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Block Copolymerization Of Poly(Diethylene Glycol Phthalic Anhydride) And Acrylate Initiated By Potassium Diperoiodocuprate(III)



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ABSTRACT

Block copolymers of methyl acrylate(MA), methyl methacrylate(MMA) and poly(diethylene glycol phthalic anhydride)(PPAG) were synthesized using a novel redox system-potassium diperoiodocuprate(III)[DPC]/PPAG system in alkaline medium. Block copolymers with high total conversion were obtained, which indicated that DPC/PPAG redox system was an efficient initiator for this blocking. The total conversion at different conditions (concentration of reactants, temperature, concentration of the DPC, reaction time) was investigated. The overall activation energy of this blocking is 44.57 kJ/mol. The ¹HNMR analysis and infrared spectra proved that the block copolymers were synthesized successfully. 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.

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KEYWORDS

Diperoiodocuprate(III);
Acrylates;
Poly(diethylene glycol
phthalic anhydride);
Redox initiation;
Block copolymerization

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INTRODUCTION

There are many reports on the synthesis of block copolymers in the literature. Marc Hillmyer^[1] 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, due to 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 was mild and the range of monomers is wide.

Now, the mostly 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 diperiodato nickelate(IV)^[12-15] were found that could be used as initiator in radical grafting copolymerization. It has been demonstrated that DPC is the most efficient initiator. We do not find any reports on radical block copolymerization of PPAG with various monomers so far. This paper investigated the block copolymerization of MA, MMA with PPAG using DPC in an alkaline mix solution. The effects of variables on the blocking were studied. The block copolymers were also characterized by FT I.R. ¹HNMR and TGA.

EXPERIMENTAL

Materials

The solution of DPC was prepared according to reference^[16]. The concentration of DPC was measured by its absorption at $\lambda = 414$ nm using a shimadzu UV-265 spectrophotometer (Japan). MA, MMA, analytical reagent, were purchased from

huadong reagent factory (Tianjin), and were distilled before used. Poly(diethylene glycol phthalic anhydride)(PPAG-10000 molecular weight)(purchased from Jufeng reagent factory, Shanxi) was used as received. The other reagents were all of analytical reagent and used as received.

Block copolymerization

Required amounts of PPAG-10000 (molecular weight) solution, MA or MMA and water were placed in the reaction tube, flushed with pure nitrogen and the reaction system was maintained at $30 \pm 0.1^\circ\text{C}$ in a thermostatic reservoir. Appropriate amounts of DPC were then added under nitrogen. Hold the reaction at $30 \pm 0.1^\circ\text{C}$ 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) was defined and calculated as follows:

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

Instrumentation

IR spectroscopy

The FT I.R. spectra of PPAG and block copolymer were recorded on an FTS-40 spectrometer (BIO RAD Co. U.S.A.) using potassium bromide pellets technique.

¹HNMR spectroscopy

The ¹HNMR spectroscopy of block copolymer was obtained from CDCl₃ solution on a JNH-FX100(JBOX),300MHz NMR spectroscopy.

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.

RESULTS AND DISCUSSION

Effect of temperature and time

The effects of temperature and time on the block-

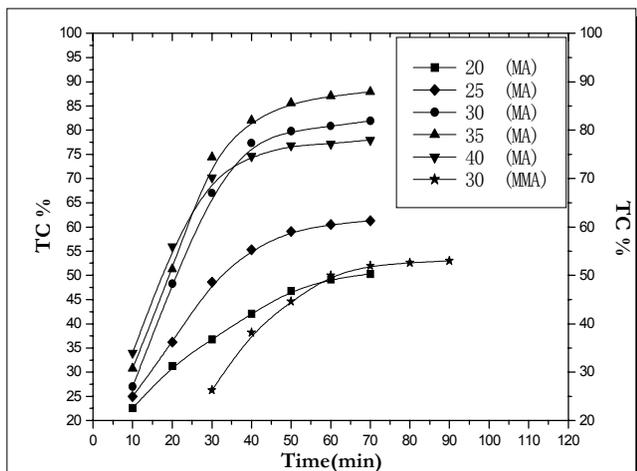


Figure 1: Effect of temperature and time on the TC%
[DPC] = 7.02×10^{-5} mol/L, W(MA) or W(MMA)/W(PPAG) = 10

