Effect of polydimethylsiloxane incorporation on the properties of polyimides synthesized from newly designed α,α' -bis(2-aminophenoxy)-p-xylene

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Abstract. A novel diamine monomer α,α' -bis(2-aminophenoxy)-p-xylene (2APX) was synthesized and condensed with four different dianhydrides to prepare a series of polyimides. Aminopropyl terminated polydimethylsiloxane (PDMS) was incorporated within the backbone of polyimides for the preparation of poly(imide siloxane) copolymers. Fourier transform infrared (FTIR), ¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopic studies accompanied by elemental and single crystal X-ray analysis were performed for structure elucidation of 2NPX and 2APX. The crystal system of the 2NPX was found to be monoclinic, belonging to space group $P2_1/n$ while 2APX was triclinic with space group $P\bar{1}$. The structural elucidation of polymers was carried out by FTIR and ¹H NMR spectroscopy and their properties were studied by solubility testing, wide angle X-ray diffraction (WAXRD), thermogravimetric analysis (TGA) and viscosity measurement along with laser light scattering technique (LLS). WAXRD pattern showed the semicrystalline nature of polyimides which was decreased in case of copolymers. The poly(imide siloxane) copolymers displayed slightly lower temperature resistance but improved solubility as compared to polyimides. Maximum degradation temperature (T_{max}) of polyimides was in the range of 523–570°C while that of copolyimides, ranged between 483–525°C. Similarly, a decline in inherent viscosities and increase in molecular weight was noticed while moving from polyimides to copolyimides.

Keywords: polymer synthesis, molecular engineering, 2APX, single crystal, poly(imide siloxane) copolymers, laser light scattering

1. Introduction

The advances in the field of high performance materials demand a unique combination of properties i.e. good oxidative and thermal stability, high glass transition temperature, excellent mechanical properties, good adhesion along with chemical, wear, fire and radiation resistance for diverse range of applications including aerospace, automotive and micro-electronic industries, as films, adhesives, sealants, coatings, insulators, gas separation membranes etc. In this regard, large number of polymeric materials such as polyamides, polyimides, poly(amide-imide)s

polybenzimidazoles, polyethers, polyketones, polysulphones, and polyesters have been developed in order to replace metal, ceramic or glass and reduce the cost of present day industrial processes [1–7]. Polyimides especially aromatic polyimides have attracted the attention of scientists and engineers more than any other polymer as they have great potential to serve this purpose due to favorable combination of aforementioned sought properties [8]. At present time, polyimides are considered as versatile polymers with an almost unlimited spectrum of applications in advanced technologies. The

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exceptional properties displayed by the polyimides are reliant on their chemical structure, composition, molecular aggregation and intra or interchain molecular interactions, hence can be tailored to desired ones through changing the chemical structure and molecular composition of polyimides. In this respect, various strategies can be applied i.e. modification of monomers in order to endow the polymer chain with new functionalities, composite engineering or copolymerization etc. Therefore, the curiosity of academic and industrial research is the production of new polyimide based materials so as to further enhance their properties and diversify applications. Much research has been carried out in last few years to improve certain properties of polyimides for specific applications. For instance, main disadvantage associated with the application of polyimide films in optoelectronic industry is their yellowish nature. This is attributed to the intra or intermolecular charge transfer complex (CTC) formation between the alternating electron-acceptor dianhydride and electron-donor diamine moieties in the polymer chain [9]. It was prophesied that use of weak electron-accepting dianhydrides or electron-donating diamines will suppress these charge transfer (CT) interactions. Keeping this in mind Haixia Yang and coworkers prepared fluorinated polyimides from diamines bearing electron withdrawing trifluoromethyl substituents (lowering its electron-donating ability) and observed significantly enhanced optical transparency [10]. Semi-aromatic polyimides derived from alicyclic dianhydride i.e. 1,2,4,5-cyclohexanetetracarboxylic dianhydride (weak electron-accepting) and different aromatic diamines also produced alike results [11]. Likewise, introduction of flexible spacers ($-\text{O}-$, $-\text{CO}-$, $-\text{SO}_2-$) [12], kink in structure through *ortho* or *meta* catenation instead of *para* [13], bulky pendant groups or hinge atoms [14] or trifluoromethyl groups ($-\text{CF}_3$) [15] in the structure of either diamine or dianhydride led to improvement in processability and solubility of polyimides while upholding their beneficial properties. Polyimides with significantly enhanced thermal and mechanical properties were produced by the incorporation of heterocyclic rings of benzimidazole, benzoxazole, pyrimidine and benzoxadiazole into the backbone of polyimides [16]. Juntao Wu studied the influence of nano-sized Al_2O_3 content on various properties of PI/ Al_2O_3 nanocomposites and found that the incorporation of Al_2O_3 in the

