

Graft Copolymerization of Methyl Acrylate onto Nylon1010 Initiated by Potassium Diperiodatonickelate(IV)

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ABSTRACT: In this article, the graft copolymerization of methyl acrylate (MA) onto nylon1010 by using potassium diperiodatonickelate(IV) [Ni(IV)]–nylon1010 redox system as initiator was studied in alkaline medium. The effect of different factors on grafting parameters was investigated. The structure of the graft copolymer was determined by infrared (IR), X-ray diffraction, and scanning electron microscope (SEM). It was found that Ni(IV)–nylon1010 system is an efficient redox initiator for this graft copolymerization. A single-electron transfer mechanism is proposed to explain the formation of radicals and the initiation. The graft copolymer was used as the compatibilizer in blends of poly(methyl methacrylate) (PMMA) and nylon1010. The SEM photographs indicate that the graft copolymer greatly improved the compatibility of the blend. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2636–2640, 2001

Key words: potassium diperiodatonickelate(IV); nylon1010; PMMA; methyl acrylate; graft copolymerization; compatibility

INTRODUCTION

Nylon1010 is one of the normally used engineering plastics. It has good general properties, but due to its bad endurance to water, the strength and stability of its size decrease after absorbing water. With the continuous developing of nylon1010, the graft and modification of nylon1010 has attracted more attention. Nylon1010 is difficult to be grafted because of the weak reducibility

of its characteristic group $\begin{array}{c} \text{O} \\ \parallel \\ (\text{—C—NH—}) \end{array}$. There

are a few reports on graft copolymerization of acrylate onto nylon and most of them were completed by traditional chain transfer method, which leads to lower grafting efficiency. Many

studies were reported on the blend of nylon and PP¹, nylon, and PE,² and nylon and PS.³ The compatibility of nylon1010 and PMMA is bad and the graft copolymer used as compatibilizer of blends of nylon1010 and PMMA was not reported. In recent years, we have obtained some achievements on vinyl monomer polymerization and graft copolymerization initiated by supernormal valence transition–metal, such as Ag(III)⁴ and Cu(III).⁵ However, there are no reports on graft copolymerization of vinyl monomer onto nylon1010 using the Ni(IV) redox system as initiator. Most experts think that the mechanism of oxidation of Ni(IV) is a two-electron-transfer process without radicals, and Ni(IV) cannot initiate polymerization of vinyl monomer.^{6,7,8} However; under our experimental conditions, the results show that polymerization of monomers such as acrylamide⁹ and acrylonitrile¹⁰ can be initiated by the Ni(IV) redox system. A two-step single-electron transfer mechanism is proposed to explain the produce of radicals and the initiation. In

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this article, graft copolymerization of MA onto nylon1010 was carried out, Ni(IV) as oxidant, and nylon1010 itself as reductant. Then the graft copolymer was used as the compatibilizer to improve the compatibility of nylon1010 and PMMA. The effects of temperature, monomer concentration, and initiator concentration on grafting parameters such as conversion of monomers ($C\%$), efficiency of grafting ($E\%$), percentage of grafting ($P\%$) used to characterize the nature of the copolymer were studied. The structure of graft polymer was determined by SEM, X-ray diffraction, and IR. The morphology blend of PMMA and nylon1010 was investigated by SEM.

EXPERIMENTAL

Materials

Methacrylate (MA) was washed successively with sodium hydroxide aqueous and distilled water to remove inhibitor, dried over anhydrous sodium sulfate, and then finally distilled under vacuum. Nylon1010 supplied by the Boye Chemical Co. (Boye, China) was dried under vacuum at 60°C for 10 h before being used. Ni(IV) was synthesized and measured according to the reported procedure.¹¹ The other solvents (analytical grade) were used without any further purification. All the other materials used in this experiment were supplied by the Beijing Chemical Reagent Co. (Beijing, China).

