

Synthesis and characterization of hydroxy-terminated polyether-polydimethylsiloxane-polyether (PE-PDMS-PE) triblock oligomers and their use in the preparation of thermoplastic polyurethanes

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ABSTRACT: A series of hydroxy-terminated polyether-polydimethylsiloxane-polyether (α,ω -dihydroxy-(PE-PDMS-PE)) ABA triblock oligomers were synthesized from silanic fluids and methyl polyallyloxy polyethers. The reaction was a one-step solventless hydrosilylation reaction with chloroplatinic acid (CPA) catalyst in the presence of heat. These ABA oligomers were characterized *via* $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, $^{29}\text{Si-NMR}$, FT-IR, and GPC to demonstrate that they exhibit a 100% linear ABA structure with a siloxane Si—O chain in the center and polyether ethylene oxide (EO)/propylene oxide (PO) chains on the two sides terminated by hydroxy groups. The triblock oligomers were used to form thermoplastic polyurethanes (TPUs) using two-step solventless bulk polymerization. The investigation of triblock oligomers impact on TPUs mechanical properties, thermal performance, surface water repellency, and morphology performance were analyzed by Instron material tester, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), water contact angles (WCA), scanning electron microscope (SEM), and transmission electron microscope (TEM). DSC and TGA indicated that PE-PDMS-PE modified TPUs had a clear lower T_g under -120°C and the temperature of 50% weight loss was improved from 280 to 340°C . PE-PDMS-PE-modified TPU did not have the marked reduction on mechanical properties than pure polyether produced TPU. Tensile strength was maintained at 13 MPa and elongation was maintained at 300%. SEM and TEM were used to investigate the copolymers' morphology performance and found that all PO PE-PDMS-PE had a pseudo-three phase separation. WCA analysis confirmed that PE-PDMS-PE-modified TPU had significantly improved hydrophobic performance because the silicone structure linked into TPU copolymers. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42521.

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INTRODUCTION

Polyurethanes (PU) have excellent mechanical properties, such as tensile strength, elongation, tear strength, toughness, and elasticity. However, PU has poor thermal performance, such as PU does not have a lower glass-transition temperature (T_g). And PU has the poor biomaterial compatibility performance and hydrophobic performance. The disadvantages of PU limited it to be introduced to biomaterial application. Silicone has the excellent thermal performance, hydrophobic property, and biomaterial compatibility. The way to produce thermoplastic polyurethanes (TPUs) is to use difunctional polyether polyol, polyester polyol, or polycarbonate polyol reacting with 4,4'-methylenediphenyl diisocyanate (MDI) to formulate the soft segments for the TPUs, and difunctional a low-molecular-weight glycol or difunctional amine was reacted with MDI to

formulate the hard segments for the TPUs. The soft and hard segments phase separate, resulting in domains of hard segments. This has influence on mechanical properties.^{1,2} However, polyether polyol produced TPUs typically exhibit poor thermal properties, with a higher soft-segment T_g of -20°C , and poor water repellency, with water contact angles (WCAs) of approximately 70° , which are typically believed to accelerate the degradation of TPUs when these materials are used as an implant biomaterial.^{3,4}

Silicone elastomers have been known to exhibit outstanding biocompatibility and biostability but to also exhibit mechanical properties that render them unsuitable for use in many medical device applications.^{5,6} However, silicone is a nonpolar material that encounters difficulty in conjunction with a polar urethane matrix, di-functional hydroxyl terminated polydimethylsiloxane

(PDMS) was used to replace polyether polyol to produce PU which resulted in poor reactivity and mechanical properties.⁷ To overcome these difficulties, the ideal technical approach is to synthesize a series of polyether-PDMS-polyether ABA block oligomer with the combination of silicone chain and polyether chain. And the polyether-PDMS-polyether oligomers were used to produce TPUs instead of polyether polyol. But it was difficult and challenged to synthesize the ABA oligomer and characterize the structure. Therefore, numerous approaches to synthesizing PDMS-based polyurethanes *via* physical mixing of a relatively hydrophilic (e.g., polyether) macrodiol with a PDMS-based macrodiol to provide compatibility between the polar urethane hard domains and the nonpolar siloxane soft domains have been reported.^{8,9} The mixing of hydroxyl-terminated PDMS or amino-terminated PDMS with polyether polyol seems to resolve the solubility problems and to result in the formation of a larger molecular with better mechanical properties and morphological performance.^{10–12} Rebeca *et al.*^{13,14} blended amino-terminated PDMSs with polyether polyols such as polytetramethyleneoxide (PTMO) or poly(hexamethylene oxide) (PHMO) to synthesize thermoplastic polyurethane, which they investigated using small-angle X-ray scattering (SAXS) on the microdomain morphology and further analyzed using a pseudo-two-phase model and a modified three-phase core-shell model. Raju *et al.*¹⁵ mixed different low-molecular-weight silicone or silyl-ethylene chain extenders with 1,4-BDO as a chain extender to react with MDI to formulate hard segments for polyurethanes. Other researchers' results indicated that approximately 20% poly(hexamethylene oxide) (PHMO) in the soft segment produced polyurethanes with a combination of good biostability and mechanical properties.^{16,17} DSC analysis of the effect of silicone chain extenders on the polyurethane morphological properties revealed that silicone chain extenders did not significantly disrupt the crystallinity of the hard segment. These modified TPUs exhibited a unique morphological feature that resulted in poor polyurethane mechanical properties.

Other researchers used polycaprolactone-blocked PDMS to produce siloxane-modified TPUs.¹⁸ Antic *et al.*¹⁹ synthesized a series of novel thermoplastic elastomers based on poly(butylene terephthalate) (PBT) and polycaprolactone-*block*-polydimethylsiloxane-*block*-polycaprolactone (PCL-PDMS-PCL) with various mass fractions *via* melt polycondensation. In the preparation of the poly(ester-siloxane)s, the PCL blocks served as a compatibilizer for the nonpolar PDMS blocks and the polar co-monomers of dimethyl terephthalate and 1,4-butanediol. The introduction of PCL-PDMS-PCL soft segments improved the reaction mixture and resulted in a high-molecular-weight polymer with reduced hard-segment crystallinity. This process altered related properties such as the melting temperature and storage modulus and also modified the surface properties.²⁰

In addition, different chain extenders have been investigated in the siloxane-modified synthesis of TPUs to improve the cross-linking density and thermal performance. Pergal *et al.*²⁰ synthesized novel modified polyurethanes using a hydroxyl-terminated hyperbranched polyester (BH-20) reacted with MDI as the hard segments and hydroxyl-terminated ethylene oxide-polyol(dimethylsiloxane)-ethylene oxide triblock copolymer (EO-PDMS-EO)

reacted with MDI as the soft segments, with soft segment content ranging from 30 to 60 wt %.^{21,22} The results showed that the TPUs' cross-linking density and T_g increased with increasing hard segment content. The preparation of TPUs using high-molecular-weight hydroxybutyl-, hydroxyhexyl-, aminopropyl- and methylaminopropyl-terminated PDMS oligomers has been reported.^{23–25} However, all of these functional PDMS-modified polyurethane preparations involved the use of solvents for the polymerization, which had the unfortunate effect of leaving solvent residues even after the solvent was removed by stripping. The residual solvents would be categorized as hazardous chemicals if these biomaterials were to be used in implant vessels or other applications. Selected strategies have been implemented to prepare a polyethylene-glycol-blocked polydimethylsiloxane for use in TPU preparation. Ciolino *et al.*²⁶ synthesized polybutadiene-*graft*-poly(dimethylsiloxane) and polyethylene-*graft*-poly(dimethylsiloxane) copolymers (PB-*g*-PDMS) *via* hydrosilylation.²⁶ The reaction was performed in a solution catalyzed by *cis*-dichlorobis(diethylsulfide)platinum(II) salt.