polyimide triggered an increase in thermal stability, Young's modulus and electrical aging performance of hybrid films as compared to pure polyimide [17]. Copolymerization strategy i.e. synthesis of polymers from two different diamines or dianhydrides is also applied to modify the properties of polyimides [18–20]. In this regard, aminopropyl terminated polydimethylsiloxane (PDMS) is often covalently incorporated within the polyimide chain. Polydimethylsiloxane is a flexible inorganic elastomer having very low glass transition temperature (-123°C) and imparts several beneficial properties to the polymeric system into which it is co-reacted e.g. improved solubility and flame resistance, increased permeability, permselectivity, adhesive ability and impact resistance, reduced water absorption and dielectric constant, modified surface properties, superior electrical properties etc. [21–27]. Therefore, silicone containing polyimides have attracted significant attention recently and studies are mainly focused on investigating the effects of polydimethylsiloxane incorporation on the aforementioned properties of polyimides. In this context, Othman reported a series of poly(siloxane-imide) block copolymers and concluded that incorporation of silicon units into the polyimide chains significantly reduced the refractive index and dielectric constant with reasonably low dielectric loss [28]. Similarly, Ku and coworkers observed that pyridine-containing poly(imide-siloxane)s showed stronger adhesion to copper foils along with lower moisture absorption as compared to conventional aromatic polyimides [29]. While improving a particular property of polyimide, it has to be remembered that their thermal and mechanical properties for which these are known for, must not be compromised. Therefore, an adjusted degree of structural modification should be applied so as to optimize the balance of properties. This article reports the synthesis of polyimides and siloxane-containing copolyimides derived from a newly designed ether based diamine monomer i.e. α,α' -bis(2-aminophenoxy)-p-xylene. This new diamine was characterized by FTIR and NMR spectroscopic techniques along with elemental and single crystal X-ray diffraction analysis. FTIR and NMR spectroscopy, solubility, WAXRD, thermal, viscometric and laser light scattering analysis were carried out for the synthesized polymers and copolymers. The emphasis of the study was to evaluate the properties of polyimides derived from diamine hav-

ing amino group at ortho position with respect to ether linkage and monitor the influence of polydimethylsiloxane incorporation on solubility, crystallinity, thermal stability, viscosity, and molecular weight of parent polyimides.

2. Experimental

2.1. Materials

All chemicals and reagents used for the synthesis of diamine, polyimides and poly(imide siloxane) copolymers were of highest purity and were used as received. 2-nitrophenol (2NP), potassium carbonate anhydrous (K_2CO_3), pyromellitic dianhydride (PMDA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and oxydiphthalic anhydride (ODPA) were purchased from Fluka Chemie GmbH (Buchs, Switzerland). While 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA), 1,4-bis(chloromethyl) benzene (CMB), 5% palladium on activated carbon (Pd/C) and aminopropyl terminated polydimethylsiloxane (PDMS) of $M_n = 2500$ were obtained from Sigma Aldrich Chemie GmbH (Schnellendorf, Germany). Hydrazine monohydrate was procured from Merck (Darmstadt, Germany). Solvents, N-methylpyrrolidone (NMP), N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), tetrahydrofuran (THF) ethanol, were acquired from various commercial sources and were dried before use [30].

2.2. Instrumentation and measurements

Melting temperatures of the aromatic dinitro and diamine compounds were determined in a capillary tube using Gallenkamp electrothermal melting point apparatus (Staffordshire, UK). The solid state Fourier transform infrared (FTIR) spectra ($400\text{--}4000\text{ cm}^{-1}$) were obtained using Thermo Nicolet-6700 spectrophotometer (Madison, USA). Nuclear magnetic resonance (NMR) spectra were recorded

in deuterated DMSO- d_6 using Bruker spectrometer (Bruker NMR Instruments) operating at 300 MHz for 1H NMR and at 75 MHz for ^{13}C NMR using tetramethylsilane (TMS) as internal reference. The elemental analyses were performed using CHNS-932 LECO instrument (Michigan, USA). Single crystal X-ray data of α,α' -bis(2-nitrophenoxy)-p-xylene and α,α' -bis(2-aminophenoxy)-p-xylene were obtained on a Bruker Apex II CCD diffractometer (Bruker XRD Instruments) at 150 K. Wide-angle X-ray diffractograms were obtained using PANalytical PW 3040/60 X'Pert PRO diffractometer (Almelo, Netherlands). Thermogravimetric analysis (TGA) were carried out using Perkin-Elmer Pyris instrument (Waltham, USA) at a heating rate of $20^\circ\text{C}/\text{min}$ in a nitrogen atmosphere up to a maximum temperature of 800°C . The inherent viscosities of the polyimides were determined using Ubbelohde's viscometer at 25°C by dissolving 0.2 g/dL of sample in DMSO. Molecular weights and radius of gyration (R_g) of polymers were determined by dissolving 0.8 g/dL of sample in DMSO through static laser light scattering technique using Brookhaven's BI-200 SM instrument (Holtville NY, USA) fitted with Argon-Ion laser (Coherent Innova) with vertically polarized incident light of wavelength 637 nm and a BI 900 At digital correlator.