Graft Copolymerization and Treatment of Copolymer

Graft copolymerization was carried out in a 50-mL four-necked flask equipped with thermometer, condenser, stirrer, and gas inlet. In a typical reaction, 0.5 g nylon1010 was added with constant stirring under nitrogen. The required amount of monomer was added, followed by Ni(IV) aqueous solution, and the total volume 20 mL with distilled water. The graft copolymerization was performed on the conditions of different temperature, monomer concentration, and initiator concentration. After completion of the reaction, the reactant was cooled and poured in aqueous hydrochloric acid solution, filtered through weighted sintered glass funnel, washed to neutral, and then dried to a constant weight under vacuum. The homopolymer of methyl acrylate (PMA) was removed from the crude graft copolymer by exhaustive Soxhlet extraction with ace-

tone for 48 h. The final copolymer was then dried to a constant weight under vacuum. The grafting parameters were defined and calculated as follows:

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

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

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

Preparations of Nylon1010/Nylon1010-g-PMA/PMMA and Nylon1010/PMMA Blends

A mixture of PMMA and nylon1010 pellets or a mixture of PMMA, nylon1010, and nylon1010-g-PMMA pellets was premixed and then melted. All materials were dried under vacuum before use. An inert atmosphere was used to reduce polymer degradation.

Measurements

Nylon1010-g-PMA was characterized after exhaustive Soxhlet extraction to remove PMA by IR analysis by using an FTS-40 spectrophotometer in a 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 nylon1010, graft copolymer, and the blends.

RESULTS AND DISCUSSION

Effect of Different Factors on Grafting Parameters

The graft copolymerization of MA onto nylon1010 was investigated at various monomer concentrations [MA], when the total volume, the weight of nylon1010, concentrations of initiator [Ni(IV)], and reaction temperature was kept unchanged. The results are shown in Figure 1. It is seen that an increase in the monomer concentration increased the grafting parameters of $C\%$, $P\%$, and $E\%$, and then they all leveled off. This may be due to the fact that as the total volume was fixed, [Ni(IV)] increases relatively in aqueous phase with the amount of MA increased. Ni(IV) not only reacts with reductant to produce radicals initiating poly-

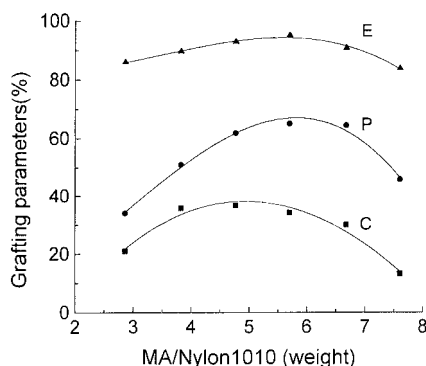


Figure 1 Effect of [MA] on grafting parameters: $[\text{Ni(IV)}] = 6.33 \times 10^{-4} \text{ mol/L}$, 35°C , 1.5 h.

merization of vinyl monomer, but also reacts with radicals terminating polymerization. Though the total weight of PMA increased, related to the MA charged, the relative weight of PMA decreased. The result is the reduction of $C\%$. As a result, $P\%$ decreases. In addition, the more MA added, the more chance of transfer reaction to monomer. The increase of homopolymerization results in the decrease of $P\%$ and $E\%$.

At the fixed concentration of MA, Ni(IV) , and the amount of nylon1010, the relationship between temperature and grafting parameters was investigated and is shown in Figure 2. In accordance with the general rule of radical polymerization, the grafting parameters, $C\%$, increases as the reaction temperature rises. As shown in Figure 2, $P\%$ and $E\%$ are increased and then decreased with the increase in temperature. This may be due to the chance of chain transfer reaction being sped up with the increase of temperature, which results in the increase of homopolymerization of MA and the decrease of $P\%$ and $E\%$. However, at the very high temperature, the mixture becomes viscous and congeals

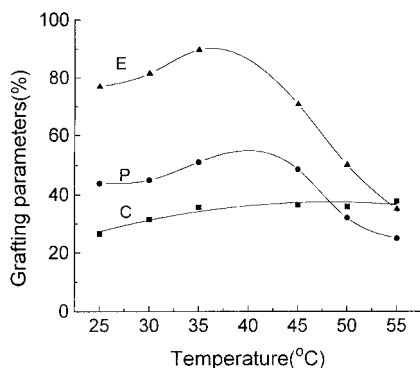


Figure 2 Effect of temperature on grafting parameters: $\text{MA/Nylon1010} = 3.8(\text{weight})$, $[\text{Ni(IV)}] = 6.33 \times 10^{-4} \text{ mol/L}$, 1.5 h.

