

Synthesis and Characterization of Silicon-Containing Cardo Polyesters

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ABSTRACT: New polyesters containing both silane and “cardo” groups were synthesized by solution polycondensation involving the reaction of bis(4-chlorocarbonylphenyl)dimethylsilane with cardo bisphenols, namely, phenolphthalein, phenolphthalimidine, and phenolphthalein anilide. Copolyesters were obtained by using different proportions of phenolphthalein and phenolphthalein anilide. Polyesters had inherent viscosities in the range 0.22–0.70 dL/g and were readily soluble in chlorinated hydrocarbons and polar aprotic solvents. Polyesters showed glass transition temperatures in the range 168–255°C as measured by DSC and thermogravimetric analysis indicated no weight loss below 416°C in a nitrogen atmosphere. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1329–1335, 1997

Key words: cardo polyesters; phenolphthalein–anilide; bis(4-chlorocarbonyl phenyl)dimethylsilane; differential scanning calorimetry; thermal degradation

INTRODUCTION

The continued interest in polyesters is demonstrated by the range of topics covered and exploited by researchers.^{1,2} The ordering and varying of backbone functions has a profound effect on the final properties of the polymer.³ Aromatic silane functions have been incorporated into thermally stable polymers such as polyimides,⁴ polyamides,^{5–8} polyamideimides, poly(1,3,4-oxadiazole)s, polybenzimidazoles, poly-1,2,4-triazoles, polybenzoxoles, and polyesters⁹ with an effort to improve their processing characteristics. The introduction of “cardo” groups into the backbone of polymers is another approach for improving solubility and thereby processibility. Cardo polymers exhibit a valuable set of properties: the combination of an increased thermal stability with an in-

creased solubility in organic solvents because of the specific contribution of the cardo group.

Phenolphthalein is becoming an important building block for condensation polymers and polyesters derived from it have been reported to exhibit interesting properties. Recently, Zhang et al. studied the gas transport properties of silicon-containing polyesters based on phenolphthalein.³

We now report the synthesis and characterization of polyesters based upon bis(4-chlorocarbonylphenyl)dimethylsilane (BCPDMS) and cardo bisphenols, namely, phenolphthalein, phenolphthalimidine, and phenolphthaleinanilide, and copolyesters synthesized by polymerization of bis(4-chlorocarbonylphenyl)dimethylsilane with different proportions of phenolphthalimidine and phenolphthaleinanilide and their properties.

EXPERIMENTAL

Materials

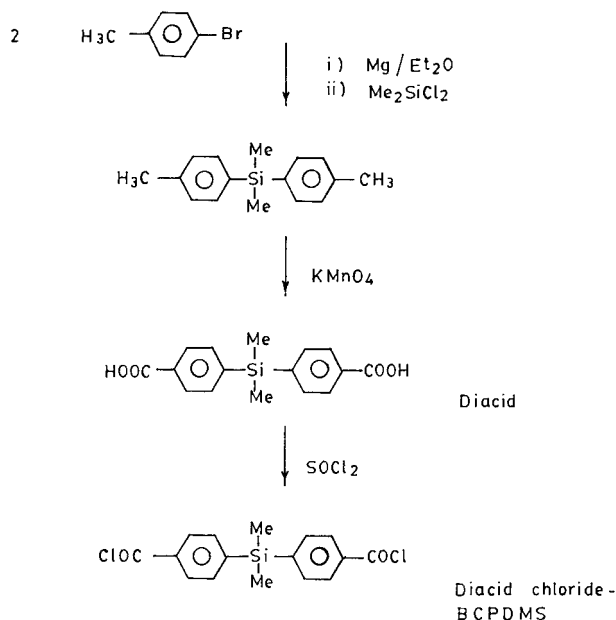
Bis(4-chlorocarbonylphenyl)dimethylsilane was prepared according to the reported method. Phenol-

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Scheme 1 Synthesis of organosilicon diacid chloride (BCPDMS).

phthalein (PPH) (Aldrich Chemical Co., analytical grade) was recrystallized from methanol to give a melting point of 261–262°C. Phenolphthalimidine (PPI) and phenolphthalein anilide (PPA) were prepared as described in the literature.¹⁰ 1,2-Dichloroethane and triethylamine were distilled prior to use.