2.3. Monomer synthesis

2.3.1. Synthesis of

α,α' -bis(2-nitrophenoxy)-p-xylene (2NPX)

2NPX was synthesized by the Williamson's etherification reaction of 2-nitrophenol with 1,4-bis(chloromethyl)benzene according to Figure 1. For this purpose, a 250 mL two neck round-bottom flask fitted with reflux condenser and nitrogen tube was charged with 11.12 g of 2-nitrophenol (80 mmol), 7.00 g of 1,4-bis(chloromethyl)benzene (40 mmol), 11.00 g of potassium carbonate (anhydrous) and 60 mL of

Figure 1. Scheme for synthesis of 2APX

DMF. The resulting mixture was heated at 120°C for 16 hrs. The color of solution was changed from yellow to dark brown. It was then cooled to room temperature and poured into 800 mL of ice cold water. Light yellow precipitates were formed which were filtered, washed with ethanol and dried. The yield of reaction was found to be 78% and melting point of the product determined was 165°C.

2.3.2. Synthesis of

α,α' -bis(2-aminophenoxy)-p-xylene (2APX)

For the synthesis of 2APX, 3.0 g of the obtained dinitro compound (2NPX) (7.89 mmol), 0.10 g of 5% Pd/C and 50 mL ethanol were introduced in a two neck round-bottom flask, to which 10 mL of hydrazine monohydrate was added dropwise. After the addition was complete, the reaction was continued at reflux temperature for 12 hrs. Then the mixture was filtered in hot form to remove Pd/C and solvent was rotary evaporated to get the solid product. The crude product was washed with water to remove any trapped hydrazine and finally recrystallized from ethanol. White colored diamine was obtained in 69% yield having melting point at 124°C.

2.4. Synthesis of polyimides

Polyimides were synthesized from diamine 2APX and dianhydrides via a two-step route as shown in Figure 2a. The synthesis of polyimide PMDA-2APX is used as an example to illustrate the general synthetic procedure: a 50 mL two neck round-bottom flask (prebaked on vacuum to exclude any moisture) was charged with 0.320 g of 2APX (1 mmol) and 4 mL DMF. After the complete dissolution of diamine, 0.218 g of PMDA (1 mmol) was added to this solution by dissolving it in 4 mL DMF. The mixture was allowed to stir at room temperature under the inert atmosphere of nitrogen for 24 hrs. The resulting poly(amic acid) solution was thermally imidized by casting it on a clean glass plate followed by curing with a programmed procedure in a vacuum oven: 18 hrs. at 80°C, 1 hr at 150°C, 1 hr at 200°C, 1 hr at 250°C and 2 hrs at 300°C to produce a fully imidized polyimide. Similarly, 2APX was condensed with 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA), oxydiphthalic anhydride (ODPA) and 2,2-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) for the preparation of BTDA-2APX, ODPA-2APX and 6FDA-2APX polyimides.

2.5. Synthesis of poly(imide siloxane) copolymers

The poly(imide siloxane) copolymers were synthesized by one-step condensation polymerization reactions of equimolar amounts of diamine 2APX and different dianhydrides in the presence of amino-propyl terminated polydimethyl siloxane (PDMS). The synthesis of PMDA-2APX-PDMS is presented as an example to describe the synthetic procedure: a 50 mL two neck round-bottom flask (prebaked on vacuum to exclude any moisture) equipped with nitrogen tube, reflux condenser, magnetic stirrer and Dean-Stark trap was charged with 0.218 g of PMDA (1 mmol) and 3 mL of NMP/THF (1:1) mixture. Then 0.250 g of PDMS (0.1 mmol) dissolved in 2 mL of THF was added slowly to the dianhydride solution. After stirring the mixture for 1 hr, 0.288 g of 2APX (0.9 mmol) dissolved in 2 mL NMP was added and allowed to stir at room temperature for 16 hrs. The resulting poly(amic acid) solution was imidized by heating in a mixture of toluene/NMP (2:5) at reflux temperature for 8 hrs. The toluene was distilled off under vacuum, the solution was cooled to room temperature and poured in a large quantity of water to give a rubbery material, which was filtered and dried in vacuum oven at 80°C for 24 hrs. In the same way BTDA-2APX-PDMS, ODPA-2APX-PDMS and 6FDA-2APX-PDMS copolyimides were synthesized by using BTDA, ODPA and 6FDA respectively according to Figure 2b.