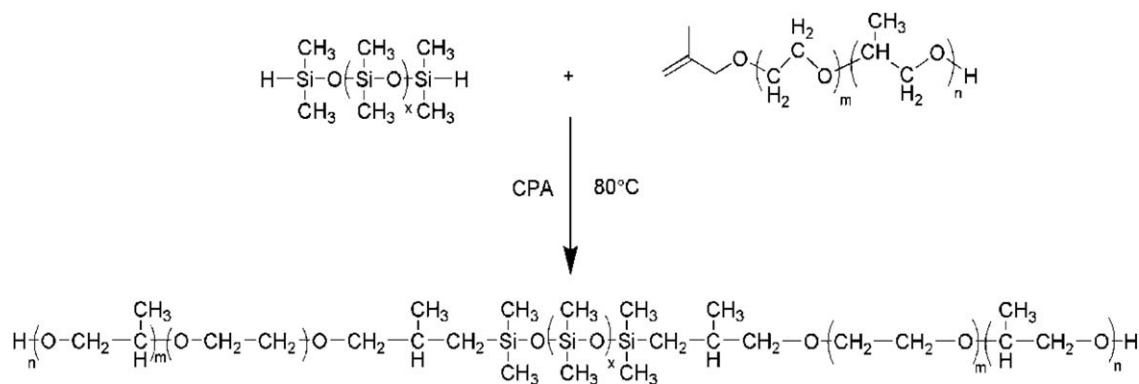
In this work, to efficiently combine the thermal performance benefit of PDMS and the good mechanical properties of polyether polyol in TPUs used as biomaterials in implant-vessel applications, a series of polydimethylsiloxane-polymethylallyloxy polyether (α,ω -dihydroxy-(PE-PDMS-PE)) ABA triblock oligomers were investigated. The PE-PDMS-PE triblock oligomers were synthesized using silanic fluids and methyl polyallyloxy polyethers in a one-step, solventless hydrosilylation reaction. The synthesized α,ω -dihydroxy-(PE-PDMS-PE) ABA copolymers contained different ethylene oxide (EO) and propylene oxide (PO) concentrations, which were characterized by ¹H-, ¹³C and ²⁹Si NMR spectroscopy techniques, and the molecular weights and distributions were analyzed by gel-permeation chromatography (GPC). The α,ω -dihydroxy-(PE-PDMS-PE) triblock oligomers were used to prepare thermoplastic polyurethanes that were reacted with MDI as soft segments, and 1,4-butanediol (BDO)/trimethylolpropane (TMP) were mixed and reacted with MDI to formulate the hard segments in a two-step, solventless, bulk polymerization. The mechanical performance, thermal performance, water contact angles, and morphological properties of the α,ω -dihydroxy-(PE-PDMS-PE)-modified TPUs were investigated in this work.

EXPERIMENTAL

Materials

Methyl hydrogen siloxanes ($\text{HMe}_2\text{SiO}(\text{Me}_3\text{SiO})_x\text{SiMe}_2\text{H}$ ($\text{M}^{\text{H}}\text{D}_x\text{M}^{\text{H}}$), $x = 8, 15, 20, 30, 40,$ and 50 , supplied by Momentive) were dried at room temperature under vacuum for 2 h. ¹H-NMR, ¹³C-NMR and ²⁹Si-NMR spectroscopy methods were used to analyze the molecular weights (M_n) of $\text{M}^{\text{H}}\text{D}_x\text{M}^{\text{H}}$, which varied in the range of 726–3836 g/mol. Methyl allyloxy polyether ($\text{CH}_2=\text{CH}(\text{CH}_3)-\text{CH}_2-\text{O}-(\text{EO})_m-(\text{PO})_n-\text{H}$ supplied by Huangma ($m = 0-10.5$; $n = 0-24$) was dried at 100°C under vacuum for 4 h. Chloroplatinic acid (CPA) in ethanol solution (Momentive) was used as a hydrosilylation catalyst.

4,4'-Methylenediphenyl diisocyanate (MDI, Bayer) with an isocyanate content of 33.6 wt % was used as received. 1,4-Butanediol (BDO, Aldrich) was purified by vacuum distillation. Trimethylolpropane (TMP, BASF) was dissolved in BDO at a



Scheme 1. α,ω -dihydroxy-(PE-PDMS-PE) hydrosilylation reaction.

weight ratio of 1 : 20 (this solution is hereafter referred to as BDP) and used as a chain extender for producing TPUs. Acrol 1021, a polypropylene glycol (PPG) with a 2-functional hydroxyl group and a molecular weight of 2000, was supplied by Bayer.

Synthesis

α,ω -Dihydroxy-(PE-PDMS-PE) ABA Triblock Oligomers. An olefinically substituted polyoxymethylalkylene with an average formula of $\text{CH}_2=\text{CH}(\text{CH}_3)-\text{CH}_2-\text{O}-(\text{EO})_m-(\text{PO})_n-\text{H}$ and an organohydrogen polysiloxane with an average formula of $\text{HMe}_2\text{SiO}(\text{Me}_3\text{SiO})_x\text{SiMe}_2\text{H}$ were combined in a mole ratio of 2 : 1 in a well-stirred mixture that was subsequently slightly sparged with nitrogen. The flask was then heated to 80°C . A solution of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in ethanol was added to the mixture in a sufficient amount to provide 10 ppm Pt. The heat source was removed, and the exothermic hydrosilylation reaction was allowed to proceed until no further temperature increase was

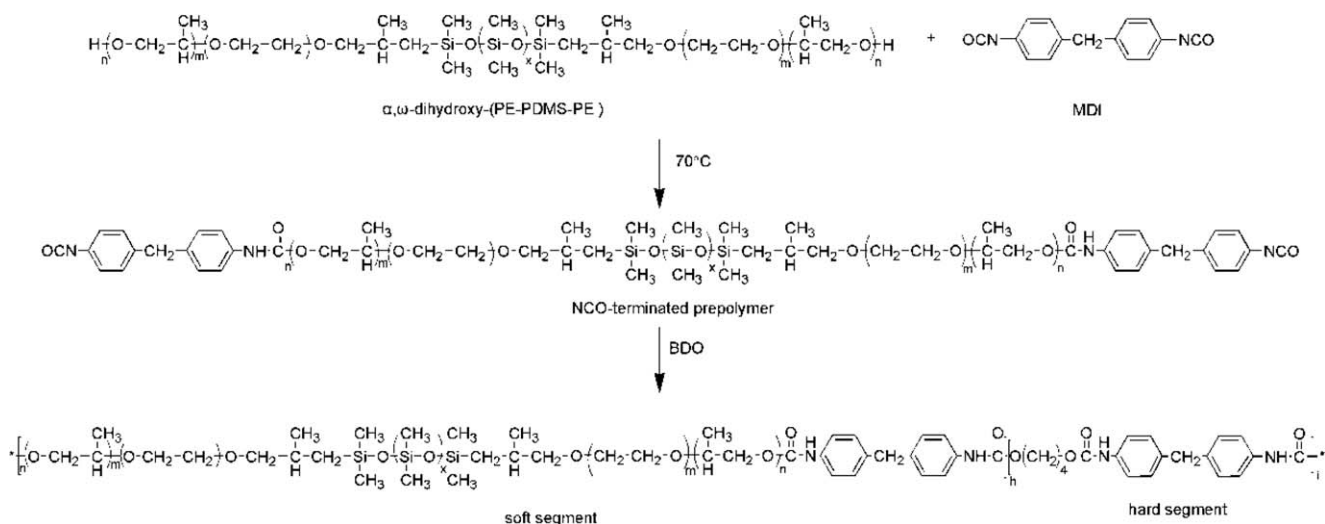
noted. The maximum temperature reached was 105°C , and the flask was allowed to maintain this temperature for 1.5 h. The residual silanic hydrogen (SiH) content was measured and was observed to be undetectable, which meant that the hydrosilylation reaction was complete. The copolymer was stripped at 100°C for 4 h to remove residue dimethylsiloxane tetramer (D4) from the copolymer, and the copolymer was allowed to cool to 25°C before being filtered. The α,ω -dihydroxy-(PE-PDMS-PE) hydrosilylation reaction is shown in Scheme 1.

A series of α,ω -dihydroxy-(PE-PDMS-PE) ABA triblock oligomers were prepared according to the compositions listed in Table I.

α,ω -Dihydroxy-(PE-PDMS-PE) ABA Triblock-Oligomer-Prepared TPUs. TPUs were synthesized using a two-step bulk polymerization method without a solvent. The reactants were MDI, BDO, TMP, and α,ω -dihydroxy-(PE-PDMS-PE) (M_n range from 2270 to 5100 g/mol). The molar ratio between

Table I. α,ω -Dihydroxy-(PE-PDMS-PE) ABA Triblock Oligomers Composition

ABA series	B Block M'DxM' D number x	A Block $\text{CH}_2=\text{CH}(\text{CH}_3)-\text{CH}_2-\text{O}-(\text{EO})_m-(\text{PO})_n-\text{H}$				ABA M_w calculated (g/mol)	
		EO number number m	PO number n	M_w (g/mol)	EO % PO %		
ABA-1	15	10	0	512	100	0	2270
ABA-2	15	10.5	8	1000	50	50	3246
ABA-3	20	10.5	8	1000	50	50	3616
ABA-4	30	10.5	8	1000	50	50	4356
ABA-5	20	10	0	512	100	0	2640
ABA-6	30	10	0	512	100	0	3380
ABA-7	40	10.5	8	1000	50	50	5096
ABA-8	50	10.5	8	1000	50	50	5836
ABA-9	40	10	0	512	100	0	4120
ABA-10	50	10	0	512	100	0	4860
ABA-11	15	0	16	1000	0	100	3246
ABA-12	15	0	24	1500	0	100	4246
ABA-13	8	0	16	1000	0	100	2728
ABA-14	20	0	16	1000	0	100	3616
ABA-15	30	0	16	1000	0	100	4356
ABA-16	40	0	16	1000	0	100	5096



