

Block Copolymerization of Poly(diethylene glycol phthalic anhydride) and Methyl Methacrylate Initiated by Potassium Diperiodatonickelate(IV)

Yinghai Liu,¹ Libin Bai,¹ Weiqi Zhou,¹ Yuanwei Liu,¹ Yanxiang Li,¹ Kuilin Deng²

¹College of Chemistry and Environmental Science, Hebei University, Baoding 071002, China

²Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

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ABSTRACT: Block copolymers of methyl methacrylate (MMA) and poly(diethylene glycol Phthalic Anhydride) (PPAG) was synthesized using a novel redox system—potassium diperiodatonickelate(IV) [DPN]/PPAG system in an alkaline medium. Block copolymers with high percentage of blocking were obtained, which indicated that DPN/PPAG redox system was an efficient initiator for this blocking. Effects of different factors on the blocking parameters were examined. The overall activation energy of this blocking was calculated to be 55.12 kJ/mol. The structure of the block copolymer was determined by infrared, X-ray diffrac-

tion, and scanning electron microscope (SEM). A mechanism is proposed to explain the generation of radicals and the initiation of block copolymerization. The block copolymer was used as the compatibilizer in blends of PMMA and Nylon6. The SEM photographs show that the block copolymer greatly improved the compatibility of the blend. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1312–1317, 2006

Key words: diperiodatonickelate; methyl methacrylate; poly(diethylene glycol phthalic anhydride); redox initiation; block copolymerization

INTRODUCTION

There are many reports on the synthesis of block copolymers in the literature. Hillmyer¹ generalized the methods for the preparation of di- and tri-block copolymers, including ionic polymerization, free radical polymerization, and metal-catalyzed polymerization. In these three kinds of methods, ionic polymerization was mostly used. However, because of the rigor condition and the narrow range of the monomers, the application of ionic polymerization in the chemistry industry is limited. In the last few years, chemistry scientists pay their attention to free radical block copolymerization, because the reaction condition of radical polymerization is mild and the range of monomers is wide.

Now, the most used initiators are Ce(IV)^{2–3} and Mn(III).^{4–6} Although ceric ion is an excellent initiator, its high price and acid medium limited its application. Therefore, to find new supernormal valence transition-metals as oxidant and polymer as reductant to form redox initiating system is very important in the synthesis of block copolymers.

During the recent years, some supernormal valence transition-metals, such as diperiodatocuprate(III),^{7–9}

diperiodatoargentate(III),^{10–11} and diperiodatonickelate(IV) (DPN),^{12–15} were found, which could be used as initiator in radical grafting copolymerization. It has been demonstrated that DPN is the most efficient initiator. We do not find any reports on radical block copolymerization of poly(diethylene glycol phthalic anhydride) (PPAG) with various monomers so far. This study investigated the block copolymerization of methyl methacrylate (MMA) with PPAG, using DPN in an alkaline mix solution. Then, the block copolymer was used as the compatibilizer to improve the compatibility of Nylon6 and PMMA. The effects of variables on the blocking were studied. The block copolymers were also characterized by FTIR, SEM, and X-ray diffraction. The morphology blend of PMMA and Nylon6 was investigated by SEM.

EXPERIMENTAL

Materials

The solution of diperiodatonickelate(IV) (DPN) was synthesized and measured according to the reported method.¹⁶ MMA (analytical reagent) was purchased from Huadong reagent factory (Tianjin, China), and was distilled before use. PPAG (PPAG-10000 molecular weight), purchased from Jufeng reagent factory (Shanxi, China) was used as received. The other reagents were all of analytical reagent and were used as received.

Correspondence to: Y. Liu (zhonggou556@163.com).

Block copolymerization

Required amounts of PPAG-10000 (molecular weight) solution, MMA, and water were placed in the reaction tube, flushed with pure nitrogen, and the reaction system was maintained at $(40 \pm 0.1)^\circ\text{C}$ in a thermostatic reservoir. Appropriate amounts of DPN were then added under nitrogen. The reaction was held at $(40 \pm 0.1)^\circ\text{C}$ for a period of time, then stopped by adding hydrochloric acid. The block copolymer was precipitated in water, filtered through a weighted sintered glass crucible, washed well with water, and then dried under vacuum to constant weight.

