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Synthesis and thermal properties of soluble silicon containing phenylated aromatic–aliphatic polyamides

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Abstract Aromatic polyamides find many applications in diverse and critical areas due to their high thermal stability coupled with high mechanical properties. However most of such aramides are difficult to fabricate because of their limited solubility and high melting temperature. Improvements in processability have been reported by incorporating bulky pendant groups and aliphatic spacer groups. Similarly to improve the solubility of polymers approaches of incorporating silicon in main polymer chain and copolymerization techniques were useful. We report the synthesis and characterization of a series of phenylated silicon containing aromatic–aliphatic polyamides from a mixture of 2, 5-bis (4-carboxy methylene phenyl)-3, 4-diphenyl thiophene (CMPDT) and bis-(4-carboxy phenyl) dimethyl silane (BCPDS) in various mole proportions, with commercial aromatic diamine. Thus a series of novel copolyamides having pendant phenyl groups, methylene spacer and silicon moiety was prepared by judicious combination of (CMPDT); BCPDS and aromatic diamine; bis-(4-aminophenyl) ether (ODA), by direct polycondensation using Yamazaki's phosphorylation method. These high molecular mass polyamides were obtained in high (89–98%) yields and had viscosities in the range of 0.23–0.57 dL/g in DMAc. Polyamides showed improved solubility in polar aprotic solvents, like NMP, DMAc, DMSO and DMF; had high thermal stability; with no mass loss below 335 °C.

Keywords 2, 5-bis (4-carboxy methylene phenyl)-3, 4-diphenyl thiophene · bis-(4-carboxy phenyl) dimethyl silane · bis-(4-amino phenyl) ether · Copolyamides · Solubility · Thermal stability

Introduction

Aromatic polyimides, polyamides have the poor processability due to their insolubility in common organic solvents and extremely high glass transition or melt temperature. The synthesis of soluble polyimides/polyamides without deteriorating their excellent properties [1–6] include the preparation of copolymers, introduction of bulky pendant groups, flexible linkages and kinked or unsymmetrical structures or cardo moiety into the polymer backbone. DSC studies of some polyamides [7, 8] were reported in literature. We successfully prepared aromatic polyamides [9], polyimides, poly (amide–imide)s, polybenzimidazoles [10], polyesters, polyquinoxalines, from a number of new cardo/methylene containing and phenylated functional monomers. Thermal behaviour of silicon containing poly(ester-imide)s [11] showed good thermal stability. Some aramides with silicon moieties in the backbone have been reported in the literature [12–15] however they were prepared from bis-(4-carboxy phenyl) dimethyl silane (BCPDS) or from bis [(4-carboxy phenyl) 4-benzamide] dimethyl silane, BCPBDS; with aromatic diamines. These aromatic polyamides contained 'Si' but no methylene spacer in combination with phenylated thiophene moiety. Thus, there are no reports on phenylated methylene spacer and silicon containing polyamides. Therefore it was worth to synthesize copolyamides which have all structural units namely pendant phenyl, methylene spacer, silicon moiety and ether linkages; to study their overall effects on resulting polyamides.

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The purpose of the present study is to synthesize and characterize the series of aromatic–aliphatic polyamides from a mixture of 2, 5-bis (4-carboxy methylene phenyl)-3,4-diphenyl thiophene, (CMPDT) and BCPDS in various mole proportions, with commercial aromatic diamine such as bis-(4-aminophenyl) ether (oxydianiline, ODA).

In the present investigation dicarboxylic acid 2, 5-bis (4-carboxy methylene phenyl)-3, 4-diphenyl thiophene (CMPDT) and polyamides therefrom were synthesized. In the present study a well developed solution polycondensation method has been used to prepare these copolyamides from dicarboxylic acids with a diamine by direct polycondensation method [16] to yield high molecular mass copolyamides. Resulting copolymers were characterized by measurement of viscosity, solubility, film-forming property, IR-spectroscopy and thermal analysis. The effect of copolymerization by varying ratio of BCPDS to CMPDT on properties of copolymers is reported.

