Synthesis and Characterization of Siloxane Copolyesters Containing Phenylindane Linkages

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ABSTRACT: A novel series of siloxane copolyesters containing 1,1,3-trimethyl-3-(p-hydroxyphenyl)-5-indanol (phenylindane bisphenol), diphenyl terephthalate (DPT), diphenyl isophthalate (DPI), and eugenol end-capped siloxanes in varying ratios were prepared at a temperature range of 200–290°C under reduced pressure using dibutyl tin dilaurate catalyst by melt polycondensation. The siloxane-containing copolyesters were characterized by infrared and ^{1}H NMR spectroscopy, elemental analysis, solution viscosity, thermogravimetric analysis, differential scanning calorimetry, and X-ray diffraction. The effect of incorporation of siloxane moiety was studied on the properties of phenyl indane/DPT/DPI coplyester. The glass transition temperatures of copolyesters were decreased from 235 to 124°C by incorporation of 10% eugenol end-capped siloxane without affecting the thermal properties. All copolyesters were found to be soluble in commonly used organic solvents and had film forming properties. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 2668–2674, 2006

Key words: phenylindane bisphenol; siloxane copolyesters; melt polymerization; eugenol end capped siloxane

INTRODUCTION

Aromatic polyesters (polyarylates)[1,2] are derived from aromatic dicarboxylic acids and diphenols. These are known as engineering polymers because of their high glass transition temperature (T_g), high flame resistance, and high thermal stability. They have excellent mechanical and thermal properties, and therefore find applications in transportation (interior panels in buses and aircrafts), glazing parts (solar collectors and appliances), and other optical uses.

Aromatic polyesters undergo a Photo Fries rearrangement when exposed to sunlight or an artificial source of UV radiation. This results in the formation of *o*-hydroxybenzophenone moieties. The *o*-hydroxybenzophenone moieties are efficient UV light absorbers based on a tautomeric keto-enol equilibrium, which dissipates the energy of absorbed incident light in a radiationless manner. Therefore, once sufficient rearrangement product has formed, the aromatic polyester becomes inherently UV stable. Aromatic polyesters are also used for the coating of PVC, Nylon 6,6, and PET. These polymers also have high tensile recovery and are being preferred to be used in making clips, springs, and fasteners.

There are different methods for the synthesis of polyarylates namely, direct condensation between a aromatic diol(s) and a aromatic dicarboxylic acid(s) especially in the presence of a proper catalyst,[3,4] interfacial polycondensation of diacid dihalide(s) with diol(s), low temperature Schotten-Baunmann[5,6] solution polycondensation between diacid dihalide(s) and a diol(s) in the presence of an acid acceptor, high temperature solution polycondensation[7,8] of a diacid dihalide(s) and a diol(s), transesterification[9,10] of an aromatic dicarboxylic acid(s) with a diacetate of an aromatic diol(s) at a high temperature, and polymerization of a diaryl (e.g., phenyl) ester[11,12] of an aromatic dicarboxylic acid(s) with an aromatic diol(s) via transesterification. All of the preparation methods possess certain advantages as well as disadvantages and selection of a particular method is governed by factors such as economics, reliability of the process, and product quality.

In the past the copolyesters of 1,1,3-trimethyl-3-(p-hydroxyphenyl)-5-indanol with isophthaloyl/terephthaloyl chloride were prepared by interfacial polymerization.[13] The copolyesters prepared by this method possess very high T_g because of the incorporation of phenylindane ring in the polymer backbone.

