

Synthesis and Characterization of Aromatic Copolyesters Containing Siloxane Linkages in the Polymer Backbone

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ABSTRACT: A new series of aromatic copolyesters containing siloxane linkages were prepared by the melt polymerization of bisphenol A (BPA) with eugenol end-capped siloxane (EuSi), diphenyl terephthalate (DPT), and diphenyl isophthalate (DPI) in varying ratio in the temperature range 220–290°C under reduced pressure in the presence of dibutyl tin dilaurate (DBTL) catalyst. The siloxane copolyesters prepared were characterized by FTIR, ¹H-NMR spectroscopy, solution viscosity, thermogravimetric analysis, differential scanning calorimetry, and X-ray diffraction. The effect of incorporation of eugenol end-capped siloxane was stud-

ied on the properties of BPA/DPI/DPT copolyesters. The glass-transition temperature of copolyester was decreased from 184 to 70°C by incorporation of 20% of eugenol end-capped siloxane. All copolyesters were found to be soluble in commonly used aprotic polar solvents and had film-forming properties. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3222–3228, 2006

Key words: aromatic copolyesters; melt polymerization; eugenol end-capped siloxane; bisphenol A; diphenyl terephthalate; diphenyl isophthalate

INTRODUCTION

Aromatic polyesters (polyarylates) are polyesters derived from aromatic diols and dicarboxylic acid.^{1,2} They belong to a class of engineering plastics and are characterized by their inherent flame retardance, resistance to UV, and relatively high glass-transition temperatures (T_g). The copolyesters prepared from bisphenol A (BPA), terephthalic acid (TPA), and isophthalic acid (IPA) are the representative examples of polyarylates. These polyesters are expected to find applications in transportations (interior panels for buses and aircrafts), glazing parts (solar collectors and appliances), and other optical uses.

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-Baumann^{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 aro-

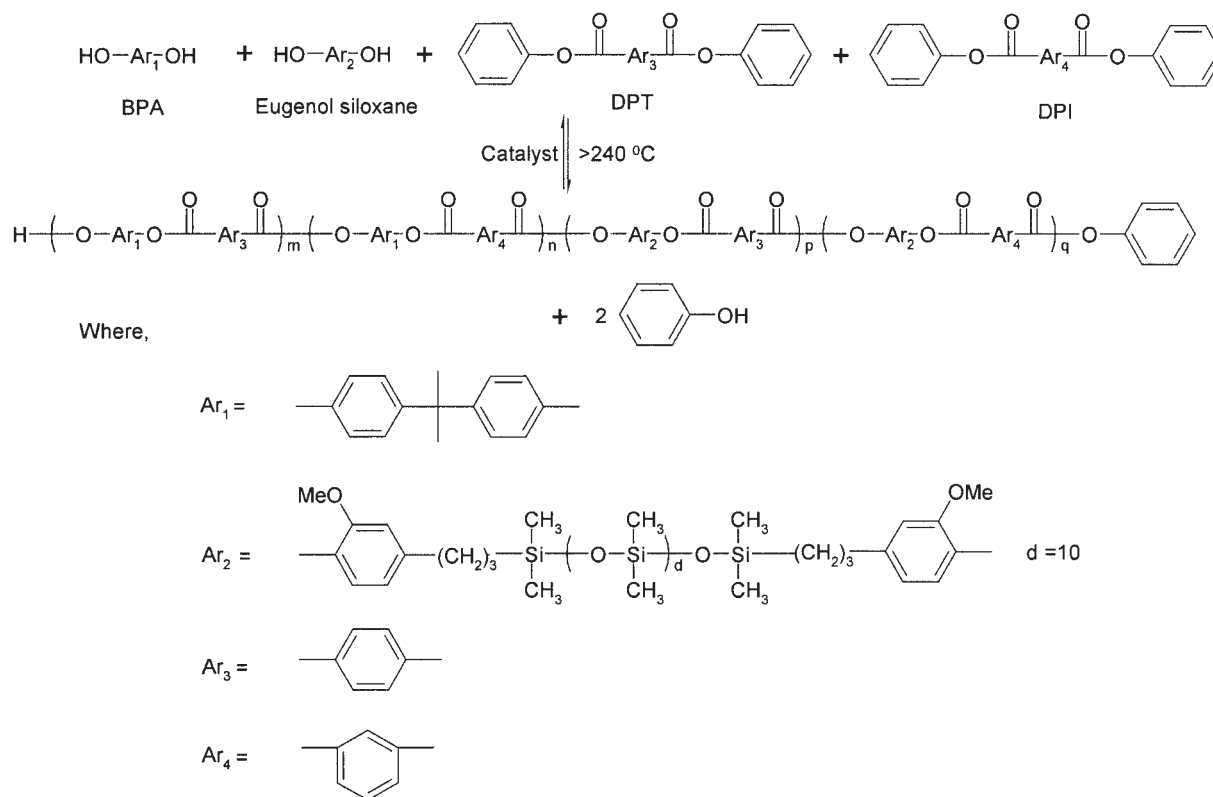
matic dicarboxylic acid(s) with an aromatic diol(s) *via* transesterification. All of the preparation methods possess certain advantages as well as disadvantages and selection of a particular method is governed by factors such as economics, reliability of the process, and product quality.

