

SYNTHESIS AND CHARACTERIZATION OF SI-CONTAINING POLYESTER-POLYETHER MULTIBLOCK COPOLYMERS

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ABSTRACT

A series of Si-containing polyester-polyether multiblock copolymers were synthesized by transesterification and melt copolycondensation of organosilicon monomers [1, 1, 3, 3-tetramethyl-1, 3-bis (p-carbomethoxyphenyl) disiloxane] (I) or dimethyl bis (p-carbomethoxyphenyl) silane] (II) and dimethyl terephthalate (DMT), with 1, 4-butanediol, polytetramethylene glycol (PTMG) respectively. The organosilicon monomers were prepared by Grignard reaction, oxidation and esterification. The structures of the above monomers (I), (II) and the copolymers were characterized by MS anal. and $^1\text{H-NMR}$.

INTRODUCTION

In recent years, the studies on the improvements of polymer properties by organosilicon compounds have been developed rapidly, since organosilicon compounds incorporated into polymers display many outstanding properties such as heat resistance, oxidation resistance, hydrophobicity, gas permeability and so on. The organosilicon modification of polyester-polyether multiblock copolymers had been reported only on the alteration of soft segment by using α , ω -dihydroxy silicon oil (PDMS) with low molecular weight partly instead of PTMG^[1]. But Si-containing polyester-polyether copolymers in hard segment have not been reported to the present. In this paper, the synthesis and characterization of Si-containing polyester-polyether copolymers in hard segment have been described.

EXPERIMENTAL

1. Materials

p-Bromotoluene, dimethyldichlorosilane and methyl iodide were obtained commercially from Beijing Chemical Factory and distilled before use. All solvents were

dried and purified according to the method described in the literature^[2]. Dimethyl terephthalate (DMT) is the commercial product from Japan, 1, 4-butanediol was dried by 4A molecular sieve and then distilled. PTMG (M. W. 1000) is the industrial product from DuPont and used without further purification.

2. Measurements

Elemental analyses of the organosilicon monomers **I** and **II** were run on a Heraeus CHN-RADID instrument. Mass spectra of the monomers were recorded on VG-IBA-HS instrument. ¹H-NMR spectra were taken on a JEOL FX 100 NMR spectrometer by using CDCl₃ as the solvent at room temperature. The intrinsic viscosity number of the copolymers were measured in m-cresol solution using an Ubbelohde capillary viscometer at 30.0±0.1°C. Before measurements of viscosities the copolymers were purified by reprecipitation using CHCl₃ as solvent and CH₃OH as precipitant. Generally, two times of reprecipitation were necessary. The precipitate was dried in a vacuum oven at 80°C for 4h.

RESULTS AND DISCUSSION

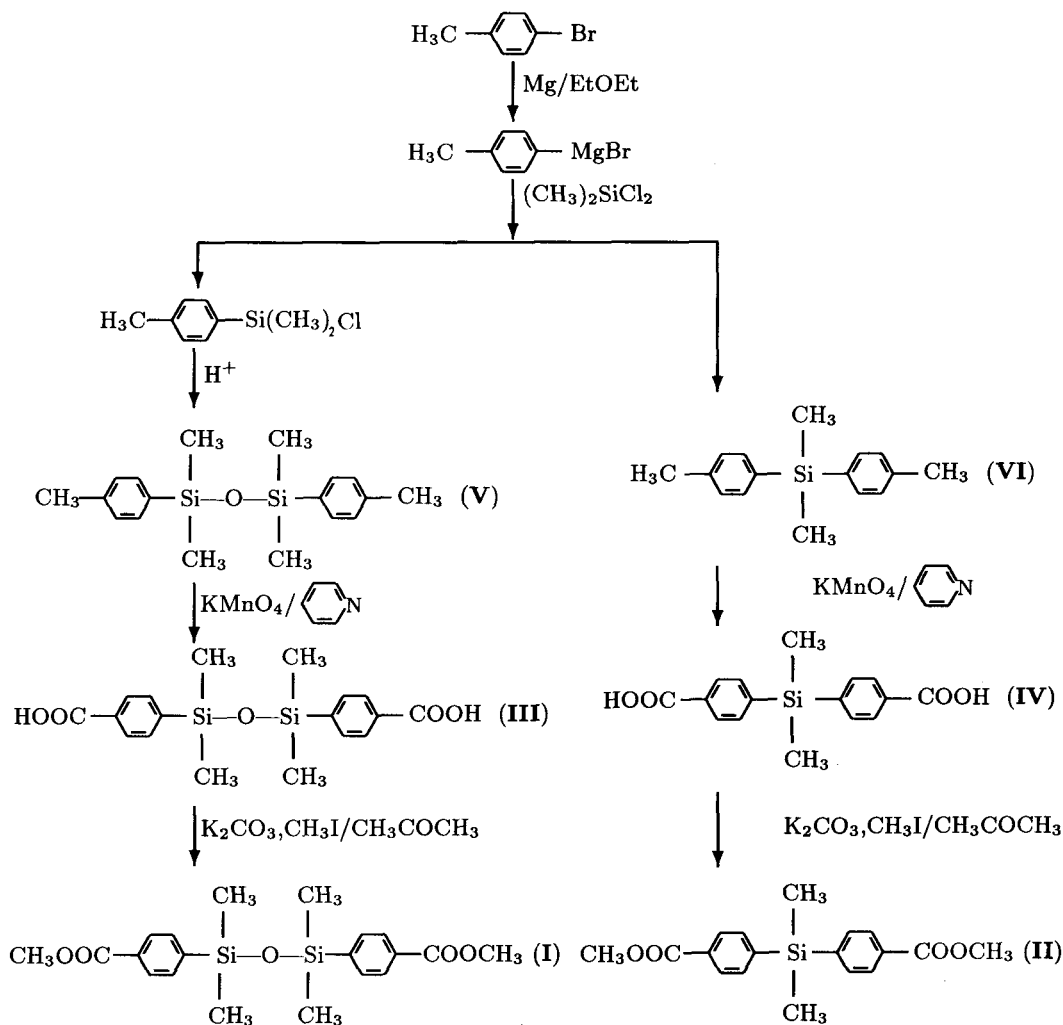
1. Preparation of two organosilicon monomers