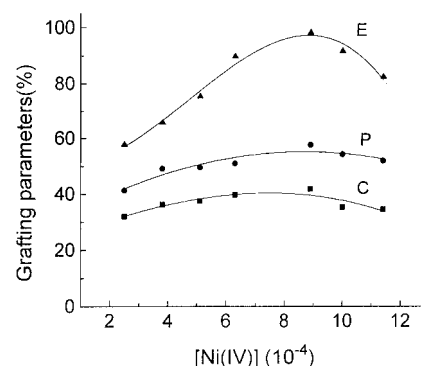


Figure 3 Effect of $[\text{Ni(IV)}]$ on grafting parameters: $\text{MA/Nylon1010} = 3.8$, 35°C , 1.5 h.

quickly and it is difficult for the grafting reaction to be carried out.

The effect of Ni(IV) concentration on grafting parameters when the other reaction conditions were invariable is shown in Figure 3. Grafting parameters, $C\%$, $P\%$, and $E\%$, all show the tendency of increasing first and then decreasing with the increase of Ni(IV) concentration. Ni(IV) reacts with the characteristic group of nylon1010

$$\begin{array}{c} \text{O} \\ \parallel \\ (-\text{C}-\text{NH}-) \end{array}$$
 to form a large number of grafting dots, which initiate the polymerization of MA. As a result, $C\%$ and $P\%$ increased. However, the reaction of Ni(IV) and radicals, living center formed in the polymerization, was accelerated by the further increase of Ni(IV) concentration, at the same time terminated the chain growing reaction. At the same time, the chance of a transfer reaction to monomer is increased, and the homopolymerization of MA was raised with increasing Ni(IV) concentration. These all resulted in the decrease of grafting parameters.

Characterization of Graft Copolymer and the Blends

The X-ray diffraction spectra of pure nylon1010 and nylon1010-g-PMA were measured, as shown in Figure 4. The results of X-ray diffraction illustrate that nylon1010 has a part of crystal ($X = 0.581$) and nylon1010-g-PMA also has a part of crystal ($X = 0.438$). The crystallinity of the graft copolymer obviously decreased.

The IR spectra of pure nylon1010 and nylon1010-g-PMA, which was extracted to remove homopolymer of MA, are shown in Figure 5. Compared with pure nylon1010, the final product has characteristic absorption of nylon1010 at 3300

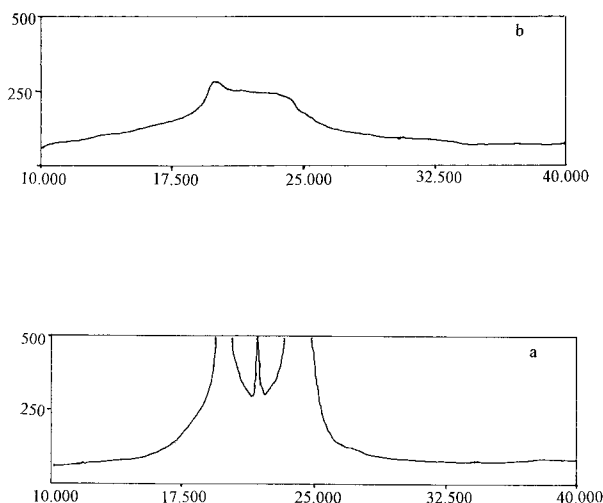


Figure 4 X-ray diffraction of Nylon1010 (a) and graft copolymer (b).

cm^{-1} ($\nu_{\text{N-H}}$) and 1655 cm^{-1} ($\nu_{\text{(C=O)-N}}$) and also has characteristic absorption of PMA at 1730 cm^{-1} ($\nu_{\text{C=O}}$) and 1160 cm^{-1} ($\nu_{\text{(C=O)-C}}$). It is demonstrated that the final product was a graft copolymer of nylon1010 and MA.