Aromatic polyesters of this class, however, are generally difficult to process 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 aromatic polyesters without affecting their thermal properties and much work has been expended in this area. One of the approaches to improve the solubility of polymers without extreme loss of their high thermal stability has been the introduction of polar and flexible groups into the polymer backbone.

The siloxane group has been known to meet this requirement, and some siloxane group containing polymers have been reported in the literature.^{13–16} 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 series of new siloxane copolyesters by melt polymerization of BPA, EuSi with mixtures of DPT and DPI in varying ratio. The effect of eugenol end-capped siloxane was studied on the properties of copolyesters derived from bisphenol A with diphenyl isophthalate and diphenyl terephthalate. The properties such as glass-transition temperature, crystalline melting temperature, crystallinity, and solubility were studied.

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Scheme 1 Preparation of siloxane copolyesters.

EXPERIMENTAL

Materials

Bisphenol A (BPA) was procured from Sigma-Aldrich, St. Louis, MO. Eugenol end-capped siloxane (EuSi) (D₁₀) was obtained from General Electric Company. Benzyltriethyl ammonium chloride (BTEAC) was procured from Sigma-Aldrich, St. Louis, MO. All these chemicals were 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 the reaction of 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 136–138°C.

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

TABLE I
Properties of Siloxane Copolyesters

Polymer code	Reactants				Yield (%)	η_{inh} (dL/g)
	BPA (%)	EuSi (%)	DPT (%)	DPI (%)		
PES-1	100		50	50	98	0.50
PES-2	95	5	50	50	99	0.46
PES-3	90	10	50	50	97	0.44
PES-4	85	15	50	50	98	0.43
PES-5	80	20	50	50	99	0.42

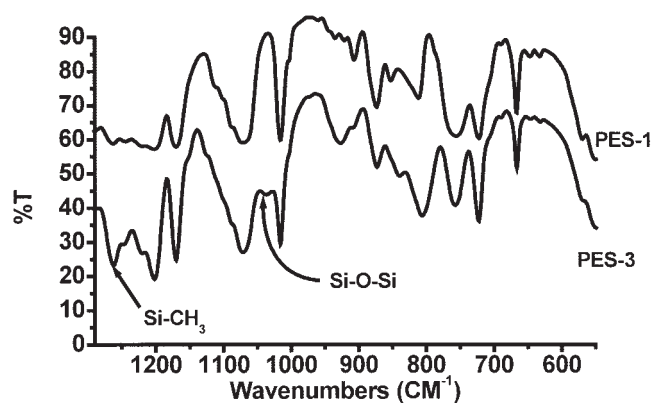


Figure 1 FTIR spectra of aromatic copolyesters (PES-1 and PES-3).