3. Results and discussion

3.1. Synthesis and characterization of monomer

The ether-based diamine α,α' -bis(2-aminophenoxy)-p-xylene (2APX) was synthesized via a two-step approach according to scheme shown in Figure 1. Firstly, dinitro compound α,α' -bis(2-nitrophenoxy)-p-xylene (2NPX) was synthesized by the Williamson's etherification of 2-nitrophenol with 1,4-bis(chloromethyl)benzene in dimethylformamide catalysed by anhydrous potassium carbonate. Then the 2NPX was reduced to corresponding diamine 2APX with hydrazine monohydrate and Pd/C in ethanol. The structures of 2NPX and 2APX were confirmed by FTIR, ^1H NMR, ^{13}C NMR spectroscopic studies, elemental and single crystal X-ray analysis. Data obtained from these techniques is presented in Table 1. The FTIR spectrum of 2NPX

Figure 2. Scheme for synthesis of polyimides (a) and poly(imide siloxane) copolymers (b)

Table 1. FTIR, NMR and elemental analysis data of 2NPX and 2APX

Technique	2NPX	2APX
FTIR	3114 (Ar–H), 2879 (CH ₂), 1580 (NO ₂ asym), 1342 (NO ₂ sym), 1253 (C–O–C)	3460, 3435 (NH ₂), 3056 (Ar–H), 2865 (CH ₂), 1275 (C–O–C)
¹ H NMR	7.90 (1H, m, H ³), 7.68–7.63 (1H, m, H ⁵), 7.50–7.44 (3H, m, H ⁴ , H ⁹ , H ^{9'}), 7.16–7.11 (1H, m, H ⁶), 5.33 (2H, s, H ^{7,7'})	7.51 (2H, s, H ⁹ , H ^{9'}), 6.89–6.86 (1H, m, H ⁴), 6.70–6.68 (2H, m, H ⁵ , H ⁶), 6.55–6.49 (1H, m, H ³), 5.09 (2H, s, H ^{7,7'}), 4.74 (2H, s, –NH ₂)
¹³ C NMR	151.2 (C ₁), 140.2 (C ₈), 136.3 (C ₅), 135.2 (C ₂), 128.7 (C ₉), 125.5 (C ₃), 121.3 (C ₄), 116.4 (C ₆), 70.50 (C ₇)	145.7 (C ₁), 138.4 (C ₈), 137.4 (C ₂), 128.2 (C ₉), 121.6 (C ₄), 116.6 (C ₅), 114.6 (C ₃), 112.6 (C ₆), 69.5 (C ₇)
Elemental	% Calcd: C = 63.16, H = 4.21, N = 7.37 % found: C = 62.93, H = 4.18, N = 7.25	% Calcd: C = 75.00, H = 6.25, N = 8.75 % found: C = 74.60, H = 6.35, N = 8.50

displayed the characteristic absorption bands of ether linkage (C–O–C) at 1253 cm^{−1} and nitro functionality (NO₂) at 1580 and 1342 cm^{−1} correspon-

ding to asymmetric and symmetric stretches respectively. The reduction of 2NPX to 2APX was confirmed by disappearance of NO₂ absorptions and

advent of typical N–H stretching bands for primary amines at 3460 and 3435 cm^{-1} in the FTIR spectrum of 2APX. Structures of 2NPX and 2APX were also elucidated by ^1H NMR spectroscopic technique. Phenyl protons were verified by the appearance of signals in the characteristic region between 6–8 ppm according to substituents attached. The protons of aromatic ring at ortho and para positions of nitro group ($\text{H}^{3\&5}$) resonated at the farthest downfield (7.90–7.63 ppm) in the ^1H NMR spectrum of 2NPX which is attributed to the deshielding engendered by electron withdrawing effect of NO_2 group. However, in case of 2APX resonance signals for these protons were shifted to upfield region (6.70–6.49 ppm) which is clear evidence in favor of nitro

group reduction to amine. Moreover, presence of amine functionality in the structure of 2APX was also certified by the advent of two protons singlet at 4.74 ppm in the ^1H NMR spectrum as shown in Figure 3a. Appearance of two protons singlets at 5.33 and 5.09 ppm for 2NPX and 2APX respectively due to methylene protons (H^7) proves the formation of ether linkage. ^{13}C NMR spectroscopic study also supported the structures of compounds as the characteristic signals for all the carbon atoms were observed as shown in ^{13}C NMR spectrum of 2APX presented in Figure 3b. Like the proton NMR, a slight upfield shift observed for carbon atoms at ortho and para positions of NH_2 group ($\text{C}_{3\&5}$) in the ^{13}C NMR spectrum of 2APX as compared to 2NPX

Figure 3. ^1H NMR (a) and ^{13}C NMR (b) spectra of 2APX

is attributed to the electron donating effect of amine group. This also supports the successful conversion of NO₂ group to NH₂ moiety. Elemental analysis shows that found and calculated ratios of carbon (C), hydrogen (H) and nitrogen (N) are in good agreement with each other. It also supports the successful synthesis of monomers.

