Study On Kinetics Of Graft Copolymerization Of Poly (Hexanedioic Acid Ethylene Glycol) And Methyl Acrylate Initiated By Potassium Diperiodatonickelate(IV)

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ABSTRACT

A redox system-potassium diperiodatocuprate(III)[DNC]/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 (Rp) is as follows: $Rp=k[MA]^{1.70}[Ni(IV)]^{0.66}$ and that the overall activation energy of graft polymerization is 40.9kJ/mol. The total conversion at different conditions (concentration of reactants, temperature, concentration of the DNC, reaction time) was investigated too. 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.
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INTRODUCTION

In the last two decades, along with the application of the biodegradable polymer materials in the diagnosing disease, therapy and repairing or replacing material field etc, the people paid more attention to them. Now the biodegradable polymer materials mainly include collagen, gelatin, collagen hydroly-sate, chitin, chitosan, poly (ortho esters), polycarbonates, and polyphosphoester etc[1-4]. And the biodegradable polycarbonates are one of important branch. 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

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classes: aliphatic polycarbonates and aromatic polycarbonates in view of their main chain structure. The aromatic polycarbonates mainly used as artificial kidney, artificial skull, but the aliphatic polycarbonates could not cause people's interest in a long time due to their low melting temperature, low glass transition temperature and bad 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 enzymatic polymerization[6], ATRP condensation polymerization[7] and so on. But the enzymatic polymerization and the ATRP condensation polymerization reaction condition is rigor and their expense is high. Those shortcomings limited their application in the chemistry industry. In the last years chemistry scientists pay 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 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 diperiodato cuprate(III)[8-10]diperiodatoargentate(III)[11-12] and diperiodatonickelate(IV)[13-14]. It has been demonstrated that [Ni(IV) is an efficient initiator. This paper investigated the graft copolymerization of MA with PEA using DNC in an alkaline solution. The results indicate that the equation of the polymerization rate (Rp) is as follows: $Rp = k [MA]^{1.70}[[Ni(IV)]^{0.66}$ and that the overall activation energy of graft polymerization is 40.9kJ/mol and the effects of variables on the

grafting were studied in detail too. The graft copolymers were also characterized.

EXPERIMENTAL

Materials

The solution of DNC was prepared according to reference[15]. The concentration of DNC was measured by its absorption at $\lambda=414$ nm using a shimadzu UV-265 spectrophotometer (Japan). MA, analytical reagent, was purchased from Huadong reagent factory (Tianjin), which was distilled before used. PEA (purchased from Jufeng reagent factory, Shanxi) was used as received. Other reagents were all of analytical reagent and used as received.

Experimental procedure

Required amounts of PEA solution(dissolved in 1,4-dioxane), MA and water were put into the glass tube, flushed with pure nitrogen and then the reaction system was maintained at $35\pm0.1°C$ in a thermostatic reservoir. Appropriate amounts of DNC were then added under nitrogen, hold at $35\pm0.1°C$ for a period of time, 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 subtracted from the constant weight and got the weight of PMA.

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

TC /% = (weight of PMA/weight of MA charged)×100%
Rp = weight of PMA/time

Measurements

FT

I.R. spectroscopy The FT I.R. 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 dissolved in the acetone, stirred, dried then got the blend PEA/PMA. The PEA, PMA -PEA and PMA dissolved in the acetone, stirred, dried then got the blend PEA/PMA-PEA/

