

STUDY ON THE SYNTHESIS AND PROPERTIES OF POLY(ESTER-IMIDE-ETHER) MULTIBLOCK COPOLYMERS*

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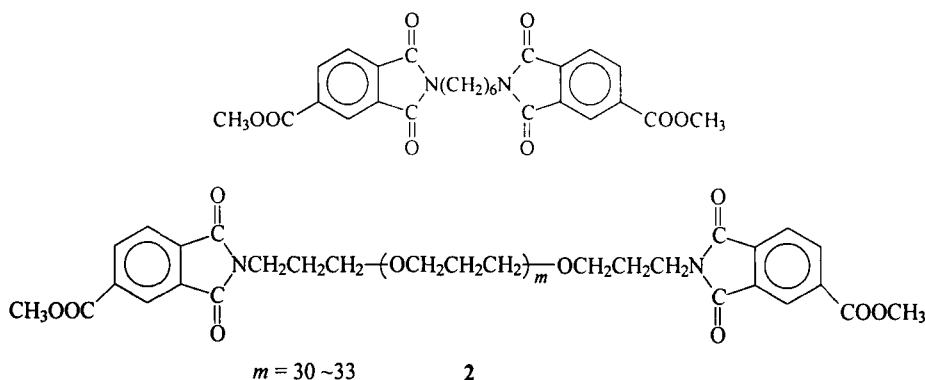
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Abstract A new class of poly(ester-imide-ether) multiblock copolymers was synthesized by transesterification and melt copolymerization of dimethyl terephthalate (DMT) and *N*-(4-carbomethoxyphenyl)-4-(carbomethoxy)-phthalimide with ethylene glycol (EG) and polytetramethylene glycol (PTMG). The structure of the above copolymers was characterized by ¹H-NMR and IR spectroscopy. Some properties of the copolymers were also examined. It was found that their mechanical properties and heat stability, compared with poly(ether-ester) copolymers, were obviously improved.

Keywords *N*-(4-carbomethoxyphenyl)-4-(carbomethoxy)-phthalimide, Polyester-polyether copolymer, Poly-(ester-imide-ether) multiblock copolymer, Imide modification

INTRODUCTION

In recent years, studies on the improvement of polymer properties by introducing imide component were extensively performed. For poly(ester-ether) multiblock copolymers, it was also reported^[1-4] that poly(ester-imide-ether) multiblock copolymers were synthesized by copolymerization of DMT, diols, compound **1** and compound **2**.



However, the imidation of polyoxylpropylene diamine (Jeffamine 2000) is complicated and the procedure for the synthesis of the poly(ester-imide-ether) multiblock copolymers is also difficult.

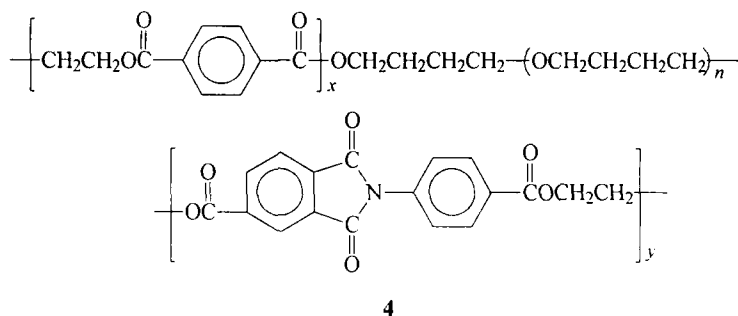
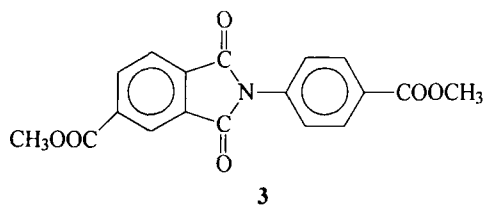
In this paper, a new pathway which can be easily incorporated with the routine procedure for the synthesis of poly(ester-ether) multiblock copolymers, has been developed. First, *N*-(4-carbomethoxyphenyl)-4-(carbomethoxy)-phthalimide with structure **3** as shown below, was synthesized. Then, it was used to synthesize a new poly(ester-imide-ether) copolymers (structure **4**) by transesterification and melt copolycondensation of **3** and

* This work was supported by 863 Programme of China (No. 715-004-0010).

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Received April 16, 1998; Revised July 31, 1999

DMT with EG and PTMG. The characterization and the study of some properties of the multiblock copolymers thus obtained have also been conducted.



