

Synthesis and Characterization of Poly(ether sulfone)-graft-polydimethylsiloxane Copolymers

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ABSTRACT: Novel poly(arylene ether sulfone) (PAES) polymers containing polydimethylsiloxane (PDMS) side chains were synthesized and characterized with NMR and Fourier transform infrared spectroscopy. The thermal properties of the copolymers were evaluated with differential scanning calorimetry and thermogravimetric analysis. The polymers showed perfect thermal stability, as the decomposition temperatures were all above 380°C, and exhibited glass-transition temperatures in the range 130–188°C. Furthermore, the surface properties

of the copolymers were evaluated by X-ray photoelectron spectroscopy and contact angle analysis. The results show that the hydrophobic abilities of the graft copolymer surfaces were improved significantly compared to PAES through the introduction of the PDMS chains. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 2434–2441, 2010

Key words: graft copolymers; poly(ether sulfones); polysiloxanes; surfaces

INTRODUCTION

Poly(arylene ether sulfone)s (PAESs) are a well-recognized class of high-performance thermoplastic polymers with useful properties, including high glass-transition temperatures (T_g 's), good mechanical strengths and stiffnesses, and outstanding resistances to thermal and oxidative degradation. They are used in a variety of applications, including ultrafiltration, coatings, adhesives, composites, molded components, and toughening agents.¹ When they are used for engineering applications, a high-temperature performance is desirable to facilitate injection or compression molding. To obtain a broad and, therefore, useful temperature range, the combination of a low- T_g rubber with a high- T_g thermoplastic is a commonly used method.^{1–3}

Another class of polymers, polydimethylsiloxanes (PDMSs), serve as a good toughening agents for thermosetting resins because of their silicon-based molecular structure, which afford good electrical properties, both low- and high-temperature resistances, low stress, and excellent hydrophobic behavior.^{2–4} Thus, many researchers have focused their attention on combining the excellent properties of both PAES

and PDMS. Given the success of PAES in coating applications, its surface properties could be improved by the introduction of PDMS into PAES and the enhancement of the hydrophobic properties of the copolymers.⁵ However, because of the incompatibility between PDMS and carbon-based polymers, it is challenging to obtain composite polymers by physical blending.^{6–17} To overcome this limitation, many methods have been reported in the literature^{6–19} over the past few decades.

We envisioned that novel PAES-g-PDMS copolymers (P4) that possessed PDMS side chains could offer a useful solution to this problem. In this report, we show that such copolymers had high thermal stabilities and reasonable solubilities. Additionally, the hydrophobic properties of the copolymer surfaces were significantly enhanced compared to PAES.

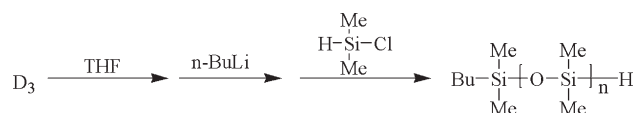
EXPERIMENTAL

Reagents and solvents

1,4-Benzoquinone, 4-amidobenzomethylether, 4,4'-dihydroxydiphenyl sulfone, and 4,4'-dichlorophenylsulfone and were purified by recrystallization. Tetramethylene sulfone (TMS) was purified by vacuum distillation before use. Hexamethylcyclotrisiloxane (D_3 ; Gelest, Inc.) was purified by stirring overnight over calcium hydride at 80°C followed by subsequent vacuum distillation under nitrogen into a preweighed, flame-dried flask. The initiator, *n*-butyl lithium, was kindly donated by the Lithco Division

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Scheme 1 Preparation of the hydrosilyl-terminated PDMS oligomer.

of the FMC Corp. and was approximately 1.6M in hexane. Tetrahydrofuran (THF; 99.5%, E. M. Sciences) was dried by calcium hydride. A Pt(0) (1,3-divinyl-1,1,3,3-tetramethyldisiloxane) 1.5 complex catalyst in xylene (2.1–2.4 wt % Pt0, Karstedt's catalyst, Gelest, Inc.) was used as received.

Characterization methods

$^1\text{H-NMR}$ (300-MHz) spectra were recorded in CDCl_3 or hexadeuterated dimethyl sulfoxide ($\text{DMSO-}d_6$) solution on a Bruker 300 MHz NMR instrument, and the resulting chemical shifts were reported in parts per million downfield from tetramethylsilane. IR spectral analysis was performed on a Nicolet Impact 410 Fourier transform infrared (FTIR) spectrometer. Differential scanning calorimetry (DSC) analyses were performed on a Rigaku Themoflex DSC8131 at a scan rate of $20^\circ\text{C}/\text{min}$. Thermogravimetric analysis (TGA) was performed under an atmosphere of N_2 with a heating rate of $10^\circ\text{C}/\text{min}$. The contact angle was determined with a FTA200 dynamic contact angle analyzer. X-ray photoelectron spectroscopy (XPS) was determined using an Esca Lab Mark II instrument.