ing of PPAG with MA were determined at 20, 25, 30, 35, 40°C. As shown in figure 1 the curves for TC vs. time, it is seen that for a given temperature, the TC increased steadily with the increasing reaction time to a certain value, and then leveled off. The initial increase in the TC has clearly indicated that both DPC and blocking sites 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 as well as a reduction in the number of active sites on PPAG. In addition, increasing the temperature results, as expected, in an increased initial rate of polymerization (R_p). The acceleration in R_p upon increasing temperature is consistent with the general principle of conventional radical polymerization. However, at the latter stage (after 40 min), the tendency of the TC comes forth a peak value. The tendency of lower TC at higher temperature (40°C) 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. In addition, we can see clearly that the TC of MA is much higher than the TC of MMA at 30°C, this may be due to the difference in the diffusive ability of MMA and MA in the system. From the Arrhenius plot (Figure 2), the activation energy of MA block with PPAG was calculated as 44.57 kJ/mol

Effect of temperature of MMA with PPAG on TC

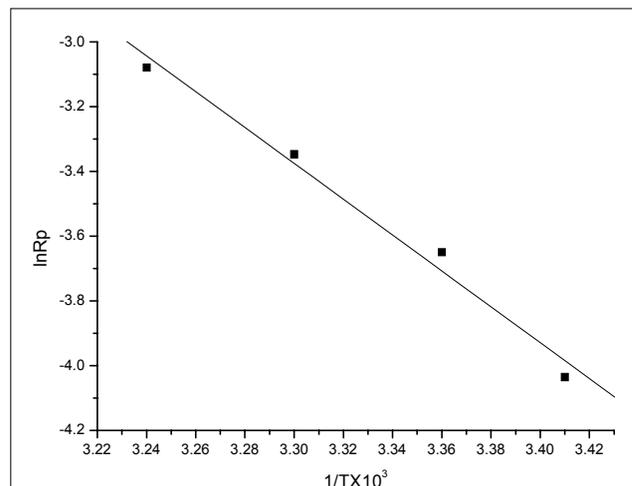


Figure 2: The activation energy
Arrhenius plot relative to the R_p , [DPC] = 7.02×10^{-5} mol/L, W(MMA)/W(PPAG) = 10.