Polymerization Procedure

Polyester-E from PPA and BCPDMS

Into a 100 mL three-necked round-bottom flask equipped with a magnetic stirrer, a nitrogen gas inlet, and a calcium chloride guard tube were placed 0.393 g (0.001 mol) of PPA, 2.5 mL dichlo-

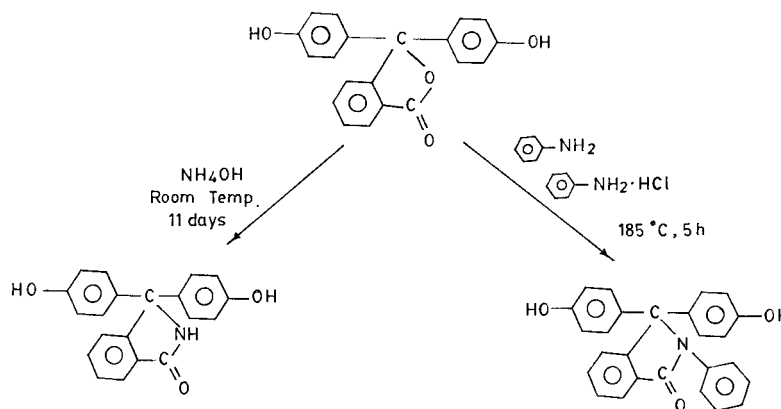
roethane, and 2 mL triethylamine. The mixture was stirred at 25°C for 5 min and then placed in an ice bath at 0°C. A solution of 0.337 g (0.001 mol) of BCPDMS in 2.5 mL of dichloroethane was added dropwise over a period of 30 min. The reaction mixture was stirred at 0°C for 1 h and at 25°C for 12 h, after which it was poured into 40 mL hexane with stirring. The precipitated polymer was isolated by filtration, washed with methanol (50 mL), water (50 mL), and dried. The polymer was purified by dissolving it in dichloromethane and by reprecipitation in excess hexane. Finally, the polymer was dried at 50°C under a vacuum. The yield was 0.602 g (91.5%). The other polyesters (A–D and F) were synthesized following a similar procedure.

