

Kinetics of Graft Copolymerization of Poly(hexanedioic acid ethylene glycol) and Methyl Acrylate Initiated by Potassium Diperiodatocuprate(III)

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Received 26 May 2006; accepted 17 August 2006

DOI 10.1002/app.25331

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A redox system, potassium diperiodatocuprate(III) [DPC]/poly(hexanedioic acid ethylene glycol) (PEA) system, was employed to initiate graft copolymers of methyl acrylate (MA) and PEA in alkaline medium. The results indicate that the equation of the polymerization rate (R_p) is as follows: $R_p = k [\text{MA}]^{1.62} [\text{Cu(III)}]^{0.69}$, and that the overall activation energy of graft polymerization is 42.5 kJ/mol. The total conversion at different conditions (concentration of reactants, temperature, concentration of the DPC,

and reaction time) was also investigated. The infrared spectra proved that the graft copolymers were synthesized successfully. Some basic properties of the graft copolymer were studied by instrumental analyses, including thermogravimetry and scanning electron microscope. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2376–2381, 2007

Key words: diperiodatocuprate(III); acrylates; poly(hexanedioic acid ethylene glycol); redox initiation; graft copolymerization

INTRODUCTION

In the last two decades, biodegradable polymer materials, along with their application in diagnosing disease, therapy, and repairing or replacing material field, etc., have gained more attention. The biodegradable polymer materials mainly include collagen, gelatin, collagen hydrolysate, chitin, chitosan, poly(ortho esters), polycarbonates, polyphosphoester, etc.^{1–4} And the biodegradable polycarbonates are one of most important branches. Because of their excellent properties such as mechanical properties and biocompatibility, and so on, the biodegradable polycarbonates have attracted much attention in biomedical application. Usually, biodegradable polycarbonates are divided into two classes: aliphatic polycarbonates and aromatic polycarbonates, in view of their main chain structure. The aromatic polycarbonates are mainly used as artificial kidney and artificial skull, but the aliphatic polycarbonates could not get people's interest for a long time because of their low melting temperature, low glass transition temperature, and poor hydrolysis stability. Recently, increasing effort was taken to adjust the structure and properties of the aliphatic polycarbonates to meet a range of different demands in biomedical application.⁵

There are many reports in the literature on the graft aliphatic polycarbonates synthesis, for example, enzy-

matic polymerization,⁶ ATRP condensation polymerization,⁷ and so on. But the enzymatic polymerization and the ATRP condensation polymerization reaction condition are rigor and their expense is high. These shortcomings limited their application in the chemical industry. In the last years, chemists paid their attention to the free-radical polymerization, because the reaction depends on the condition a little, although there are some difficulties in free-radical polymerization. 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. Some of the radical copolymerization was carried out in the aqueous solution initiated with ceric ammonium nitrate. Although ceric ion is an excellent initiator, it is expensive, and the copolymerization, which it initiated, must be implemented in the acidic medium. Therefore, to find new supernormal valence transition metals as oxidant and polymer as reductant for the redox system, which initiates the radical graft copolymerization, is very important.

During the recent years, we have obtained some achievements on polymerization initiated by supernormal valence transition metals, such as diperiodatocuprate(III),^{8–10} diperiodatoargentate(III),^{11,12} diperiodatonickelate(IV),^{13,14} and Mn(III).^{15–19} It has been demonstrated that Cu(III) is an efficient initiator. This study investigated the graft copolymerization of methyl acrylate (MA) with poly(hexanedioic acid ethylene glycol) (PEA) using diperiodatocuprate(III) (DPC) in an alkaline solution. The results indicate that the equation of the polymerization rate (R_p) is

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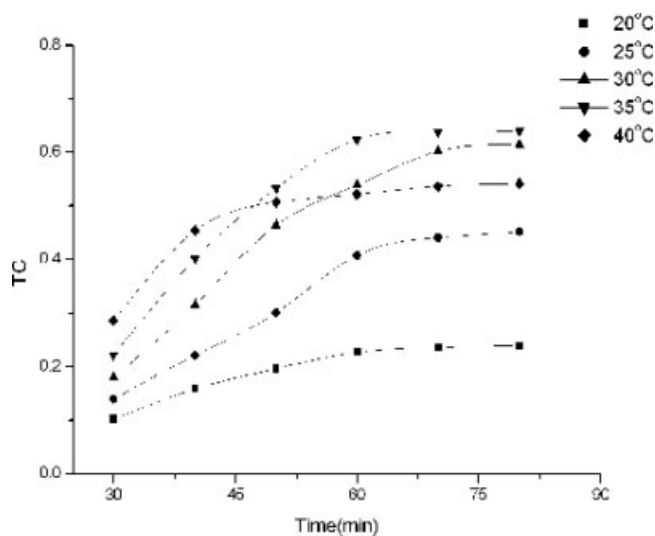