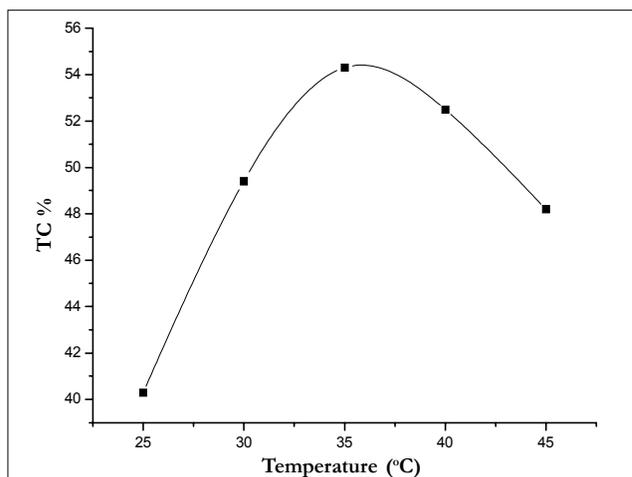


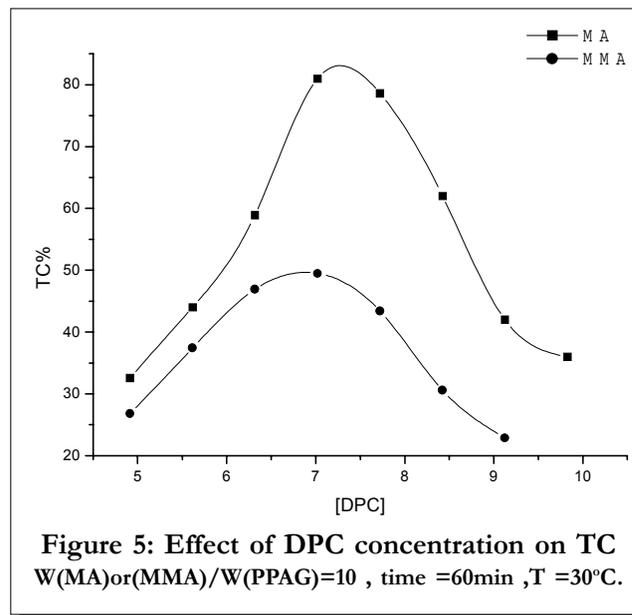
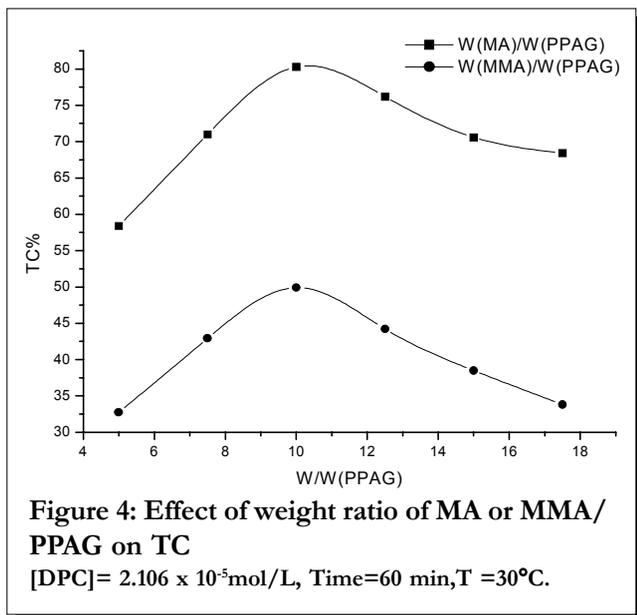
Figure 3: Effect of temperature on copolymerization of MMA with PPAG.
[DPC] = 7.02×10^{-5} mol/L, W(MMA)/W(PPAG) = 10, Time = 60 min.

In figure 3, it is the effect of temperature on copolymerization of MMA with PPAG. The trend is consistent with the blocking of PPAG with MA but lower than the MA.

Effect of weight ratio of MA or MMA/PPAG on TC

When kept all the other variables unchanged, the effect of weight ratio of MA or MMA/PPAG on TC had been investigated. The results are shown in figure 4. It can be seen that TC increased with an increasing weight ratio of MA or MMA/PPAG at first and then declined. The declined trend of TC at too

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higher monomer amount may be explained as follows: although the MA and polymerized with PPAG increased, however, it became less when compared with the fast increment of the added monomer, namely TC declined. At the same time, because the total volume was unchanged, increasing monomer was equal to increase DPC in aqueous, namely TC was decreased under the condition of higher monomer amount.

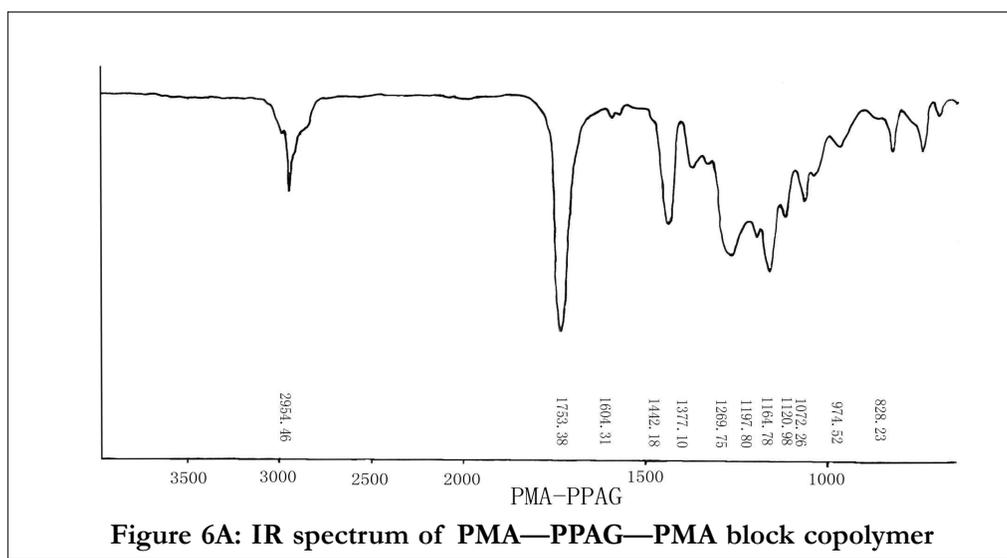
Effect of DPC concentration on TC

Figure 5 shows the effect of initiator concentration on TC. It can be seen that TC increased 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 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.