TABLE II
Determination of % Composition of BPA and EuSi
in Copolyesters by $^1\text{H-NMR}$ Spectroscopy

Polymer code	Feed composition		Composition by $^1\text{H-NMR}$	
	BPA	EuSi	BPA	EuSi
PES-2	95	5	95.2	4.8
PES-3	90	10	90.5	9.5
PES-4	85	15	84.5	15.5
PES-5	80	20	80.5	19.5

Measurements

FTIR spectra of neat aromatic copolyester films were recorded on Perkin–Elmer 16 PC FTIR spectrophotometer.

$^1\text{H-NMR}$ 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 solvent due to the potential overlap with the methyl protons in the siloxane polymer. The chloroform reference peak at 7.28 ppm was used to ensure accuracy of peak assignments.

Ubbelohde viscometers were used to determine the inherent viscosities (η_{inh}) at $30 \pm 0.1^\circ\text{C}$ of polymer solutions having concentrations of 0.5 g/100 mL in chloroform.

Differential scanning calorimetry (DSC) thermograms were obtained with a Perkin–Elmer DSC-7, at a heating rate of $10^\circ\text{C min}^{-1}$.

Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) were carried out with a Perkin–Elmer TGA-7 thermogravimetric analyzer, under nitrogen atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$.

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_α radiation.

Preparation of siloxane copolyesters

All copolyesters were prepared by the melt polymerization technique. Since the preparation methods were similar, only a representative polymerization method is given for the copolyester of PES-2.

A 100-mL three-necked cylindrical glass reactor was equipped with a mechanical stirrer, a nitrogen gas inlet, a vacuum-jacketed Vigreux column, and distillation head. The reactor was charged with 4.33 g (0.019 mol) of BPA, 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 0.5 wt % (based on BPA) of DBTL catalyst. The melt polymerization was carried out 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 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, and no phase separation was observed. The reaction product is homogeneous in nature. The product 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), *N,N*-dimethyl formamide (DMF), *N,N*-dimethylacetamide (DMAC), *N*-methyl-2-pyrrolidone (NMP), and *N,N*-dimethyl sulfoxide (DMSO).

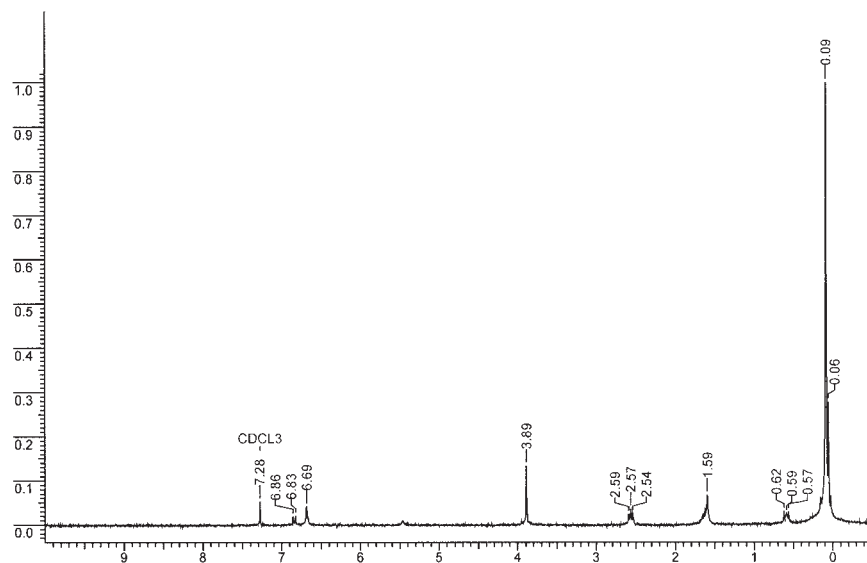
RESULTS AND DISCUSSION

The aromatic copolyesters containing siloxane linkages were prepared by the melt polymerization of DPT, DPI, and EuSi with BPA in varying ratios in the temperature range of $220\text{--}290^\circ\text{C}$ under reduced pressure in the presence of DBTL catalyst. The copolyesters prepared were homogeneous in nature, and no phase separation was observed due to incorporation of siloxane blocks. The preparation of siloxane copolyesters is shown in Scheme 1.