It is very difficult to process these aromatic polyesters into fibers and films because of their limited solubility in organic solvents and their high softening or high melting temperatures. There has been a constant need to improve the solubility of polyarylates without affecting their thermal properties and much work has been expended in this area. The introduction of polar and flexible groups into the polymer backbone is one of the better approaches to improve the solubility of

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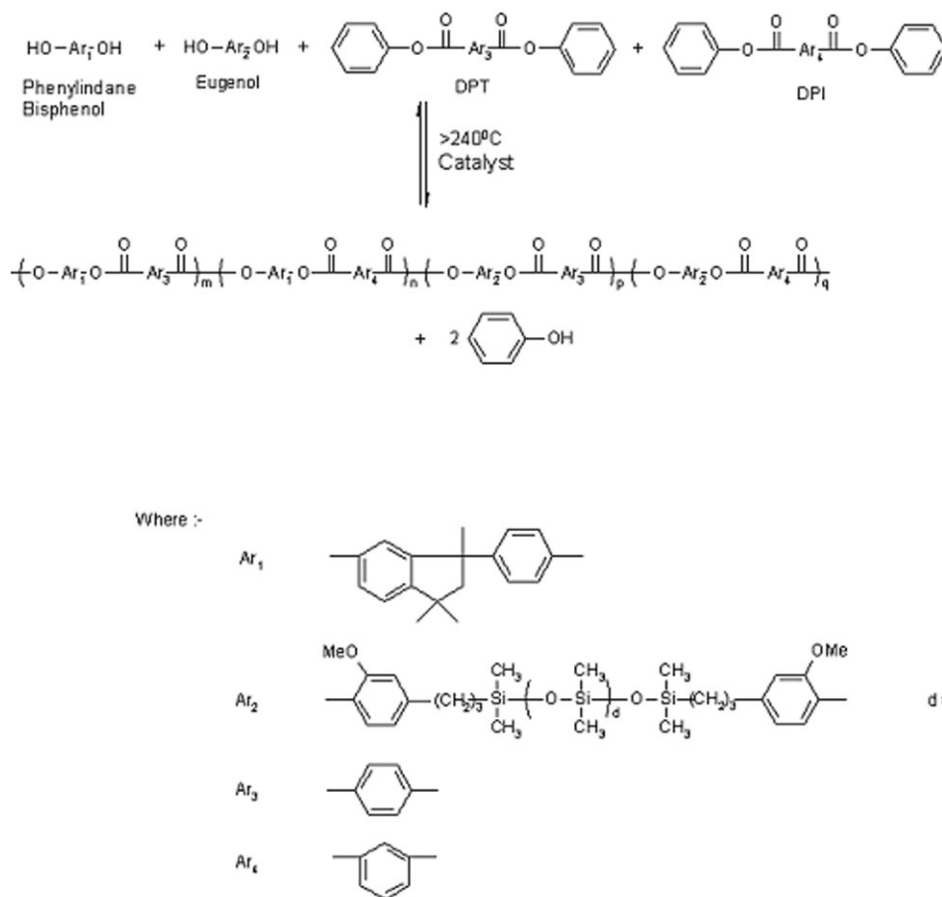
Scheme 1 Preparation of siloxane copolyesters.

polymers without extreme loss of their high thermal stability. The siloxane group has been known to meet this requirement and some siloxane group containing polymers have been reported in the literature.[14–17] Siloxane copolyesters are well known thermoplastic resins, which have good flow and mold release characteristics in injection molding applications.

In the present work, we have prepared a novel series of siloxane copolyesters of 1,1,3-trimethyl-3-(*p*-hydroxyphenyl)-5-indanol (phenylindane bisphenol)

and EuSi with mixtures of diphenyl terephthalate (DPT) and diphenyl isophthalate (DPI) in varying ratios by melt polymerization technique. The effect of incorporation of eugenol end-capped siloxane was studied on the properties of copolyesters derived from phenylindane bisphenol with DPT and DPI. The copolyesters were characterized by infrared, proton NMR spectroscopy, solution viscosity, elemental analysis, thermal behavior, and crystallinity.