Figure 1 Effects of temperature and time on TC [MA] = 4.7 mol/L, [Cu(III)] = 2.106×10^{-3} mol/L.

as follows: $R_p = k[\text{MA}]^{1.62}[\text{Cu(III)}]^{0.69}$ and that the overall activation energy of graft polymerization is 42.5 kJ/mol, and the effects of variables on the grafting were also studied in detail. Then the graft copolymers were also characterized.

EXPERIMENTAL

Materials

The solution of diperiodatocuprate(III) (DPC) was prepared according to Ref. 10. The concentration of DPC was measured by its absorption at $\lambda = 414$ nm using a Shimadzu UV-265 spectrophotometer (Japan). Methyl acrylate (MA), an analytical reagent, was purchased from Huadong reagent factory (Tianjin), which was distilled before use. Poly(hexanedioic acid ethylene glycol) (PEA) (purchased from Jufeng reagent factory, Shanxi) was used as received. Other reagents were all of analytical reagent grade and were used as received.

Measurements

FTIR spectroscopy

The FTIR spectra of PEG and graft copolymer were recorded on an FTS-40 spectrometer (BRVKER IFS-25) using potassium bromide pellets technique.

SEM

The PEA and PMA were dissolved in the acetone, stirred, and dried to get PEA/PMA blend. The PEA, PMA-PEA, and PMA were dissolved in the acetone, stirred, and dried to get the PEA/PMA-PEA/PMA blend. Scanning electron microscope, AMKAY-1000B,

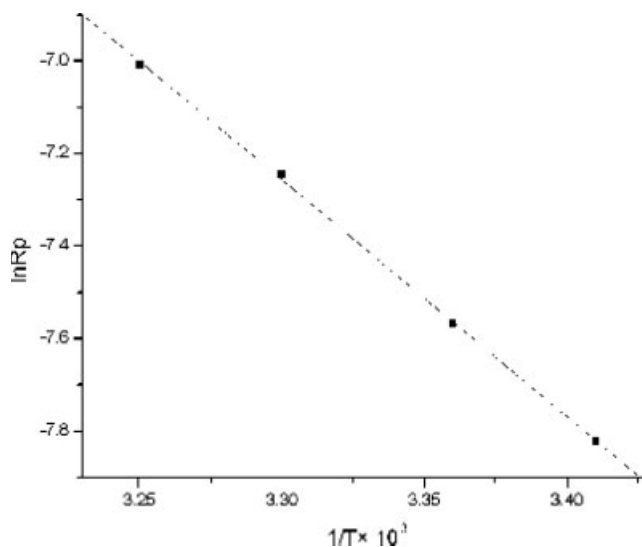


Figure 2 Arrhenius plot relative to the R_p [MA] = 4.7 mol/L, [Cu(III)] = 2.106×10^{-3} mol/L.

was used to observe the morphologies of PEA/PMA and the PEA/PMA-PEA/PMA.

Thermal analysis

TGA curve of the graft copolymer was carried out on a Shimadzu apparatus (DGC-40 DTA-TG) at a heating rate of $10^\circ\text{C}/\text{min}$ in a static air atmosphere.