Single crystal X-ray analysis also confirmed the structure of 2NPX and 2APX. Crystals of compounds suitable for single crystal X-ray analysis were developed by slow evaporation of DMSO and ethanol respectively at room temperature to identify their structures. Crystallographic data was collected at 150(2) K on a Bruker Apex II CCD diffractometer using Mo-K α radiation ($\alpha = 0.71073$ Å). The structure was solved by direct methods and refined on F² using all the reflections [31]. All the non-hydrogen atoms were refined using anisotropic atomic displacement parameters and hydrogen atoms bonded to carbon were inserted at calculated positions using a riding model. The amine hydrogens in 2APX were located from difference maps and their coordinates refined. Parameters for data collection and refinement are summarised in Table 2. The structures of 2NPX and 2APX are shown in Figure 4 and 5 respectively. The dinitro molecule (2NPX) is centrosymmetric having no obvious π - π stacking interactions in the lattice although there are some weak

Figure 4. Molecular structure of 2NPX. Non-hydrogen atoms shown with 50% probability ellipsoids. Atoms with suffix 'A' generated by symmetry operation 1-x, 1-y, 1-z.

Figure 5. Molecular structure of 2APX. Non-hydrogen atoms shown with 50% probability ellipsoids.

CH $\cdots$ O interactions. The central ring makes an angle of 52.41(5)° with the outer rings. The molecule of 2APX has no internal symmetry since the terminal rings are at different angles to the central phenyl group (78.87(4) and 34.52(4)° for rings containing N1 and N2, respectively). No convincing hydrogen bonding was observed in the structure,

Table 2. Crystal data and structure refinement for 2NPX and 2APX

Parameter	2NPX	2APX
Empirical formula	C ₂₀ H ₁₆ N ₂ O ₆	C ₂₀ H ₂₀ N ₂ O ₂
Formula weight	380.35	320.38
Temperature	150(2) K	150(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic
Space group	P2 ₁ /n	P $\bar{1}$
Unit cell dimensions	$a = 7.4203(4)$ Å $\alpha = 90^\circ$ $b = 11.7771(6)$ Å $\beta = 90.8180(10)^\circ$ $c = 9.7275(5)$ Å $\gamma = 90^\circ$	$a = 8.7516(6)$ Å $\alpha = 64.8160(10)^\circ$ $b = 10.1550(7)$ Å $\beta = 68.0410(10)^\circ$ $c = 11.0313(8)$ Å $\gamma = 77.8430(10)^\circ$
Volume	850.00(8) Å ³	821.28(10) Å ³
Z	2	2
Density (calculated)	1.486 Mg/m ³	1.296 Mg/m ³
Absorption coefficient	0.112 mm ⁻¹	0.084 mm ⁻¹
F(000)	396	340
Crystal size	0.37×0.21×0.17 mm ³	0.60×0.24×0.21 mm ³
Crystal description	orange block	colourless rhomb
Theta range for data collection	2.72 to 30.56°	2.15 to 28.34°
Reflections collected	9717	8491
Independent reflections	2583 [$R(\text{int}) = 0.0224$]	4059 [$R(\text{int}) = 0.0196$]
R [$F^2 > 2\sigma(F^2)$]	0.042	0.043
$wR(F^2)$	0.119	0.113
Goof	1.06	1.07
CCDC number	1056786	1056787

Figure 6. Weak intermolecular interactions in the lattice of 2APX

although there are some $\text{NH}\cdots\pi$ and $\text{CH}\cdots\pi$ interactions as shown in Figure 6 and these seem to be the most significant intermolecular effects.

3.2. Synthesis and characterization of polyimides and copolyimides

The newly designed diamine 2APX was condensed with four commercially available dianhydrides i.e. PMDA, BTDA, ODP, 6FDA to synthesize simple polyimides. Then this diamine was polymerized with same dianhydrides along with aminopropyl terminated polydimethylsiloxane (PDMS) oligomer of $M_n = 2500$ to synthesize poly(imide siloxane) copolymers. The synthesis of the polyimides and copolyimides was confirmed by FTIR and $^1\text{H-NMR}$ spectroscopic techniques. FTIR spectra of polyimides displayed characteristic absorption bands associated with five membered imide ring around 1780 and 1715 cm^{-1} attributed to asymmetric and symmetric C=O stretches respectively, along with C-N stretching absorptions around 1375 cm^{-1} . The completion of the reaction i.e. conversion of polyamic

acid to fully cyclized polyimide was confirmed by disappearance of: carboxyl and NH bands in the region of $3100\text{--}3500\text{ cm}^{-1}$ (at the polyamic acid stage) and the appearance of the characteristic absorption bands of the imide ring accompanied by shifting of carbonyl stretching vibrations towards higher frequency i.e. from 1650 to 1715 cm^{-1} . However, polyimide derived from BTDA displayed absorption bands around 1645 cm^{-1} along with typical peaks of imide group even after imidization which is attributed to the presence of ketonic carbonyl moiety in its structure. Similarly appearance of characteristic peaks for siloxane moieties i.e. Si-O-Si and Si-CH_3 around 1080 and 792 cm^{-1} respectively along with typical peaks of imide structure in the FTIR spectra of PDMS containing copolyimides confirmed the synthesis of poly(imide siloxane) copolymers. FTIR data of polyimides and copolyimides is listed in Table 3. Representative FTIR spectra of polyimide PMDA-2APX at poly(amic acid) stage and after imidization are shown in Figure 7.