Preparation of the starting materials

Preparation of the hydrosilyl-terminated PDMS oligomers

Hydrosilyl-terminated PDMS oligomers were prepared by the anionic ring-opening polymerization of D_3 with *n*-butyl lithium followed by termination with dimethylchlorosilane. The synthetic route of the PDMS was done according to refs. 18 and 19 (see Scheme 1). A colorless clear liquid was obtained (7.2 g, 95% yield).

IR (KBr, cm^{-1}): 1052 (vs, Si—O—Si), 1261 (vs, Si— CH_3), 800 (vs, Si—C), 2130 (vs, Si—H), 2960 (vs, C—H), 1028 (vs, Si—O—Si). $^1\text{H-NMR}$ (CDCl_3 , ppm):

4.71 (m, 1H), 1.32 (m, 4H), 0.88 (m, 3H), 1.32 (m, 2H), 0.19 (d, 6H), 0.07 (s, 6H).

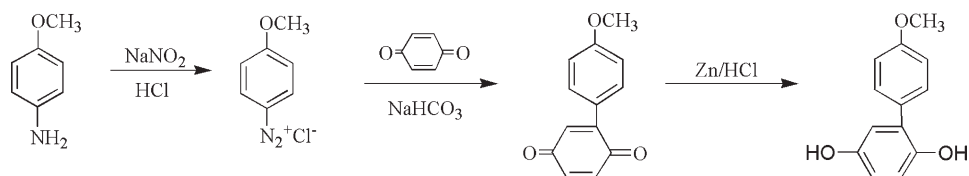
Synthesis of (4-methoxy)phenyl hydroquinone (MPQ)

Into a 200-mL beaker equipped with a mechanical stirrer, a dropping funnel, and a thermometer were placed hydrochloric acid (11.8M, 34 mL), water (20 mL), and ice (20 g). 4-Amidobenzomethylether (12.30 g, 0.10 mol) was added dropwise into the stirred mixture through the dropping funnel, and then, 20 mL of a concentrated water solution of sodium nitrite (6.90 g, 0.10 mol) was added dropwise. The mixture was stirred for 2 h at $0\text{--}5^\circ\text{C}$; this yielded a clear solution. The resulting solution was filtered and added dropwise to a mixture of 1,4-benzoquinone (10.8 g, 0.1 mol), sodium bicarbonate (25.20 g, 0.30 mol), and water (50 mL). The reaction mixture was stirred at $8\text{--}12^\circ\text{C}$ for about 2 h and then at room temperature for 2 h. The precipitate was collected by filtration, washed thoroughly with water, and dried at 60°C in a vacuum oven. The product was recrystallized from *n*-butanol and gave grey crystals (17.55 g, 82% yield; see Scheme 2).

IR (KBr, v , cm^{-1}): 3061 (v, C=C—H); 2950 (v_{as} , CH_3); 1660 (vs, C=O); 1589, 1454 (vs, Ar); 1099 (vs, $\text{CH}_3\text{—O—Ar}$). $^1\text{H-NMR}$ ($\text{DMSO-}d_6$, δ , ppm): 7.98 (d, 4H), 7.92 (d, 4H), 7.85 (d, 2H), 7.37 (d, 2H), 7.28 (d, 4H), 7.15 (s, 4H), 7.04 (d, 1H), 6.86 (d, 2H), 3.67 (s, 1H). $^{13}\text{C-NMR}$ (CDCl_3 , ppm): 55.23, 113.79, 124.87, 130.58, 130.93, 135.94, 137.21, 144.46, 160.66, 187.61. mp = 116°C (DSC). m/z = 214.

Synthesis of 2-(4-methoxyphenyl)-1,4-dihydroxybenzene (MPH; Fig. 1)

MPQ (10.70 g, 0.05 mol), Zn powder (9.81 g, 0.15 mol), and 40 mL of deionized water were placed into a 100-mL, three-necked flask equipped with a mechanical stirrer, a condenser, and a dropping funnel. The mixture was heated to 90°C with stirring; then, 12 mL of HCl (11.8M) was added dropwise at a rate of 0.5 drops/s. After complete addition, the reaction mixture was allowed to reflux for 3 h. The hot mixture was then filtered. The filtrate was cooled to room temperature and poured into a large amount of deionized water. The white solid was collected and recrystallized from toluene (7.56 g, 70% yield; see Scheme 2).