Scheme 2. ABA-modified thermal polyurethane elastomers 2-step bulk polymerization.

the reacting $-\text{NCO}$ groups (from MDI) and the $-\text{OH}$ groups (from BDP and α,ω -dihydroxy-(PE-PDMS-PE), respectively) was fixed at 1.02. The content of the hard segment was fixed at 30% by weight, and the reaction temperature was optimized at 70°C . All of the TPU synthesis was performed in a four-neck, round-bottom flask equipped with a mechanical stirrer, a dry nitrogen inlet, a reflux condenser and a dropping funnel. The flask was placed in a silicone oil bath. A typical synthesis for the sample TPU-4 copolymer using α,ω -dihydroxy-(PE-PDMS-PE) with a molecular weight of 3700 g/mol soft segment is described as an example. The starting reaction mixture of 60 g (0.162 mol) of α,ω -dihydroxy-(PE-PDMS-PE) and 33.3 g (0.133 mol) of MDI was added to a flask at room temperature and heated to 70°C under a nitrogen atmosphere. Next, the remaining 40 g (0.108 mol) of α,ω -dihydroxy-(PE-PDMS-PE) was added dropwise to the flask *via* the dropping funnel. The reaction mixture was stirred for 150 min at 70°C to prepare the isocyanate-terminated prepolymer. The NCO content during the reaction was analyzed using the standard dibutylamine back-titration method.²⁷ The first-step prepolymer preparation was completed when the prepolymer NCO content reached 6.69%. Next, 60 g of prepolymer and a stoichiometric amount of BDP (3.85 g, 0.428 mol) were blended together using a stirring machine. The mixture was

stirred for 3 min and cast onto a Teflon[®] plate, which was placed in an oven at 100°C for 1 h and subsequently dried under vacuum at 90°C for 12 h. The cast TPU materials were maintained at room temperature for 7 days before their properties were tested. The TPU elastomer preparations are shown in Scheme 2.

Three different α,ω -dihydroxy-(PE-PDMS-PE) triblock oligomers were used to prepare thermoplastic polyurethane elastomers; their compositions are listed in Table II.

Characterization

Infrared Spectroscopy (FT-IR). A Fourier-transform infrared spectrophotometer (FT-IR) (Nicolet 6700 spectrometer, USA) was used to identify α,ω -dihydroxy-(PE-PDMS-PE) ABA copolymer functional groups. The scanning range spanned 500 to 4000 cm^{-1} at a resolution of 4 cm^{-1} , and 64 scans were collected for each sample.

Gel-Permeation Chromatography. Gel-permeation chromatography (GPC) was performed on a Waters 600E chromatograph equipped with a refractive-index detector and three Supelco PL-Gel columns. As a mobile phase, THF was used at 60°C and with a flow rate of 1.0 mL/min, and a GPC universal calibration curve was established using polystyrene as the calibration standard.

Table II. Thermoplastic Polyurethane Elastomers Composition

TPU Series	Composition molar ratio ^a	PDMS block M_w (g/mol)	A block type	A block M_w (g/mol)	Theoretic NCO content (%)
TPU-1 ^b	0.56 : 1.59 : 1.00	/	PPG	2000	5.56
TPU-2 ^c	0.38 : 1.41 : 1.00	1600	All EO	512	6.19
TPU-3 ^d	0.25 : 1.28 : 1.00	1600	EO/PO	1000	6.69
TPU-4 ^e	0.25 : 1.28 : 1.00	1600	All PO	1000	6.69

^a ABA:MDI:BDP:NCO/OH = 1.02.

^b TPU-1 is made by Arcol 1021.

^c TPU-2 is made by ABA-5 with 20 Siloxane D units, all EO with 512 M_w .

^d TPU-3 is made by ABA-3 with 20 Siloxane D units, 50%EO and 50% PO with 1000 M_w .

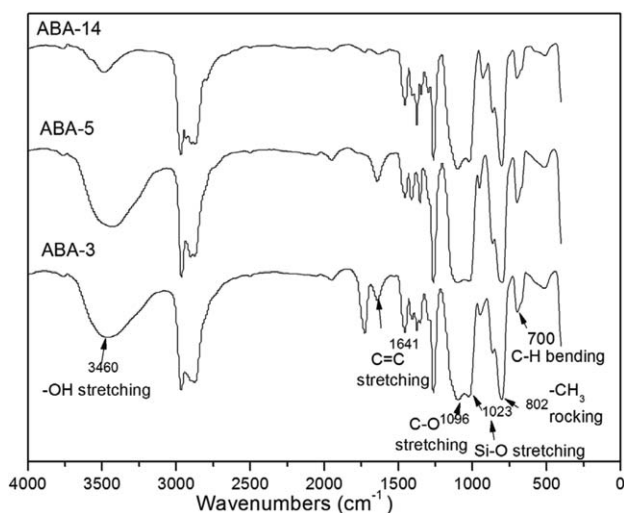
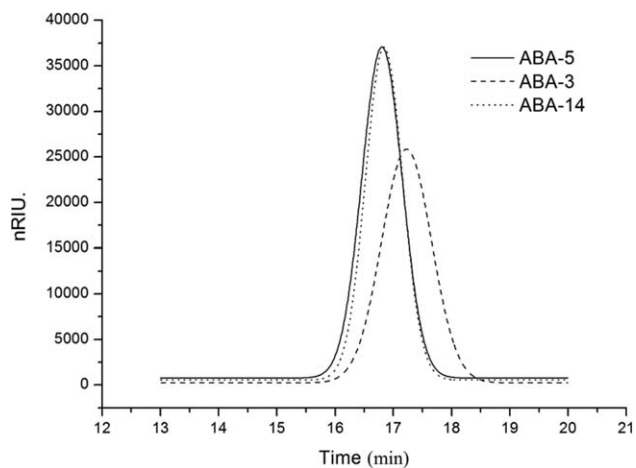
^e TPU-4 is made by ABA-14 with 20 Siloxane D units, 100% PO with 1000 M_w .

Table III. GPC Analysis of the α,ω -Dihydroxy-(PE-PDMS-PE) ABA Copolymers

Polymer	M_n (g/mol)	M_w (g/mol)	$D (M_w/M_n)$
ABA-1	2500	4500	1.29
ABA-2	3600	4700	1.32
ABA-3	4500	5400	1.20
ABA-4	5000	6300	1.27
ABA-5	2700	3600	1.31
ABA-6	3300	4600	1.39
ABA-7	5600	7200	1.29
ABA-8	5900	7900	1.32
ABA-9	3900	5500	1.41
ABA-10	4200	6300	1.48
ABA-11	3500	4400	1.26
ABA-12	4600	5700	1.22
ABA-13	3700	4000	1.09
ABA-14	3700	4900	1.34
ABA-15	4200	5600	1.31
ABA-16	5400	6900	1.27

The experimental results of these characterizations are summarized in Table III.

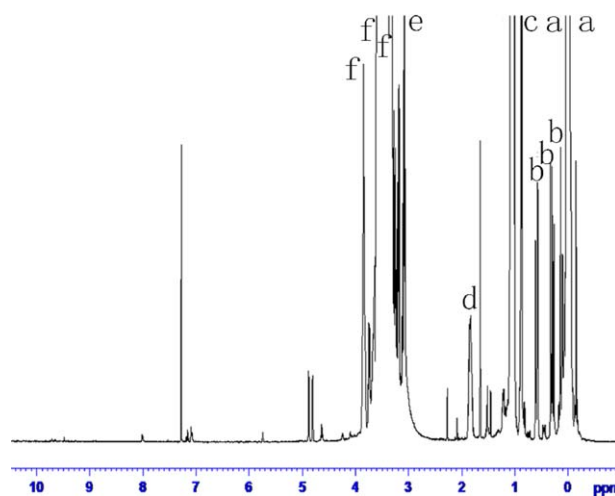
^1H , ^{13}C , and ^{29}Si NMR Analyses. The NMR experiments were performed on Bruker UltrashieldTM 400 spectrometer equipped with a 4-mm inverse-detection z-gradient probe. The ^1H , ^{13}C , and ^{29}Si NMR spectra were measured at 25°C using 0.5 ml of CDCl_3 to dissolve 40 mg samples. The ^1H NMR spectra were recorded at 127°C with an accumulation of 16 scans to determine the chemical structure of methyl allylpolyoxide and the EO/PO units of the α,ω -dihydroxy-(PE-PDMS-PE) ABA copolymers. The ^{13}C NMR spectra were recorded at 127°C with an accumulation of 1024 scans (0.29 Hz/point resolution) to determine the chemical structure of siloxane grafted by polyether.