The blocking parameters, such as total conversion (TC) and percent of blocking (PB) were defined and calculated as follows:

$$\text{TC}\% = (\text{weight of PMMA}/\text{weight of MMA charged}) \times 100\%$$

$$\text{PB}\% = (\text{weight of PMMA}/\text{weight of PPAG}) \times 100\%$$

Preparations of Nylon6-block copolymer-PMMA and Nylon6-PMMA

A mixture of PMMA and Nylon6 pellets or a mixture of PMMA, nylon6 pellets, and block copolymer was dissolved in formic acid. All materials were dried under room temperature before use.

Measurements

FTIR spectroscopy

The FTIR spectra of PPAG and block copolymer were recorded on an FTS-40 spectrometer (BIO RAD Co., Cambridge, Massachusetts), using potassium bromide pellets technique.

Thermal analysis

TGA curve of the block 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.

Scanning electron microscope

AMKAY-3000B was used to observe the morphologies of PMMA, PPAG-*b*-PMMA, Nylon6, PMMA-NY-LON6, and PMMA-block copolymer-Nylon6.

X-ray diffraction

X-ray diffractions of PMMA and PPAG-*b*-PMMA were measured using a Ya 900 X-ray diffractometer.

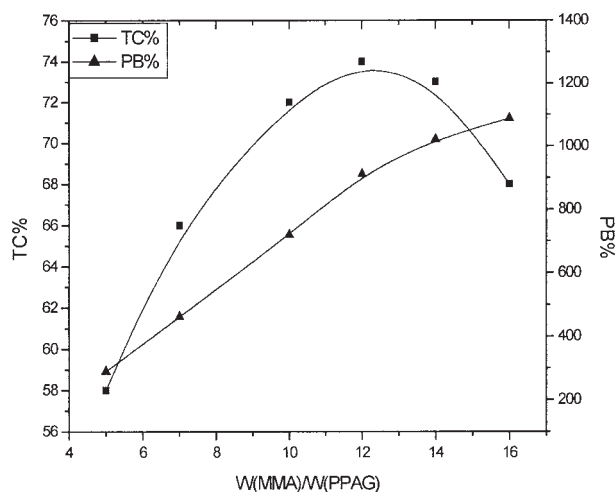


Figure 1 Effect of weight ratio of MMA/PPAG on the blocking parameters. [DPN] = 3.52×10^{-5} mol/L, Time = 80 min, $T = 40^\circ\text{C}$.

The X-ray diagrams were made with Ni-filtered Cu $K\alpha$ radiation at 30 kV and 20 mA.

RESULTS AND DISCUSSION

Effect of weight ratio of MMA/PEG on the blocking parameters

By keeping all the other variables unchanged, the effect of weight ratio of MMA and PPAG [W(MMA)/W(PPAG)] on the block parameters has been investigated. The results are shown in Figure 1. It can be seen that TC increased with an increasing ratio of W(MMA)/W(PPAG) at first and then declined. However, PB increased all along in the range studied. The declined trend of TC at too higher monomer amount may be explained as follows: although the MMA polymerized with PPAG increased (as evidenced by the increased PB at all times), it became less when compared with the fast increment of the added monomer, that is, TC declined.

Effect of the reaction time on the blocking parameters

When the other reaction conditions were invariable, the effect of reaction time on TC and PB was investigated and shown in Figure 2. The initial increase in the TC and PB clearly indicated that both DPN and macro radicals could keep its activity for a period of time. The following trend of leveling off can be attributed to the decrease in monomer concentration and initiator concentration.

Effect of DPN concentration on the blocking parameters

Figure 3 shows the effect of initiator concentration on TC and PB. It can be seen that TC and PB increased

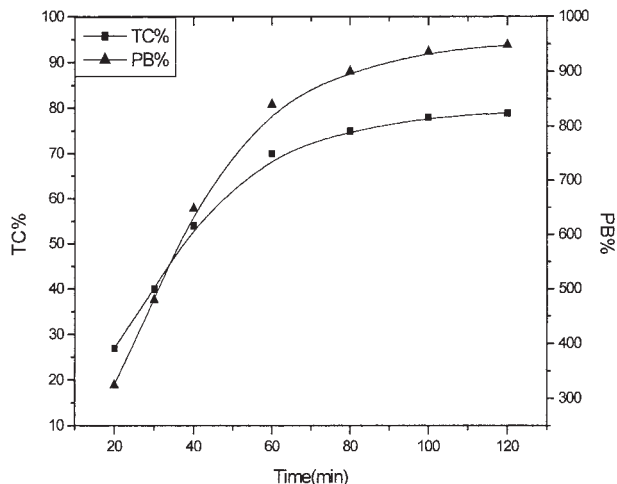


Figure 2 Effect of the reaction time on the blocking parameters. $[DPN] = 3.52 \times 10^{-5}$ mol/L, $W(MMA)/W(PPAG) = 12$, $T = 40^\circ\text{C}$.

significantly first, passed through a maximum, and then decreased. 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 DPN. However, abundance of primary radicals may accelerate the rate of termination by coupling. At the same time, an excess of DPN may also increase the chance of encounter between DPN and propagating chain radicals, which will terminate the reaction too.