The two organosilicon monomers **I** and **II** were synthesized by Grinard reaction using p-bromotoluene and dimethyldichlorosilane as starting materials, oxidation and esterification using CH₃I as esterifying agent, as shown in Scheme 1.

Grinard reaction and oxidation reaction have been completed by following a general procedure as presented in Ref. [3 – 6]. In short, compounds **V** and **VI** can be obtained through Grinard reaction of p-tolylmagnesium bromide and dimethyldichlorosilane respectively, and compounds **III** and **IV** can be obtained by oxidation reaction of **V** and **VI** with KMnO₄ as oxidizer respectively. The last step, esterification reaction, is rather difficult to be completed. It has not been reported in the literatures. The acid **III** and **IV** are almost insoluble in general solvents so that the above reactions were proceeded between phases of solid-liquid or solid-solid in low rate. It also should be emphasized that the esterification can not be simply completed by using CH₃OH in presence of concentrated sulfuric acid because Si-O bonds and Si-C bonds are easily destroyed by alcohols, acids, etc. The mild conditions have been established for esterification reactions in this work. The synthesis is described as the following:

11.22g (about 0.03 mol) compound **III** was added into solution of 13g K₂CO₃ (about 0.095 mol) in 60ml distilled water and stirred until **III** was completely dissolved. Then 250 ml acetone was added into the reaction mixture, a large amount

of white precipitate appeared. 16 ml (about 0.256 mol) CH_3I was added and the reaction mixture was heated to reflux under N_2 atmosphere for about 10 hours, then cooled to room temperature and evaporated to remove the solvent. 250 ml 10% K_2CO_3 water solution and 250 ml ether were added into the residue. The ether solution was washed by saturated NaCl solution until the pH value was 7, dried over anhydrous Na_2SO_4 and then evaporated. The product **I** is about 8.66g. (yield 71%). The melt point was 62°C after recrystallization in hexane. The synthesis of compound **II** was the same as that of monomer **I**. The yield of monomer **II** was about 80%, m.p. 83.4°C . The melt points of the products are concordant with the data in the literature^[3].



Scheme 1

2. Characterization of organosilicon monomers

All data of $^1\text{H-NMR}$, MS and C. H. Anal. of organosilicon monomers were summarized in Table 1.

Table 1 Characterization of organosilicon compounds

Compounds	Protons	δ	Peak		MS	Elemental analysis (%)	
			shape	area		Calcd	Found
VI	Si-CH ₃	0.1-0.2	s	6	240		
	-CH ₃	2.1-2.2	s	6			
	-Ar	6.9-7.4	quart	8			
V	Si-CH ₃	0.1-0.2	s	12	314		
	-CH ₃	2.1-2.2	s	6			
	-Ar	6.9-7.4	quart	8			
IV					300	C64.00	C64.18
						H5.33	H5.27
III					374	C57.75	C57.65
						H5.88	H5.90
II	Si-CH ₃	0.24	s	6	328	C65.86	C65.63
	-CH ₃	3.56	s	6			
	-Ar	7.14-8.15	quart	8		H6.10	H6.24
I	Si-CH ₃	0.35	s	12	402	C59.70	C59.64
	-CH ₃	3.92	s	6			
	-AR	7.45-8.05	quart	8		H6.47	H6.57

From the data of Table 1, it can be concluded that the designed organosilicon monomers were obtained.