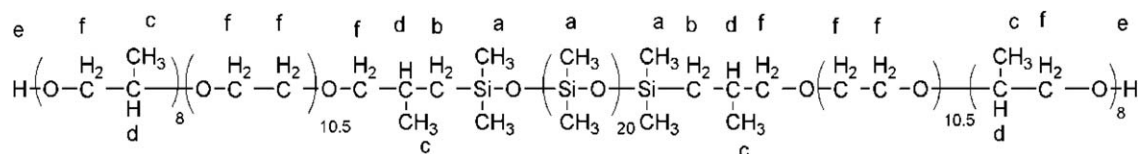
**Figure 1.** ATR-FTIR Spectrum of α,ω -dihydroxy-(PE-PDMS-PE) ABA-3, ABA-5, and ABA-14.**Figure 2.** GPC Spectrum of α,ω -dihydroxy-(PE-PDMS-PE) ABA-3, ABA-5, and ABA-14.

The ^{29}Si NMR spectra was used to determine the siloxane repeat number and the Si—C structure.

Differential Scanning Calorimetry. Differential scanning calorimetry (DSC) was performed on a Q2000 V23.12 Build 103 differential scanning calorimeter; the samples were scanned under a nitrogen atmosphere at a heating rate of 10°C/min and a cooling rate of 20°C/min over a temperature range of -150 to 200°C. The weight of the samples was approximately 5 mg. In the first scan, the samples were heated from room temperature to 220°C to eliminate their thermal history. The samples were subsequently cooled to -150°C and finally heated to 220°C.

Scanning Electron Microscopy. The surfaces or “air exposed” areas and cross-section morphologies of urethane-siloxane-based TPUs were analyzed *via* field-emission scanning electron microscopy. The samples were adhered to aluminum sample holders and sputter-coated with an Au layer. The TPU images were obtained using a JEOL JSM-6460LV microscope, and

**Figure 3.** ^1H NMR of α,ω -dihydroxy-(PE-PDMS-PE) ABA-3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Scheme 3. ABA-3 structure with marking alphabet linked to ^1H NMR.

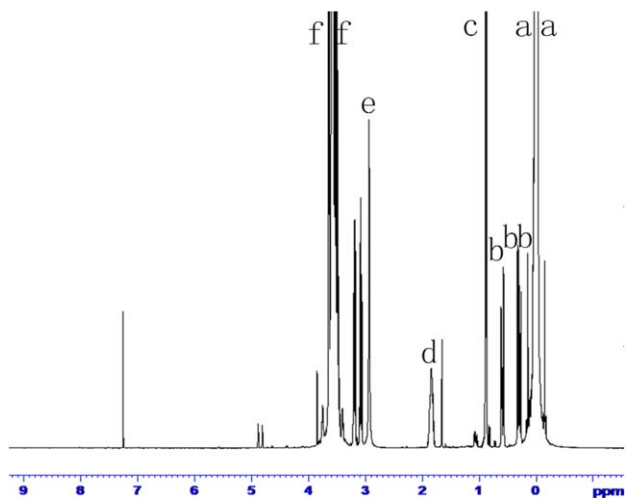


Figure 4. ^1H NMR of α,ω -dihydroxy-(PE-PDMS-PE) ABA-5. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

microphotographs were obtained at a working distance of 10 mm and an acceleration voltage of 20 kV.

Transmission Electron Microscopy. TPU copolymers morphology performance was investigated *via* transmission electron microscopy (TEM). TEM model was JEM-1230EX and an acceleration voltage was 120 kV. The samples were cut under liquid N_2 cooling condition and the sample thickness was 70–100 nm.

Water Contact Angle (WCAs). The water contact angles of the TPU copolymer films were measured using a Krüss DSA100 machine according to the sessile drop method. A single, 20- μL drop of distilled water was deposited onto the TPUs' film surface, and the contact angle at 26°C was recorded after 30 s using a camera connected to a computer. The final contact-angle values were taken as the average of five measurements.

Thermogravimetric Analysis (TGA). The thermal stability of the copolymers was determined using a Q5000 V3.5 Build 252 thermogravimetric analyzer; the samples were heated in the temperature range of 25 to 700°C at a heating rate of 10°C/min. The TGA scans were recorded under a dynamic nitrogen

atmosphere with a flow rate of 25 ml/min. The average weight of the samples was approximately 10 mg.

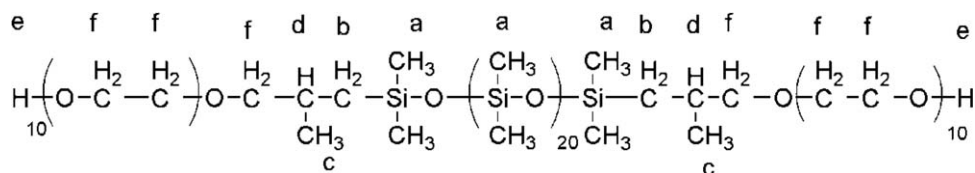
Mechanical Property Tests. Mechanical property tests were performed using an Instron 4302 universal testing machine with a 1-kN load cell and a crosshead speed of 500 mm/min. At least three pieces of each sample were tested to determine the ultimate tensile strength, ultimate elongation and elastic modulus at 100% elongation. The average results for three pieces of each sample were used as the final data values. The sample length for the tensile tests was 12.5 cm.

RESULTS AND DISCUSSION

α,ω -Dihydroxy-(PE-PDMS-PE) ABA Triblock Oligomer Characterization

FT-IR Spectra. Figure 1 displays a portion of the IR spectra of the α,ω -dihydroxy-PE-PDMS-PE triblock oligomers and their various copolymer series with different EO and PO concentrations. The absorption of the characteristic peak at 802 cm^{-1} (Si-CH₃ rocking band) showed incorporation of the PDMS segment with methyl allylpolyethers to formulate the ABA copolymer structure. The absorption of the characteristic peaks occurred at approximately 700 cm^{-1} (symmetric C-H bending band), 1023 cm^{-1} (Si-O-Si stretching band), and 1097 cm^{-1} (C-O stretching band), and no peak was observed at 2200 cm^{-1} (Si-H stretching band), which doubly confirmed that the siloxane chain was well coordinated with the methyl allylpolyether. The absorption of the characteristic peak at approximately 3460 cm^{-1} (—OH stretching band) indicated that the ABA copolymers were capped by hydroxyl groups. The FT-IR spectra of ABA-3, ABA-5 and ABA-14 were similar to each other.

GPC Analysis. The different structures of α,ω -dihydroxy-(PE-PDMS-PPE) ABA triblock oligomers and their molecular weights and distributions were analyzed by GPC; the results are shown in Table III. The molecular-weight data showed that the M_n values of 16 ABA copolymers were in the range of 2,400 to 6,000. The GPC curves of ABA-3, ABA-5 and ABA-14 are presented together in Figure 2 and are representative of the entire set. We observed that the ABA copolymers exhibited a large and sharp high molecular weight curve, which indicates that methyl allylpolyether hydrosilylated ABA oligomers created a pure



Scheme 4. ABA-5 structure with marking alphabet linked to ^1H NMR.

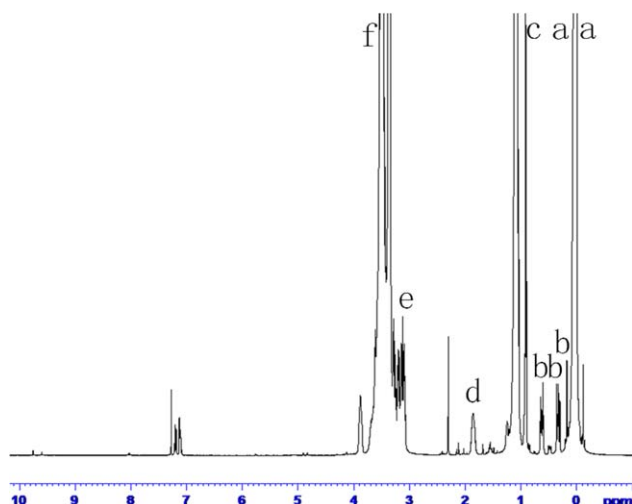


Figure 5. ^1H NMR of α,ω -dihydroxy-(PE-PDMS-PE) ABA-14. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

copolymer in the absence of excess methyl allylpolyether. If the ABA copolymers were created by allylpolyethers, this process would require at least a 30% allylpolyether excess to reach 100% hydrosilylation completion, so there was mono allylpolyethers residue in the final ABA oligomers. The mono polyether reacted with NCO to terminate the polymerization resulting in poor mechanical properties. As shown in Figure 2, the GPC curve of ABA-14 shows a single sharp peak at $M_n = 3,700$, which is similar to the methodologically calculated ABA-14 M_n of 3,675. The results show that ABA-14 had a calculated structure with 20 units of D in the central siloxane backbone linearly linked by methyl allyl polyether polyol ($M_n = 1,000$) in the absence of excess methyl allyl polyether polyol.