EXPERIMENTAL

Materials

DMT was a commercial product from Japan. Trimellitic acid anhydride (TMA) was obtained from American Acros company. PTMG (M.W. 1000) was an industrial product from Du Pont Company. Other chemicals and solvents were obtained from Beijing Chemical Company. All the chemicals were used without further purification unless specified.

Preparation of *N*-(4-Carbomethoxyphenyl)-4-(carbomethoxy)-phthalimide

N-(4-carboxyphenyl)-4-carboxy-phthalimide

To a 500 mL three-necked round bottom flask fitted with a condenser and magnetic stirrer, 41.15 g (0.3 mol) 4-amino-benzoic acid and 168 mL *N,N*-dimethylacetamide (DMAC) were added. The mixture was cooled to 0°C, 57.6 g (0.3 mol) TMA was added under the protection of N₂, stirred for 18 h at room temperature, 54 mL (0.57 mol) acetic anhydride and 12.5 mL (0.165 mol) pyridine were added and the mixture was stirred for 5 h at 154°C. A white solid was precipitated, filtered and dried in vacuum for 20 h at 90°C to give 65 g of a crude product. After recrystallization with DMF, it was dried in vacuum for 12 h at 80°C to afford 59.7 g *N*-(4-carboxyphenyl)-4-carboxy-phthalimide, yield 63.9%.

N-(4-carbomethoxyphenyl)-4-(carbomethoxy)-phthalimide

To a 500 mL round bottom flask fitted with a condenser and magnetic stirrer, 20 g *N*-(4-carboxyphenyl)-4-carboxy-phthalimide, 300 mL methanol and 15 g concentrated sulfuric acid were added. The mixture was refluxed for 15 h with stirring, filtered after evaporating off most of CH₃OH and dried in vacuum for 8 h at 50°C. The product was purified by reprecipitating from benzene into *n*-hexane, filtered, dried in vacuum for 10 h at 80°C, 15 g *N*-(4-carbomethoxyphenyl)-4-(carbomethoxy)-phthalimide was obtained, yield 75.7%, m.p. 197°C. ¹H-NMR: δ 3.8~4.0 (OCH₃, 6H), 7.6~8.5 (Ar H, 7H). IR: 1735, 1785 cm⁻¹ (imidecarbonyl stretching); 1720 (Ar carbonyl stretching). Elemental analysis: found: C 63.71%, H 3.83%, N 4.13%; calcd: C 63.69%, H 3.87%, N 4.01%.

Synthesis and Purification of the Poly(ester-imide-ether) Multiblock Copolymers.

The synthesis of poly(ester-imide-ether) multiblock copolymers was achieved according to the previously reported

method^[5] for poly(ester-ether) multiblock copolymers, except that the monomer *N*-(4-carbomethoxyphenyl)-4-(carbomethoxy)-phthalimide, partly instead of DMT, was introduced into the hard segments of the copolymers.

The copolymers were purified by reprecipitating from CHCl_3 solution with CH_3OH . Generally, two times of reprecipitation were necessary.

Measurements

Structure characterization

Elemental analysis was carried out with a Heraeus, CHN-Rapid instrument. Infrared spectra and differential infrared spectra were taken on Perkin-Elmer 683 and System FT-IR spectrometers, respectively. $^1\text{H-NMR}$ were recorded by Varian Unity 200 spectrometer using CDCl_3 as solvent.

Melting point, intrinsic viscosity, TGA and DSC

Melting points were determined with a microscope fitted with a hot stage. Intrinsic viscosities of the copolymers were determined in *m*-cresol solution ($C = 0.5 \text{ g/dL}$) using an Ubbelohde viscometer at $30.0 \pm 0.1^\circ\text{C}$. TGA and DSC analysis were carried out on a Perkin-Elmer 7 series Thermal Analysis System using annealed copolymer samples.