Measurements

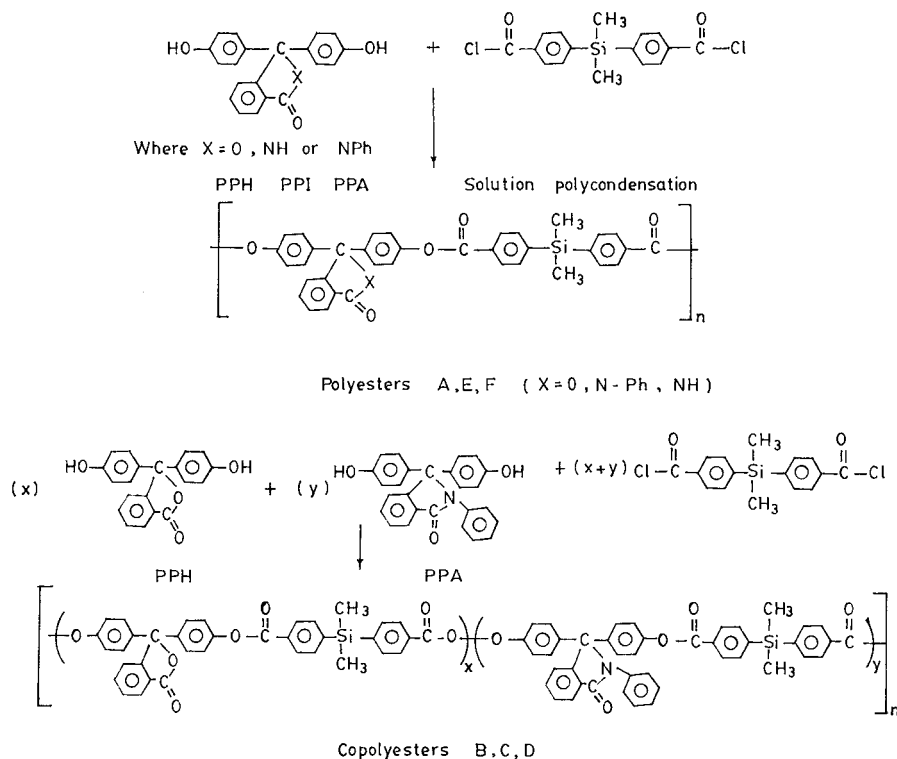
The reduced viscosities (η_{red}) were measured with a 0.5% concn sym tetrachloroethane at 25°C using a suspended-type Ubbelohde viscometer. IR spectra were recorded using a KBr pellet technique on a Perkin-Elmer 883 spectrophotometer. ¹H-NMR were recorded in CDCl₃ on a Bruker 200 MHz spectrometer using TMS as the internal reference. Thermogravimetric analysis and differential scanning calorimetry were performed on a Perkin-Elmer TGA-7 and a Perkin-Elmer DSC-7, respectively, at a heating rate of 10°C/min. The X-ray diffractograms were obtained with a Phillips X-ray unit (Phillips generator, PW-1730) and nickel-filtered CuK α radiations.

RESULTS AND DISCUSSION

The synthesis of BCPDMS is reported (Scheme 1) and involves the reaction of 4-bromotoluene



Scheme 2 Synthesis of phenolphthalimidine and phenolphthalein anilide bisphenols.



Scheme 3 Synthesis of silicon-containing cardo polyesters.

with magnesium followed by reaction with dichlorodimethylsilane. The resulting bis(4-tolyl)dimethylsilane was oxidized to the dicarboxylic acid with KMnO_4 and subsequently converted to the diacylchloride. Aminated phenolphthalein bisphenols were prepared as shown in Scheme 2.

Polyesters were synthesized by polycondensa-

tion of BCPDMS with PPA by the solution polymerization technique (Scheme 3). The polycondensation was carried out in 1,2-dichloroethane using triethylamine as an acid acceptor. In a similar manner, copolyesters were also prepared from BCPDMS and a mixture of PPA and PPH (Scheme 3). The results of the synthesis of the

Table I Synthesis of Silicon-containing Cardo Polyesters

Entry	Polymer	Composition of Diols (mol %)		Yield (%)	η_{red}^a (dL/g)
		PPH	PPA		
1	A	100	00	91.9	0.22
2	B	75	25	83.3	0.27
3	C	50	50	84.7	0.38
4	D	25	75	91.1	0.54
5	E	00	100	91.5	0.70
6	F	PPI (100)		87.8	0.40

^a Measured with 0.5% (w/v) solution of polyester in 1,1,2, 2 sym tetrachloroethane at 25°C.