Experimental

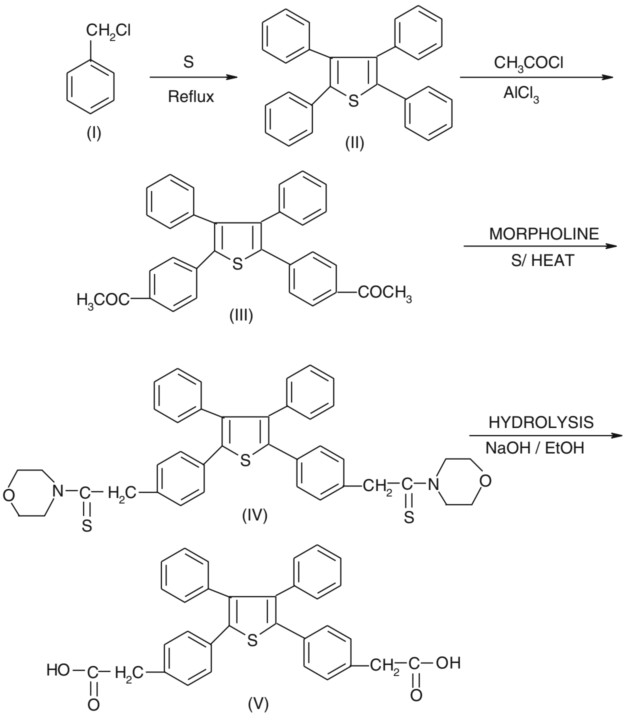
Materials

Commercially available sulfur was purified before use. Benzyl chloride was fractionally distilled. *N*-methyl-pyrrolidone was dried by azeotropic removal of water with benzene for 6 h, distilled under reduced pressure and stored over Linde Type 4Å molecular sieves. *N*, *N* Dimethylacetamide was refluxed over barium oxide for 4 h, the liquid was decanted in a separate round bottom flask and distilled at reduced pressure over calcium hydride and stored over Linde type 4Å molecular sieves. Lithium chloride was dried under vacuum at 150 °C for 6 h. Pyridine was refluxed with potassium hydroxide pellets, fractionally distilled and stored over Linde type 4Å molecular sieves. 4, 4′-Diaminodiphenyl ether (ODA), was recrystallized from alcohol. *p*-Bromotoluene was purified by distillation. Dichloro dimethyl silane and magnesium metal turnings were used as received.

Synthesis of monomer

Synthesis of aromatic diacid, 2, 5-bis (4-carboxy methylene phenyl)-3, 4-diphenyl thiophene CMPDT was performed in several steps (Scheme 1).

Tetraphenyl thiophene (II) was prepared in good yields by refluxing benzyl chloride with sulfur. The IR spectrum (KBr) of II exhibited absorption bands at 3,060 (aromatic C–H), 1,595 (aromatic C = C), and 1,435 cm^{-1} (thiophene). The diacetyl derivative (III) was synthesized by acetylation of (II) using the acetyl chloride and anhydrous aluminum chloride as catalyst in nitrobenzene. The infrared spectrum (KBr) of (III) exhibited an absorption bands at 1,680 cm^{-1} (C = O). 2, 5-bis (4-thioacetomorpholide phenyl)-3, 4-diphenyl thiophene (IV) was prepared by refluxing the (III) with sulfur and morpholine. The infrared spectrum (KBr) of IV exhibited an absorption band at 1,278 cm^{-1} (C = S).