Figure 6 shows the SEM micrographs of nylon1010 and nylon1010-*g*-PMMA. Compared with

pure nylon1010, the morphology of graft copolymer obviously changed. The SEM micrographs of nylon1010/PMMA and nylon1010/nylon-*g*-PMA/PMMA blends are shown in Figure 7. It was seen that the uncompatibilized blend of nylon1010/PMMA had a coarse morphology, and the addition of graft copolymer made the interface of two phases indistinctly. The above features suggest that the graft copolymer is efficient to improving the compatibility of nylon1010 and PMMA.

The Initiation Mechanism of Grafting Reaction

The IR spectrum has shown the formation of graft copolymer nylon1010-*g*-PMA, having a characteristic absorption of —CONR— at 1640 cm^{-1} . This illustrates that the grafting reaction proceeds on the nitrogen atom. The initiation mechanism, which belongs to a single electron transfer, may be shown as follows⁹:

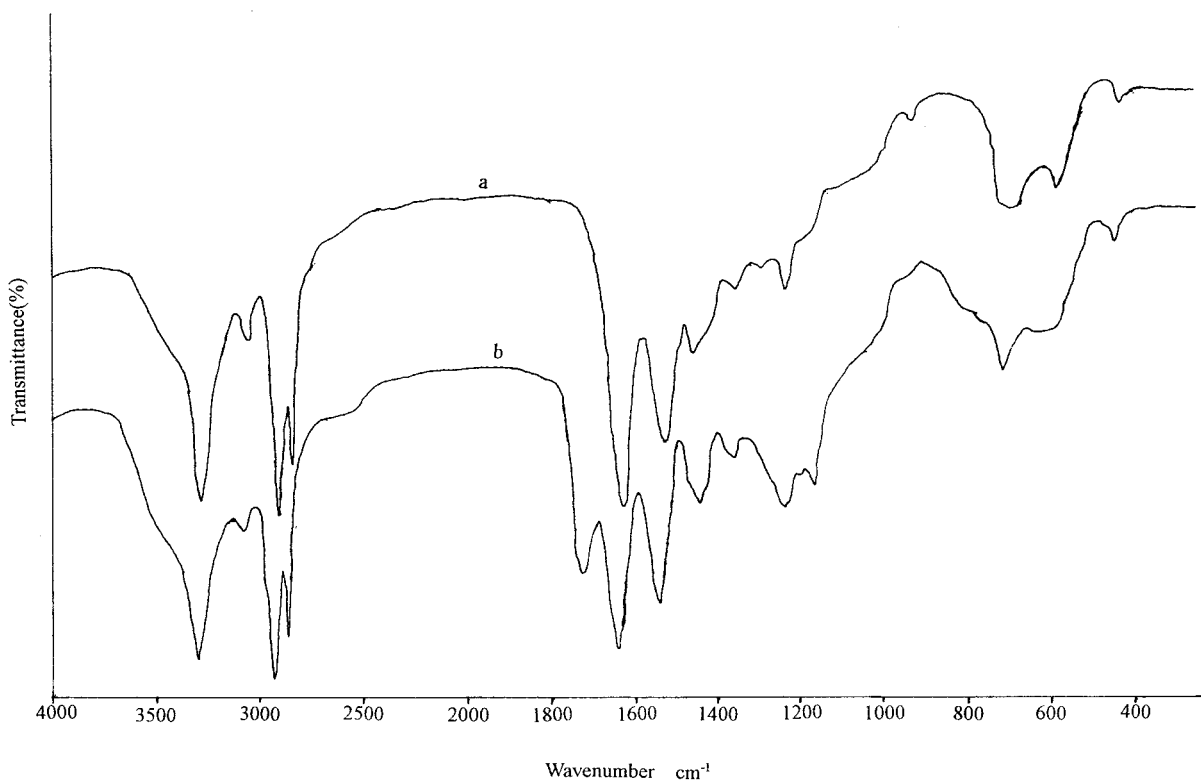
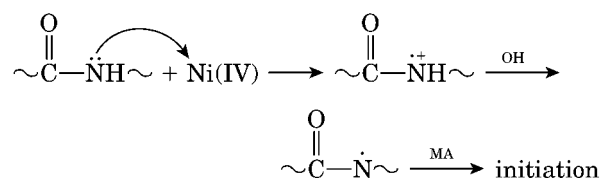


Figure 5 IR spectra of Nylon1010 (a) and graft copolymer (b).

