



Synthesis and characterization of the copolymers containing blocks of polydimethylsiloxane in low boiling point mixtures



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HIGHLIGHTS

- Copolymers containing siloxane were prepared in an azeotrope.
- An Azeotrope of monomers is favorable for the polycondensation reaction.
- Polycondensation is preceded at low temperature, short time and low vacuum degree.
- The copolyester shows larger elastic elongation and recovery than those of pure PTT.
- Microphase separation and aggregation of Siloxane blocks occur in the material.

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ABSTRACT

Block copolyesters containing both polydimethylsiloxane and poly(trimethylene terephthalate) (PTT) blocks were prepared by polycondensation reaction. Although hydroxyl-terminated siloxane oligomer (H-PDMS) and 1,3-propanediol are immiscible, their mixture can form an azeotrope with a low boiling point. It was found that the reactions were preceded at lower temperature, shorter reaction times and lower degree of vacuum than the traditional way. With increasing H-PDMS content, the occurrence time of Weissenberg effect is gradually shortened. The structure and thermal performances of the block copolymers was characterized by using the Fourier transform infrared spectroscopy (FTIR), ¹H NMR, Ubbelohde viscometer, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA) and polarizing microscopy, respectively. The block copolymers have lower glass transition temperatures, cold-crystallization temperatures, melting points, starting decomposition temperatures but higher maximum decomposition rate temperatures and higher amount of residue than those of pure PTT. The block copolymers with less H-PDMS content have larger storage modulus and loss modulus than those of pure PTT. The copolyester is easier to form banded spherulites at lower temperatures than that of pure PTT. Microphase separation and aggregation of polydimethylsiloxane blocks occurs in the material that is favorable for improving the impact strength of the material.

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1. Introduction

The traditional thermoplastic aromatic polyesters are all prepared by transesterification and melt-polycondensation methods with two monomers (M1 and M2), such as the poly(trimethylene terephthalate) (PTT) that is prepared by dimethyl terephthalate and 1,3-propanediol (PD) [1], and they are regarded as the reaction with equal mole number of functional groups. The dynamic reaction

equation of M1 and M2 monomers with equal mole number of functional groups is as follows [2,3],

$$\frac{dp}{dt} = A \left[(1-p)^2 - \frac{pn_w}{K} \right] \quad (1)$$

where A is a constant related with the reaction system; p is the extent of reaction; K is the equilibrium constant; n_w is the residual concentration of the water or alcohol in the system.

Because K is small, the boiling points of the monomers are high and the melt viscosity is large, the polymer with high molecular weight can only be obtained at high temperature and very low pressure within long reaction times. These strict conditions have

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increased the cost of the industrial production. Therefore, the reaction at low temperature and proper pressure within short reaction times is a worthy goal to strive for.

If another monomer, M3 (it is immiscible with M1 or M2), is added into the transesterification reaction system, and also if M2 and M3 can form a mixture with low boiling point (such as an azeotrope) [4], *K* will increase and the transesterification and polycondensation reaction may be occurred at lower temperature, shorter reaction times and lower degree of vacuum than those in traditional way. On the other hand, if M3 can be incorporated into the polymer molecular chains, a new kind of polymer will be synthesized. Copolycondensation is one of the effective means to seek new materials and modify the existing materials. There have been many reports for copolycondensation of PTT, such as PTT-TI [5], PTT-POB [6], PTT-PEG [7,8], PU-PTT [9], PTT-PTMG [10], and so on. Polysiloxane is a widely used monomer for preparing new copolymers [11–15] and it can offer some new properties to the copolymers.

In this work, hydroxyl-terminated polydimethylsiloxane (H-PDMS) was used as the third monomer (M3) to adding into the reaction system contained with dimethyl terephthalate (DMT) and PD; as a result, H-PDMS not only can promote the reaction proceeding to the positive direction by decreasing the reaction temperature and time, but also can be imbedded into the molecular chains by forming block copolymers that will have some unexpected properties. Some copolymers with different polydimethylsiloxane contents were synthesized and their properties were investigated in detail.