PMA. Scanning electron microscope, AMKAY-1000B was used to observe the morphologies of PEA /PMA and the PEA / PMA -PEA /PMA.
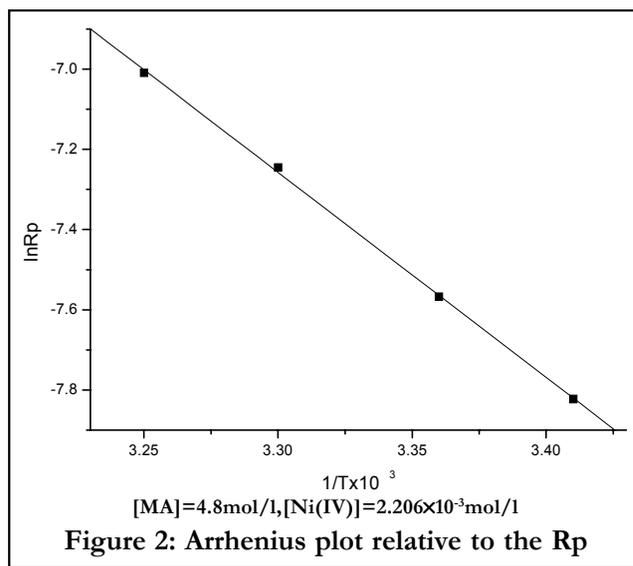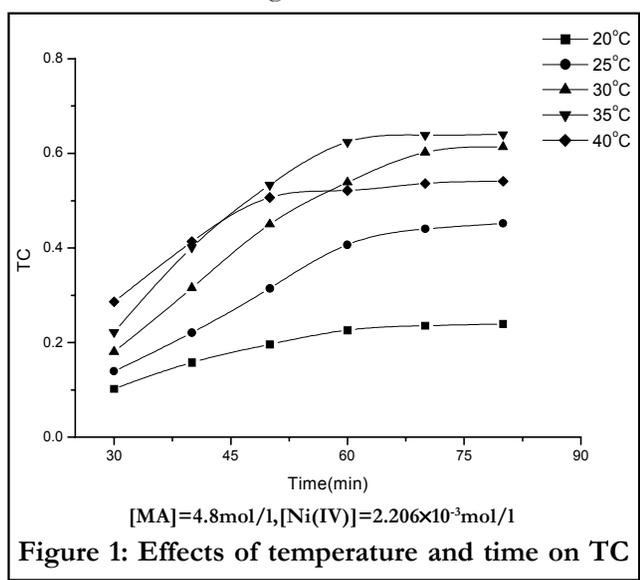
Thermal analysis

TGA curve of the graft copolymer was carried out on a Shimadzu apparatus (DGC-40 DTA-TG) at a heating rate of 10ºC /min in a static air atmosphere.

RESULTS AND DISCUSSION

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, 40°C. Figure 1 gives the curves of TC vs. time .It is seen that for a given temperature, the TC increase steadily with the increasing reaction time to a certain value, and then levels off. The initial increase of the TC indicates clearly that both DNC 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 (Rp) is seen as temperature increasing. The acceleration in Rp upon increasing temperature is consistent with the general principle of conventional radical polymerization. And at the 35°C the reaction time reach 60min (exclude the 40°C), the tendency of the TC comes forth a peak value. The decreasing of TC at 40°C in the latter

[MA]=4.8mol/l,[Ni(IV)]=2.206×10⁻³mol/l

Figure 2: Arrhenius plot relative to the Rp

stage may be ascribed to a faster termination rate of the growing chain through oxidation by DNC, which, in reverse, accelerate the consumption of the DNC. From the Arrrhenius plot (Figure 2), the activation energy of MA graft with PEA is got as 40.9 kJ/mol.

Effect of MA concentration and time on TC

When kept all the other variables unchanged, the curves of TC vs. time at [MA]=2.0, 2.9, 3.9, 4.8, 5.6, 6.3mol/l is figure 3. The explanation of the TC vs. time at a given MA concentration is similar with the figure 1. To the change trend of [MA] vs. time can be explained as follow: It can be seen that TC increase with increasing concentration of MA at first and then decline. 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 small. With increasing concentration of MA, the graft polymers could bring into self-emulsification so as to absorb more monomers on 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 approach of both Ni(IV) and PEA, therefore TC declined.

Effect of DNC concentration and time on TC

Figure 4 shows the curves of TC vs. time at [DNC] =0.71×10⁻³, 1.153×10⁻³, 1.504×10⁻³, 1.855×10⁻³, 2.206×10⁻³, 2.557×10⁻³, 2.908×10⁻³mol/l. To the curves of TC vs. time we can explain as figure 1. And to the change trend of TC vs. DNC concentration, it