RESULTS AND DISCUSSION

Experimental procedure

Required amounts of PEA solution (dissolved in 1,4-dioxane), MA, and water were put into a glass tube, flushed with pure nitrogen, and then the reaction system was maintained at $(35 \pm 0.1)^\circ\text{C}$ in a thermo-

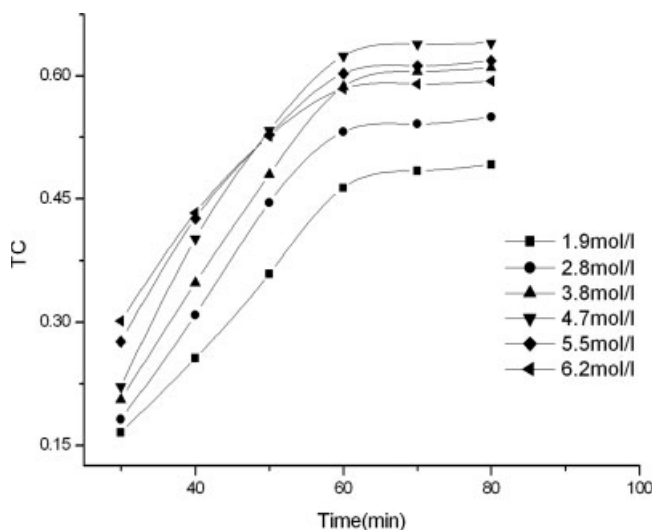


Figure 3 Effect of MA concentration and time on TC [Cu(III)] = 2.106×10^{-3} mol/L, $T = 35^\circ\text{C}$.

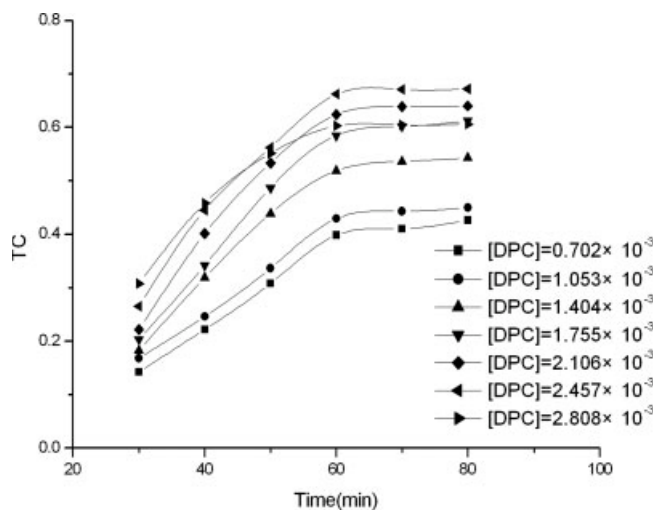


Figure 4 Effect of DPC concentration and time on TC [MA] = 4.7 mol/L, $T = 35^{\circ}\text{C}$.

static reservoir. Appropriate amounts of DPC were then added under nitrogen, hold at $(35 \pm 0.1)^{\circ}\text{C}$ for a period of time, and then stopped by adding hydrochloric acid. The graft copolymer was precipitated in salt water, filtered through a weighted sintered glass crucible, washed well with water, and then dried under vacuum to constant weight, and then the weight of PEA was subtracted from the constant weight to get the weight of PMA.

The total conversion (TC) and the polymerization rate (R_p) were defined and calculated as follows:

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

$$R_p = \text{weight of PMA}/\text{time}$$

Effects of temperature and time on TC

The effects of temperature and time on the grafting of PEA with MA were determined at 20, 25, 30, 35, and 40°C . Figure 1 gives the curves of TC versus time. It is seen that, for a given temperature, the TC increases steadily with the increasing reaction time to a certain value, and then levels off. The initial increase of the TC indicates clearly that both DPC and grafting sites could keep its activity for a period of time. The following trend of leveling off can be attributed to the decrease in monomer and initiator concentration, as well as a reduction in the number of active sites on PEA. In addition, an increased initial rate of polymerization (R_p) is seen as the temperature increases. The acceleration in R_p upon increasing temperature is consistent with the general principle of conventional radical polymerization. And at 35°C , the reaction time reaches 60 min (exclude the

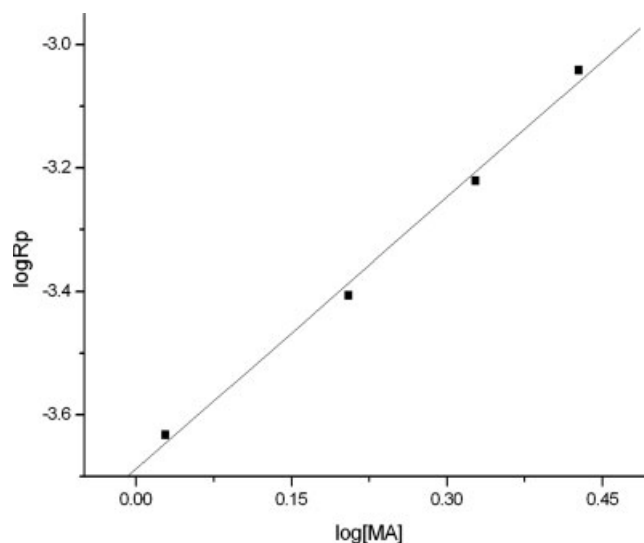


Figure 5 Double logarithmic plot of R_p versus [MA] [Cu(III)] = 2.106×10^{-3} mol/L, $T = 35^{\circ}\text{C}$.