Table 3. FTIR data of polyimides and copolyimides

Polymer	Before imidization		After imidization					
	OH, NH	C=O (amide)	OH, NH	C=O (imide)	C-N (imide)	Si-O-Si	Si-CH ₃	CH ₃
PMDA-2APX	3524	1627	—	1704, 1779	1349	—	—	—
PMDA-2APX-PDMS	3435	1643	—	1722, 1778	1376	1088	792	2961
BTDA-2APX	3432	1655	—	1716, 1779	1373	—	—	—
BTDA-2APX-PDMS	3446	1652	—	1717, 1780	1378	1087	794	2961
ODPA-2APX	3465	1660	—	1715, 1777	1374	—	—	—
ODPA-2APX-PDMS	3462	1637	—	1717, 1780	1377	1078	792	2961
6FDA-2APX	3496	1655	—	1716, 1786	1378	—	—	—
6FDA-2APX-PDMS	3458	1648	—	1716, 1785	1380	1094	793	2962

Figure 7. FTIR spectra of PMDA-2APX at poly(amic acid) stage (a) and after imidization (b)

Soluble polymers i.e. 6FDA-2APX, 6FDA-2APX-PDMS and ODPA-2APX-PDMS were also characterized by ^1H NMR spectroscopy and data obtained is presented in Table 4. Appearance of characteristic signals of aromatic protons along with methyl-

ene protons supported the proposed structures of polymers. Representative ^1H NMR spectrum of the 6FDA-2APX with the assignment of protons is shown in Figure 8 which is in complete agreement with the proposed structure of polyimide. In case of

Table 4. ^1H NMR data of polymers

Polymer	^1H NMR ($\text{DMSO}-d_6$) chemical shifts in ppm					
	Ar-H	O-CH ₂	CH ₂			Si-CH ₃
6FDA-2APX	8.38–7.03 (9H, m, $\text{H}^{1,2,3,4,5,6,7,9,9'}$)	5.08	—	—	—	—
6FDA-2APX-PDMS	8.43–7.18 (9H, m, $\text{H}^{1,2,3,4,5,6,7,9,9'}$)	5.23	3.58	1.60	0.47	–0.001
ODPA-2APX-PDMS	8.16–7.35 (9H, m, $\text{H}^{1,2,3,4,5,6,7,9,9'}$)	5.12	3.62	1.59	0.48	–0.053

Figure 8. ^1H NMR Spectrum of 6FDA-2APX

6FDA-2APX, resonance signals in the range of 8.38–7.74 ppm are assigned to the phenyl protons of dianhydride segment i.e. H^1 , H^2 and H^3 in the polymer chain. This downfield shift is attributed to electron withdrawing nature of carbonyl groups present in it. Aromatic protons of the diamine fragment appeared slightly upfield between 7.48–7.03 ppm. Two proton singlet signal present at 5.08 ppm in spectrum is ascribed to methylene group present in structure inherited from diamine. The disappearance of signals for amine protons and downfield shift observed for phenyl proton adjacent to $-NH_2$ functionality (H^3 in diamine and H^4 in polymer) from 6.52 to 7.74 ppm (owing to electron withdrawing effect of dianhydride segment) as compared to 1H NMR spectrum of 2APX, validated the establishment of imide linkage from amine and dianhydride. Moreover, imidization of poly(amic acid) was also confirmed by the fact that 1H NMR spectra of polymer showed no signals in the characteristic region of amide protons i.e. between 9–11 ppm. In addition to aforementioned peaks, 1H NMR spectra of 6FDA-2APX-PDMS and ODPA-2APX-PDMS displayed resonance signals around 3.60, 1.60, 0.47 and 0.00 ppm which are characteristic peaks for: methylene protons adjacent to imide ring (H^{10}), central methylene of propyl (H^{11}), methylene next to Si (H^{12}) and methyl protons adjacent to Si (H^{13}) respectively. These signals suggest that aminopropyl terminated polydimethylsiloxane (PDMS) segments have been incorporated successfully into the polyimide chain.