Scheme 2 Synthesis of MPH.

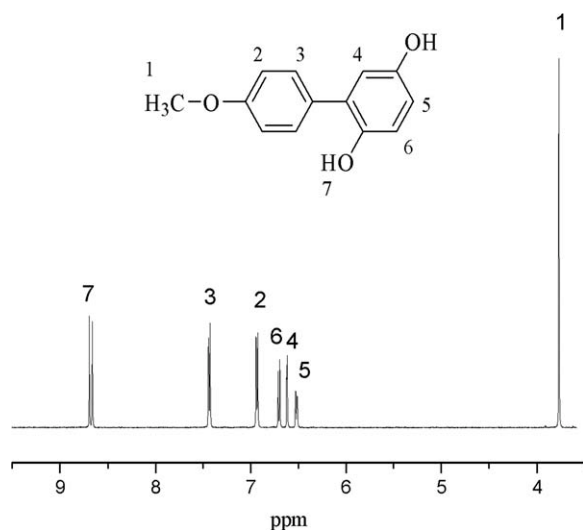


Figure 1 $^1\text{H-NMR}$ spectrum of MPH.

IR (KBr, ν , cm^{-1}): 3277 (v, Ar—OH); 2917 (ν_{as} , CH₃); 1600, 1496 (vs, Ar); 1099 (vs, CH₃—O—Ar). $^1\text{H-NMR}$ (CDCl_3 , ppm): 7.33 (t, 1H), 7.24 (d, 1H), 7.22 (d, 1H), 7.20 (s, 1H), 6.85 (d, 1H), 6.73 (d, 1H), 6.72 (s, 1H), 4.90 (s, 2H), 2.40 (s, 3H). $^{13}\text{C-NMR}$ (CDCl_3 , ppm): 54.99, 113.30, 114.32, 116.20, 116.68, 127.80, 129.96, 130.11, 131.04, 146.59, 150.01, 157.92. mp = 113°C (DSC). m/z = 216.

Preparation of the copolymers

We adjusted the PDMS content of the polymers to 40, 60, and 80% by controlling the ratios of MPH to 4,4'-dihydroxydiphenylsulfone (bisphenyl S) to 4 : 1, 3 : 2, and 2 : 3, respectively.

Synthesis of methoxyl-PAES (MO-PAES) (P1)

A three-necked flask equipped with a mechanical stirrer, a nitrogen inlet, a Dean-Stark trap, and a condenser was charged with MPH (4.32 g, 20.0 mmol), 4,4'-dihydroxydiphenylsulfone (1.25 g, 5.0 mmol), 4,4'-dichlorophenyl sulfone (7.50 g, 26.2 mmol), and K_2CO_3 (3.80 g, 27.5 mmol). TMS (50 g) and 40 mL of toluene were then added. The reaction mixture was refluxed for 2 h. The toluene was removed by distillation, and the polymerization was then completed at 220°C after 4 h. The mixture was poured into 300 mL of water. The polymer was pulverized into powder after cooling. The powder was washed with water three times and then dried at 120°C for 10 h to give the desired polymer as a white powder (10.27 g; see Scheme 3).

IR (KBr, cm^{-1}): 2832 (m, CH₃O—Ar); 1152, 1325 (vs, O=S=O); 1585, 1458 (vs, Ar); 1242 (v, Ar—O—Ar); 1101 (vs, Ar—O—R). $^1\text{H-NMR}$ ($\text{DMSO-}d_6$, ppm): 7.98 (d, 4H), 7.92 (d, 4H), 7.85 (d, 2H), 7.37

(d, 2H), 7.28 (d, 4H), 7.15 (s, 4H), 7.04 (d, 1H), 6.86 (d, 2H), 3.67 (s, 1H).

Synthesis of hydroxyl-PAES (HO-PAES) (P2)

Into a 250-mL, three-necked, round-bottom flask equipped with a magnetic stirrer, a condenser, and nitrogen inlet, P1 (6.5 g) and freshly prepared pyridine hydrochloride (100 g) were placed.²⁰ The mixture was heated under reflux until the solution became homogeneous, which took about 4 h. After it was cooled to 120°C, the mixture was poured into water. The resulting precipitate was collected and dried to give a yellow solid (5.6 g; see Scheme 3).

IR (KBr, cm^{-1}): 3430 (m, HO—Ar); 1152, 1325 (vs, O=S=O); 1587, 1456 (vs, Ar); 1241 (v, Ar—O—Ar). $^1\text{H-NMR}$ ($\text{DMSO-}d_6$, ppm): 8.70 (s, 1H), 7.98 (d, 4H), 7.84 (d, 4H), 7.68 (d, 2H), 7.27 (d, 4H), 7.12 (d, 4H), 7.11 (s, 1H), 7.02 (d, 2H), 6.69 (d, 2H).