Effect of temperature on the blocking parameters

The relationship between the temperature and TC as well as PB was investigated and shown in Figure 4. It

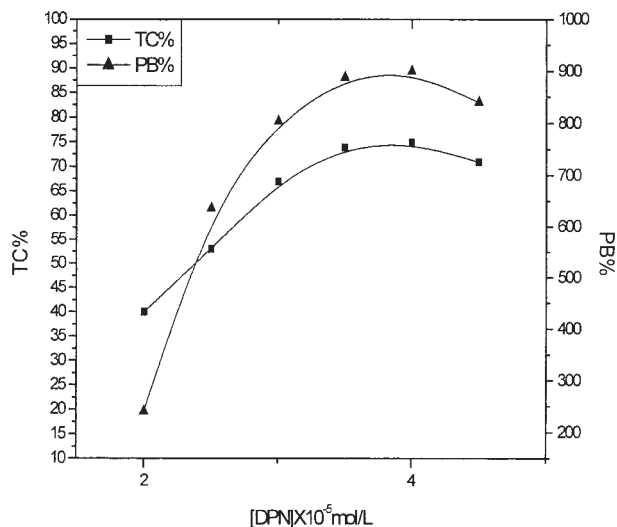


Figure 3 Effect of DPN concentration on the blocking parameters. $W(MMA)/W(PPAG) = 12$, Time = 80 min, $T = 40^\circ\text{C}$.

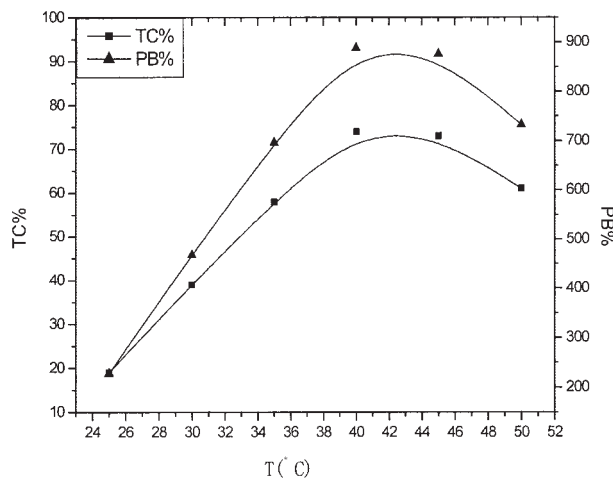


Figure 4 Effect of weight ratio of MA or MMA/PPAG on TC. $[DPN] = 3.52 \times 10^{-5}$ mol/L, $W(MMA)/W(PPAG) = 12$, Time = 80min.

can be seen that the TC and PB showed a similar trend, which increased with the rise of temperature at first and then increased slowly even, declined at too high temperature. The tendency of lower TC and PB at higher temperature may be ascribed to a faster termination rate of the growing chain through oxidation by DPN, which, in reverse, accelerate the consumption of the DPN.

The activation energy

To calculate the activation energy of the reaction, the R and $\ln R$ of each temperature was shown in the Table I. Based on the Arrhenius, the overall activation energy was got as 55.12 kJ/mol.

Proof of blocking

Figure 5 shows the absorption peaks at 2950 and 1440 cm^{-1} come from C-H_{atr} and C-H_{def} of $-\text{CH}_2-$. Absorption at 1120 and 1600 cm^{-1} come from C-O_{str} and of PPAG. The sharp peak at 1750 cm^{-1} , corresponding to C=O , is a clear indication of the presence of PMMA segment in the block copolymer.