TABLE I
Properties of Siloxane Copolyesters

Sample ID	Phenyl indane (%)	EuSi (%)	DPT (%)	DPI (%)	Yield (%)	η_{inh}[a] (dL/g)	Elemental analysis[b]	
							C (%)	H (%)
PES-1	100	–	100	–	99	0.44	78.10 (78.39)	5.68 (5.52)
PES-2	100	–	–	100	98	0.40	78.12 (78.39)	5.73 (5.52)
PES-3	100	–	50	50	98	0.41	78.12 (78.39)	5.70 (5.52)
PES-4	95	5	50	50	97	0.40	73.80 (73.66)	6.01 (5.82)
PES-5	90	10	50	50	99	0.38	70.08 (69.80)	6.18 (6.06)

[a]Determined in chloroform at 30°C.
[b]Numbers in parentheses indicate the calculated values.

TABLE II
Properties of Siloxane Copolyesters

Sample ID	$M_w{}^a$	$M_n{}^a$	PDI
PES-1	36,200	16,500	2.20
PES-2	35,600	16,000	2.22
PES-3	36,000	15,600	2.30
PES-4	32,700	13,100	2.50
PES-5	32,400	13,500	2.40

[a]Determined in chloroform at 30°C.

EXPERIMENTAL

Materials

Phenylindane bisphenol was prepared by following the method given in the literature.[16] The product had a melting point of 189–191°C.

Eugenol end-capped siloxane (EuSi) (D_{10}) [M_n = 1240 g/mol as determined by vapor pressure osmometry (VPO) in chloroform at 30°C] received from General Electric, USA was used as such without further purification.

Diphenyl terephthalate (DPT) was prepared by the reaction of terephthaloyl chloride with sodium salt of phenol using benzyltriethyl ammonium chloride (BTEAC) as phase transfer catalyst and purified by recrystallization from methylene chloride. The crystallized product had a melting point of 197–199°C.

Diphenyl isophthalate (DPI) was prepared by reacting isophthaloyl chloride with sodium salt of phenol using BTEAC as phase transfer catalyst and purified by recrystallization from methylene chloride. The crystallized product had a melting point of 135–137°C.

Dibutyl tin dilaurate (DBTL) procured from Sigma-Aldrich, USA was used as such without further purification.

Measurements

Infrared spectra were recorded on PerkinElmer 16 PC FTIR spectrophotometer in chloroform.

Proton NMR spectroscopy was used for compositional and structural analysis of polymers. Proton NMR spectra were obtained using a Bruker 500 MHz spectrometer in deuterated chloroform. No tetramethylsilane (TMS) was used in the deuterated chloroform sample solvent because of the potential overlap with the methyl protons in the siloxane polymer. The chloroform reference peak at 7.28 ppm was used to ensure the accuracy of peak assignments.

The number average (M_n) and weight average (M_w) molecular weights were determined with thermoquest gel permeation chromatography (GPC) equipped with RI detector and column sets of PSS SDV 8 μm 100 Å and linear mixed bed column in chloroform at a flow rate of 1 mL/min at room temperature. The calibration curves for GPC were obtained by using polystyrene standards. The polydispersity index (PDI) was determined by taking the ratio of M_w and M_n.

Ubbelhode viscometers were used to determine the inherent viscosities (η_{inh}) at 30 °C ± 0.1°C of polymer solutions having concentrations of 0.5 g/100 mL in chloroform.

The elemental analyses for carbon and hydrogen in siloxane copolyesters were determined using the standard techniques.

Differential scanning calorimetry (DSC) thermograms were obtained with a PerkinElmer DSC-7 under dry nitrogen atmosphere with a flow rate of 50 mL/min at a heating rate of 10°C min^{-1}. About 8–10 mg of sample was used for DSC analysis and the samples were scanned in the temperature range of 50–300°C.

Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) were carried out with a PerkinElmer TGA-7 thermogravimetric analyzer under dry nitrogen atmosphere with a flow rate of 50 mL/min at a heating rate of 10°C min^{-1}. About 4–5 mg of sample was used for TGA analysis and the samples were scanned in the temperature range of 50–900°C.