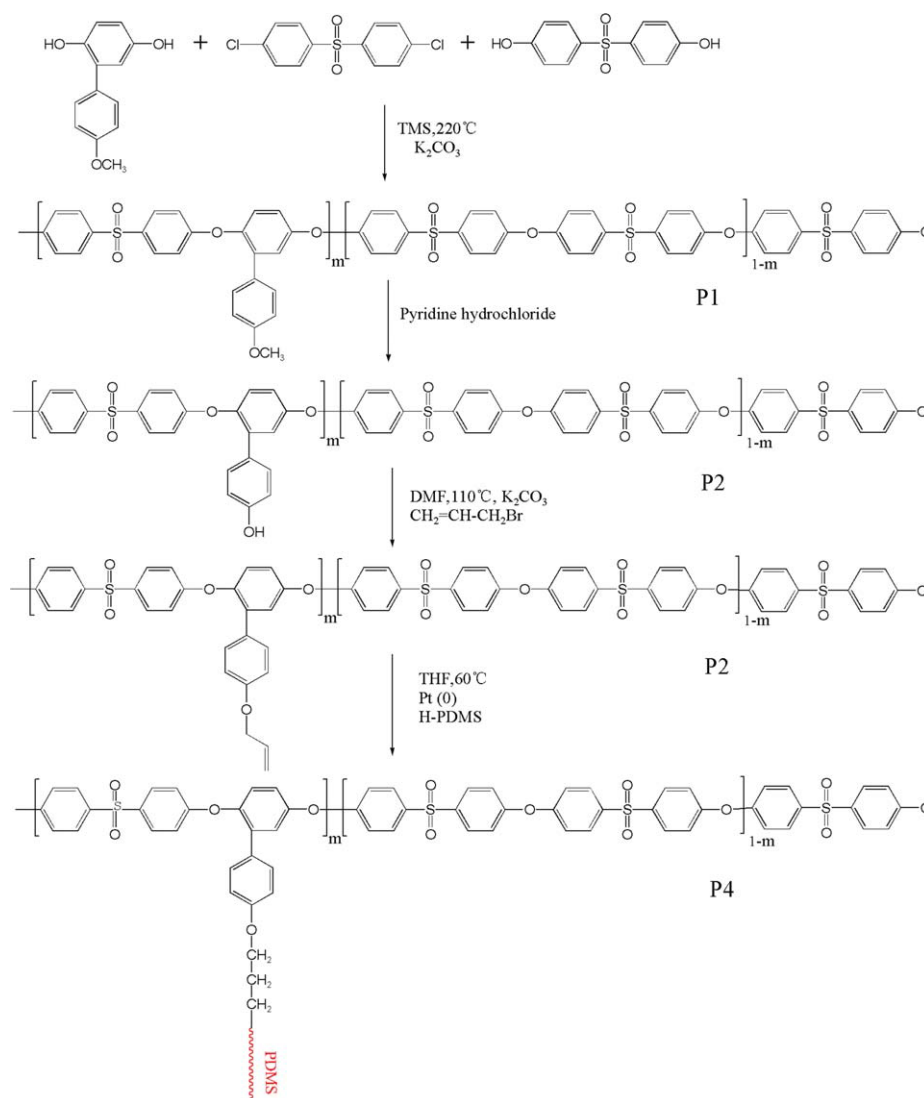
Synthesis of allyl-PAES (P3)

To a stirred solution of hydroxyl-side-chain poly(ether sulfone) (PES) oligomer (5.0 g) in 60 mL of dimethylformamide, anhydrous potassium carbonate (0.25 g, 1.5 mmol), and allyl bromide (1.09 g, 9.0 mmol) were added, and the mixture was allowed to react under nitrogen for 12 h at 110°C. The mixture was poured into 300 mL of water, and the product was precipitated from water and then filtered and washed with distilling acetone (2 × 30 mL) and water (4 × 30 mL) at room temperature. A whitish yellow powder was obtained (4.82 g; see Scheme 3).

IR (KBr, cm^{-1}): 3067, 3090 (vs, C=CH₂); 1325, 1152 (vs, O=S=O); 1648 (vs, CH₂=CH—); 1584, 1455 (vs, Ar); 1240 (v, Ar—O—Ar); 1106 (vs, Ar—O—R). $^1\text{H-NMR}$ ($\text{DMSO-}d_6$, ppm): 7.98 (d, 4H), 7.85 (d, 4H), 7.70 (d, 2H), 7.38 (d, 4H), 7.27 (d, 4H), 7.14 (d, 2H), 7.02 (d, 2H), 6.88 (d, 5.6 Hz, 2H), 6.69 (s, 1H), 5.97 (5, 1H), 5.32 (d, 1H), 5.19 (d, 1H), 4.49 (d, 2H).