3. Synthesis of Si-containing hard segment polyester-polyether multiblock copolymers

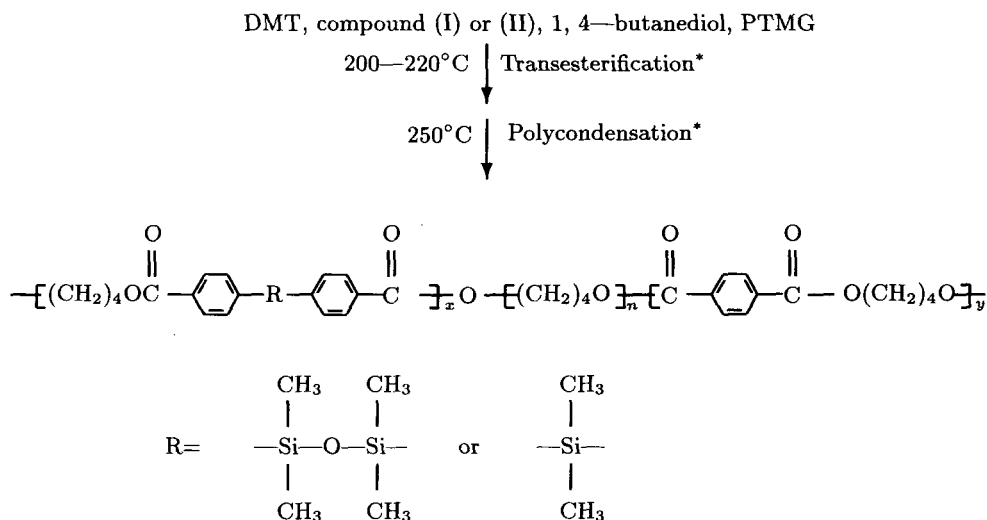
Scheme 2 describes the synthetic route for Si-containing polyester-polyether multiblock copolymers. For all copolymers, the ratio of hard segment and soft segment by weight is 30:70 according to the added amount. The amount of organosilicon monomers added in hard segment is 0, 10 and 20 mole % respectively.

The choice of binary alcohol was important to get the Si-containing copolymers. The 1, 4-butylene glycol was assigned binary alcohol in this work, the more active binary alcohol, e.g. ethylene glycol, would cleave organosilicon monomers so that the synthesis of Si-containing polyester-polyether copolymers unavoidably failed.

4. Characterization of Si-containing polyester-polyether copolymers

The structures of Si-containing hard segment polyester-polyether multiblock copolymers have been characterized by $^1\text{H-NMR}$ spectra. The segment structures

of copolymers were shown in Scheme 3. Chemical shifts of all kind of protons in the copolymers were listed in Table 2.



(when monomer I was used.) (when monomer II was used.)

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

* the catalysts and procedures of esterification and polycondensation were the same as the Ref. [7].