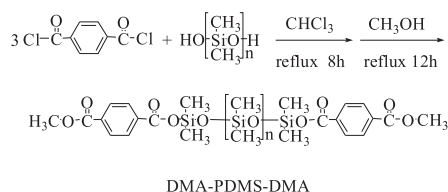
2. Experimentals

2.1. Raw material

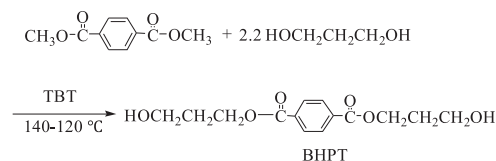
Dimethyl terephthalate (DMT), AR, white flakes, m.p.139–142 °C, acid value ≤ 0.2(KOH mg/g), Sinopharm Chemical Reagent Co.(China); 1,3-propanediol (PD), AR, Tianjin Guangfu Institute of Fine Chemicals(China); hydroxyl-terminated polydimethylsiloxane(H-PDMS, *M* = 425, OH% = 8.0%), Wuxi Quanli Chemical Co. Ltd.(China); chloroform, AR, Tianjin Kermel Chemical Reagent Co.(China); tetrabutyl titanate (TBT), AR, Tianjin Kermel Chemical Reagent Co.(China); antimony trioxide (Sb₂O₃), AR, Tianjin Chemical Reagent Plant III(China); tetrachloroethane, AR, Tianjin Guangfu Institute of Fine Chemicals(China).

2.2. Determining of boiling point of the mixture of PD and H-PDMS

10 mL of PD and 10 mL of H-PDMS were placed into a round-bottomed flask under stirring, then the mixture was rapidly heated to 140 °C at the beginning and then was slowly heated at 1 °C/min until some bubbles appeared in the bottom of flask at the temperature about 160 °C, which was regarded as the boiling point of the mixture.



Scheme 1. Preparation of DMA-PDMS-DMA.



Scheme 2. Preparation of BHPT.

2.3. Preparation of DMA-PDS-DMA

5 g of terephthaloyl chloride was dissolved in 35 mL of chloroform in a three-neck round-bottom flask, stirred and heated to reflux. Using atmospheric pressure drop funnel, 3.5 g of H-PDMS was dropwise added within 2 h. The reaction was continued for 6 h until no chloride hydrogen gas escapes, and then 10 mL of methanol was added and the reaction was continued for 12 h until no chloride hydrogen gas escapes. Then filtered and washed the crude product with chloroform, ethanol for several times. The product was dried at 50 °C in vacuum for 24 h. **Scheme 1** is the reaction equation.

2.4. Preparation of block copolyesters

2.4.1. Transesterification

80 g (0.4120 mol) of dimethyl terephthalate, 69 g (0.9067 mol) of PD, and 0.03 g of tetrabutyl titanate were placed into a three-neck round-bottomed flask. The system was gradually heated to 140 °C under nitrogen protection, stirred when the solid was molten; then gradually heated to 220 °C until no methanol distilled. **Scheme 2** was the transesterification reaction.

2.4.2. Melt-polycondensation

15 g of BHPT, 0.01 g of Sb₂O₃ and 0 g, 4 g, 6 g, 8 g H-PDMS were placed respectively in the flask under nitrogen atmosphere. The mixture was gradually heated to 160 °C until the solid was completely molten and then stirred continuously. The mixture was then gradually heated from 160 °C to 190 °C within 1 h, and during the heating process the distillate came into being at 180 °C, and it stratified into two layers in the bottle. Then the system was heated continuously to 230 °C within 1 h, and finally the distillate was collected and poured into a graduated cylinder and the volume of H-PDMS (upper layer) and PD (lower layer) were counted respectively after standing for 4 h, and listed in **Table 1**. At 230 °C, the

Table 1

Experimental parameters of the polycondensation for various PTT-b-SI copolymers.

Samples	H-PDMS (mL)		PD (mL)		<i>m</i> ^c (g)	<i>t</i> ^d /min	Product's characteristics
	V1 ^a	V ^b	V1 ^a	V ^b			
15/0 PTT-b-SI	0	0	0.1	3.8	10.85	>30 ^f	Slightly yellowish Transparent Brittle
15/4 PTT-b-SI	0.3	0.5	1.2	4.0	13.75	20	Milky white Translucent A little Tough
15/6 PTT-b-SI	0.3	0.6	1.2	4.4	15.33	15	White opaque Tough
15/8 PTT-b-SI	0.4	1.0	1.4	5.0	16.35	8	White opaque Very Tough

eV1 of 15/16 PTT-PTMEG is gotten after 225 °C and V is all the volume of PD and PTMEG distilled from the system.

^a the volume of the distillates before decompression.

^b full volume of the distillates when the reaction was completed.

^c *m* is the product's weight.

^d *t* is the time that the melt undergone until the Weissenberg effect begins.

^f 15/0 PTT-B-SI has no Weissenberg effect within 30 min.

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