^1H NMR Spectroscopy. The ^1H NMR spectra of ABA-3, ABA-5 and ABA-14 displayed the following results. The first integrated peak area appeared as two resonance peaks between -0.3 and 0.1 ppm and was marked as “a”. These peaks were assigned to the contribution of ^1H from methyl silicone groups ($-\text{Si}(\text{CH}_3)-\text{CH}_2-$), and their presence indicated that methyl allylpolyether links combined with $\text{Si}-\text{H}$ groups. The second integrated peak areas appeared as three resonance peaks between 0.2 - 0.6 ppm and were marked as “b”; these peaks were assigned to the contribution of ^1H from methylallyl groups ($-\text{Si}(\text{CH}_3)-\text{CH}_2-$). The next integrated peak area with a resonance peak at approximately 1.0 ppm was marked as “c”; these peaks were assigned to the contribution of ^1H from methyl groups linked with $-\text{CH}-\text{CH}_2-$ ($\text{CH}_3-\text{CH}(\text{CH}_2)-$). The integrated peak area marked as “d” with a resonance peak between

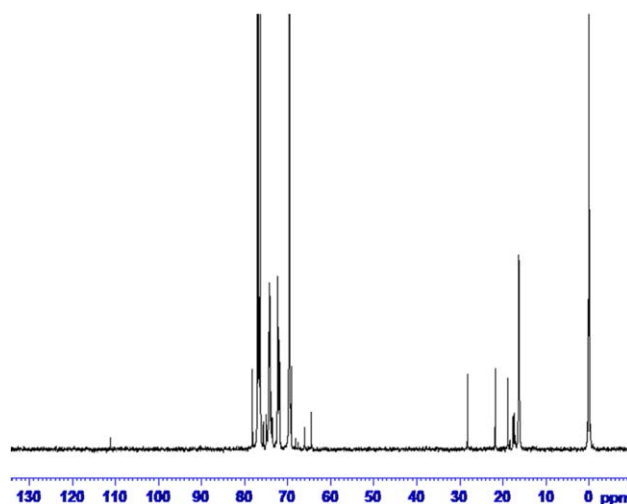


Figure 6. ^{13}C NMR of α,ω -dihydroxy-(PE-PDMS-PE) ABA-3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

1.2 and 1.8 ppm was assigned to the contribution of ^1H from the carbon hydrogen groups ($-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{CH}_2$). The integrated peak marked as “e”, with a resonance peak between 3.2 and 3.4 ppm, was assigned to the contribution of ^1H from the hydroxyl groups. The integrated peak marked as “f”, with a resonance peak between 3.5 and 3.8 ppm, was assigned to the contribution of ^1H from the $-\text{CH}_2-\text{O}$ groups ($-\text{CH}_2-\text{O}-$).

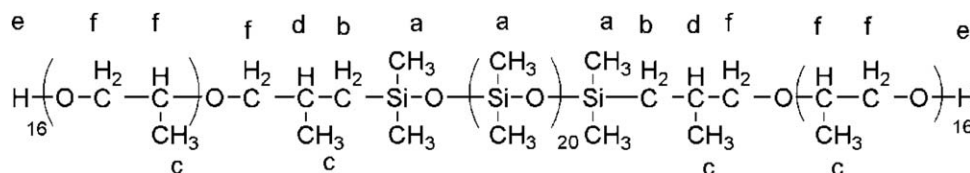
The ^1H NMR spectrum of ABA-3 is shown in Figure 3; it indicates that ABA-3 has a $\text{Si}-\text{C}$ backbone, 10.5 repeated EO units and 8 repeated PO units. The structure of ABA-3 is shown in Scheme 3.

The ^1H NMR spectrum of ABA-5 is shown in Figure 4; it indicates that ABA-5 has a $\text{Si}-\text{C}$ backbone, 10 repeated EO units and no PO units. The structure of ABA-5 is shown in Scheme 4.

The ^1H NMR spectrum of ABA-14 is shown in Figure 5; it indicates that ABA-14 has a $\text{Si}-\text{C}$ backbone, 16 repeated PO units and no EO units. The structure of ABA-14 is shown in Scheme 5.

^{13}C NMR Spectroscopy. The ^{13}C NMR determination of the chemical structure of polyalkylene glycol and the capping group is a well-established method. In the ABA copolymer spectra, the signals corresponding to $\text{Si}-\text{CH}_3$ appeared at 0 ppm, those corresponding to the $-\text{CH}_2-\text{CH}-$ and $-\text{CH}_2-\text{CH}_2-$ groups appeared between 18 and 27 ppm, and that corresponding to the $-\text{CH}_2-\text{O}$ groups appeared between 60 and 78 ppm.

The ^{13}C NMR spectrum of ABA-3 is shown in Figure 6; it indicates that ABA-3 has a $\text{Si}-\text{C}$ backbone and random repeated



Scheme 5. ABA-14 structure with marking alphabet linked to ^1H NMR.

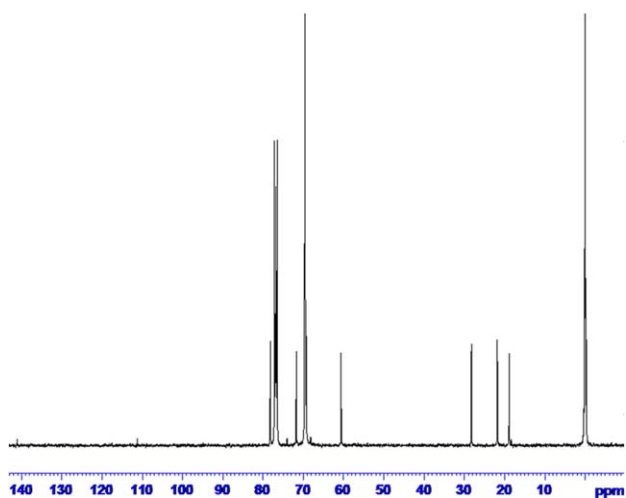


Figure 7. ^{13}C NMR of α,ω -dihydroxy-(PE-PDMS-PE) ABA-5. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

EO/PO units with hydroxyl capping groups. The structure of ABA-3 is shown in Scheme 3.

The ^{13}C NMR spectrum of ABA-5 is shown in Figure 7; it indicates that ABA-5 has a Si—C backbone and 100% EO units with hydroxyl capping groups. The structure of ABA-5 is shown in Scheme 4.

The ^{13}C NMR spectrum of ABA-14 is shown in Figure 8; it indicates that ABA-14 has a Si—C backbone and 100% random repeated PO units with hydroxyl capping groups. The structure of ABA-14 is shown in Scheme 5.

^{29}Si NMR Spectroscopy. The ^{29}Si NMR technique is an efficient and accurate method for determining the structure of silicone polymers, which are composed of Si—O and Si—CH₂— groups. The ABA-3, ABA-5 and ABA-14 ^{29}Si NMR spectra are, respectively displayed in Figures 9–11. The signal at 7 ppm was

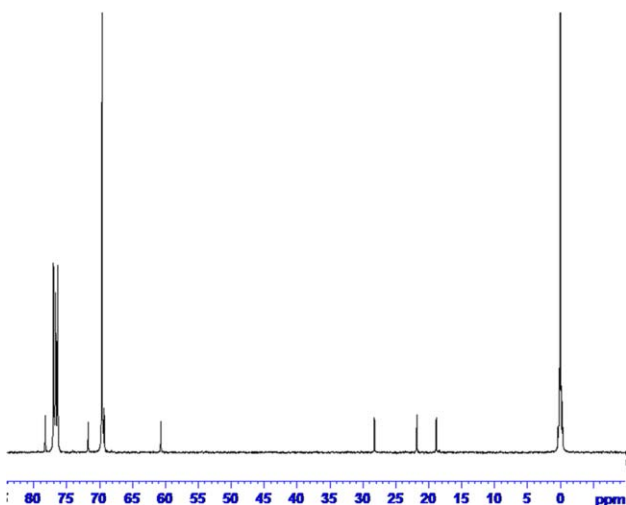


Figure 8. ^{13}C NMR of α,ω -dihydroxy-(PE-PDMS-PE) ABA-14. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

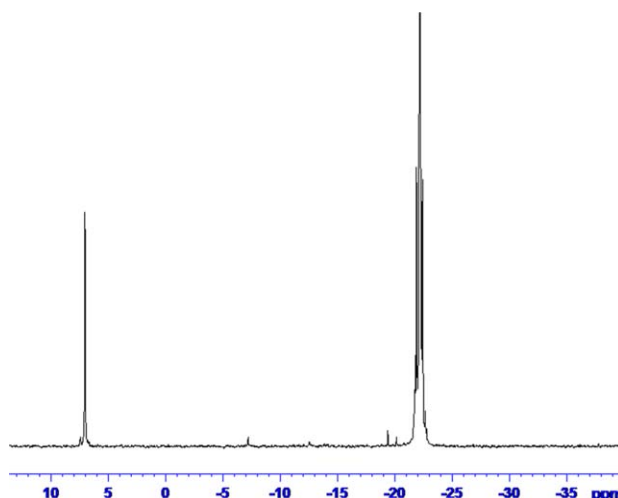


Figure 9. ^{29}Si NMR of α,ω -dihydroxy-(PE-PDMS-PE) ABA-3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

assigned to —Si—CH₂— groups, and the signals between —20 and —23 ppm were assigned to —Si—O groups. The presence of two Si—CH₂ groups indicates that the copolymers have linear backbones, and the 20 Si—O groups indicate that the polymer contained the designed number of repeated D units. The ^{29}Si NMR spectra doubly confirmed the ABA copolymer structures shown in eqs. (3), (4) and (5).