Scheme 1 Synthesis of 2, 5-bis (4-carboxymethylene phenyl) 3, 4-diphenyl thiophene (CMPDT)

Treatment of (IV) with 10% ethanolic sodium hydroxide solution at reflux temperature, 80–85 °C, gave 2, 5-bis (4-carboxy methylene phenyl)-3, 4-diphenyl thiophene (CMPDT) [9]. In a one liter round bottom flask equipped with reflux condenser and magnetic stirrer were placed 33.7 g (0.05 mol) IV and 500 mL 10% ethanolic sodium hydroxide solution. The reaction mixture was refluxed with stirring for 12 h. after which the most of the ethanol was distilled out under reduced pressure. To the residual product, 500 mL hot water was added and filtered. The filtrate was acidified by 1:1 hydrochloric acid. The precipitated product was filtered, washed thoroughly with hot water and dried. The product was recrystallized from ethanol to get white pure CMPDT (V). Yield: 16.38 g (65%), m.p. 238–240 °C. IR spectrum (KBr) of CMPDT showed absorptions at 3,500–3,250 (–OH); 1,726 cm^{-1} (–C=O).

Synthesis of BCPDS

Synthesis of bis (4-carboxy phenyl) dimethyl silane was performed in two steps as reported earlier [12]. Bis (4-tolyl) dimethyl silane (BTDS) was prepared in 77% yields from magnesium metal turnings, dichloro dimethyl silane in diethyl ether with *p*-bromo toluene by using iodine as initiator; finally product was purified by distillation under reduced pressure. Bis (4-carboxy phenyl) dimethyl silane was synthesized (in 56% yields) by oxidation of BTDS with potassium permanganate, and it was purified by recrystallisation from aqueous alcohol.

Polymerization

Direct polycondensation of diacid and diamine using Yamazaki's Phosphorylation method is the most convenient approach for synthesizing high molecular mass polyamides. Therefore polymerization of CMPDT and BCPDS with aromatic diamine ODA was performed by this method to yield phenylated, methylene and silicon moiety containing copolyamides. A typical procedure for synthesis of copolyamides is given below.

Synthesis of copolyamides

In a 100 mL three neck round bottom flask equipped with reflux condenser, magnetic stirrer, calcium chloride guard tube and nitrogen gas inlet were placed 0.252 g (0.5 mmol) CMPDT, 0.150 g (0.5 mmol) 4-BCPDS, 0.200 g (1 mmol) ODA; 0.200 g lithium chloride [8 wt% based on solvent *N*-methyl pyrrolidone (NMP) and pyridine mixture] and 0.744 g (0.63 mL, 2.4 mmol) triphenyl phosphite (TPP), 0.5 mL pyridine and 2 mL NMP. The mixture was stirred well and temperature was slowly raised to 100 °C over a period of 30 min and the mixture maintained at 100 °C for 3 h. After cooling the resultant viscous solution was poured into rapidly stirred 200 mL of methanol. The precipitated polymer (PA-3) was filtered, washed with methanol and dried. The polymer was purified by dissolving in *N*, *N*-dimethylacetamide (DMAc) and reprecipitating in methanol. It was filtered, washed with methanol and dried under vacuum at 100 °C for 8 h. The yield was 99% and the viscosity of polymer in DMAc was 0.57 dL/g.

The series of copolyamides was synthesized by above procedure, where in a mixture of different mol % proportion of CMPDT and BCPDS were polycondensed with ODA. Percentage yields and viscosities of copolyamides are shown in Table 1.

Table 1 Synthesis of copolyamides[a] from ODA and (CMPDT + BCPDS[b])

Polymer code	Diamine (ODA)	Diacid (mol %)		Yield (%)	Viscosity dL/g[c]
		BCPDS	CMPDT		
PA-1	100	100	00	98.49	0.35
PA-2	100	75	25	98.83	0.41
PA-3	100	50	50	97.52	0.57
PA-4	100	25	75	98.27	0.41
PA-5	100	00	100	89.22	0.23

[a] Polymerization was carried out with 1 mmol of ODA and 1 mmol of CMPDT and/or BCPDS