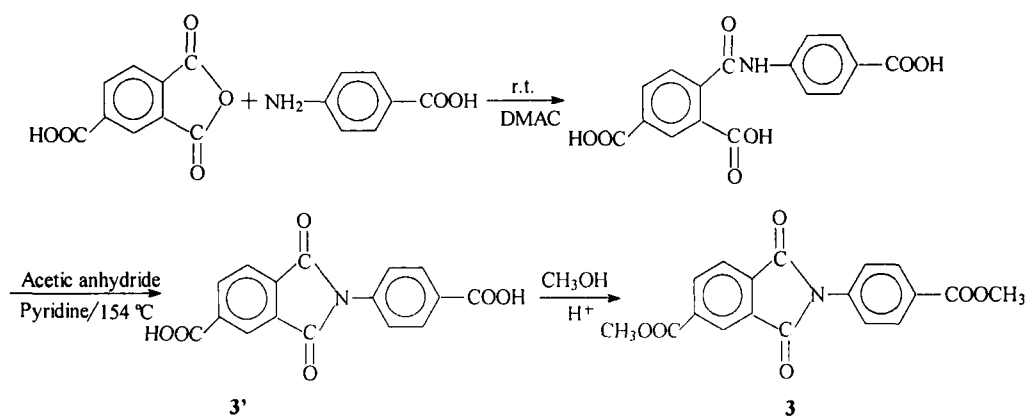
Mechanical properties

The sample films were prepared by casting a copolymer solution (5 wt%) on a glass slide, following by evaporating the solvent at room temperature. The films were peeled off and annealed at 80°C in vacuum for 12 h. The specimens thus obtained were cut into dumb-bell test pieces. Tensile strength and elongation at break were measured on an Instron 1122 at room temperature.

RESULTS AND DISCUSSION

Monomer Synthesis

The monomer, *N*-(4-carbomethoxyphenyl)-4-(carbomethoxy)-phthalimide **3** was synthesized by the following reaction routes (Scheme 1).

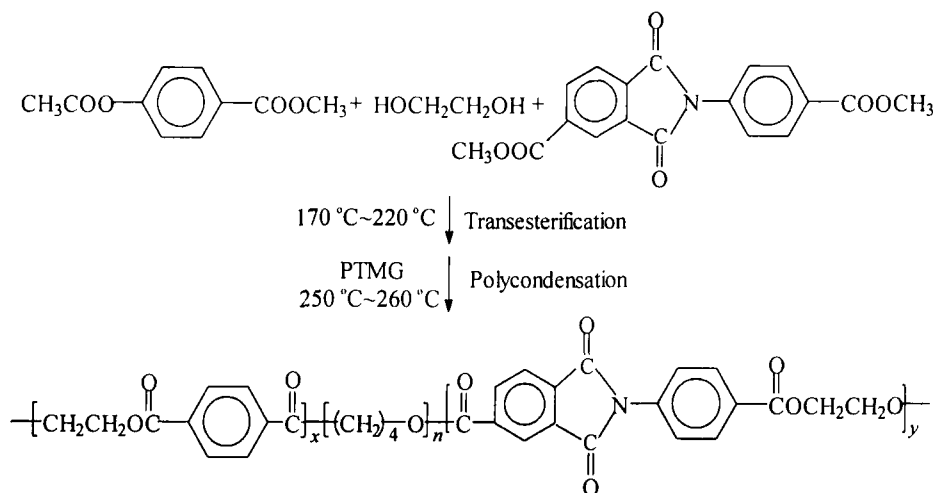


Scheme 1

N-(4-carboxyphenyl)-4-carboxy-phthalimide (**3'**) was synthesized according to the procedure presented in Ref. [6]. The monomer (**3**) has not been reported in the literature. Three methods had been tried to accomplish the esterification: (1) reaction of (**3'**) with CH_3OH using concentrated sulfuric acid as catalyst as described in the experiment; (2) reaction of acyl chloride of (**3'**) with CH_3OH and (3) reaction of (**3'**) with methyl iodide. Because the solubility difference between (**3**) and (**3'**) is so small that the separation of (**3**) and (**3'**) is difficult, which is the key problem of obtaining the best yield so that the compounds introduced into the reaction should be as few as possible. Compared with the methods (2) and (3), the first method is the easiest and the reaction conditions are more moderate. The repeated experiments indicated that the first one gave the best yield.

Copolymers Synthesis

The copolymers were synthesized by the following reactions (Scheme 2).