Synthesis of the PAES-g-PDMS copolymer (P4)

The PAES-g-PDMS copolymer was prepared by the hydrosilylation of P3 with hydrosilyl-terminated PDMS, as shown in Scheme 3. The general procedure was as follows. A solution of 1.0 g of P3 (1.7×10^{-3} , 1.0×10^{-3} , and 0.6×10^{-3} mol of allyl groups corresponded with 80, 60, and 40% allyl group contents of P3 by the theoretical calculations) and 2.1 g (5 mmol) of hydrosilyl-terminated PDMS [average degree of polymerization (m) = 4, M (MW) = 413] was prepared by dissolution in 20 mL of dry tetrahydrofuran. To this solution, 50 μL of a 0.1M isopropyl alcohol solution of chloroplatinic acid was added, and the reaction mixture was stirred for 24 h at 60°C. Then, the reaction mixture was poured into



Scheme 3 Synthesis of P1–P4. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

50 mL of ethanol, and the polymer was subsequently reprecipitated several times from its chloroform solution into excess ethanol. A pale yellow solid powder was obtained (1.53 g, see Scheme 3).

IR (KBr, cm⁻¹): 1371, 1153 (vs, O=S=O); 1262 (v, Si–CH₃); 1240 (v, Ar–O–Ar); 1108 (vs, Ar–O–R); 1079 (vs, Si–O–Si); 798 (vs, Si–C). ¹H-NMR (CDCl₃, ppm): 7.90 (d, 4H), 7.73–7.79 (d, 4H), 7.33 (d, 2H), 7.15 (d, 4H), 7.07 (d, 4H), 6.89–6.92 (d, 4H), 6.82 (d, 2H), 6.74 (s, 1H), 3.87 (t, 2H), 1.79 (m, 2H), 1.30 (d, 4H), 0.865 (t, 2H), 0.626 (t, 2H), 0.523 (t, 2H), 0.195 (s, 6H), 0.068 (s, 6H).

RESULTS AND DISCUSSION

Preparation of PDMS

The PDMS oligomers were prepared by the reaction shown in Scheme 1, which shows the triorganosila-

nol, the molar ratio of D₃ to the initiator (silanolate anion), and the theoretical and observed *m* values of the resulting PDMS oligomer. All of the triorganosilanols were efficiently converted to their corresponding silanolate anion with *n*-butyl lithium. We controlled *m* easily by changing the ratio of D₃ to the initiator.

Preparation of MPH

The synthesis of MPH was accomplished in two steps. The coupling²¹ of 4-methoxyphenyldiazonium chloride with 1,4-benzoquinone in the presence of NaHCO₃ to yield MPQ was followed by reduction with Zn/HCl to give the desired product. The structure of MPQ was confirmed by mass spectrometry, FTIR spectroscopy, and ¹H-NMR spectroscopy. In the FTIR spectra, MPQ showed an absorption band around 1660 cm⁻¹ due to the symmetric stretching

TABLE I
Grafting Degree of the PAES-g-PDMS Copolymers

Theoretical content (%)	PAES-CH ₂ CH=CH ₂ (%)	PAES-PDMS (%)	Convert ratio (%)
80	58.9	60	100
60	40.9	40	100
40	28.6	16.25	54

The PDMS theoretical contents of the graft copolymers were determined by the ratio of MPH units to 4,4'-dihydroxydiphenylsulfone units, and the real contents were determined by the ratio of peak intensity.

of carbonyl groups. After reduction, this characteristic absorption disappeared, and the characteristic band attributed to a hydroxyl group appeared around 3270 cm⁻¹. The peak at 4.50–5.00 ppm in the ¹H-NMR spectra of MPH was assigned to the hydroxyl proton, which was absent in the spectrum of MPQ. The peaks at 2.40 and 7.33–6.72 ppm were assigned to the methyl and aromatic protons, respectively.

Preparation of P3

Scheme 3 outlines the synthetic route used to obtain the desired copolymers. The ¹H-NMR spectrum of the copolymers showed a signal at 6.69–7.98 ppm, which was attributed to the aromatic protons of the PAES segments. The proton signal attributed to the –OCH₃ groups of the PAES segments was found at

3.87 ppm in the ¹H-NMR spectrum of P1. After polymerization, this signal disappeared, and a new signal corresponding to the –OH protons of the side groups of PAES segments was observed at 9.56 ppm. This gave evidence that all of the –OCH₃ groups were converted to –OH groups. In the ¹H-NMR spectrum of P3, signals attributed to the methylene (4.47 ppm) and vinyl protons (6.00, 5.34, and 5.24 ppm) of the allyl group were observed, and the signal at 9.56 ppm attributed to –OH disappeared completely (see Scheme 3).