[b] 4-BCPDS, bis (4-carboxyphenyl) dimethyl silane

[c] Measured at concentration of 0.5 g/dL in DMAC at 30 °C

Measurements

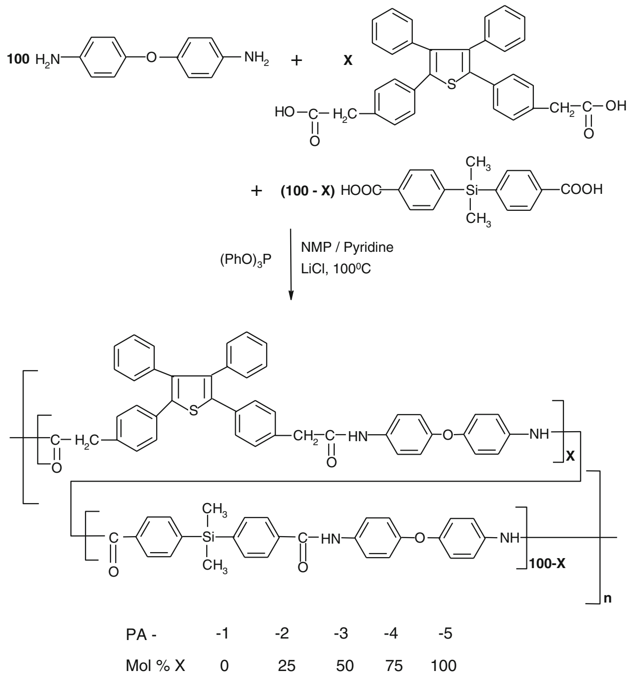
The viscosities of the polyamides were measured in DMAc at 30 °C using Ubbelohde suspended level dilution viscometer (USLV) at polymer concentration of 0.5 g/dL. Solubility of polyamides was determined at 1% (w/w) concentration in different solvents at room temperature or on warming, if needed. Infrared spectra were recorded on a Perkin-Elmer Spectrum GX spectrophotometer using KBr pellet. Thermogravimetric analysis of polyamides was performed on TA Instrument TGA Q-5000 system at a heating rate of 10 °C/min under nitrogen atmosphere for ~5 mg sample mass. DSC analysis of polyamides was carried out on TA Instruments DSC Q10, at a heating rate of 10 °C/min in nitrogen atmosphere.

Results and discussion

Aromatic polyamides with bulky pendant tetraphenyl thiophene moiety; and aliphatic methylene linkage in polymer backbone have been reported earlier from our laboratory [9] wherein better solubility/processability without loss in thermal stability were observed. In continuation of earlier work studies were undertaken to incorporate silicon moieties along with bulky tetraphenyl thiophene moiety and methylene spacer linkages in polyamides; by utilizing BCPDS as a comonomer (Scheme 2). The structure of these copolyamides was as identified by infrared and NMR spectra.

All copolyamides showed an absorption band at 3,299, a sharp peak at 1,540 (characteristic for –NH) and peak at 1,660 cm^{-1} (due to C = O in amide group). The absorption band at 3,053, characteristic for aromatic –CH stretching; and absorption band at 2,954 cm^{-1} corresponding for aliphatic (–CH stretch) methylene linkage were observed (Fig. 1). Disappearance of absorption bands at 3,450 and 3,350 cm^{-1} indicated that all the acid and amine groups reacted completely to yield copolyamide.

The copolyamides were characterized by ^{1}H-NMR spectroscopy. The ^{1}H-NMR spectrum (Fig. 2) of copolyamide PA-4 showed peak at 3.38 δ; assigned to $–CH_2–CO–$