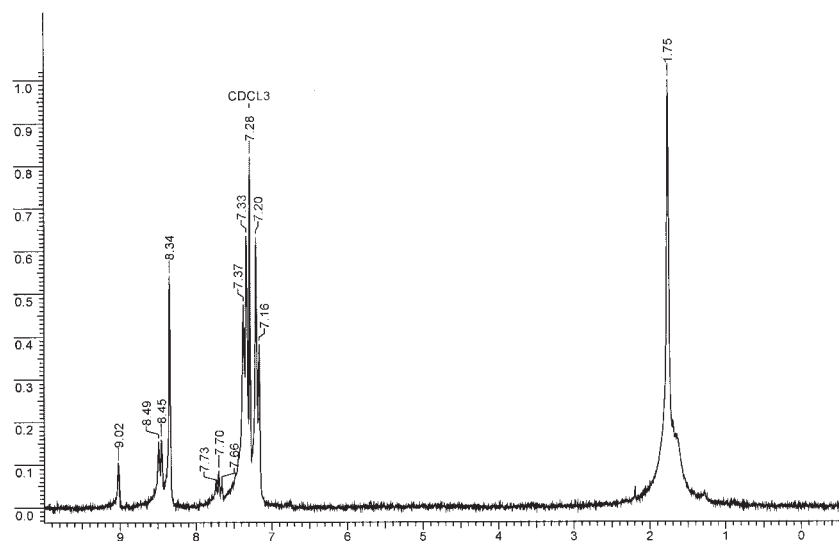
The siloxane copolyesters were characterized by FTIR spectra, $^1\text{H-NMR}$ spectra, solution viscosity, thermogravimetric analysis, differential scanning calorimetry, and X-ray diffraction. The properties of copolyesters are summarized in Table I.

The copolyesters were obtained in quantitative yields. The solution viscosities of copolyesters were varied from 0.42 to 0.50 dL/g. A decrease in the solution viscosity of copolyester was observed with an increase in the incorporation of siloxane from 5 to 20%. This may be due to the flexible nature of the siloxane linkages.

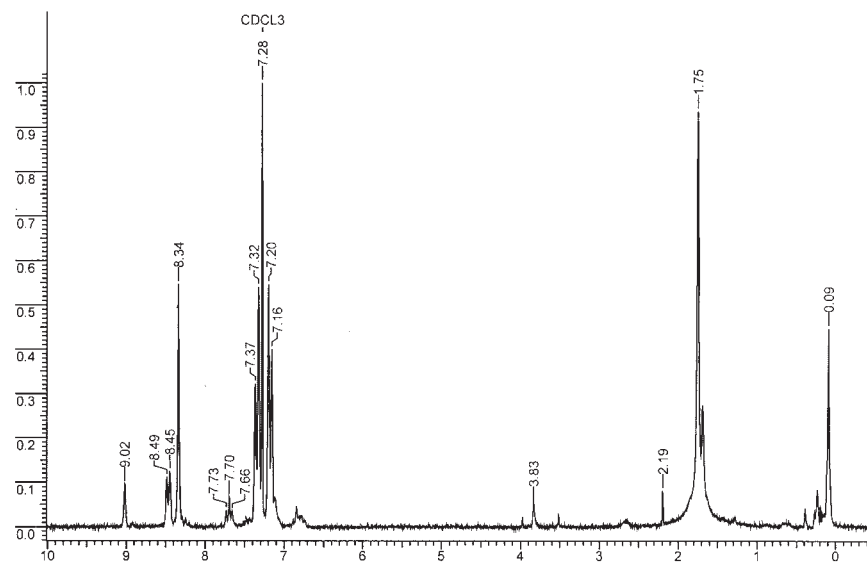
The solubility behavior of siloxane-containing copolyesters was checked at 5 wt % concentration in different solvents. All copolyesters were found to be soluble in the polar solvents, namely chloroform, methylene chloride, THF, and aprotic polar solvents, namely DMF and NMP. However, all the copolyesters were found to be insoluble in DMSO. None of the copolyester was soluble in ethanol, methanol, and petroleum ether. All copolyesters have film-forming properties, and the films were flexible in nature.