Proof of blocking

Figure 6A and figure 6B are the IR spectra of block copolymer PMA-PPAG and PMMA-PPAG. The absorption peaks at 2950 and 1440 cm^{-1} come



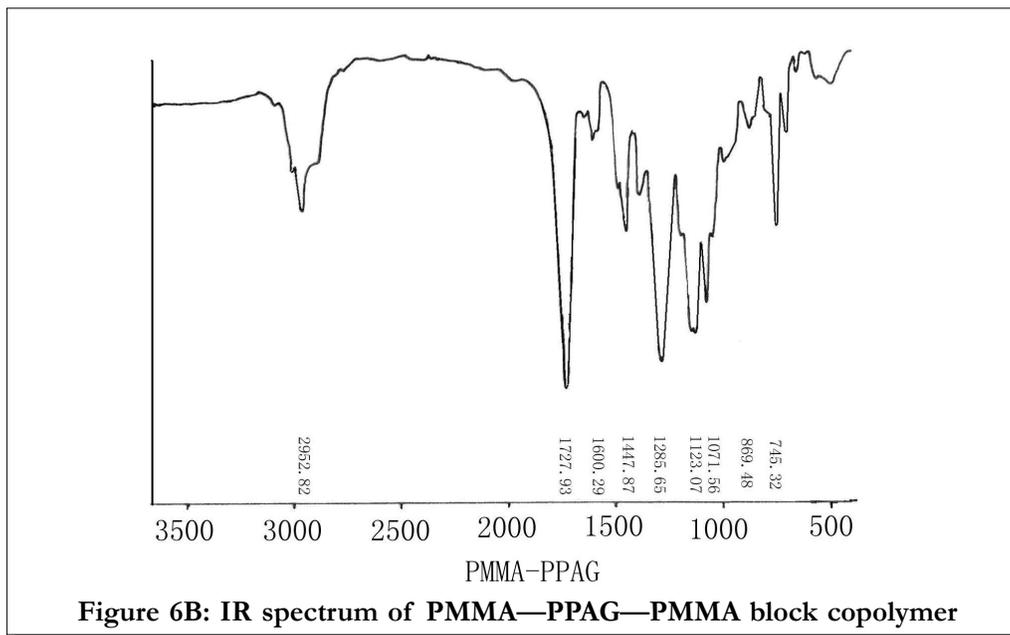
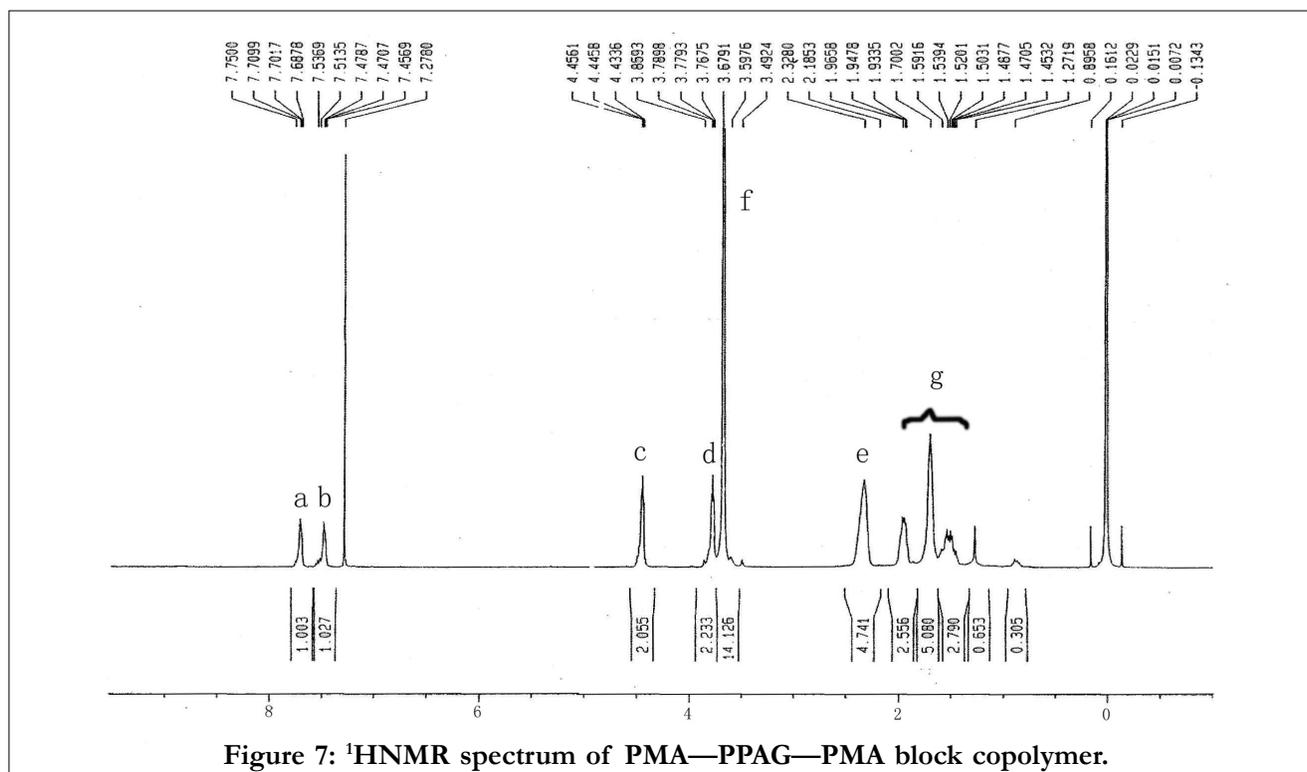