Scheme 2 Synthesis of copolyamides from ODA and (CMPDT + BCPDS)

and peak at 0.62 *δ* assigned to silicon attached methyl protons. Aromatic protons appeared in the range of 7.94 to 6.99 *δ*; whereas amide -NH- appeared at 10.3 *δ*. These peaks correlated well with the proposed structure of copolymer. NMR spectrum was used to calculate the quantitative proportions of comonomers, namely CMPDT and BCPDS, in the copolymer, by comparing the relative intensities of the NMR signals of methylene/methyl protons. Thus PA-4 contained 75% moles of CMPDT and 25% moles of BCPDS and the relative intensities of NMR peaks at 3.38/0.62 *δ* corresponded well with the structure. CMPDT contained two methylene groups (4H) and it is 75% mole in PA-4; therefore peak at 3.37 *δ* is due to three protons; whereas BCPDS contained two methyl groups (6H) and it is 25% mole in PA-2; hence peak at 0.62 *δ* is due to 1.5 protons. In brief the relative intensities of NMR signal at 3.37 and 0.62 *δ* are expected to be 2:1 and that is found in NMR spectrum of PA-4. (There is little contribution to the intensity of the peak at 3.37 *δ* by the peak at 3.58 *δ* due to traces of water in solvent d_6-DMSO). Relative intensity of total aromatic protons also matched well to expected values.

Fig. 1 Infrared spectra (KBr) of PA-5. **a** Infrared spectrum (KBr) of PA-3

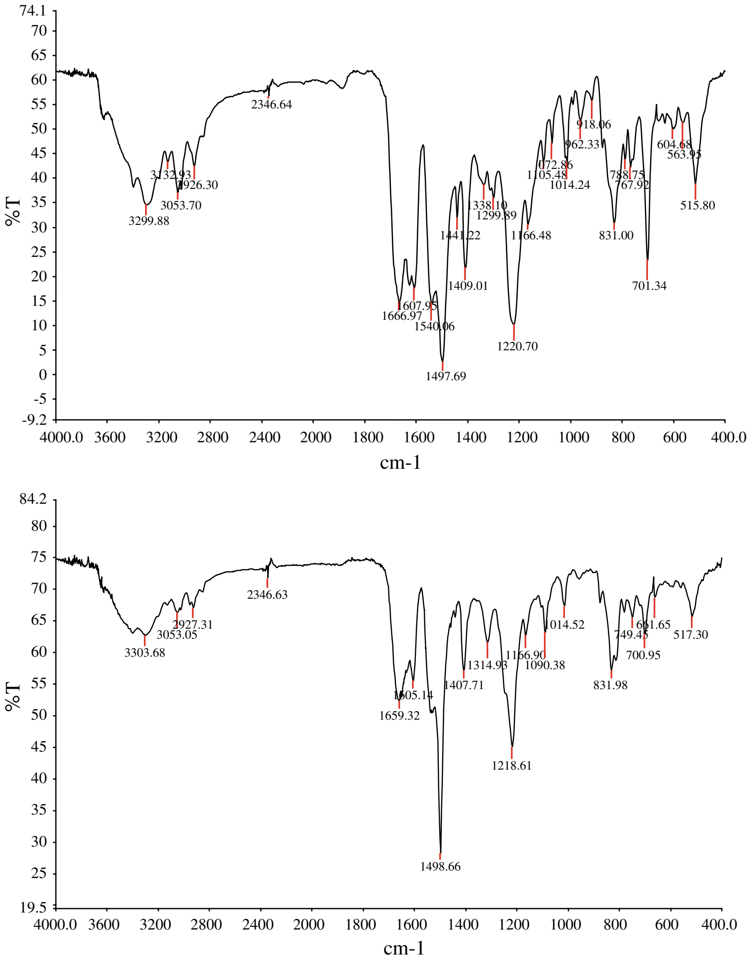


Table 2 Thermal analysis[a] of copolyamides from ODA and (CMPDT + BCPDS)

Polymer code	Temperature for various % decomposition		Residual % wt. at 900 °C	Tg (°C)[b]
	T_i^c	T_{10}^d		
PA-1	350	465	50	263
PA-2	360	428	53	242
PA-3	340	435	60	250
PA-4	335	456	62	228
PA-5	340	435	60	216