(a)



(b)



(c)

Figure 2 $^1\text{H-NMR}$ spectra of (a) Eugenol end-capped siloxane, (b) PES-1, and (c) PES-2 in CDCl_3 .

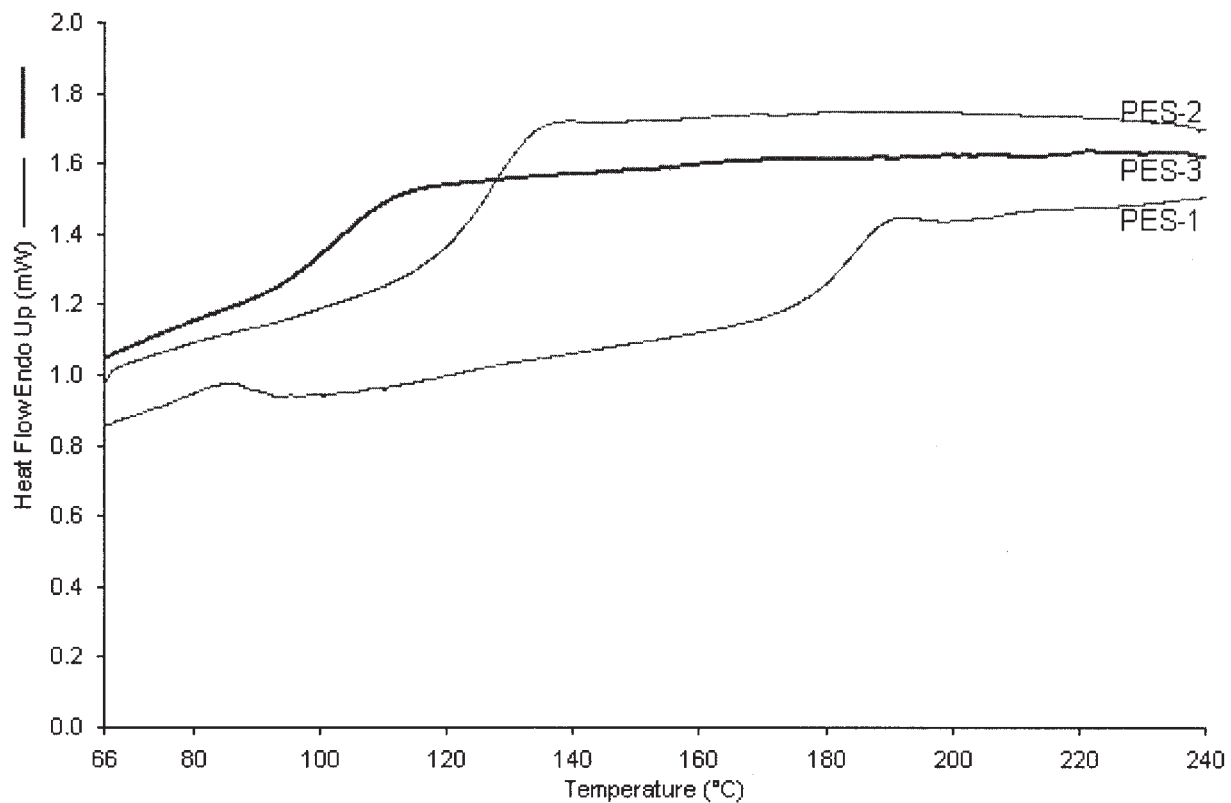


Figure 3 DSC thermograms of siloxane copolyesters.