40°C), and the tendency of the TC comes forth a peak value. The decreasing of TC at 40°C in the latter stage may be ascribed to a faster termination rate of the growing chain through oxidation by DPC, which, in reverse, accelerates the consumption of the DPC. From the Arrhenius plot (Fig. 2), the activation energy of MA graft with PEA is 42.5 kJ/mol.

Effect of MA concentration and time on TC

When keeping all the other variables unchanged, the curves of TC versus time at [MA] = 1.9, 2.8, 3.8, 4.7, 5.5, and 6.2 mol/L (Fig. 3). The explanation of the TC versus time at a given MA concentration is simi-

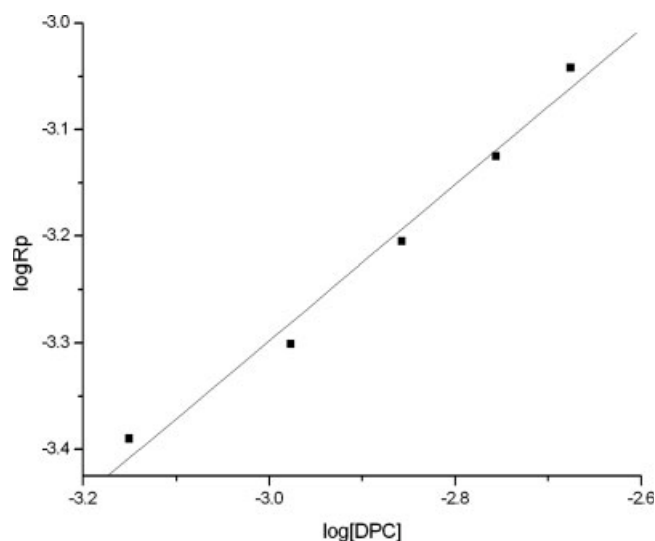


Figure 6 Double logarithmic plot of R_p versus [Cu(III)] [MA] = 4.7 mol/L, $T = 35^{\circ}\text{C}$.