[a] Thermogravimetric analysis at heating rate of 10 °C/min under nitrogen

[b] Determined by DSC

[c] Temperature at which initial loss of mass observed

[d] Temperature at which 10% mass loss observed

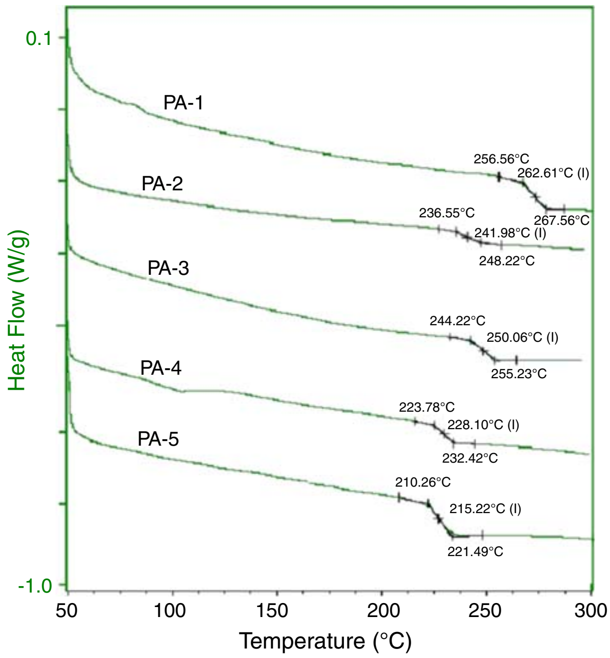


Fig. 3 DSC curve of PA-1 to PA-5

These copolyamides had inherent viscosities in the range of 0.23–0.57 dL/g indicating built-up of a moderately high molecular masses. The inherent viscosities of PA-1 and PA-5, those containing either BCPDS alone or CMPDT alone are lower than those of copolyamides. Higher viscosities of copolyamides are possibly due to random structure of copolyamides favoring enhanced solubility in reaction medium and therefore enhancing the extent of polymerization favoring molecular mass build up. These polyamides were obtained in good yields (97–99%), except for PA-5. the lower yield of PA-5 may be due to formation of lower molecular mass polymer (viscosity, 0.23 dL/g), reflecting lower % conversion and possibly that more amounts of lower molecular mass compounds remained dissolved when reaction mixture was precipitated