Figure 6B: IR spectrum of PMMA—PPAG—PMMA block copolymer

Figure 7: ^1H NMR spectrum of PMA—PPAG—PMA block copolymer.

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

^1H NMR spectra in figure 7 confirmed the structures of the copolymers obtained. At 7.5369, 7.6879 ppm (a,b as shown in the molecular formula below)

for hydrogen of the phenyl, at 3.7675 and 4.4336 ppm (d, c as shown in the molecular formula below) for hydrogen of the $-\text{[CH}_2\text{CH}_2\text{O]}_n-$ protons, 3.6791 ppm (f as shown in the molecular formula below) for $-\text{OCH}_3$, at 2.328 (e as shown in the molecular formula below), 1.9335, 1.5394, 1.4532 (g as shown in the molecular formula below) for $-\text{CH}_2\text{CH}-$ of PMMA. According the integral area

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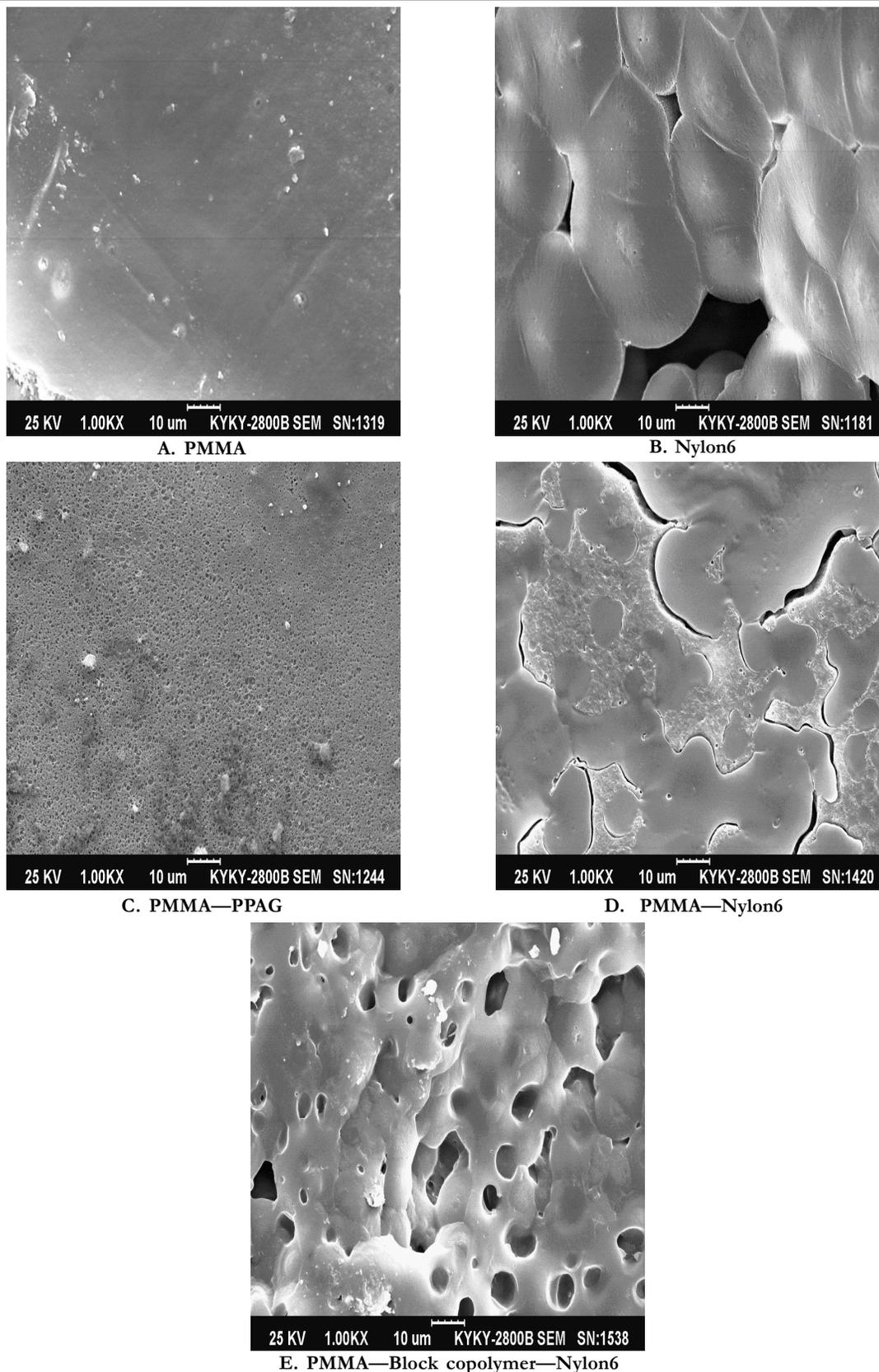
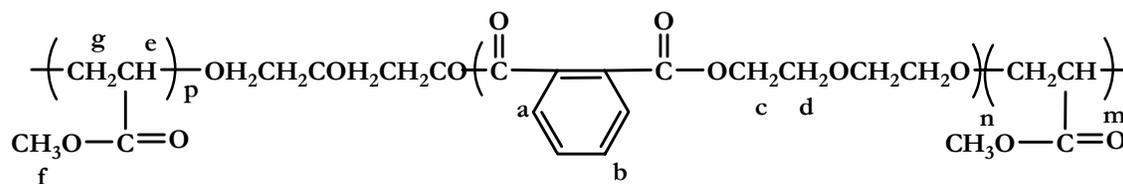
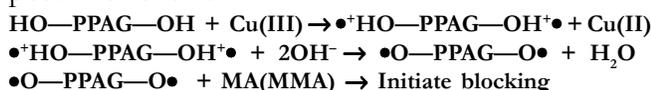


Figure 8: The SEM of PMMA(A), Nylone6(B), PMMA—B—PPAG(C), PMMA—Nylone6(D) and PMMA— Block copolymer—Nylone6(E)



of the hydrogen, we can calculate the result of $(m+p)/n$ as 9.27, then get the molecular weight (33000).

A plausible initiation mechanism^[17-18] was proposed as follows:



Morphological studies (SEM)

The morphological characters of PMMA, Nylone6, PMMA—B—PPAG, PMMA—Nylone6 and PMMA—Block copolymer—Nylone6 were studied by SEM. As shown in figure 8, it can be seen that the surface of the PMMA(A) is smoothness, the surface of the Nylone6(B) is crystal and the surface of the block copolymer (C) was full of small holes, which is ascribed to the different strength of the molecular chain. Due to 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—Nylone6 (D). On the contrary the interstices and two phases have disappeared in the PMMA—Block copolymer—Nylone6 (E). The above features suggest that the block copolymer is efficient to improving the compatibility of nylon6 and PMMA.

CONCLUSION

In this study, block copolymerization with higher TC has been obtained using DPC in medium. Moreover, the block copolymerization can be carried out at a mild temperature due to the lower activation energy (44.57 kJ/mol) of this blocking and in an alkali mix medium. And from the TC% aspect, the MA is higher than MMA apparently. The proof of blocking was obtained from ¹HNMR and IR analysis. Another, 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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