3.3. Organosolubility of polymers

The solubility of polymers was tested quantitatively (0.1 g/5 mL) in organic solvents like DMSO, DMF, DMAc, NMP and also in H_2SO_4 . It was found that the simple polyimides except that synthesized from 4,4'-(hexafluoroisopropylidene) diphthalic anhy-

dride i.e. 6FDA-2APX were insoluble in these solvents. This is attributed to ultra-strong intermolecular interactions and good packing ability of the polymer chains which suggests their semi-crystalline behavior and it is also proved by their WAXRD analysis. Under normal circumstances, intermolecular interactions in the polyimide chains occur between electron-donating diamine segments and electron-withdrawing dianhydride moieties in the polymer chain. But in case of polyimides under discussion, in addition to these interactions, there are some other intermolecular effects responsible for enhancing chain packing ability. Luckily, we got the single crystal of 2APX and it was observed during X-ray analysis that $CH\cdots\pi$ interactions are present between the 2APX molecules as shown in Figure 6. Therefore, polyimides synthesized from this diamine displayed insolubility in spite of having ether linkage in their structure. Moreover, the existence of a large number of benzene rings in polymer backbone without bulky side groups tremendously improved the structure regularity and consequently reduced the solubility. The solubility of 6FDA-2APX is attributed to steric hindrance of bulky CF_3 groups. These groups increased the disorder in the chains and hindered compact chain stacking thus reducing the chain-chain interactions. This resulted in increase of free volume and consequently better penetration of solvent molecules into the polymer chains that enhanced solubility. However, solubility of other polyimides was improved by the incorporation of flexible PDMS segment in the backbone as it reduced the packing ability of polymer chains. Solubility data of simple polyimides and poly(imide siloxane) copolymers is given in Table 5 and results show that polyimides which were insoluble, have shown partial solubility after copolymerization. Also the polyimide ODPA-2APX which was partially soluble before copolymerization, completely

Table 5. Solubility data of polymers

Polymer	DMSO	DMF	DMAc	NMP	H_2SO_4
PMDA-2APX	–	–	–	–	+
PMDA-2APX-PDMS	+	+	+	+	++
BTDA-2APX	–	–	–	–	+
BTDA-2APX-PDMS	+	+	+	+	++
ODPA-2APX	+	+	+	+	+
ODPA-2APX-PDMS	++	++	++	++	++
6FDA-2APX	++	++	++	++	++
6FDA-2APX-PDMS	++	++	++	++	++

++: (soluble on heating), +: (slightly soluble on heating), –: (insoluble)

solubilized after introduction of flexible PDMS segment in the backbone. This improvement in solubility of copolyimides was expected as reported in literature [32, 33].

3.4. Wide angle X-ray diffraction analysis (WAXRD)

The crystallinity of the polyimides and copolyimides was examined by wide angle X-ray diffraction analysis with 3040/60 X'Pert PRO diffractometer in the region of $2\theta = 5\text{--}50^\circ$ at room temperature using the polyimide powder obtained as samples. WAXRD diffractograms shown in Figure 9 illustrate the semi-crystalline nature of polyimides and almost amorphous morphology of copolymers. Among the polyimides, the least crystalline behavior was observed for 6FDA-2APX which is attributed to reduction in chain packing efficiency due to bulky CF_3 groups. Incorporation of flexible PDMS segment led to decline in crystallinity of polyimides as it discouraged the chain symmetry thus making it harder for them to pack into the crystal lattice hence reveals a large decrease in crystallinity [34]. These results also support the observed insolubility of polyimides and partial solubility of copolyimides as the amorphous nature of the resulting polymers endows them a good solubility [35].

3.5. Thermal properties of polymers

The thermal properties of the polyimides were evaluated by means of TGA. It was observed that copolyimides are thermally less stable as compared to corresponding polyimides. The temperature at 10% weight loss (T_{10}), an important criterion for evaluation of thermal stability was in the range of 386–405°C for polyimides while for poly(imide silox-

Figure 9. WAXRD diffractograms of polyimides and copolyimides

Figure 10. Thermograms of ODPA-2APX and ODPA-2APX-PDMS

Table 6. Thermal analysis data of polymers

Polymer	T_{10} [°C] ^a	$T_{\max}$ [°C] ^b	R_{800} [°C] ^c
PMDA-2APX	395	565	48
PMDA-2APX-PDMS	386	525	34
BTDA-2APX	405	570	51
BTDA-2APX-PDMS	403	515	39
ODPA-2APX	400	540	52
ODPA-2APX-PDMS	390	495	32
6FDA-2APX	386	523	47
6FDA-2APX-PDMS	368	483	31

^atemperature at 10% weight loss

^btemperature at which maximum degradation occurs

^cresidual mass (wt%) at 800°C

ane) copolymers, it ranged between 368–403°C. Temperature range of maximum weight loss ($T_{\max}$) was 523–570°C and 483–525°C for polyimides and copolyimides respectively. Residual mass (wt%) at 800°C (R_{800}) was also measured and found between 47–52% for polyimides and 31–39% for siloxane-containing copolyimides. This decrease in thermal stability of copolyimides is ascribed to the presence of thermally less stable aliphatic portion in the form of PDMS within the copolymer backbone. Representative thermograms of polyimide ODPA-2APX and copolyimide ODPA-2APX-PDMS are shown in Figure 10. Thermal stability data for polyimides and copolyimides is listed in the Table 6 and results reveal that these polymers exhibit good thermal stability with a slight weight loss up to 400°C. This could be attributed to phenylation of the backbone and formation of imide units in the structure of polymers.