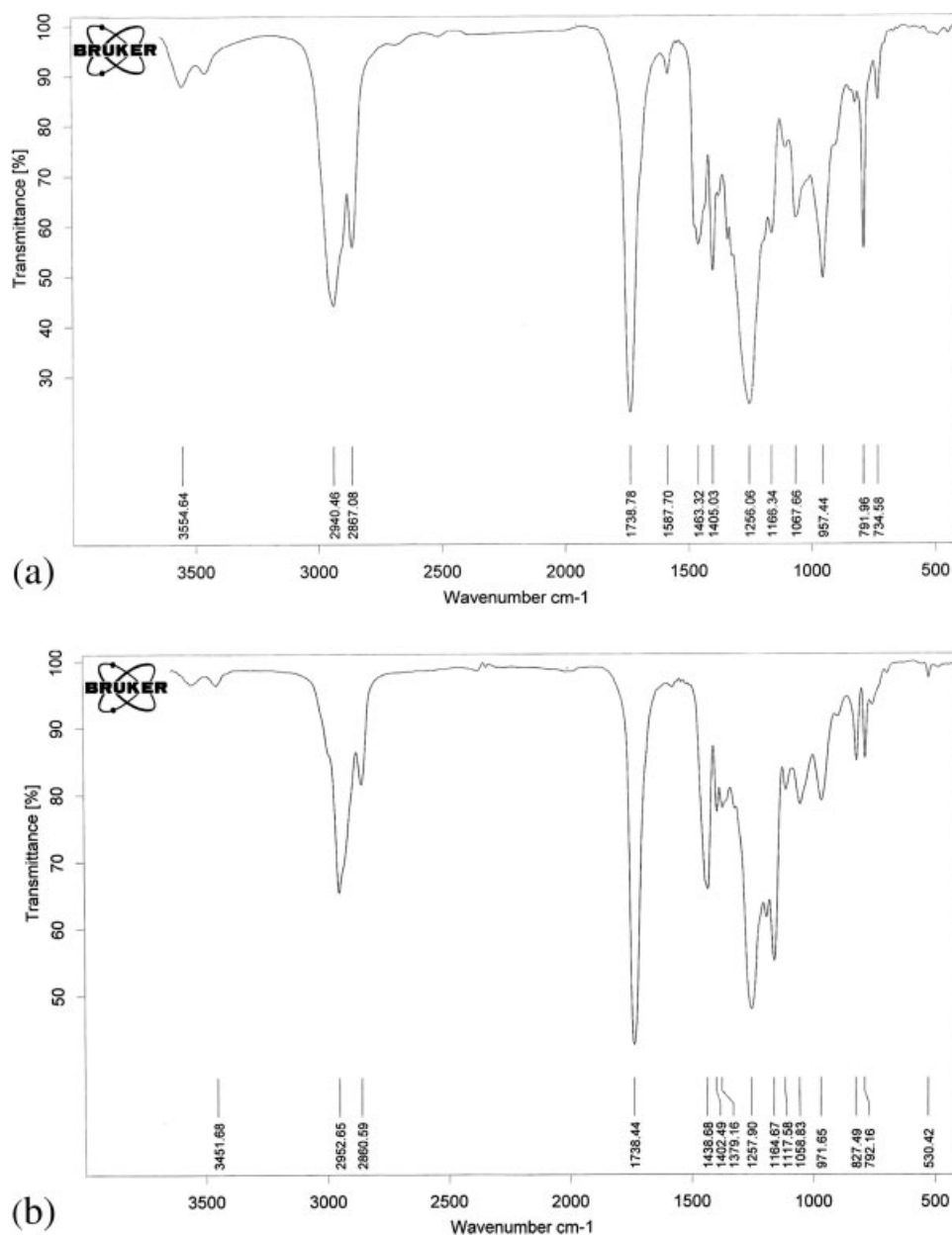


Figure 7 IR spectrum of (a) PEA and (b) PMA-PEA.

lar with that shown in Figure 1. The change in trend of [MA] versus time can be explained as follows: it can be seen that TC increases with the increasing concentration of MA at first and then declines. The trend of TC may be explained as follows: when the concentration of MA is low, the probability of interaction between PEA and MA is less. With increasing concentration of MA, the graft polymers could bring into self-emulsification so as to absorb more monomers onto the PEA surface, which considerably enhances the rate of the graft reaction. If the concentration of MA was too high, the monomers absorbed onto PEA are so great that they interfere significantly with the approach of both Cu(III) and PEA, therefore leading to the declination of TC.

Effect of DPC concentration and time on TC

Figure 4 shows the curves of TC versus time at $[DPC] = 0.702 \times 10^{-3}$, 1.053×10^{-3} , 1.404×10^{-3} , 1.755×10^{-3} , 2.106×10^{-3} , 2.457×10^{-3} , 2.808×10^{-3} mol/L. The curves of TC versus time are explained in Figure 1. Also, to the changing trend of TC versus DPC concentration, it can be seen that TC increases significantly first, reaches a maximum, and then decreases. The initial increasing trend may be a result of the increased rate of polymerization, which can be ascribed to the formation of a great number of free radical through an oxidation by DPC. However, abundance of primary radicals may accelerate the rate of termination by coupling. At the same

time, an excess of DPC may also increase the chance of encounter between DPC and propagating chain radicals, which will terminate the reaction too.

Kinetics of polymerization

Polymerization was also carried out under varying [MA], and the double logarithmic plot of R_p versus [MA] is shown in Figure 5. The slope indicates that R_p is proportional to the 1.62 power of [MA]. At the same time, the double logarithmic of R_p versus [DPC] is shown in Figure 6. The slope also indicates that R_p is proportional to the 0.69 power of [DPC].

The equation of the polymerization rate is as follows:

$$R_p = k[\text{MA}]^{1.62}[\text{Cu(III)}]^{0.69}$$

This equation includes two contents. First, MA is employed not only as the monomer taking part in the reaction of chain propagation, but also as the reductant participating in the reaction of initiation. On the other hand, the termination of the growing polymer chains would have both monoradical and biradical termination mechanisms.