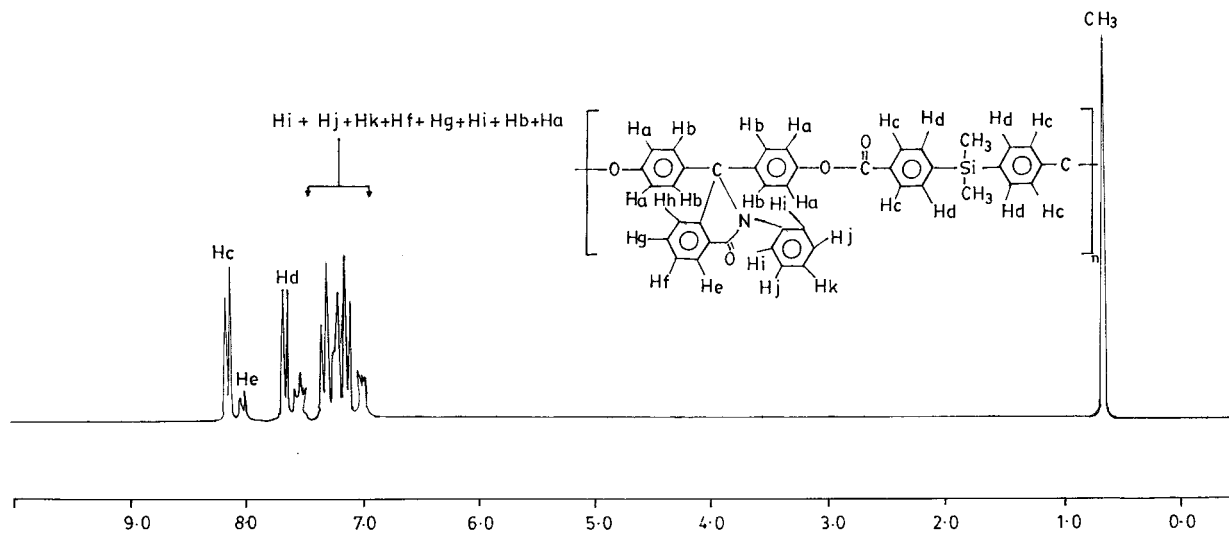


Figure 1 H-NMR (200 MHz, CDCl₃) of polyester E.

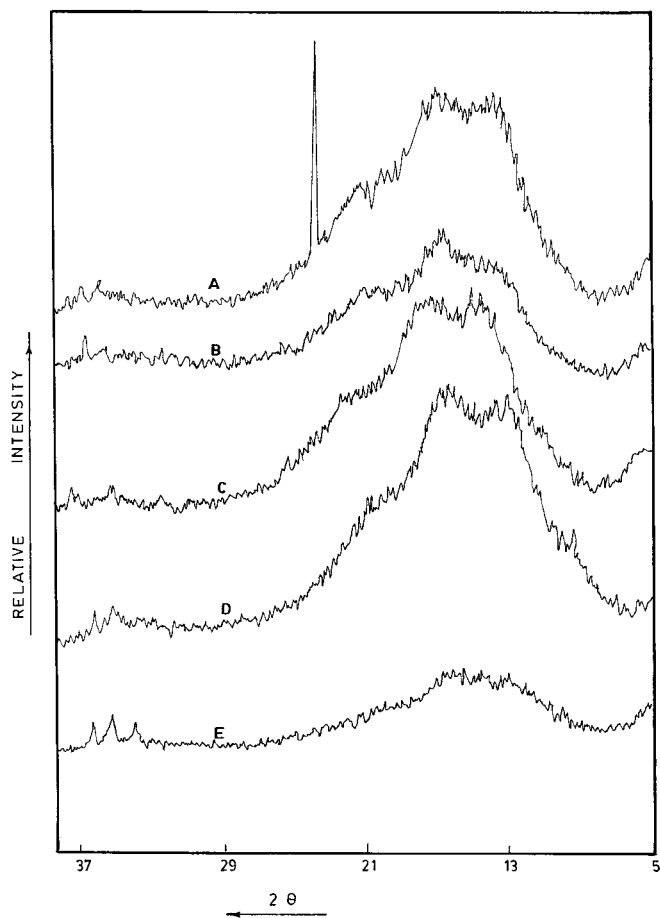


Figure 2 X-ray diffractograms of polyesters A–E.