A plausible initiation mechanism¹⁷⁻¹⁸ was proposed as follows:

TABLE I
The Activation Energy

Temperature (K)	$\ln R_p$	$1/T$	E_a
298	-13.16	0.00336	55.12
303	-12.64	0.0033	
308	-12.35	0.00325	
313	-11.94	0.00319	

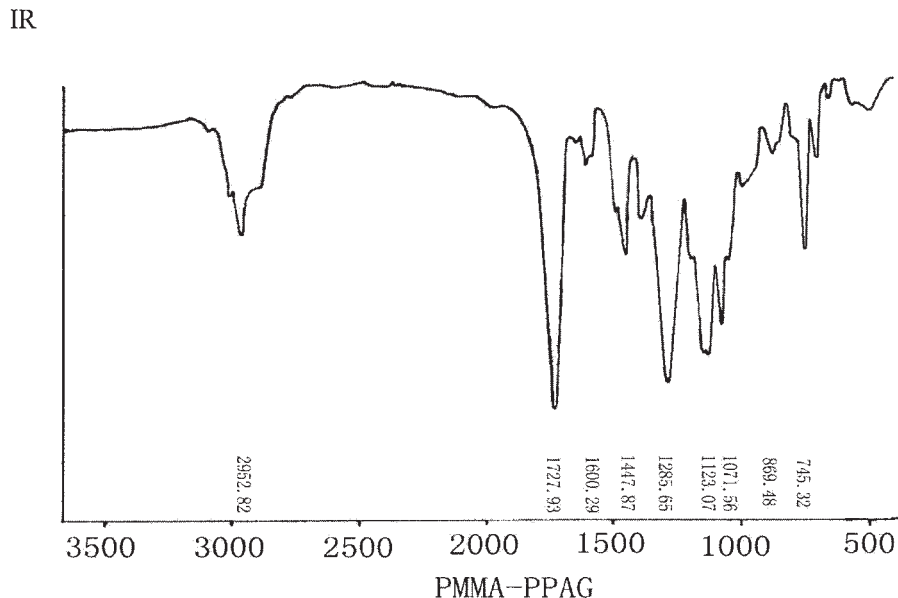
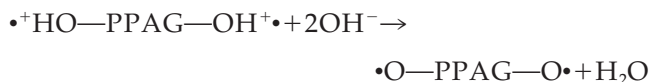
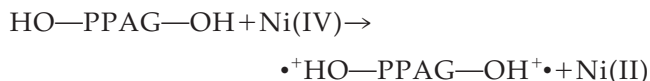


Figure 5 IR spectrum of PMMA-PPAG-PMMA block copolymer.



X-ray diffraction

To define the crystallinity of MMA and PPAG-*b*-PMMA, X-ray diffraction patterns were analyzed, as shown in Figure 6. The X-ray diffraction pattern of PMMA exhibits a much stronger peak than the PPAG-*b*-PMMA between 11.409° and 22.377°. Much bigger steric hindrance that results from the diethylene glycol part located on the consecutive position of benzene

make the molecular chain twist, so that the molecular chain's tacticity and crystallinity declined.

Morphological studies (scanning electron microscope)

The morphological characters of PMMA, Nylon6, PMMA-*b*-PPAG, PMMA-Nylon6, and PMMA-block copolymer-Nylon6 were studied by scanning electron microscope. As shown in Figure 7, it can be seen that the surface of the PMMA (A) is smooth, the surface of the Nylon6 (B) is crystal, and the surface of the block copolymer (C) is full of small holes, which is ascribed to the different strength of the molecular chain. Because of the effect of surface tension, the weaker molecular chain broke and came into being holes. There are some interstices and obvious two phases in the PMMA-Nylon6 (D). On the contrary, the interstices

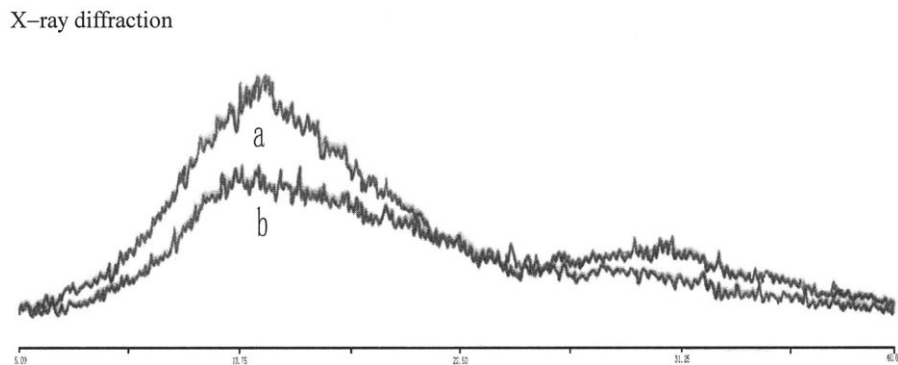
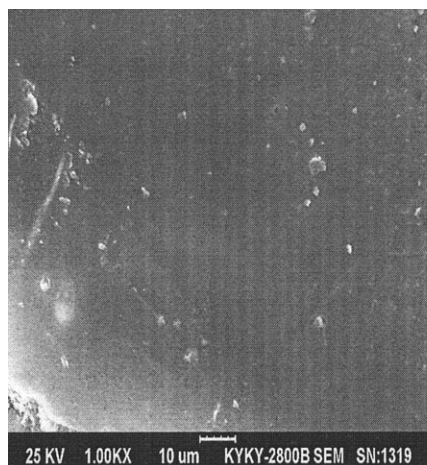
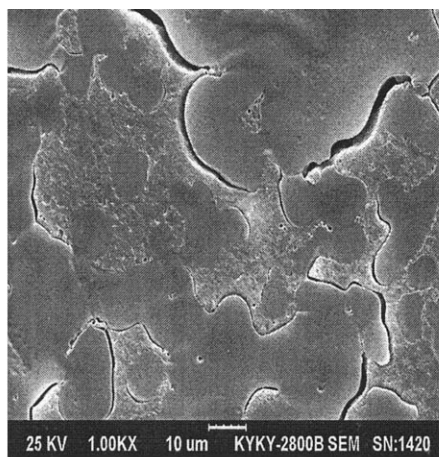