Wide angle X-ray diffractograms (WAXD) were obtained for powdered samples with a Phillips X-ray unit (Phillips generator, PW-1730) using nickel filtered CuK$_\alpha$ radiation.

Melt polymerization

All copolyesters were prepared by melt polymerization technique. The preparation of siloxane copolyester (PES-4) is given below as a representative example.

A 100-mL three-necked cylindrical glass reactor equipped with a mechanical stirrer, a nitrogen gas inlet, and a vacuum jacketed Vigreux column and distillation head was charged with 5.092 g (0.019 mol) of phenylindane bisphenol, 1.24 g (0.001 mol) of EuSi, 3.18 g (0.010 mol) of DPI, 3.18 g (0.010 mol) of DPT, and 4×10^{-4} mol (based on phenylindane bisphenol) of dibutyl tin dilaurate (DBTL) catalyst. The melt polymerization was carried out in PID controlled cylindrical furnace at 200°C under nitrogen atmosphere for 3 h; 220°C for 0.5 h at 200 mmHg, 240°C for 0.5 h at 120 mmHg, 260°C for 0.5 h at 50 mmHg; 290°C for 0.5 h at

TABLE III
Quantification of Siloxane in Copolyesters

Polymer code	Feed composition		Composition by ¹H NMR	
	Phenyl indane (%)	Siloxane (%)	Phenyl indane (%)	Siloxane (%)
PES-4	95	5	95	4.5
PES-5	90	10	90	9.5

TABLE IV
Solubility Behavior of Siloxane Copolyesters

Sample ID	CHCl$_3$	DMSO	DMF	DMAC	NMP	DCM	THF
PES-1	++	− −	++	++	++	++	++
PES-2	++	− −	++	++	++	++	++
PES-3	++	− −	++	++	++	++	++
PES-4	++	− −	++	++	++	++	++
PES-5	++	− −	++	++	++	++	++

CHCl$_3$: Chloroform; DMSO: dimethyl sulfoxide; DMF: *N,N*-dimethyl formamide; DMAC: *N,N*-dimethyl acetamide; NMP: *N*-methyl-2-pyrrolidone; DCM : dichloromethane; THF: tetrahydrofuran.

1 mmHg, and finally at 290°C for 1 h at 0.1 mmHg. The reaction mixture was stirred continuously throughout the melt polymerization at constant speed. The translucent copolyester obtained was cooled to room temperature under the flow of nitrogen, dissolved in chloroform, and precipitated in methanol. The fibrous material obtained was separated by filtration and dried at 80°C in a vacuum oven for 3 h and yield was recorded. The same procedure was used for the preparation of other siloxane copolyesters.

Polymer solubility

The solubility of siloxane copolyesters was checked at 5 wt % concentration in various polar and nonpolar solvents namely, chloroform, methylene chloride, tetrahydrofuran (THF), dimethyl formamide (DMF), dimethylactamide (DMAC), methyl pyrrolidone (NMP), dimethyl sulfoxide (DMSO), methanol, ethanol, petroleum ether etc.

RESULTS AND DISCUSSION

The aromatic copolyesters containing siloxane linkages were prepared by the melt polymerization of phenylindane bisphenol with varying ratios of DPT, DPI, and EuSi in the temperature range of 200–290°C under reduced pressure in the presence of DBTL catalyst. The preparation of siloxane copolyesters is shown in Scheme I.

The siloxane copolyesters were characterized by FTIR and ^{1}H NMR spectra, solution viscosity, TGA, DSC, and X-ray diffraction. The properties of copolyesters are summarized in Tables I–V.

The solution viscosities of copolyesters were determined in chloroform at 30°C varied from 0.38 to 0.44 dL/g. The results are summarized in Table I. No particular trend was observed in the inherent viscosities of siloxane copolyesters with the incorporation of siloxane segments. Furthermore, the deviations in the values of inherent viscosities are in the range of experimental error. The elemental analysis for carbon and hydrogen was performed using the standard techniques, and the observed values for carbon and hydrogen are in accordance with the structure of the copolyester.