3.6. Viscometric analysis

The inherent viscosities of the soluble polyimides and copolyimides synthesized were determined by

Table 7. Viscometric and light scattering data

Polymer	η_{inh} [dL/g]	M_w [g/mole]	R_g [nm]
6FDA-2APX	0.29	3.52×10^5	53
6FDA-2APX-PDMS	0.11	8.48×10^5	85
ODPA-2APX-PDMS	0.15	3.29×10^6	78

$dn/dc = 0.165 \text{ mL/g}$

Relative errors: $M_w = \pm 5\%$, $R_g = \pm 5\%$

dissolving 0.2 g/dL of sample in DMSO at 25°C using Ubbelohde's Viscometer and data obtained is given in Table 7. Inherent viscosity of polymer 6FDA-2APX was found to be 0.29 dL/g. Since the inherent viscosity is a good criterion for estimation of molecular weight, hence polyimide 6FDA-2APX is expected to show reasonable molecular weight. This supposition was supported by laser light scattering analysis as molecular weight of 3.52×10^5 was determined. The η_{inh} was declined to 0.11 dL/g for copolyimide 6FDA-2APX-PDMS as incorporation of PDMS segment, decreased the rigidity and stiffness of polymer chains owing to its flexible nature. The inherent viscosities of 0.11 and 0.15 dL/g are reasonable for this kind of copolymers as reported in the literature [36].

3.7. Laser light scattering analysis

Molecular weights of polymers were determined using static laser light scattering (SLLS) analysis technique by dissolving 0.8 g/dL of sample in DMSO. SLLS measures light intensity as a function of scattering angle and solute concentration and the relationship between the light scattering from a dilute polymer solution and the weight-average molecular weight can be described by the Zimm formalism. This allows the determination of weight-average molecular weight, radius of gyration and shape information of the solute [37]. The results revealed that copolyimide 6FDA-2APX-PDMS have higher molecular weight than corresponding polyimides (6FDA-2APX). This increase in weight is understandable as high molecular weight PDMS segment ($M_n = 2500$) is introduced in the polymer chain. Moreover, incorporation of PDMS segment imparts flexibility to chain, hence it can grow to a longer length and consequently molecular weight of polymer increases. Like the molecular weight (M_w), radius of gyration (R_g) of copolymers is also longer than simple polymers, which is again attributed to reduction in chain rigidity by PDMS. These results of molecular weight suggest that synthesized diamine

Figure 11. Zimm plot for ODPA-2APX-PDMS at 20°C

has good tendency to react with dianhydrides. Results obtained from viscometric and laser light scattering of polymers are listed in Table 7 and representative Zimm plot for ODPA-2APX-PDMS is shown in Figure 11.

4. Conclusions

Polyimides and poly(imide siloxane) copolymers were synthesized successfully from newly designed diamine monomer 2APX. The structures of diamine and polymers were verified by different techniques. The main objective of the research was to study the properties of polyimides derived from diamine having amino group at ortho position with respect to ether linkage and monitor the influence of amino-propyl terminated polydimethylsiloxane (PDMS) segment on properties of the parent polyimides. In this regard main emphasis was on solubility, crystallinity, thermal stability, viscosity and molecular weight of polymers. Polyimides, except that synthesized from 6FDA, were insoluble in organic solvents, however their solubility was improved after incorporation of siloxane units in the polymer chains. WAXRD pattern showed that polyimides are semi-crystalline in nature that was decreased in case of copolyimides. Comparison of data obtained from the thermal study of these polymers showed that poly(imide siloxane) copolymers are thermally less stable than corresponding polyimides. Viscometric analysis revealed that siloxane-containing polyimides are less viscous than simple polymers. Finally, high molecular weight polymers were synthesized successfully by introduction of PDMS segment in the backbone of polymer chain. The observed behavior of polymers suggests that the synthesized polyimides can be used as high temperature and solvent

resistant materials for applications under severe conditions where excellent thermal stability and resistivity is desired. However poly(imide siloxane) copolymers can be used in applications where improved processability is of prime importance while sacrificing some of thermal stability.

Supplementary Data

CCDC 1056786 and 1056787 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via

www.ccdc.cam.ac.uk/data_request/cif.

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