Preparation of the graft copolymers

Table I summarizes the preparation of the PAES-PDMS graft copolymers containing various side-chain concentrations, and Figure 2 shows the ¹H-NMR spectrum of the graft copolymers with 40% [Fig. 2(a)], 60% [Fig. 2(b)], and 80% [Fig. 2(c)] incorporation of side chains. The signals attributed to the methyl protons of PDMS were observed at 0.07 ppm, and the signals of Si–H, which terminated PDMS at 4.7 ppm, disappeared. In the ¹H-NMR spectrum (Fig. 2) of c (60%-PDMS-g-PAES) (a-2) and c (80%-PDMS-g-PAES) (a-3), the signals of the methylene and vinyl protons of the allyl group at 4.47, 6.00, 5.34, and 5.24 ppm disappeared, but in the ¹H-NMR spectrum of a (40%-PDMS-g-PAES) (a-1), these signals were still observed. Because during the hydrosilylation, the graft polymer precipitated from

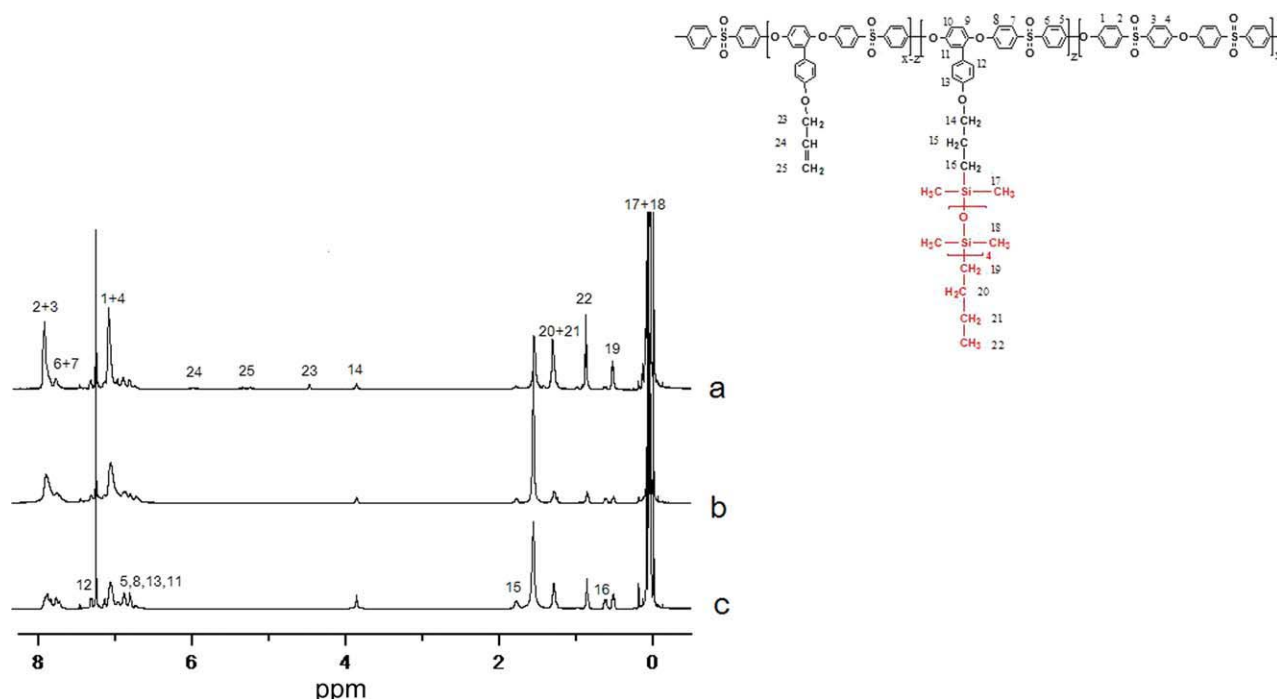


Figure 2 ¹H-NMR spectra of (a) 40, (b) 60, and (c) 80% PDMS-g-PAES (CDCl₃). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Solubility of CH₃O-PAES, HO-PAES, P3, and PDMS-*g*-PAES