The number average (M_n) molecular weight and weight average (M_w) molecular weights of copolyesters were determined in chloroform at 30°C by GPC. The results are summarized in Table II. The M_n varies from 13,100 and 16,600 g/mol, the M_w varies from 32,400 to 36,200 g/mol, and the PDI of the copolyester varies from 2.2 to 2.5. The PES-4 and PES-5 copolyesters have slightly low molecular weights as compared to that of PES-1, PES-2, and PES-3. This may be attributed to the low reactivity of the eugenol siloxane comonomer.
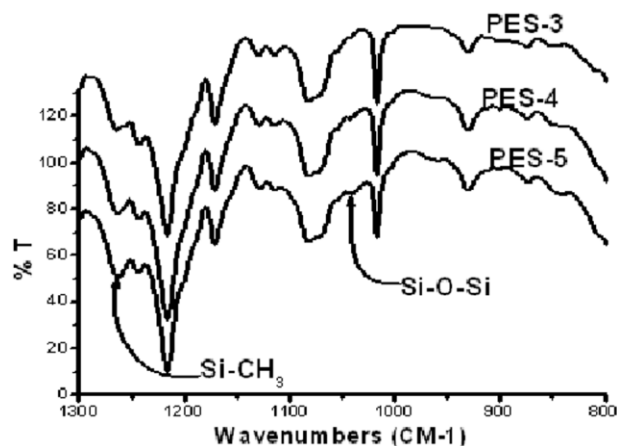
TABLE V
Thermal Behavior of Siloxane Copolyesters

Sample ID	T_g (°C)	IDT (°C)	T_{10} (°C)	T_{max} (°C)	Residue (%)
PES-1	235	447	457	490	26
PES-2	209	447	457	485	28
PES-3	221	448	455	479	26
PES-4	150	419	437	486	35
PES-5	124	399	411	485	35

T_g: Glass transition temperature; IDT: initial decomposition temperature; T_{10}: temperature for 10% weight loss; T_{max}: temperature for maximum weight loss.

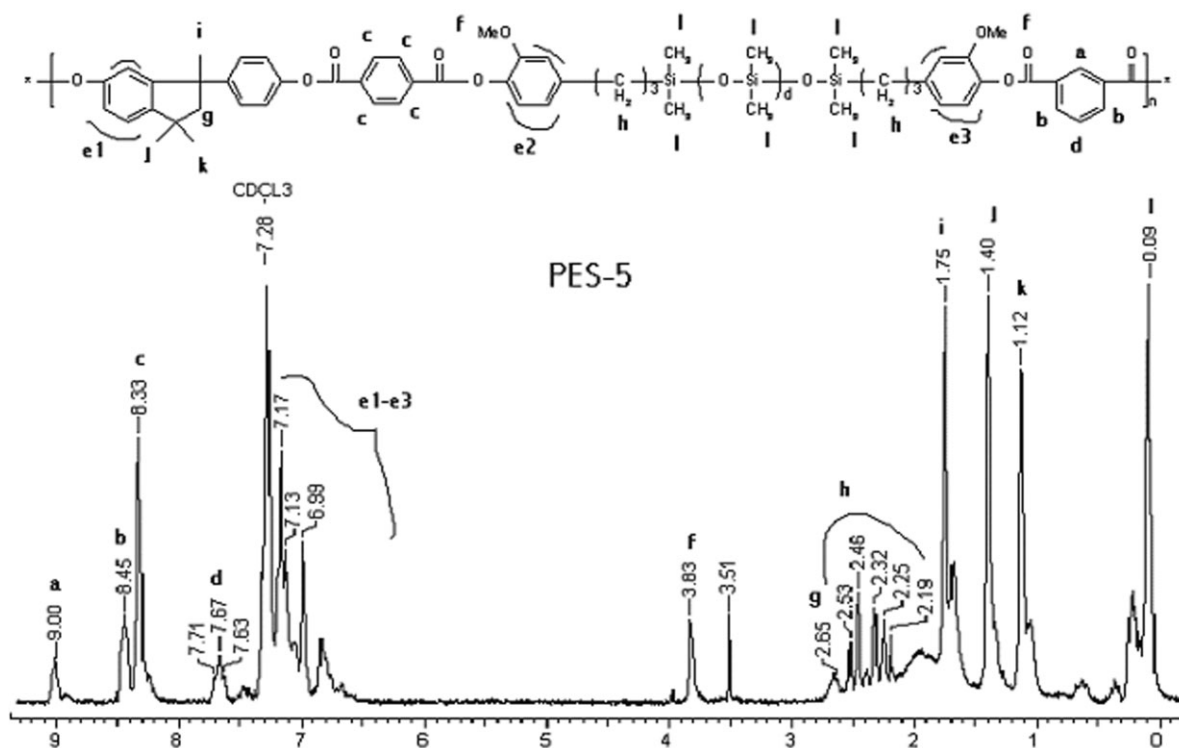**Figure 1** FTIR spectra of siloxane copolyesters.