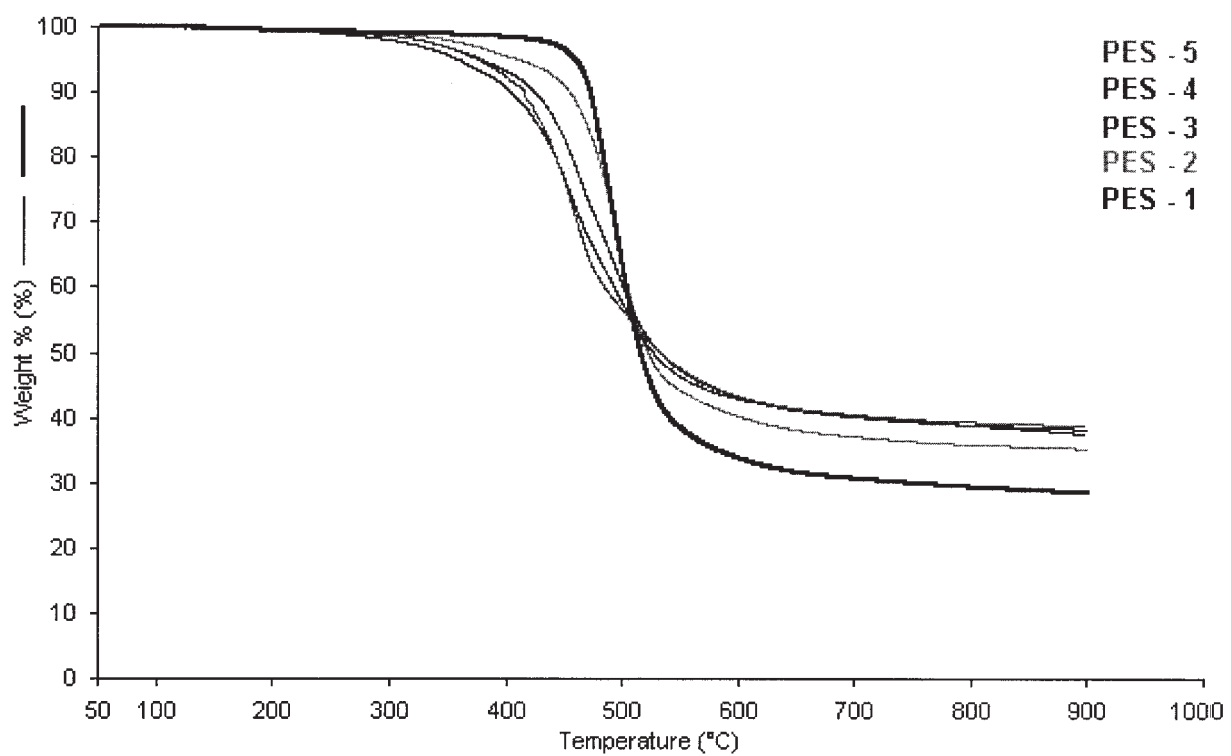


Figure 4 TGA thermograms of siloxane copolyesters.

TABLE III
Thermal Behavior of Siloxane Copolyesters

Polymer code	T_g (°C)	IDT (°C)	T_{10} (°C)	T_{max} (°C)	Residue (%)
PES-1	184	466	471	494	29
PES-2	126	445	453	497	35
PES-3	102	415	425	496	37
PES-4	79	407	414	459	38
PES-5	70	400	404	455	39

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

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} due to the presence of Si—O—Si linkages and a stretching vibration band at 1262 cm^{-1} due to the presence of Si—CH₃ linkages. The FTIR spectra of aromatic copolyester (PES-1) and siloxane copolyester (PES-3) are illustrated in Figure 1.

The incorporation of eugenol siloxane in aromatic copolyesters was confirmed and quantitatively determined by ¹H-NMR spectroscopy. The results are summarized in Table II.