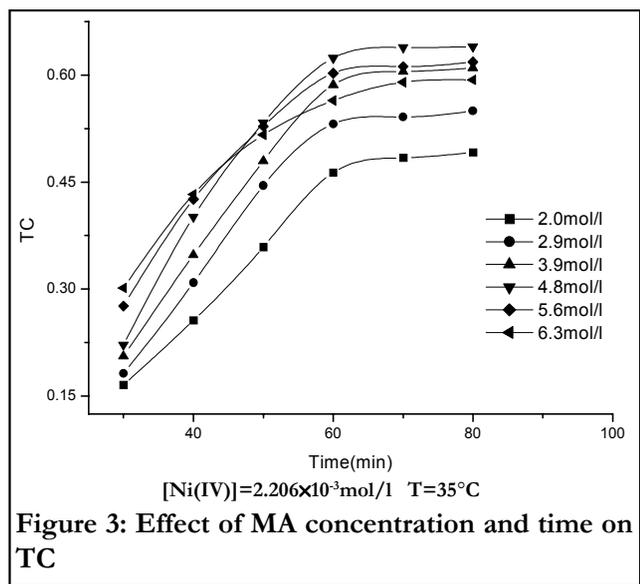[MA]=4.8mol/l,[Ni(IV)]=2.206×10⁻³mol/l

Figure 1: Effects of temperature and time on TC

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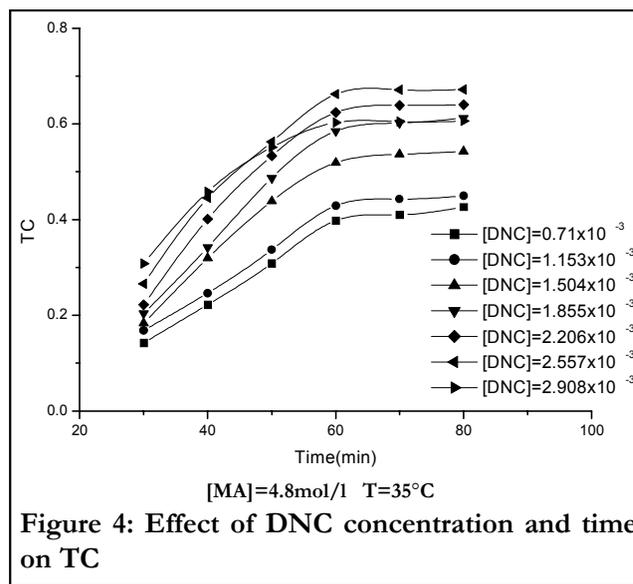**Figure 3: Effect of MA concentration and time on TC**

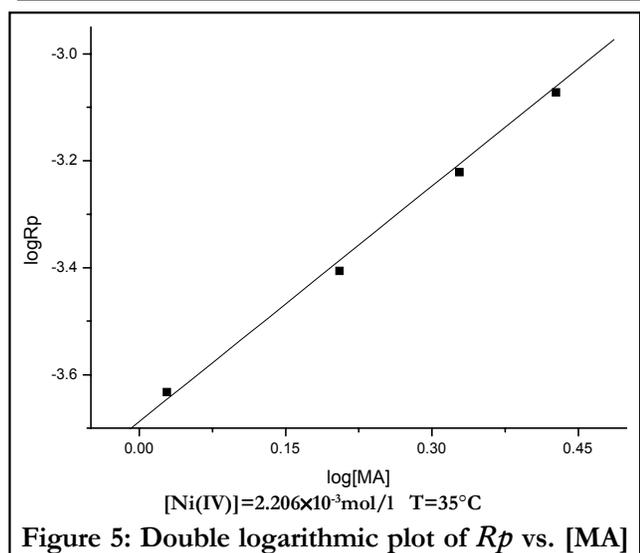**Figure 4: Effect of DNC concentration and time on TC**

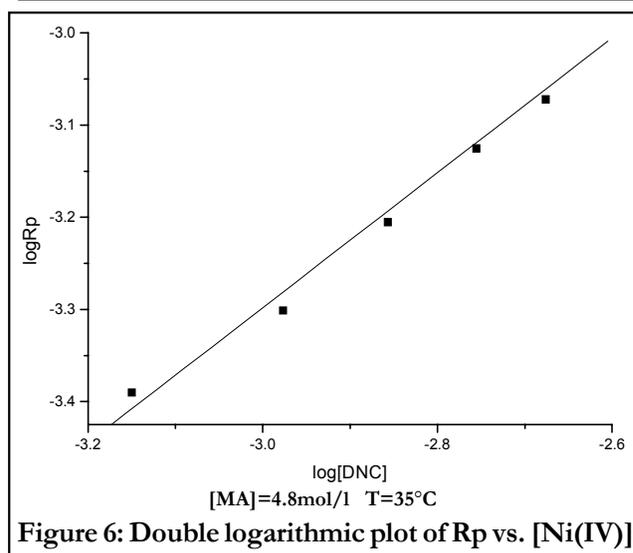**Figure 5: Double logarithmic plot of *Rp* vs. [MA]**

Figure 6: Double logarithmic plot of Rp vs. [Ni(IV)]

can be seen that TC increase significantly first. And get a maximum, then decrease. 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 DNC. However, abundance of primary radicals may accelerate the rate of termination by coupling. At the same time, an excess of DNC may also increase the chance of encounter between DNC 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 Rp vs [MA] is shown in figure 5. The slope indicates that

Rp is proportional to the 1.70 power of [MA]. At the same time the double logarithmic of Rp vs. [DNC] is shown in figure 6. The slope also indicates that Rp is proportional to the 0.66 power of [DNC].