Proof of grafting

IR spectroscopy

Figure 7(a) shows the IR spectra of pure PEA, B is the graft copolymer PMA-PEA. In Figure 7(a), the absorption peaks at 1738.78 and 1166 cm^{-1} come from C—O_{str.}. Absorption at 791.96 cm^{-1} is CH₂'s rocking vibration of O(CH₂)₂O and at 734.58 cm^{-1} is CH₂'s rocking vibration of OC(CH₂)₄CO. The sharp peak at 3554.64 cm^{-1} corresponds to —OH. In Figure 7(b), absorption at 792.19 cm^{-1} is the CH₂'s rocking vibration of O(CH₂)₂O, and the 3451.68 cm^{-1} corresponds to —OH. These are the PEA's own peaks. Pay attention to the peak of 827.49 cm^{-1} , it is the rocking vibration of CH₃ of PMA. According to these evidences, we can draw a conclusion that the copolymer is PMA-PEA.

SEM

Morphological characters of the blends PMA/PEA and PMA/graft polymer/PEA are shown in Figure 8. It can be seen that there are some convex forms in Figure 8(a) (PMA/PEA). The smooth surface is the PMA and the convex forms are the PEA, because two kinds of materials cannot be compatible after blend and have different flow capability. When the acetone vaporizes from the blend polymer, the PEA forms the convex shape. On the contrary, the convex forms have disappeared as shown in Figure 8(b) (PMA-PMA/PEA-PEA). The aforementioned features

suggest that the graft copolymer is efficient in improving the compatibility of PEA and PMA.

Thermal analysis

The thermal behavior of graft copolymer and PEA was examined by a study of their thermograms. As shown in Figure 9, Curve 1 is the pure PEA, Curve 2 is PEA-PMA (grafting percentage = 30%), and Curve 3 is PEA-PMA (grafting percentage = 50%). Thermal decomposition of the PEA takes place in two main steps. The first stage (240–300°C) is due to the break of the low molecular weight segment. The second step between 300 and 400°C may be corresponding to the break of the PEA. The Curve 2's first stage (360–400°C) is due to the break of the PEA, and the second step (400–440°C) is corresponding to the break of the PMA. The Curve 3's first step is between 364 and 402°C, and the second is between 402 and 440°C. From Figure 8, we obviously find that thermal property improves largely.

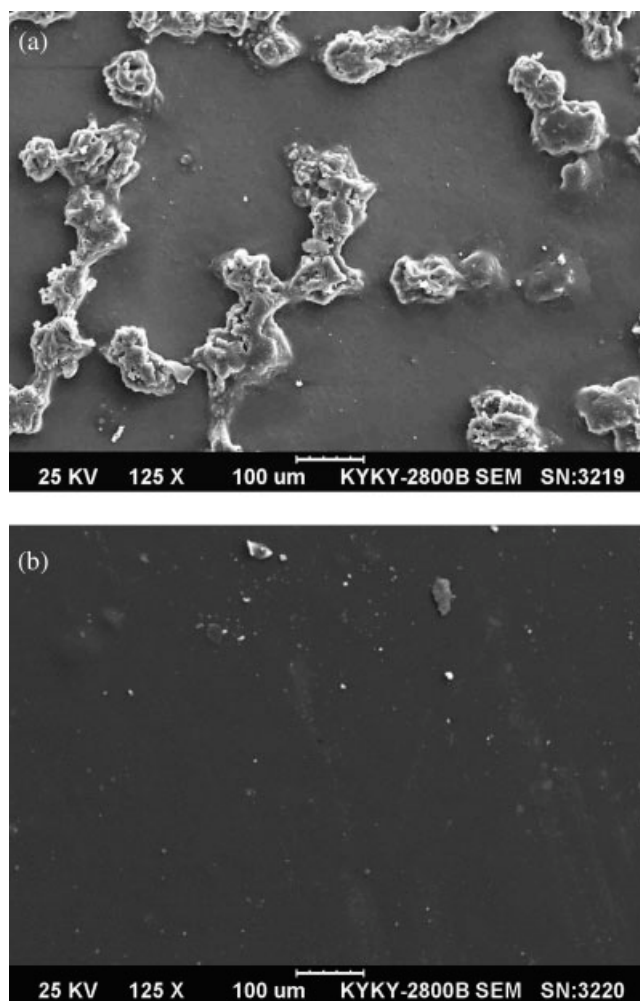


Figure 8 Scanning electron micrographs of (a) PEA/PMA and (b) PEA/PMA-PEA/PMA.