Table II Solubility of Silicon-containing Cardo Polyesters

Sample No.	Solvent	Polymer					
		A	B	C	D	E	F
1	Concn H ₂ SO ₄	++	++	++	++	++	++
2	DMAC	++	++	++	++	++	++
3	DMF	++	++	++	++	++	++
4	NMP	++	++	++	++	++	++
5	TCE	++	++	++	++	++	++
6	DCM	++	++	++	++	++	++
7	<i>m</i> -Cresol	++	++	++	++	++	++
8	DMSO	+	+–	+–	+–	+–	+–
9	Methanol	–	–	–	–	–	–

++ Soluble at room temperature; + soluble on heating; +– partly soluble; – insoluble.

polyesters are given in Table I. All the polyesters were obtained in good yields as a colorless powdery or fibrous material.

Polyesters exhibited reduced viscosities in the range of 0.22–0.70 dL/g. On comparing the reduced viscosities of polyesters A–E, it was observed that polyester A derived from PPH had a lower reduced viscosity and the reduced viscosity increases through B to E as the proportion of PPA

was increased. The formation of polyesters was confirmed by IR and ¹H-NMR spectra. The IR spectra of polyesters exhibited a characteristic strong absorption band for ester carbonyl in the range 1740–1750 cm⁻¹. Polyesters containing PPA showed a strong absorption band at 1698 cm⁻¹ assignable to amide carbonyl. Polyesters also showed a band at 1765 cm⁻¹ due to the carbonyl group of the phthalide ring. IR spectra also

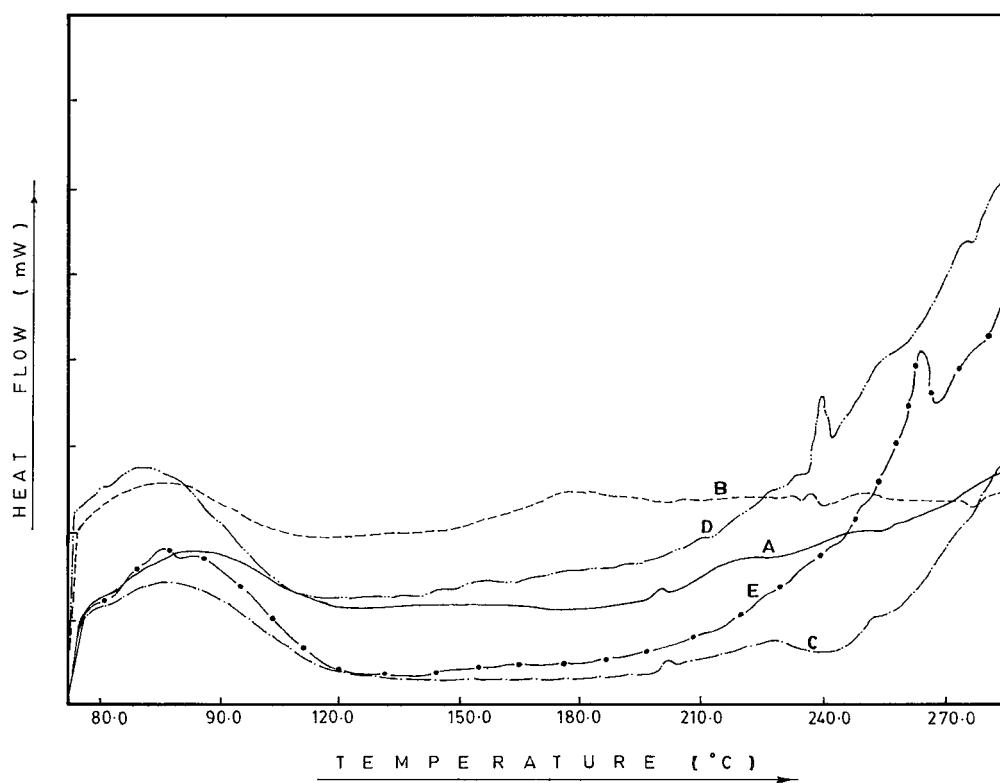


Figure 3 DSC thermograms of polyesters A–E.