Thermal Properties of the TPUs

DSC Analysis of the TPUs. T_g of synthesized TPU samples were measured *via* DSC at a heating rate of 10°C/min under nitrogen atmosphere. The DSC curves of the TPU samples obtained during the second heating run are shown in Figure 12. The values of T_g and T_m are tabulated in Table IV. On the basis of the results of the DSC curves shown in Figure 12 and the values of T_g , we concluded that TPU-1 produced by PPG did not exhibit a lower T_g . It could be explained by the structure of

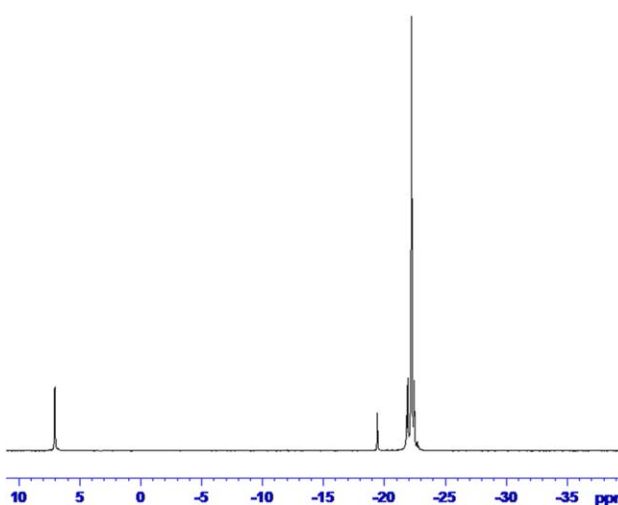


Figure 10. ^{29}Si NMR of α,ω -dihydroxy-(PE-PDMS-PE) ABA-5. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

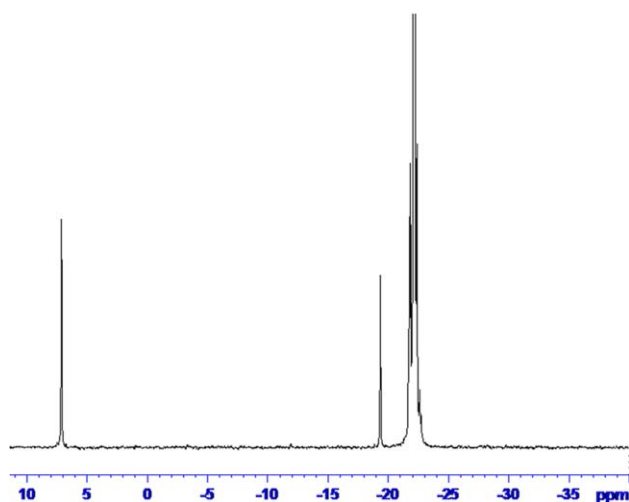


Figure 11. ^{29}Si NMR of α,ω -dihydroxy-(PE-PDMS-PE) ABA-14. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

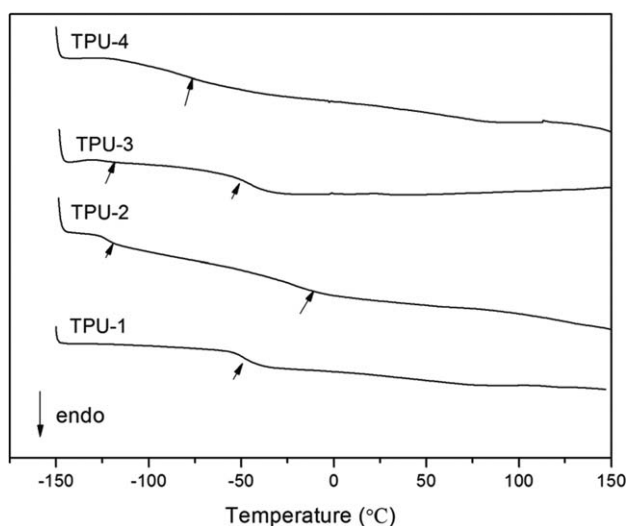


Figure 12. DSC Analysis Curves of TPUs.

urethane did not provide a low T_g under -100°C . However, TPU-2, TPU-3 and TPU-4, which were specifically produced from ABA-5, ABA-3 and ABA-14, respectively, exhibited a lower T_g (-123°C), indicating that the PDMS backbone was incorporated into the polyurethane elastomer matrix, which significantly improved its low temperature performance. It could be

explained that silicone chain had the low T_g under -120°C . T_g of the siloxane phase (-120°C) was detected in the differential thermograms of the PE-PDMS-PE triblock-oligomer-prepared TPUs but was not detected in the differential thermograms of TPU-1, which was produced using a non-PDMS-modified TPU. This result indicates that use of α,ω -dihydroxy-(PE-PDMS-PE) ABA triblock oligomers instead of polyether polyol dramatically improves the TPU's low-temperature performance and widens the material processing window.

TGA of the TPUs. The thermal stability and degradation of the TPU samples were investigated by TGA, as shown in Figures 13 and 14. The characteristic temperatures for weight losses of 5%, 50%, and 90% and the residual weight at 600°C are listed in Table IV. The weight loss of the TPU copolymers began between 281 and 295°C , as evident from the temperature of 5% weight loss. On the basis of the presented results, the thermal stability of the TPU samples was concluded to increase with increasing molecular weight of the PDMS block. The temperature of 5% TPU copolymer weight loss increases when the silicone content increases in the TPU copolymer. It could be explained that high silicone content had the better high temperature resistance performance. However, the degradation of the copolymers between 50 and 90% was strongly affected by the PDMS-block molecular weight. This result can be explained if the urethane bonds and the urethane components decomposed at temperatures lower than 350°C (50% weight loss) and the PDMS block degraded between 300 and 450°C , as indicated by the DTG curves in Figure 14. On the basis of the analysis of the TGA results, the mechanism of thermal degradation of the TPU copolymer produced by PE-PDMS-PE triblock oligomers was concluded to be slower than that of the PPG-produced TPU. Therefore, the PE-PDMS-PE triblock-oligomer-based TPUs can be used as a temperature-resistant material.

SEM Analysis of the TPUs. Scanning electron microscopy (SEM) micrographs of two representative TPU copolymer films (TPU-1 and TPU-4) are displayed in Figures 15 and 16, respectively. TPU-1 is a PPG produced TPU copolymer and TPU-4 is a PE-PDMS-PE produced TPU copolymer. The brighter regions in the micrographs represent hard domains, and the darker regions represent the soft-segment-rich matrix. TPU-1 produced by PPG clearly exhibits two clear separated phases. But the hard segments of TPU-1 are well distributed because the higher hydrogen intensity during the TPU copolymer preparation. It could be explained that soft segment and hard segment bind each other since the high hydrogen intensity. The hard domains

Table IV. Thermal Analysis Performance of TPUs

Sample	T_{g1} ($^\circ\text{C}$)	T_{g2} ($^\circ\text{C}$)	5% ($^\circ\text{C}$)	50% ($^\circ\text{C}$)	90% ($^\circ\text{C}$)	Residual weight at 600°C , %	T_{max}
TPU-1	NA*	-44.2	281	340	361	2.21	342/352/580
TPU-2	-122.2	-21.3	292	379	447	2.80	322/392/522
TPU-3	-123.5	-44.3	291	378	428	2.68	320/389/571
TPU-4	-85.51	NA*	295	350	466	3.35	345/537/646

NA*: Not analyzed.

