteristic of PMA. The final product was obviously a graft copolymer of PVA and MA.

#### SEM

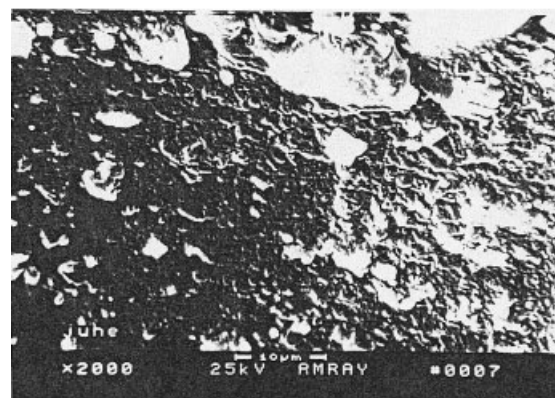
Figure 5 illustrates SEM micrographs of PVA and PVA-g-PMA. The surface of the ungrafted PVA clearly was very rough and not smooth, whereas the surface of MA-grafted PVA became smoother and almost turned into an integration. The graft reaction brought about these changes.

#### X-ray diffraction

The X-ray diffraction patterns of pure PVA and PVA-g-PMA were measured and are shown in Figure 6. The X-ray diffraction pattern of pure PVA exhibits a wide peak at 19.08, indicating high crystallinity. The pattern of



(a)



(b)

**Figure 5** SEM micrographs of (a) PVA and (b) PVA-g-PMA.

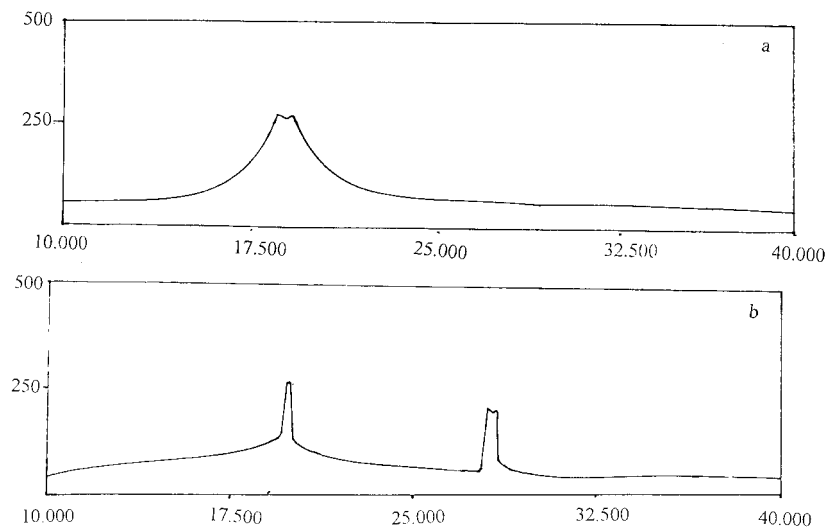


Figure 6 X-ray diffraction of (a) PVA and (b) PVA-g-PMA.

PVA-g-PMA has a sharpened peak at 19.81 and an added peak at 28.08. This suggests that the grafting polymerization of MA affected the crystal structure of PVA.

#### DSC

DSC thermograms of PVA and PVA-g-PMA are shown in Figure 7. According to documentary values, the glass-transition temperature ( $T_g$ ) of PVA is 85°C. However, the  $T_g$  value of the graft copolymer (34°C) was different by 51°C. PMA in PVA led to the reduction of  $T_g$ .

#### TGA

Figure 8 displays thermograms from TGA. The TGA curve of PVA shows two stages of decomposition marked at 313.3°C, but the copolymer curve shows only one stage. In the TGA curve of PVA, an inflexion

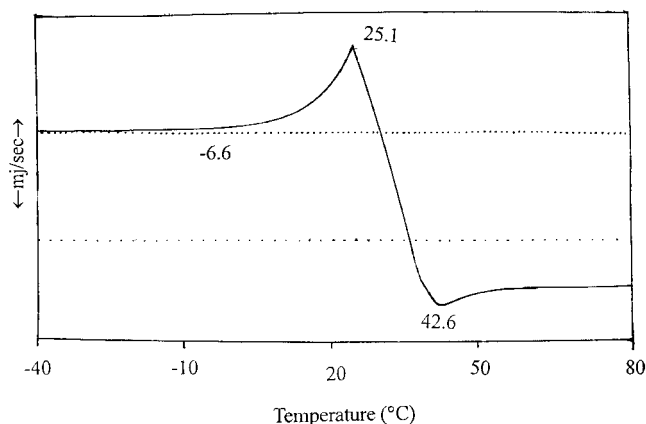


Figure 7 DSC curve of PVA-g-PMA.