Solvent	P1			P2			P3			P4		
	40%	60%	80%	40%	60%	80%	40%	60%	80%	40%	60%	80%
TMS	++	++	+	-	-	-	++	+	+	-	-	-
NMP	++	++	++	++	++	+	++	++	++	++	+	+
DMAc	++	++	++	++	++	+	++	++	++	++	++	-
DMSO	++	++	++	+	+	+	+	++	++	++	+	-
Ethanol	-	-	-	-	-	-	-	-	-	-	-	-
CHCl ₃	++	++	++	++	++	++	++	++	++	++	++	++
Toluene	-	-	-	-	-	-	-	-	-	-	-	-
THF	+	+	-	+	++	+	++	++	++	++	++	+
Acetone	-	-	-	-	-	-	-	-	-	-	-	-
Oil ether	-	-	-	-	-	-	-	-	-	-	-	-

- = insoluble; + = soluble on heating; ++ = soluble at room temperature.

the THF solution, the excess allyl compound could not react with PDMS. The real grafting degree could be calculated from the ¹H-NMR spectrum of the PAES-*g*-PDMS copolymers and is listed in Table I. In addition, according to the FTIR spectrum, absorptions attributed to sulfone groups (1317 cm⁻¹), Si-CH₃ (1261 cm⁻¹), Si-O-Si (1000-1100 cm⁻¹), and Si-CH₂ (800 cm⁻¹) supported the successful grafting of PAES and PDMS. Moreover, the absorption attributed to Si-H (2130 cm⁻¹) disappeared.

Solubility of the copolymers

Table II indicates the comparison of solubility among CH₃O-PAES, HO-PAES, P3, and the PDMS-PAES graft copolymer. The solubility of the chemically modified PAES was different from the PES. PES is soluble in only a few solvents, such as dimethylacetamide, dimethylformamide, NMP, and CHCl₃. However, P3 became soluble in other solvents, such as THF, likely because of the introduction of alkanes into the polymer framework. It was important to use a suitable solvent to prepare the graft copolymer by hydrosilylation. The graft copolymers exhibited good solubility, being soluble even in CHCl₃. It was fruitful to characterize the structures of the graft copolymers by ¹H-NMR spectroscopy. This allowed us to observe that the incorporation of PDMS into PAES afforded insolubility, even in relatively strongly polar solvents,

such as dimethyl sulfoxide (DMSO), DMAc, and TMS.

Molecular weight and thermal properties of the graft copolymers

As listed in Table III, the number-average molecular weight (*M_n*) and weight-average molecular weight (*M_w*) of the PAES-*g*-PDMS copolymers were determined by GPC against polystyrene standards. The GPC curve (Fig. 3) showed that the copolymers exhibited high molecular weights and broad molecular weights.

T_g and the 5% weight loss temperatures of the copolymers were determined by DSC and TGA, as listed in Table III. A decrease in *T_g* was observed with increasing content of the PDMS segments. There appeared to be H-bonding interactions of the OH groups, as evidenced by the high *T_g* values observed for PAES-OH(40%) [poly(a2)], PAES-OH(60%) [poly(b2)], and PAES-OH(80%) [poly(c2)] compared to the lower values for PAES-OCH₃(40%) [poly(a1)], PAES-OCH₃(60%) [poly(b1)], PAES-OCH₃(80%) [poly(c1)], PAES-Allyl(40%) [poly(a3)], PAES-Allyl(60%) [poly(b3)], and PAES-Allyl(80%) [poly(c3)], in which the OH groups were either protected by methoxyl groups or replaced by allyl groups.

The thermal stability of PAES-OCH₃ and PAES-*g*-PDMS was examined by TGA under nitrogen at a heating rate of 10°C/min, and some thermograms

TABLE III
Thermal Stability and Molecular Weight of the Copolymers

Content (%)	DSC				TGA		PAES-PDMS		
	PAES-OCH ₃	PAES-OH	Allyl-PAES	PAES-PDMS	PAES-OCH ₃	PAES-PDMS	<i>M_n</i>	<i>M_w</i>	<i>M_w/M_n</i>
40 (a)	202°C	223°C	203°C	188°C	443°C	445°C	6004	12908	2.15
60 (b)	195°C	223°C	207°C	180°C	451°C	399°C	15706	40785	2.6
80 (c)	198°C	230°C	192°C	130°C	456°C	380°C	55717	152938	2.7