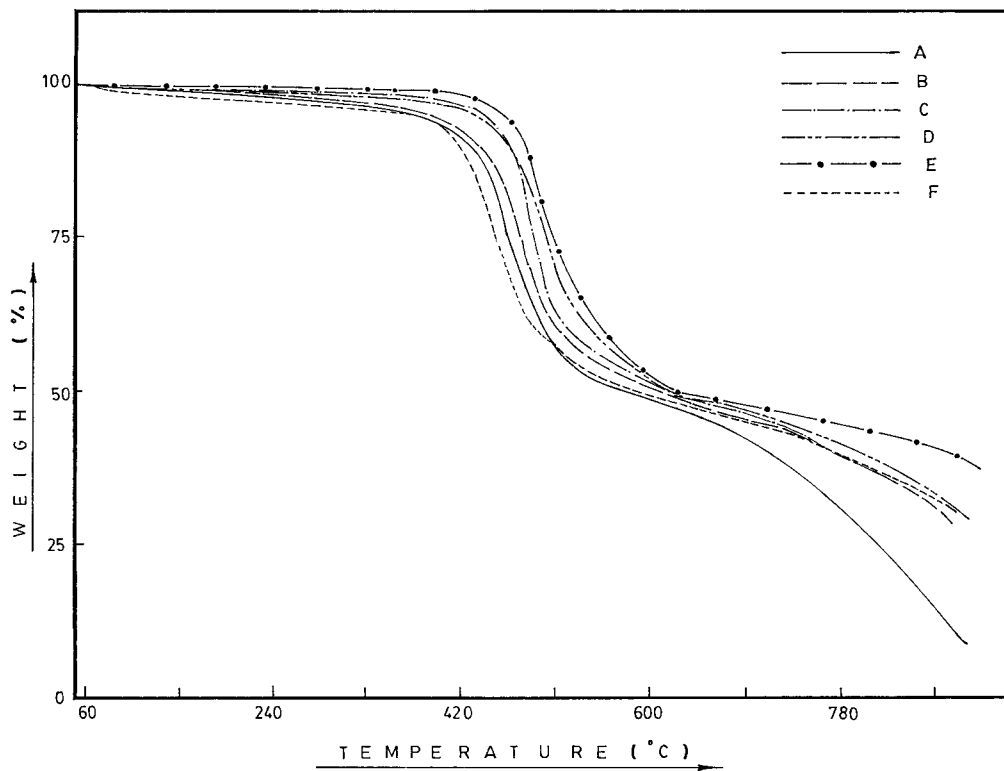


Figure 4 Thermogravimetric curves of polyesters A-F.