Figure 2 ^{1}H NMR spectrum of siloxane copolyester (PES-5).

The incorporation of eugenol siloxane in aromatic copolyester was qualitatively confirmed by the FTIR spectroscopy. The FTIR spectra showed a stretching vibration band at 1045 cm^{-1} because of the presence of Si—O—Si linkages and a stretching vibration band at 1262 cm^{-1} because of the presence of Si—CH$_3$ linkages. The FTIR spectra of aromatic copolyester (PES-3) and siloxane copolyester (PES-4 and PES-5) are illustrated in Figure 1.

The copolyesters were obtained in quantitative yields. The incorporation of siloxane in copolyesters was quantitatively determined by ^{1}H NMR spectroscopy (Fig. 2). The results are summarized in Table III. The ^{1}H NMR spectra of eugenol end-capped siloxane and phenylindane bisphenol/DPT/DPI copolyester are illustrated in Figure 3. The incorporation of eugenol siloxane in copolyester was determined by ^{1}H NMR spectroscopy, using the relative integration of the peaks of eugenol end-capped siloxane at 0.09 δ due to methyl siloxane protons (H$_a$), and at 1.40 δ due to methyl protons (H$_J$) of phenylindane moiety.

The solubility behavior of copolyester samples was checked at 5 wt % concentration in various solvents and nonsolvents and the results are summarized in Table IV.

All copolyesters were found to be soluble in polar solvents namely, chloroform, methylene chloride, THF, and aprotic polar solvents namely, *N,N*-DMF and *N*-NMP. However, all copolyesters were found to be insoluble in DMSO. None of the copolyester was

found to be soluble in the nonsolvents namely, ethanol, methanol, and petroleum ether.

The thermal behavior of siloxane copolyesters was studied by DSC, TGA, and DTG by heating the polymers at a constant rate of 10°C under nitrogen atmosphere. The DSC and TGA thermograms of siloxane copolyesters are illustrated in Figures 4 and 5. The thermal properties of siloxane copolyesters are summarized in Table V.

The DSC results showed a considerable decrease in T_g of siloxane copolyesters by the incorporation of flexible siloxane linkages into the copolyester backbone. The T_gs of copolyesters were decreased from 235 to 124°C by the incorporation of 10% of eugenol end-capped siloxane (D_{10}). This may be due to the incorporation of flexible eugenol end-capped siloxane structure into the copolyester backbone.