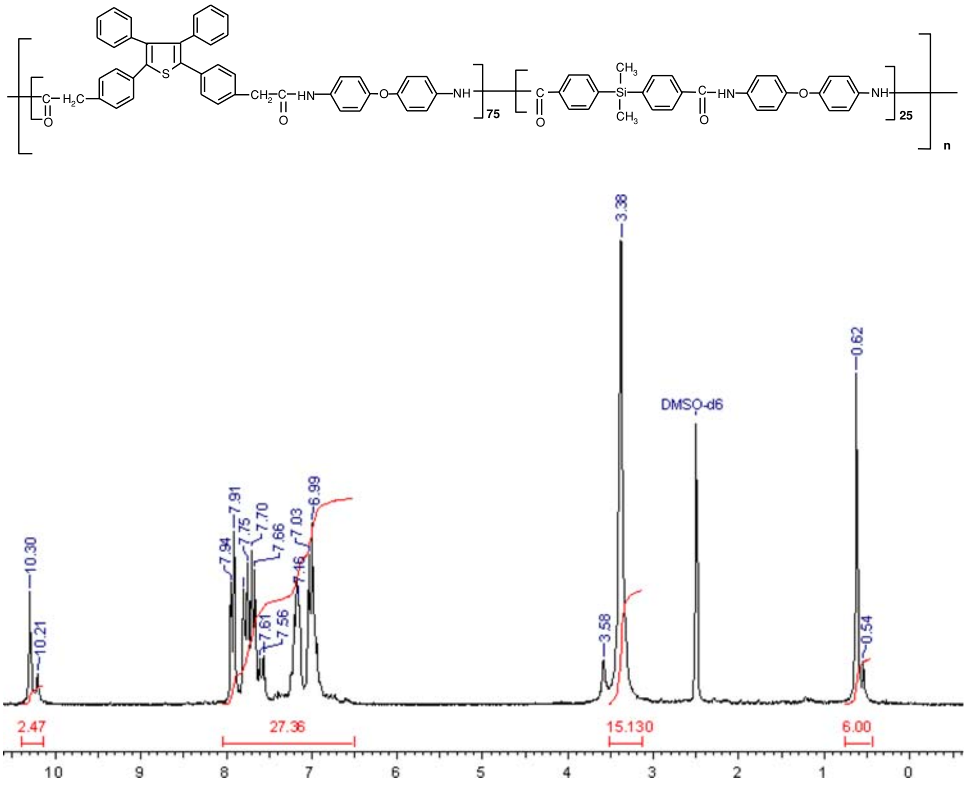


Fig. 2 ^{1}H-NMR spectrum of PA-4

Table 3 Solubility of copolyamides from ODA and (CMPDT + BCPDS)

Solvent polymer	PA-1	PA-2	PA-3	PA-4	PA-5
DMAc	+ +	+ +	+ +	+ +	+ +
DMSO	+ +	+ +	+ +	+ +	+ +
NMP	+ +	+ +	+ +	+ +	+ +
DMF	+ +	+	+ +	+ +	+ +
Pyridine	+ +	+	+ +	+ +	+ +
m-Cresol	+	+	+ +	+	+
Conc. H_2SO_4	+	+	+	+	+
Nitrobenzene	+ −	+ −	+	+ −	+ −
THF	+ −	+ −	+ −	+ −	+ −

+ + Soluble at room temperature, + soluble on heating, + − partly soluble

in nonsolvent, like methanol. The glass transition temperatures of these copolyamides were determined by differential scanning calorimeter (DSC) and the Tg values were in the range of 216–263 °C (Fig. 3). It is observed that the glass transition temperature decreased as the mole percentage of comonomer CMPDT increased; which may possibly be attributed to the increase in free volume of polymer chain and the addition of spacers allowed an earlier onset of microbrownian motion as a evident by the lowest Tg observed for PA-5. The addition of flexible spacers, methylene groups is expected to allow an earlier onset of motion which decreased the Tg along the series because along the series percentage of flexible spacers increased.

The thermal stability of the copolyamides was studied by thermogravimetric analysis and the initial decomposition temperature (T_i), temperature at which 10% mass loss (T_{10}) and char yields at 900 °C were determined from the original curves. T_i and T_{10} values range between 335 to 360 °C and 428 to 465 °C respectively (Table 2). Most of the polyamides exhibited two-stage decomposition pattern as characteristic of aramides. It was observed that residual mass % at 900 °C is higher for PA-3 to PA-5 [about 60%] compared to that of PA-1 to PA-2 [about 50%]. This is attributed to increased amount of CMPDT in PA-3 to PA-5 thereby increasing more aromatic content in PA-3 to PA-5; leading to higher residual mass at 900 °C for these aramides. These phenylated silicon moiety and methylene spacer group containing polyamides had excellent thermal stability.

All these copolyamides were readily soluble in polar aprotic solvents such as *N*-methylpyrrolidone (NMP), *N*, *N*-dimethylsulphoxide (DMSO), *N*, *N*-dimethylacetamide (DMAc), *N*, *N*-dimethylformamide (DMF) etc. These results (Table 3) are similar to those reported for CMPDT derived polyamides [9]. However the copolyamides prepared in the present studies were also partly soluble in common organic solvents like tetrahydrofuran and nitrobenzene; which may be assigned to the additional silicon units and the copolymerization effects. Thus better solubility of these polyamides; as expected; may be due to the judicious combination of copolymerization and silicon plus tetraphenyl thiophene moiety with methylene linkages in the polymer backbone.

Conclusions

A new series of copolyamides containing tetraphenyl thiophene moiety, aliphatic methylene spacer group and silicon linkage in polymer backbone have been synthesized. These copolyamides showed high solubility in organic solvents without appreciable loss in thermal stability and hence they have potential applications as high temperature film.

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