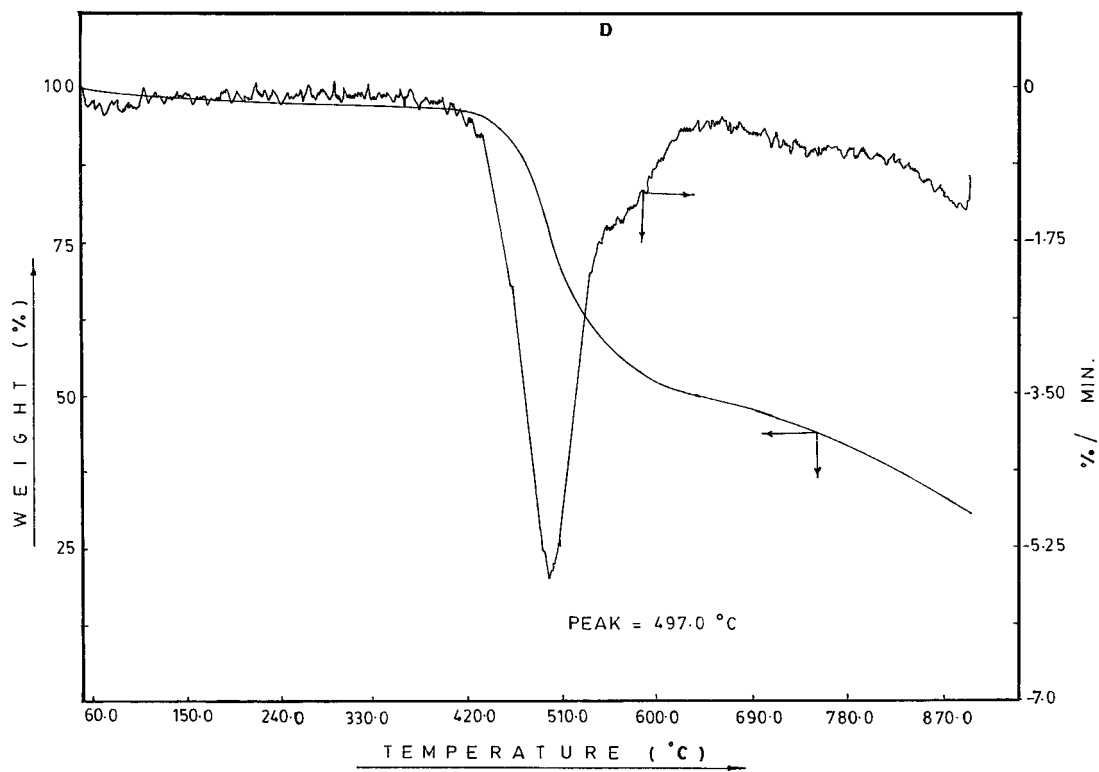


Figure 5 TG and DTG curves of polyester D.

Table III Thermal Analysis^a Data of Silicon-containing Cardo Polyesters

Entry	Polymer	T_i^b (°C)	T_{max}^c (°C)	Residual Mass % at 900°C	T_g^d (°C)
1	A	434	471	6.95	208
2	B	444	480	22.93	168
3	C	460	489	26.41	220
4	D	464	497	29.88	252
5	E	478	508	31.97	255
6	F	416	457	29.19	—

^a Thermogravimetric analysis conducted at heating rate of 10°C/min under nitrogen.

^b T_i , the temperature at which initial loss of mass was observed.

^c T_{max} , temperature of maximum rate of decomposition from DTG.

^d Determined by DSC.

showed absorption at 1250 and 840 cm^{-1} due to the silyl- CH_3 group.

¹H-NMR spectra were in good agreement with the structure of the polyesters. A representative ¹H-NMR spectrum of polyester along with its proton assignments is depicted in Figure 1. X-ray diffraction studies of the polyesters indicated that polyester E derived from PPA was amorphous while polyesters A–D showed a partial crystallinity (Fig. 2).

All the polyesters were soluble in chlorinated hydrocarbons and polar aprotic solvents. This enhanced solubility indicates that the introduction of silicon atoms in the polyester main chain and phthallide cardo moieties along the polyester chain reduces the chain stiffness. They were partially soluble in dimethylsulfoxide and insoluble in methanol (Table II). The glass transition temperature (T_g) of the polyesters, as determined by DSC, were in the range of 168–255°C (Fig. 3).

Thermogravimetric analysis (TGA) of the polyesters was carried out in a nitrogen atmosphere at a heating rate of 10°C/min. TGA and DTG curves of polyesters are shown in Figures 4 and 5, respectively. Table III incorporates thermal characteristics such as the initial decomposition temperature (T_i), maximum decomposition temperature (T_{max}), and residual weight at 900°C. No weight loss was observed below 416°C, indicating a high thermal stability of the polyesters.

CONCLUSION

Polyesters and copolyesters, containing dimethylsilyl moieties in the polymer backbone and cardo

groups along the main chain, were synthesized from BCPDMS and PPA/PPH by low-temperature solution polycondensation. These polyesters had film-forming properties, improved thermal stability, and polymer solubility in selected organic solvents.

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