The ¹H-NMR spectra of eugenol end-capped siloxane, BPA/DPT/DPI copolyester (PES-1), and BPA/EuSi/DPT/DPI copolyester (PES-2) are illustrated in Figure 2. The incorporation of eugenol siloxane in copolyester was determined by ¹H-NMR spectroscopy, using the relative integration of the peaks of eugenol end-capped siloxane at $0.09\ \delta$ due to methyl siloxane protons and at $1.75\ \delta$ due to isopropylidene group of BPA. The incorporation of EuSi in copolyester was found to be quantitative as the feed compositions.

The siloxane copolyesters prepared by the melt polymerization technique are block copolymers. The short siloxane blocks are incorporated in the polymer chains by the above technique. This was confirmed by NMR spectroscopy.

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 3 and 4. The thermal properties of siloxane copolyesters are summarized in Table III.

The DSC results showed that the glass-transition temperature (T_g) of siloxane copolyesters was considerably decreased by the incorporation of siloxane linkages into the polymer backbone. The T_g 's of copolyesters were decreased from 184 to 70°C by the incorporation of 20% of eugenol end-capped siloxane (D₁₀). The decrease in T_g is due to the incorporation of flexible structure of the eugenol end-capped siloxane. The incorporation of siloxane linkages has improved

the injection-molding properties of BPA/DPT/DPI aromatic copolyesters.

The initial decomposition temperature (IDT), temperature 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 increases from 29 to 39% due to the incorporation of siloxane in the polymer backbone when the copolyester was heated from 50 to 900°C under nitrogen atmosphere. This indicates that the siloxane copolyesters are thermally stable.

The crystalline/amorphous nature of the siloxane copolyesters was studied by wide angle X-ray diffraction (WAXD) spectroscopy. The representative X-ray diffractograms are illustrated in Figure 5. The X-ray diffraction studies showed that all the copolyesters are amorphous in nature. The amorphous nature and high solubility of the siloxane copolyesters is attributed to the flexibility and polarity of the eugenol siloxane group.

CONCLUSIONS

A new series of aromatic copolyesters containing siloxane linkages were prepared by the melt polymerization of BPA, EuSi, DPT, and DPI in varying ratios in the temperature range of 220 – 290°C under reduced pressure in the presence of DBTL catalyst. All copolyesters are homogenous in nature, and no phase separation was observed due to the incorporation of siloxane linkages. All the copolyesters were easily soluble in a wide range of solvents, and the solution had film-forming properties. The glass-transition temperatures of copolyesters were considerably decreased

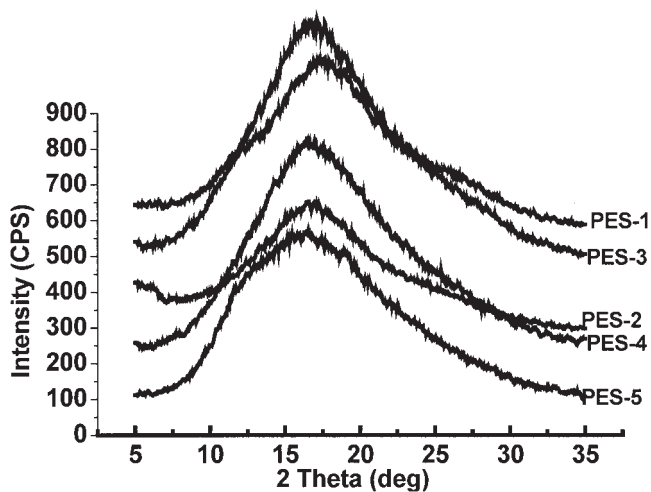


Figure 5 X-ray diffractograms of siloxane copolyesters.

without the loss of thermal stability by the incorporation of siloxane linkages into the polymer backbone. Therefore, these copolyesters may be considered to be promising soluble, high-temperature plastic materials.

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