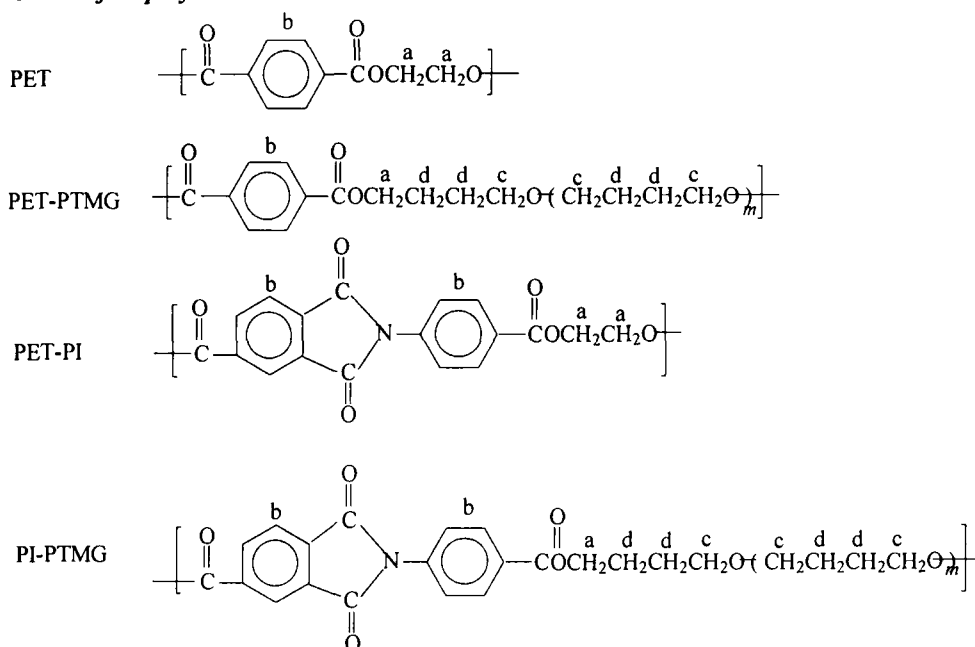
Scheme 2

where $n = 14$, the values of x and y are variable.

For all copolymers, the ratio of hard segment to soft segment is 35:65 by weight according to the added amounts. The amounts of monomer (3) added in hard segment are 0, 5 and 7 mol%, respectively.

It should be emphasized that the choice of diol is important to get a copolymer with high molecular weight. For the less active binary alcohol, e.g. 1,4-butylene glycol, the transesterification could not go to completion so the poly(ester-imide-ether) copolymer with high molecular weight can not be obtained. A possible explanation is that complexing of the imide monomer (3) with the catalyst of metallic salts destroys the monomer (3). Therefore, ethylene glycol, which is the more active one, was used as the binary alcohol in this work.

Characterization of Copolymer



Scheme 3

The structure of copolymer containing 5 mol % imide monomer was characterized by differential infrared spectra, using the copolymer without the imide monomer (3) as the reference sample. The presence of polyimide segments is confirmed by the imide carbonyl stretching vibration at 1740 and 1784 cm^{-1} . All the structures of the copolymers have been determined by $^1\text{H-NMR}$ spectra. The segment structures of copolymers are shown in Scheme 3, chemical shifts of all kinds of protons in the copolymers are listed in Table 1.

According to the peak areas at δ 4.68–4.7 (a) and 3.4 (c), the weight ratio of hard/soft segments of copolymers can be calculated. Using the peak areas at δ 4.68–4.7 (a) and 8.1 (b), the mole ratio of PET-PI was calculated. The results are showed in Table 2.

The results in Table 2 indicates that the mole ratio of PI in the copolymers synthesized is lower than that of the added amount. A possible explanation is that a small portion of compound (3) was broken under transesterification and copolycondensation conditions.

Table 1. Chemical shifts of the protons of copolymers

Proton type Group δ	a COOCH_2 4.68–4.70	b Ar 8.1	c OCH_2 3.4	d CH_2CH_2 1.6
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Table 2. Composition of the copolymers

Copolymers	Segment ratio (wt%)				PI (mol%)	
	Cald.		by $^1\text{H-NMR}$		Cacld.	by $^1\text{H-NMR}$
	hard	soft	hard	Soft		
PET-PTMG	35	65	37	63	0	0
PET-PI-PTMG(A)	35	65	37	63	5	2.4
PET-PI-PTMG(B)	35	65	35	65	7	5

Properties of Copolymers

The intrinsic viscosities $[\eta]$, thermal properties and mechanical properties of the different copolymers are summarized in Table 3.

Table 3. The properties of different copolymers

Copolymers	$[\eta]$	$T_0(^{\circ}\text{C})^a$	$T_{0.5}(^{\circ}\text{C})^b$	Tensile strength at break (kg/cm^2)	Elongation at break (%)
PET-PTMG	0.97	173.5	433.3	202.34	948
PET-PI-PTMG(A) ^c	1.19	184.7	442.5	250.07	1094
PET-PI-PTMG(B) ^d	1.12	222.6	438.1	277.20	1142

a) T_0 : The initial decomposition temperature; b) $T_{0.5}$: The decomposition temperature at 50% weight loss

c) PET-PI-PTMG (A): containing PI 2.4 mol %; d) PET-PI-PTMG (B): containing PI 5.0 mol %

It can be seen that copolymers with high intrinsic viscosity were obtained. From the change of T_0 and $T_{0.5}$ of different copolymers, it can be concluded that the thermostability and the mechanical properties of copolymers (A) and (B) are significantly improved. Furthermore, the greater the amount of compound (3), the better are its thermal stability and mechanical properties.

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