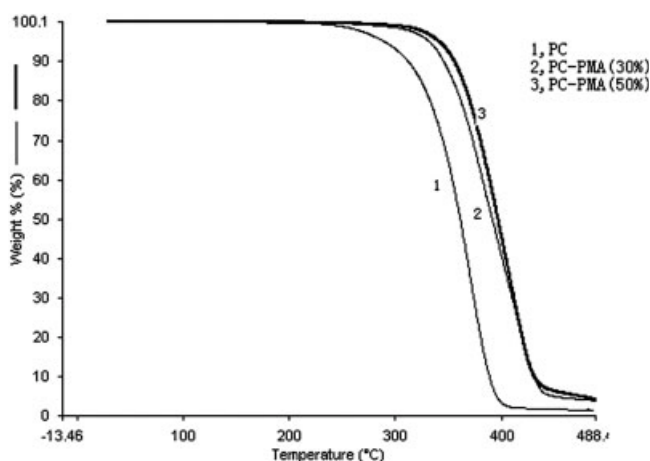


Figure 9 Thermal analysis of (1) PEA; (2) PEA-PMA (30%); (3) PEA-PMA(50%).

CONCLUSIONS

In this study, graft copolymerization with higher TC has been obtained using DPC in medium. The results indicate that the equation of the polymerization rate (R_p) is as follows: $R_p = k[\text{MA}]^{1.62}[\text{Cu(III)/PEA}]^{0.69}$, and that the overall activation energy of graft polymerization is 42.5 kJ/mol. The proof of grafting is obtained by IR analysis. On the basis of

SEM photographs and the thermal analysis, it is found that the graft copolymer greatly improved the compatibility of the blends PMA and PEA, and their thermal property improved largely.

References

1. Stock, U. A.; Vacanti, J. P. *Annu Rev Med* 2001, 52, 443.
2. Chandra, R.; Rustgi, R. *Prog Polym Sci* 2000, 25, 1273.
3. Sudesh, K.; Abe, H.; Doi, Y. *Prog Polym Sci* 2000, 25, 1503.
4. Okama, M. *Prog Polym Sci* 2002, 27, 87.
5. Rokicki, G. *Prog Polym Sci* 2000, 25, 259.
6. Gross, R. A.; Kalra, B.; Kumar, A. *Appl Microbiol Biotechnol* 2001, 55, 655.
7. Fu, Z.; Shen, D.; Yang, W. *Polymer* 2002, 42, 186.
8. Liu, Y. H.; Song, X. R.; Shi, H. M.; Xu, L. L. *Chem J Chin Univ* 1990, 11, 328.
9. Liu, Y. H.; Liu, W. H.; Yu, T. L.; Fan, Z. h. T.; Wang, F. L. *J Mol Sci* 1997, 13, 41.
10. Liu, Y. H.; Zhang, J. S.; Li, W. P. *J Hebei Univ* 2001, 21, 57.
11. Liu, Y. H.; Liu, W. H.; Zhao, M.; Meng, J. G. *Chem J Chin Univ* 1992, 13, 1151.
12. Shang, Y. J.; Liu, Y. H.; Deng, K. Li, W. P. *J Hebei Univ* 1999, 19, 356.
13. Liu, Y. H.; Shang, Y. J.; Li, W. P.; Wang, Z.; Deng, K. L. *Acta Polym Sin* 2000, 2, 235.
14. Cakmak, I. *Die Angew Makromol Chem* 1993, 211, 53.
15. Cakmak, I. *Macromol Rep A* 1994 31(Suppl. 1, 2, 9), 85.
16. Cakmak, I. *Die Angew Makromol Chem* 1995, 224, 1.
17. Cakmak, I. *Eur Polym J* 1995, 31, 1015.
18. Cakmak, I. *Macromol Rep A* 1995, 32 (Suppl. 1, 2), 197.
19. Cakmak, I. *Die Angew Makromol Chem* 1995, 224, 49.