The equation of the polymerization rate is as follows:

$$Rp = k \, [MA]^{1.70}[[Ni(IV)]^{0.66}$$

This equation includes two contents. On the one hand, MA is employed, not only as the monomer taking part in the reaction of chain propagation, but the reductant participating in the reaction of initiation. On the other hand, the termination of the growing polymer chains would have both monoradiacal and biradiacal termination mechanism.
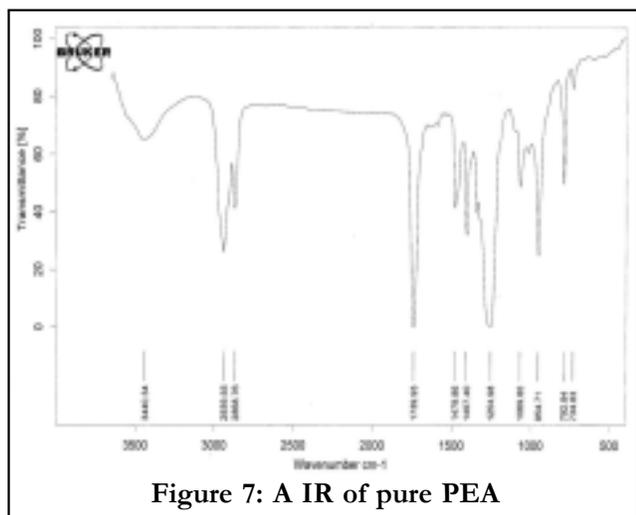
Proof of grafting
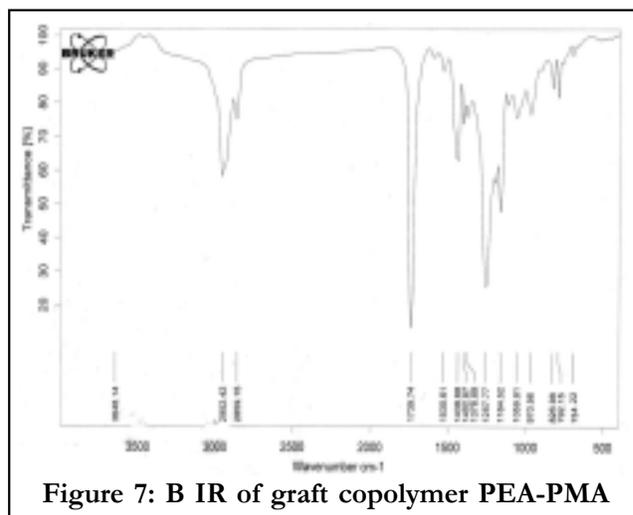
Figure 7: A IR of pure PEA

Figure 7: B IR of graft copolymer PEA-PMA

IR Spectroscopy

Figure 7 A is the IR spectra of pure PEA, B is the graft copolymer PMA-PEA. In the figure 7 A, the absorption peaks at 1739.93 cm^{-1} comes from C-O$_{str}$. Absorption at 792.84 cm^{-1} is CH$_2$'s rocking vibration of O(CH$_2$)$_2$O and the 734.83 cm^{-1} is CH$_2$'s rocking vibration of OC(CH$_2$)$_4$CO. The sharp peak at 3440.34 cm^{-1} corresponds to -OH. In the figure 7 B, at 792.15 cm^{-1} is the CH$_2$'s rocking vibration of O(CH$_2$)$_2$O,734.22 cm^{-1} is the CH$_2$'s rocking vibration of OC(CH$_2$)$_4$CO and the 3648.14 cm^{-1} corresponds to -OH. Those are the PEA own peaks. Pay attention to the peak of 826.98 cm^{-1}, it is rocking vibration of CH$_3$ of PMA. According to those evidences, we can draw a conclusion that the copolymer is PMA -PEA.