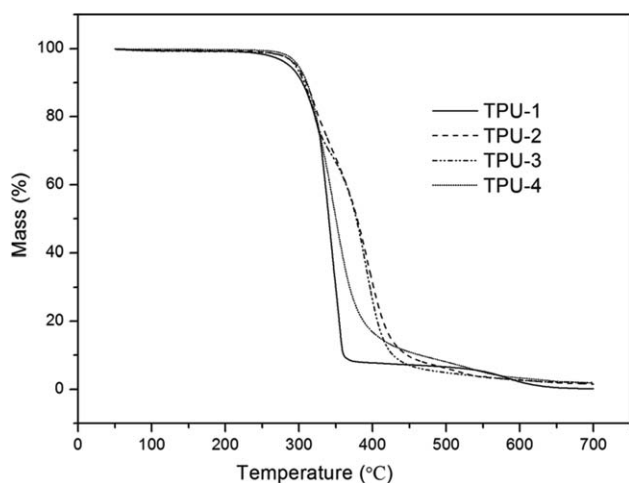


Figure 13. TGA Analysis Curves of TPUs.

provide the excellent mechanical properties which will be discussed later of this paper. TPU-4 produced by the PE-PDMS-PE oligomer contains two phases; however, the hard segment is uniformly distributed around the soft segment. This indicates that PE-PDMS-PE triblock oligomer significantly improves the soft segments and hard segments phase separation. It could be explained by two methodologies. One methodology is that PE-PDMS-PE has the less hydrogen intensity compared to polyether. The less hydrogen intensity results in less binding between soft segment and hard segment, so the two phases have the improved separation. Another methodology is that PE-PDMS-PE has the excellent surfactant performance improved the mixing efficiency during the TPU copolymer preparation. PE-PDMS-PE has hydrophobic groups (such as PDMS) and hydrophilic groups (such as PE) which give the good emulsification performance for mixing PE-PDMS-PE with MDI and BDP.

Compared the SEM micrograph of TPU-1 to TPU-4, we could clearly tell that TPU-1 has the higher intensity of brighter regions and TPU-4 has the higher intensity of darker regions. That means that PPG produced PU elastomer TPU-1 has much higher intensity of hard domains than PE-PDMS-PE produced PU elastomer TPU-4. Since the hard domain contributes to PU

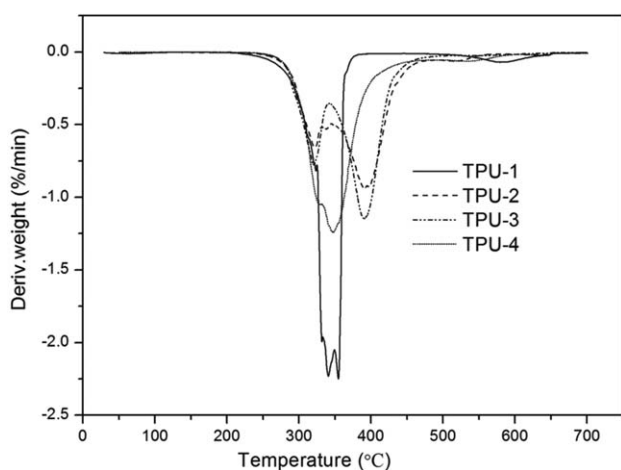


Figure 14. DTG Analysis Curves of TPUs.

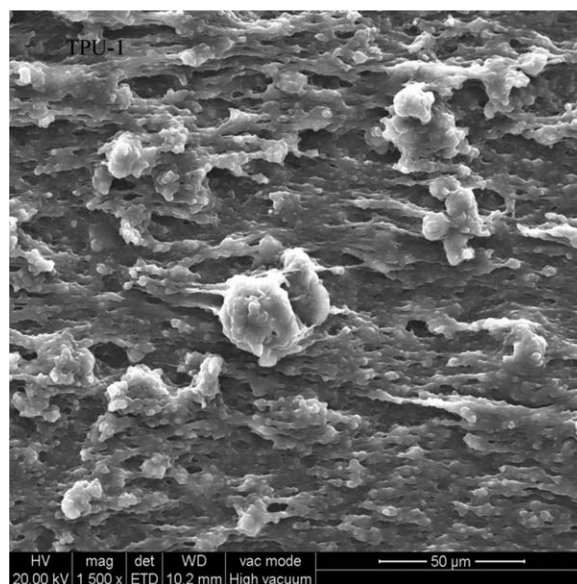


Figure 15. TPU-1 SEM.

elastomer's mechanical properties, TPU-4 has the worse mechanical properties than TPU-1, which was double confirmed to the mechanical properties discussion. PE-PDMS-PE oligomers produced PU elastomers have a two-phase separation and a higher intensity of soft domains which result in poor mechanical properties than non-silicone modified pure PPG produced PU elastomer.

As displayed in Figure 15, SEM micrograph of TPU-1 has a two-phase separation morphology performance as typical PU elastomer. However, SEM micrograph of TPU-4 displayed in Figure 16 has some domains between hard domain and soft domain, which could be silicone domain. The silicone domain helps the PE-PDMS-PE oligomer produced TPU polymer the improved thermal performance, especially the weight loss of the TPU copolymers increased from 281°C to 295°C. In TPU

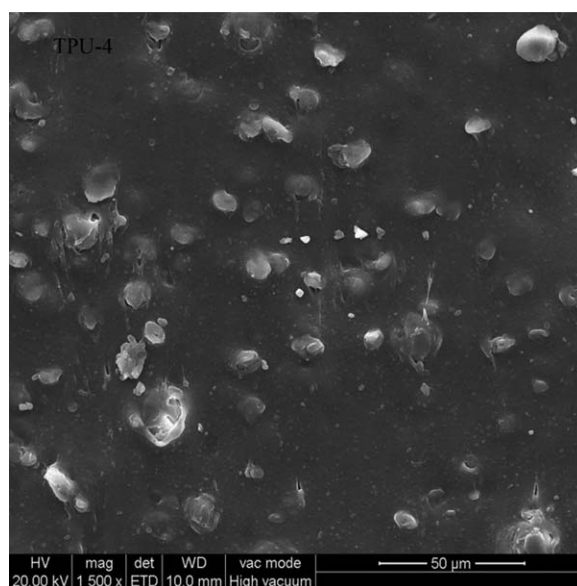


Figure 16. TPU-4 SEM.

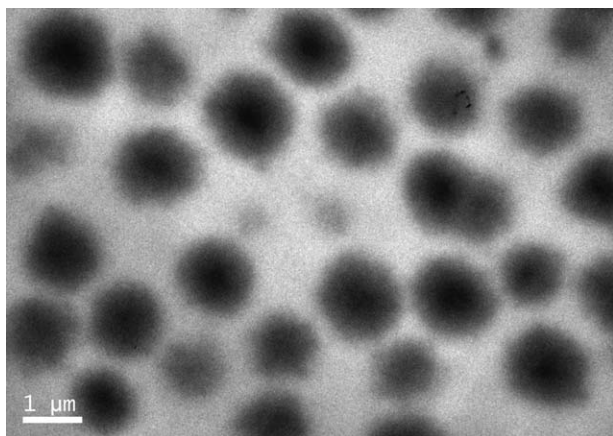


Figure 17. TEM graph of TPU-1 made by PPG.

polymer, the hard segment polymer chain with urea group starts to break out firstly when the polymer is heated to higher temperature. TPU-4 has the silicone domain as shown in the SEM micrograph that increases the thermal stability of PU elastomer. This result confirms to TPU thermal properties discussion. With the siloxane chain in the middle of PE-PDMS-PE oligomers, the final TPUs have silicone domains between hard domain and soft domain that results in PE-PDMS-PE produced PU elastomers having a lower T_g and a higher polymer weight loss temperature.

TEM Analysis of the TPUs. In order to further investigate the TPUs' morphology performance, TEM was used to analyze the phase separation and characterize the PE-PDMS-PE structure impact on the morphology. Based on the above SEM discussion, we could draw a conclusion that TPUs have the clear two phase separation and PE-PDMS-PE modified TPU-4's two phases have better separation than PPG produced TPU-1. Figure 17 is the TEM picture of TPU-1 copolymer made by PPG, MDI and BDP. In TPU-1's TEM picture, brighter domain and darker domain have a clear separation, and they bind each other tightly, which has been discussed in SEM analysis and has the same conclusion.

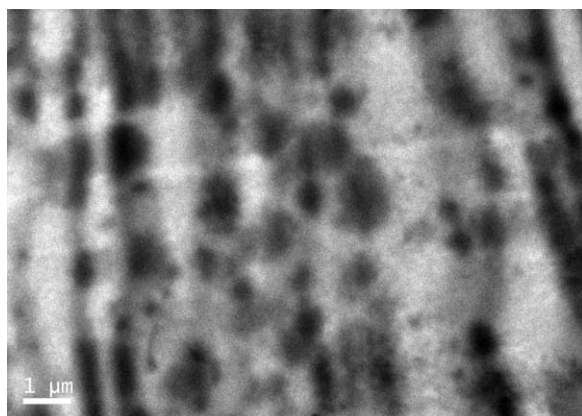


Figure 18. TEM graph of TPU-2 made by all EO PE-PDMS-PE.