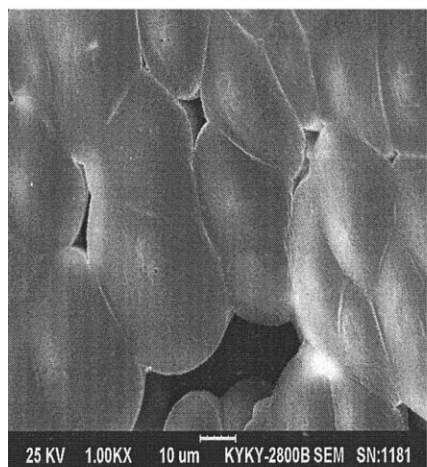
Figure 6 X-ray diffraction of PMMA (a) and PMMA-PPAG-PMMA (b).



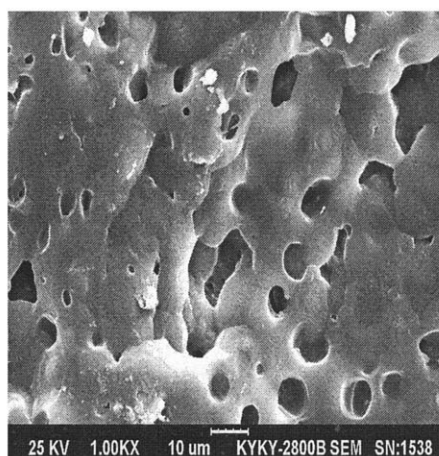
A PMMA



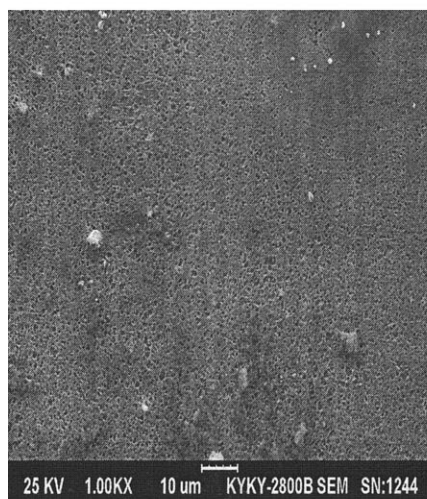
D PMMA—Nylon6



B Nylon6



E PMMA—Block copolymer—Nylon6



C PMMA—PPAG

Figure 7 SEM of PMMA (A), Nylon6 (B), PMMA-PPAG-PMMA (C), PMMA-Nylon6 (D), and PMMA-*b*-Nylon6 (E).

and two phases have disappeared in the PMMA-block copolymer-Nylon6 (E). The aforementioned features suggest that the block copolymer is efficient in improving the compatibility of Nylon6 and PMMA.

CONCLUSIONS

In this study, block copolymerization with higher TC and PB has been obtained using DPN in an alkaline medium. Moreover, the block copolymerization can be carried out at a mild temperature due to the lower activation energy (55.12 kJ/mol) of this blocking and in an alkali mix medium. The proof of blocking was obtained from ^1H NMR and IR analysis.

PPAG-*b*-PMMA is a good compatibilizer for the Nylon/PMMA blending system. Changes of morphology were obvious. We believe that the block copolymer is efficient on toughness modification of Nylon6. Further work is being carried out.

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