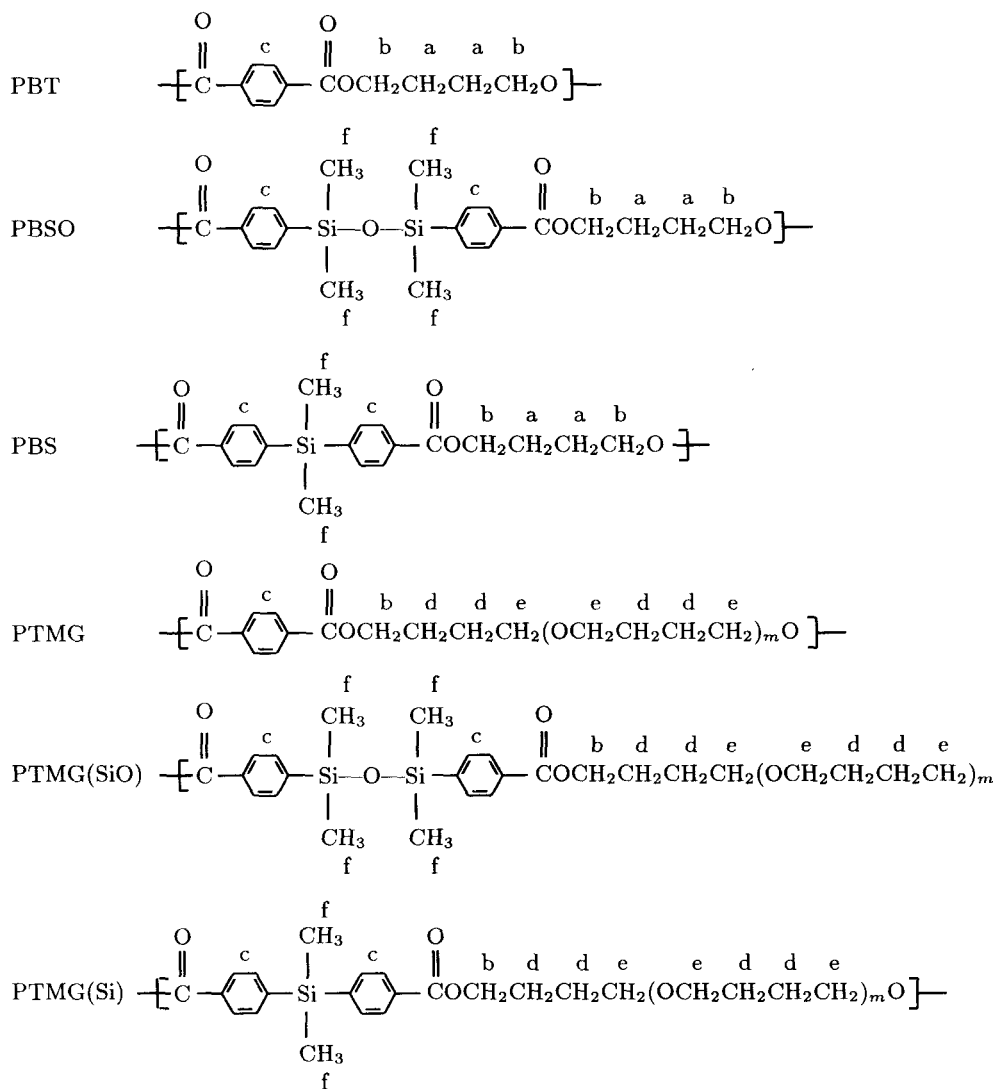
Scheme 2

Table 2 Chemical shifts of protons of copolymers

Proton type	a	b	c	d	e	f
Group	CH ₂ CH ₂	COOCH ₂	Ar	CH ₂ CH ₂	OCH ₂	Si—CH ₃
δ	1.94	4.37	8.05	1.60	3.38	0.33

Table 3 Compositions and intrinsic viscosity of copolymers

Copolymers	Segment ratio (wt%)				Si (mol %)		[η]
	Calcd.		by ¹ H-NMR		Calcd.	by ¹ H-NMR	
	Hard	Soft	Hard	Soft			
PBT-PTMG	30	70	31.1	68.9			1.373
PBT-PBSO-PTMG (PBSO:PBT=1:9)	30	70	30	70	10	6.04	1.285
PBT-PBSO-PTMG (PBSO:PBT=1:4)	30	70	30	70	20	12.53	1.265
PBT-PBS-PTMG (PBS:PBT=1:9)	30	70	34	66	10	5.6	1.468
PBT-PBS-PTMG (PBS:PBT=1:4)	30	70	34.46	65.54	20	12.48	1.465



where $m = 13$, alphabet a, b, c, d, e, f are proton types

Scheme 3

It can be proved that the copolymers contained silicon due to resonance at δ 0.33 ppm. The compositions of block copolymers synthesized are shown in Table 3. According to both the peak area at chemical shift 1.94 ppm (a) and that at 1.60 ppm (d), the weight ratio of hard/soft segments of copolymers can be calculated. And using the peak area at chemical shift 0.33 ppm (f), the mole ratio of PBT/PBSO and PBT/PBS can also be gotten.

The results in Table 3 indicated that the weight ratio of hard/soft segments of the copolymers was not affected by silicon addition, but the mole ratio of PBT/PBSO

and PBT/PBS in the copolymers synthesized was lower than that of the added amount. A possible explanation is that a few of organosilicon monomers was broken by 1, 4-butanediol under transesterification and copolycondensation conditions. It can be seen that the copolymers with high molecular weight were obtained from values of intrinsic viscosity. The properties of the Si-containing in hard segment polyester-polyether multiblock copolymers will be discussed in detail later.

Keywords:

1, 1, 3, 3-Tetramethyl-1, 3-bis (p-carbomethoxyphenyl) disiloxane; Dimethyl bis (p-carbomethoxyphenyl) silane; Polyester-polyether; Organosilicon modification

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