SEM

Morphological characters of blend of PMA/PEA and PMA/graft polymer/PEA are shown in figure 8. It can be seen that there are some convex forms in the figure 8A (PMA/PEA). The smooth surface is the PMA and the convex forms are the PEA. Because two kinds of materials can not be compatible after blend and have different flow capability. When the acetone vaporizes form the blend polymer, the PEA forms the convex shape. On the contrary, the convex forms have disappeared in the figure8 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
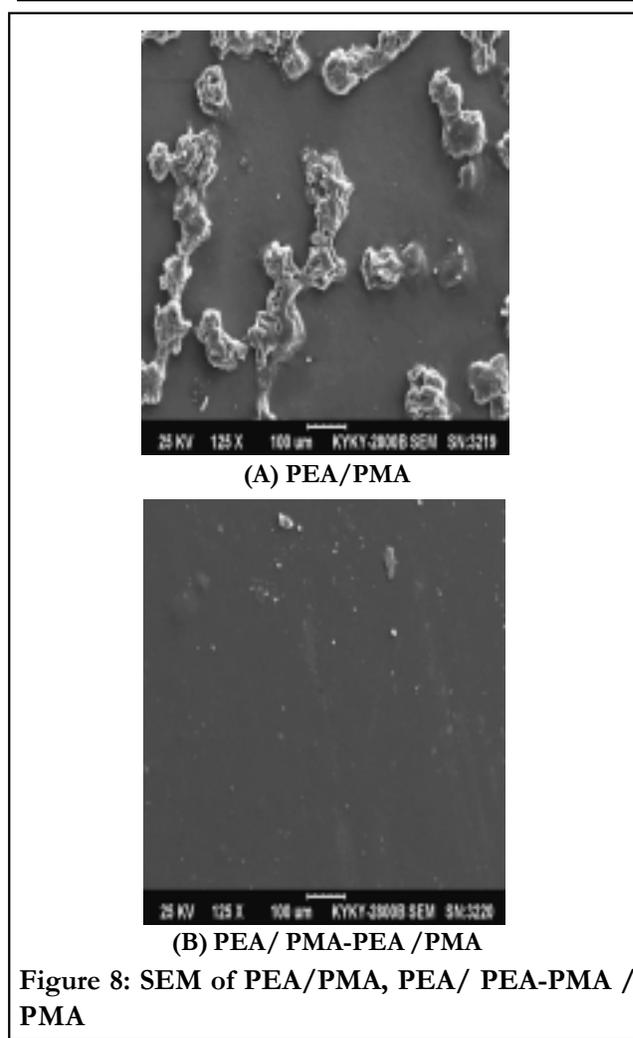

(A) PEA/PMA

(B) PEA/ PMA-PEA /PMA

Figure 8: SEM of PEA/PMA, PEA/ PEA-PMA / PMA

PEA were examined by a study of their TGA thermo grams. As shown in figure 9, curve 1 is the pure PEA, curve2 is PEA-PMA (grafting percentage=30%) and the curve3 is PEA-PMA (grafting percentage=50%). Thermal decomposition of the PEA takes place in
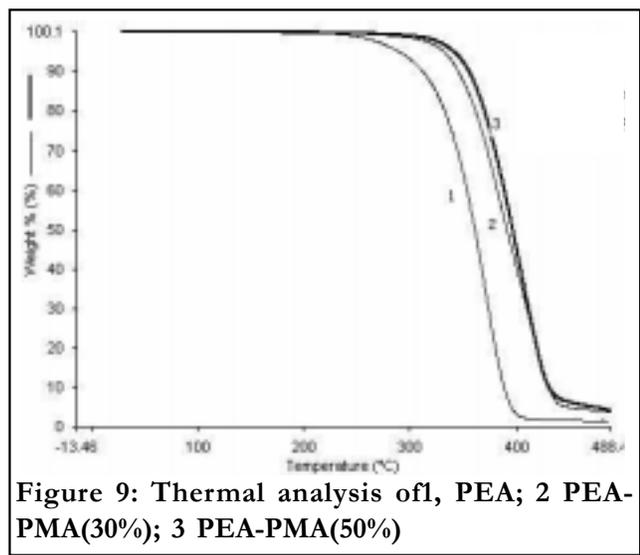
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Figure 9: Thermal analysis of 1, PEA; 2 PEA-PMA(30%); 3 PEA-PMA(50%)

two main steps. The first stage (240°C-300°C) is due to the break of the low molecular weight segment. The second step between 300°C and 400°C may be corresponding to the break of the PEA. The curve2's first stage (360°C-400°C) is due to the break of the PEA, and the second step(400°C-440°C) is corresponding to the break of the PMA. The curve3's first step is between 364°C and 402°C, the second is between 402°C and 440°C. From the figure 8, we find obviously that thermal property improves largely.

CONCLUSION

In this study, graft copolymerization with higher TC has been obtained using DNC in medium. The results indicate that the equation of the polymerization rate (Rp) is as follows: $Rp = k [MA]^{1.70}[[Ni(IV)]^{0.66}$ and the overall activation energy of graft polymerization is 40.9kJ/mol. The proof of grafting is obtained by IR analysis. Based on the 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 improves largely.

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