The initial decomposition temperature (IDT), temperatures for 10% weight loss (T_{10}), and percentage residue were determined from TGA curves. The temperature for maximum weight loss (T_{max}) was calculated from the DTG curves. The decomposition of siloxane copolyester took place in one step. A marginal decrease in the thermal stability was observed by the incorporation of siloxane linkages in the polymer backbone. The percentage of residue in copolyester increases from 26 to 35% because of the incorporation of 5–10% of siloxane in the polymer backbone when the copolyester was heated from 50 to 900°C under
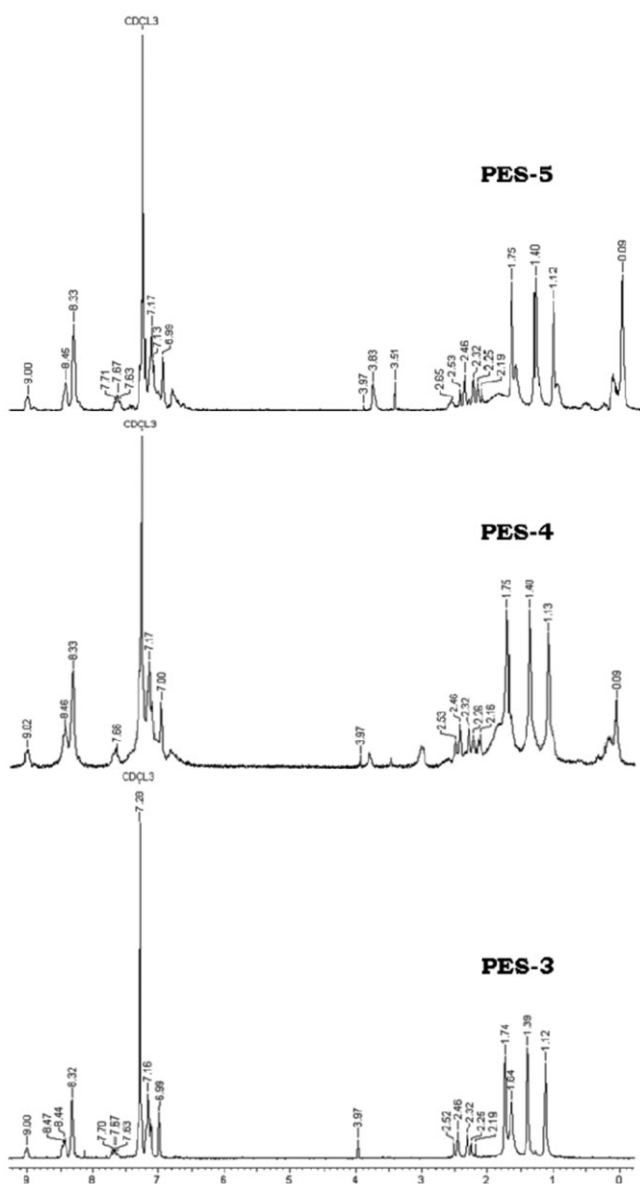
Figure 3 ^{1}H NMR spectra of siloxane copolyesters.

Figure 4 DSC thermograms of siloxane copolyesters. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

under reduced pressure in the presence of DBTL catalyst. The copolyesters were obtained in quantitative yields. All the copolyesters were easily soluble in a wide range of aprotic polar solvents and the solution had film-forming properties. The translucent copolyesters were obtained by the incorporation of eugenol end-capped siloxane. The T_gs of copolyesters were considerably decreased by the incorporation of siloxane moiety into the polymer backbone without much loss of thermal stability. This may be due to the incorporation of flexible siloxane moieties in the copolyester backbone. Therefore, these copolyesters may be considered to be, promising soluble, high temperature plastic materials.

nitrogen atmosphere. This indicates that the siloxane copolyesters are thermally stable.

The crystalline/amorphous nature of the aromatic copolyesters was studied by WAXD spectroscopy. The X-ray diffractograms of different aromatic copolyesters are shown in Figure 6. The X-ray diffraction studies showed that the aromatic copolyesters prepared from phenylindane bisphenol with varying ratios of DPT, DPI, and EuSi exhibited an amorphous behavior.