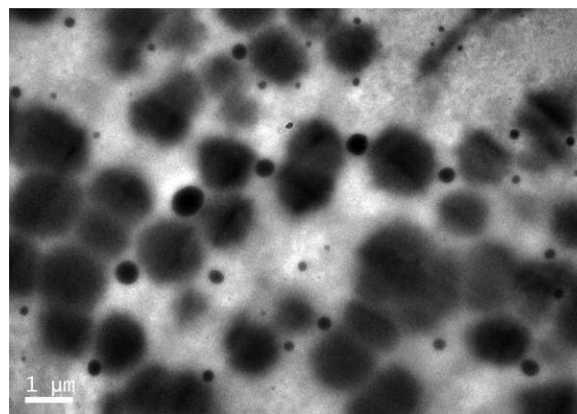


Figure 19. TEM graph of TPU-3 made by EO/PO PE-PDMS-PE.

Figure 18 is the TEM picture of TPU-2 copolymer made by PE-PDMS-PE having all EO and EO molecular weight 512. Soft segments separate away from hard segments. But in certain area, there are some polymer crystallizations which could be caused by all EO structure in the polymer matrix. Since the polymer crystallization investigated by TEM, TPU-2 has the worst mechanical properties among those four TPUs. Figure 19 is the TEM picture of TPU-3 copolymer made by PE-PDMS-PE having EO/PO random and molecular weight 1000. Soft segments clearly separate away from hard segments, and there are some round balls accumulated together between brighter domain and darker domain. They could be silicone groups accumulated together which possibly results in a pseudo-three phases' separation. And every phase is well distributed in the copolymer morphology. Figure 20 is the TEM picture of TPU-4 copolymer made by PE-PDMS-PE having all PO and molecular weight 1000. It has a clear phase separation between soft segments and hard segments, and a clear pseudo-third phase which could come from silicone chains accumulation. Since the even distribution of three-phase in TPU-4 morphology, TPU-4 has the good mechanical performance than TPU-2 and TPU-3, which will be discussed later.

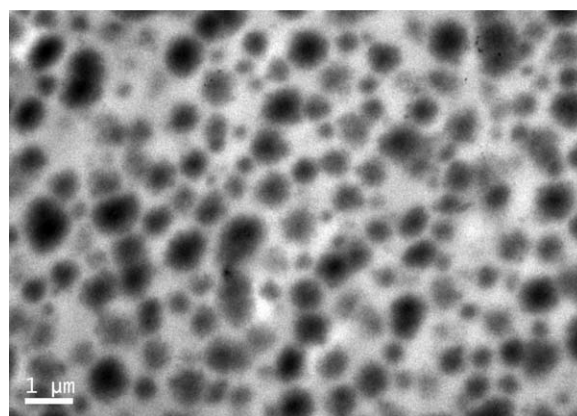


Figure 20. TEM graph of TPU-4 made by all PO PE-PDMS-PE.

Table V. Water Contact Angles (°) of TPUs

TPU series	Composition molar ratio	A Block Type/ M_w (g/mol)	WCAs (°)
TPU-1	0.56 : 1.59 : 1.00	PPG/2000	73
TPU-2	0.38 : 1.41 : 1.00	All EO/512	96
TPU-3	0.25 : 1.28 : 1.00	EO/PO/1000	110
TPU-4	0.25 : 1.28/1.00	All PO/1000	120

Water Contact Angles of the TPUs. The hydrophobicity of the surface of the TPU films was investigated using water contact angles (WCA) measurements. WCAs greater than 90° indicated hydrophobicity. Pure PPG-produced TPU-1 exhibited a lower water contact angle, which indicates poor hydrophobic performance. The TPU-2, TPU-3 and TPU-4 materials exhibited high WCAs that ranged from 96° to 120°, which indicated that the PDMS was incorporated into the urethane matrix to improve the hydrophobic property of the TPU. The PE-PDMS-PE triblock oligomers improved the TPU's hydrophobic performance, which could facilitate the use of this material as an implant biomaterial with slower degradation in the body. The WCA data are listed in Table V.

Mechanical Properties

TPU-1 was prepared with polypropylene glycol without the benefit of any silicone chain incorporation. This sample was used as the benchmark for the TPU elastomer physical properties that we evaluated. Typical polyurethane elastomers exhibit good mechanical properties. We attempted to use dihydroxyl-terminated PDMS ($M_w = 2000$) to produce TPU without solvent. However, dihydroxyl-terminated PDMS had poor reactivity with MDI, which could not produce a higher molecular weight NCO prepolymer. The TPU-2 was prepared using ABA-5 with 20 D units and 100% EO methyl allyl polyether with a molecular weight of 512 in reaction with MDI to formulate the soft segments. The TPU-3 was prepared using ABA-3 with 20 D units and 50% EO/50% PO methyl allyl polyether with a molecular weight of 1000. The TPU-4 was prepared using ABA-14 structured with 20 D units and 100% PO methyl allyl polyether with a molecular weight of 1000. The mechanical properties of four TPU elastomers are listed in Table VI. The results demonstrate that linearly structured α,ω -dihydroxy-(PE-PDMS-PE) ABA copolymers were incorporated into the polyurethane matrix, which did not significantly negatively affect the polyurethane's mechanical properties. A comparison of three different

ABA copolymers' mechanical properties reveals that all of the PO-modified ABA materials result in a final TPU elastomer with mechanical properties better than those of the EO-containing modified ABAs and similar to those of the PPG-produced TPU. This result is explained by the observation that PO exhibits the natural PPG structure, which improved the physical properties of the polyurethane. PE-PDMS-PE modified TPU did not have the dramatic reduction on mechanical properties than pure polyether produced TPU, which could be explained that PE-PDMS-PE maintains some portion of pure polyether's structure and properties, which had the similar hard domain separation.

Compared to four TPUs' hardness, they are similar since the hard segment % is fixed on 30%. TPUs' hardness is majorly affected by hard segment %, not the soft segment structure.

CONCLUSIONS

A series of hydroxyl-terminated polyether-polydimethylsiloxane-polyether (α,ω -dihydroxy-(PE-PDMS-PE)) ABA triblock oligomers were synthesized from silanic fluids and methyl polyallyloxy polyethers using a one-step solventless hydrosilylation reaction with chloroplatinic acid (CPA) as a catalyst in the presence of heat. These α,ω -dihydroxy-(PE-PDMS-PE) oligomers were characterized using $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, $^{29}\text{Si-NMR}$, FT-IR, and GPC to demonstrate that they exhibit a 100% linear ABA structure with a siloxane Si—O chain in the center and polyether ethylene oxide (EO)/propylene oxide (PO) chains on the two sides terminated by hydroxy groups. Using a two-step solventless bulk polymerization, the α,ω -dihydroxy-(PE-PDMS-PE) triblock oligomers were applied to produce thermoplastic polyurethanes (TPUs). TPUs' thermal performance was characterized by DSC and TGA, and we could tell that PE-PDMS-PE-modified TPUs had a clear lower T_g under -120°C and the temperature of 50% weight loss was improved from 280 to 340°C . PE-PDMS-PE-modified TPU did not have the marked reduction on mechanical properties than pure polyether produced TPU. Tensile strength was maintained at 13 MPa and elongation was maintained at 300%. SEM and TEM were used to investigate the copolymer morphology performance and found that all PO PE-PDMS-PE had a pseudo-three phase separation. WCA analysis confirmed that PE-PDMS-PE-modified TPU had significantly improved hydrophobic performance because the silicone structure linked into TPU copolymers. Future studies will focus on material property testing and construction of a model for the relationship between the α,ω -

Table VI. Mechanical Properties of TPUs

TPU series	Composition molar ratio	A Block Type/ M_w (g/mol)	Tensile strength (MPa)	Modulus at 100% elongation (MPa)	Elongation at break(%)	Hardness (Shore A)
TPU-1	0.56 : 1.59 : 1.00	PPG/2000	14.23	4.28	364.4	68
TPU-2	0.38 : 1.41 : 1.00	All EO/512	13.21	4.14	287.5	70
TPU-3	0.25 : 1.28 : 1.00	EO/PO/1000	12.97	4.29	340.8	69
TPU-4	0.25 : 1.28/1.00	All PO/1000	13.49	4.43	354.9	67

dihydroxy-(PE-PDMS-PE) structure and the modified TPUs' morphological performance.

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