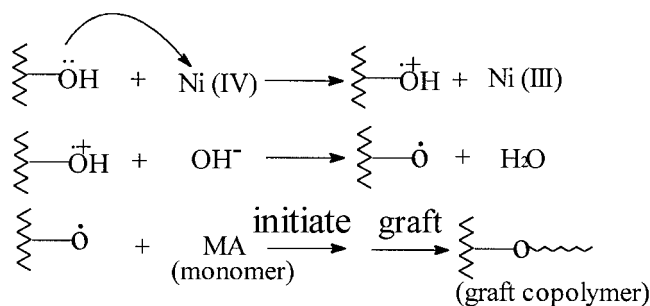
due to absorbed moisture lies between 85.6 and 150°C. No such inflexions are observed in the TGA curve of PVA-g-PMA. This may indicate that PVA-g-PMA is resistant to moisture absorption. It also shows that PVA with a crystallinity peak at 218.5°C has more oxidation peaks. This is probably true because pure PVA holds more tiny groups and hydrogen bonds than the graft copolymer.

#### Solubility testing

Solubility testing of PVA-g-PMA was also carried out. The grafted products were insoluble in solvents that suited either homopolymer. However, the graft copolymers did swell in many tested solvents, such as water, a mixture of water and acetone, and dimethylformamide. This was perhaps due to the existence of residual hydroxy groups and hydrogen bonds.

#### Initiation mechanism of the grafting reaction

The IR spectrum showed that MA was grafted onto PVA because there were many alterations in the IR spectrum of the final product. In contrast with pure PVA, the proportion of the absorption band at 1655  $\text{cm}^{-1}$  ( $\nu_{\text{O}-\text{H}}$ , distorting) to the absorption band at 1100  $\text{cm}^{-1}$  ( $\nu_{\text{C}-\text{O}}$ , stretching) obviously decreased. Therefore, it could be assumed that Ni(IV) might have reacted with hydroxyl groups on the PVA backbone to generate macroradicals first and then initiate MA grafting polymerization. The process of Ni(IV)  $\rightarrow$  Ni(II) belongs to the two-step single-electron-transfer process.<sup>26-29</sup> The graft copolymerization of MA onto PVA is proposed to occur as follows:



Again,



and so forth.

### CONCLUSIONS

Acrylate monomers can be grafted onto PVA with the Ni(IV)-PVA initiation system. The incorporation of MA into PVA was demonstrated by IR, SEM, X-ray diffraction, DSC, and TGA. Solubility testing indicated that the grafted copolymers were resistant to water and many other solvents. The crystallinity of the

grafted PVA obviously changed in comparison with that of pure PVA because of the existence of PMA.

It is generally accepted that the mechanism of oxidation of Ni(IV) is a single-step two-electron-transfer process without radicals and that Ni(IV) cannot initiate the polymerization of a vinyl monomer. During this research, a graft polymer with high  $E\%$  and  $P\%$  values was obtained. The Ni(IV)-PVA system was found to be an efficient redox initiator for this graft copolymerization. The mechanism proposed for the redox process, which includes two separate single-electron-transfer steps, is a modification of the traditional mechanism. Moreover, the graft reaction could be carried out under milder conditions because of its lower activation energy, which is superior to that of other initiators. Therefore, the Ni(IV)-PVA redox system is considered to be a practical initiator and has a good foreground. Further studies are in progress.

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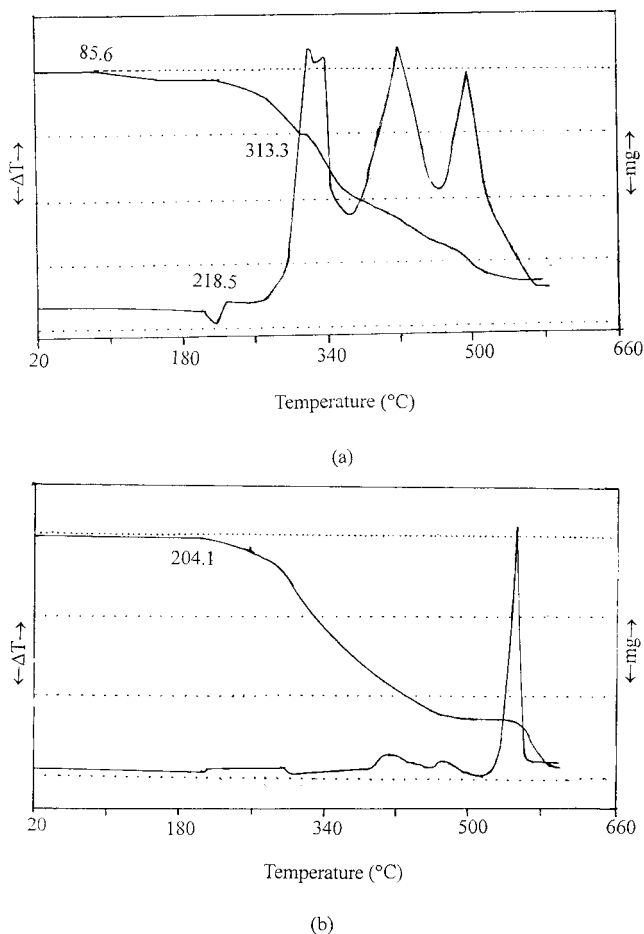


Figure 8 TGA curves of (a) PVA and (b) PVA-g-PMA.