CONCLUSIONS

A series of aromatic copolyesters containing siloxane linkages were prepared by the melt polymerization of phenylindane bisphenol with varying ratios of DPT, DPI, and EuSi in the temperature range 200–290°C
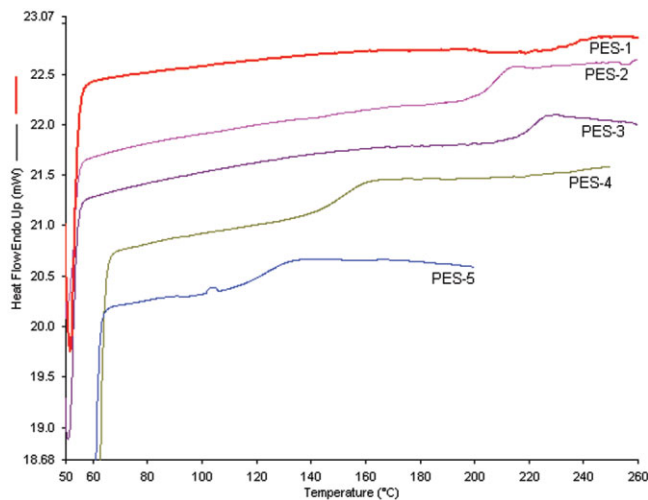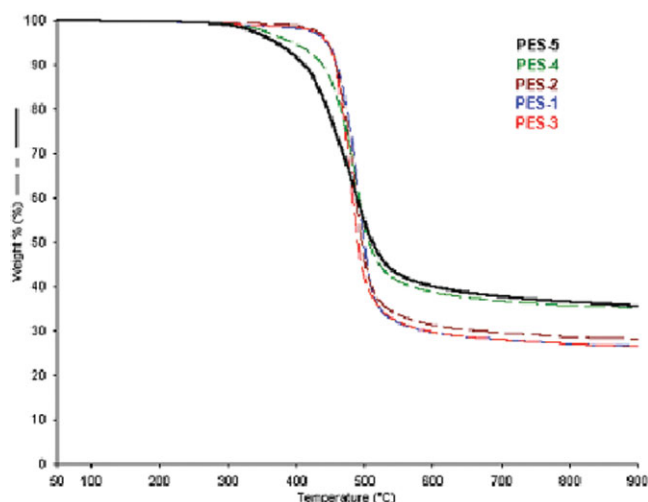

Figure 5 TGA of siloxane copolyesters. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]
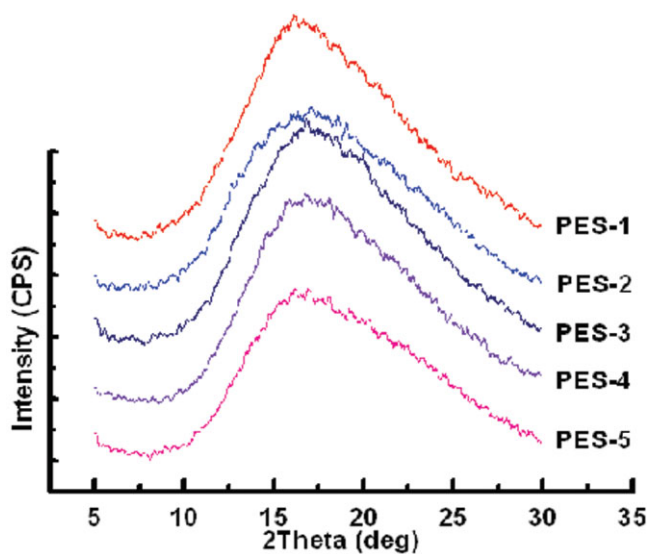
Figure 6 X-ray diffractograms of siloxane copolyesters. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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