CONCLUSION

Most experts think that the mechanism of oxidation of Ni(IV) is a two-electron-transfer process without radicals, and Ni(IV) cannot initiate polymerization of vinyl monomer. Under our experimental conditions, we studied the homopolymerization of vinyl monomer and graft copolymerization. We obtained a graft copolymer with high efficiency of grafting from a difficult grafted polymer. Ni(IV)-nylon1010 system is an efficient redox initiator for the graft copolymerization. The two-step single-electron transfer mechanism in redox process we have proposed is a modification to traditional mechanism.

Nylon1010-*g*-PMA is a good compatibilizer for the nylon/PMMA blending system. Changes of morphology were obvious. We believe that the graft copolymer is efficient on toughness modification of nylon1010. Further work is being carried out.

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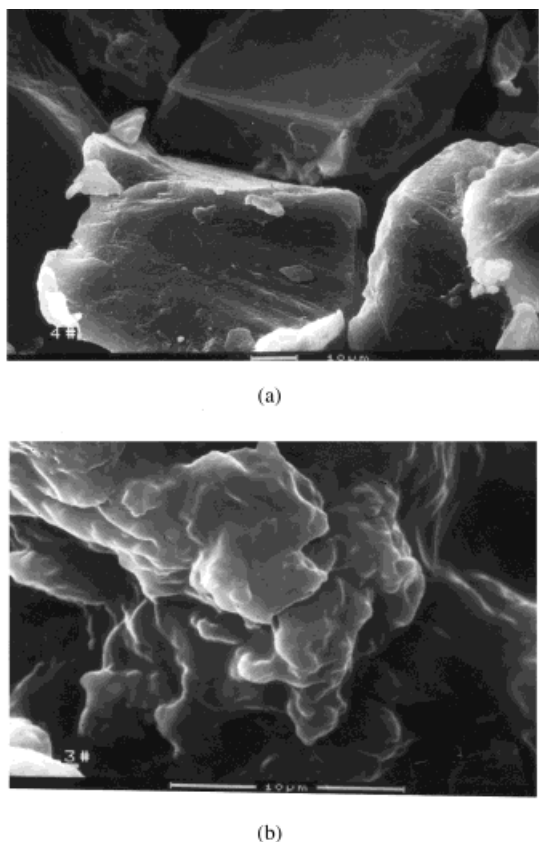


Figure 6 SEM micrographs of nylon1010 (a) and nylon1010-*g*-PMMA (b).

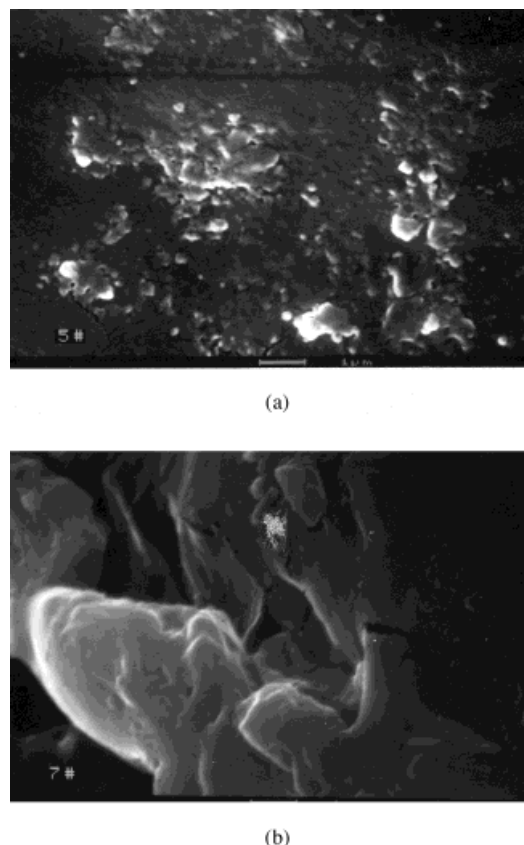


Figure 7 SEM micrographs of nylon1010/PMMA (a) and nylon1010/nylon-*g*-PMA/PMMA blends (b).

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