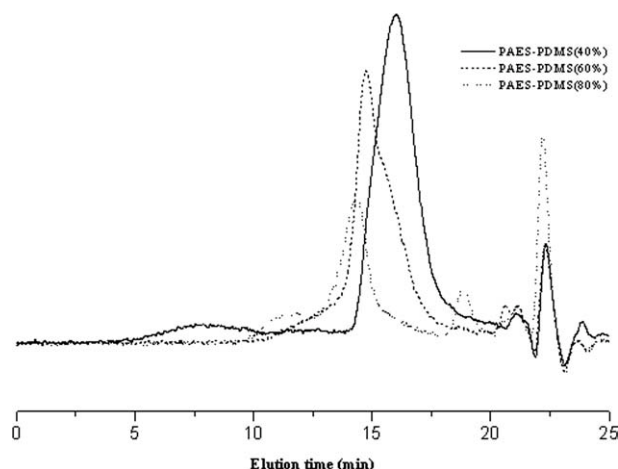


Figure 3 GPC curve of PAES-PDMS 40–60% against polystyrene standard with THF as a solvent.

are reported in Table III. All of the unmodified copolymers of PAES-OCH₃ showed excellent thermal stability, as evidenced by their TGA curves temperatures [$T_{d5\%}$ (5% weight loss temperature) = 445–456°C]. In contrast to PAES-OCH₃, the $T_{d5\%}$ traces of the PAES-g-PDMS copolymers (270°C) decreased because an increase in the content of the PDMS segments led to a decrease of the copolymer's thermal stability. However, the PAES-g-PDMS polymers with 40, 60, and 80% incorporation of side chains were thermally stable up to 445, 399, and 380°C, respectively, which demonstrated good heat resistance.

Surface properties of the graft copolymers

Many researchers have reported the phenomenon of PDMS segments enriched on the surface of copolymer films,^{11–16} which gave them desirable properties.

To confirm that the siloxane chains were separated from the PAES segment and migrated to the surface of the copolymer film, elemental analysis of the surface of the graft copolymer film was measured with XPS. The detection angle in the experiment was 15°, which gave valuable information about the conformation of the macromolecules at the surface. The degree of incorporation of PDMS in the copolymers was determined and is listed in Table IV. The atomic percentage of Si content in the polymer, as determined by ¹H-NMR, was much lower than the atomic

TABLE IV
Atomic Percentage of the PAES-g-PDMS Copolymers

PDMS content ratio (mol %)	Polymer (atom %; by ¹ H-NMR): C : O : Si	Surface (atom %; by XPS): C : O : Si
40 (a)	41.6 : 10.2 : 1	5.5 : 1.8 : 1
60 (b)	13.8 : 3.5 : 1	2.4 : 0.8 : 1
80 (b)	11.5 : 2.6 : 1	2.5 : 0.7 : 1

TABLE V
Surface Contact Angle of the PDMS-PAES Film

PDMS content ratio (mol %)	Contact angle (°)
0	81
40	97
60	108
80	106

percentage of Si on the surface, as calculated by XPS. The atom content of PDMS was determined as follows: C : O : Si = 2 : 1 : 1 (according to the structure of PDMS). These results show that the composition of the surface of the PAES-g-PDMS copolymer film was similar to that of the surface of PDMS, which suggested that the PDMS segments enriched the surface of the copolymer film.

The surface contact angles for the PDMS-PAES films were obtained by casting. The effect of the PDMS chain on the characterization of the PAES films was observed by contact angle analysis. Table V shows the surface contact angle of the PAES films that contained various amounts of PDMS. The contact angle analysis revealed that the contact angles of the PAES and PAES-g-PDMS copolymers were 81 and 97–108° correspondingly. It was evident that the contact angle increased; this revealed that the hydrophobic properties of the copolymer increased relative to PES, which provided further evidence that the PDMS segments enriched the surface of the copolymer film. On the basis of these observations, Figure 4 illustrates the composition of the film with PDMS.

CONCLUSIONS

Novel PES-graft-PDMS copolymers were synthesized with a new synthetic route. The chemical structure of the block copolymer was characterized by ¹H-NMR and FTIR. In addition, the thermal properties were evaluated by TGA and DSC. Although the thermal stability of PAES-g-PDMS decreased as the

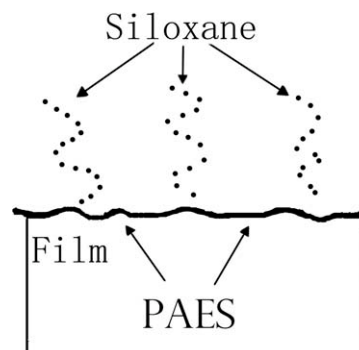


Figure 4 Illustration of film with PDMS.

content of PDMS segments increased, they exhibited good thermal stability as high-performance thermoplastic polymers. The surface properties of the graft copolymer were evaluated by XPS and contact angle measurements. These results illustrate that the PDMS segments enriched the surface of the copolymer film. Furthermore, contact angle analysis indicated that the hydrophobic properties of the polymers increased upon introduction of the PDMS oligomers.

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