Journal of Fluorine Chemistry 132 (2011) 878–884

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Optical and thermal behavior of novel fluorinated polyimides capable of preparing colorless, transparent and flexible films

Hossein Behniafar *, Narges Sefid-girandehi

School of Chemistry, Damghan University, 36715-364, Damghan, Iran

ARTICLE INFO

Article history:
Received 9 April 2011
Received in revised form 13 June 2011
Accepted 16 June 2011
Available online 23 June 2011

Keywords:
Fluorinated polyimides
Absorption edge
Heat resistant polymer
Trifluoromethyl
Gel-permeation chromatography
Differential scanning calorimetry

ABSTRACT

A new diamine, 1,5-bis(2-amino-4-trifluoromethylphenoxy)naphthalene (DA1524) was synthesized by the nucleophilic substitution reaction of 1,5-dihydroxynaphthalene and 4-chloro-3-nitrobenzotrifluoride in the presence of potassium carbonate in *N*,*N*-dimethylformamide, followed by catalytic reduction with hydrazine and Pd/C in ethanol. DA1524 was then utilized to prepare a novel class of CF_3-containing polyimides. Intrinsic viscosities [η] of the polymer solutions at 25 °C were measured by the extrapolation of their viscosity numbers till zero concentration. $\bar{M}_w$ and $\bar{M}_n$ values of the resulting polymers were determined using gel-permeation chromatography (GPC). The polymers showed a good film-forming ability, and some characteristics of their thin films including color and flexibility were investigated qualitatively. In addition, the absorption edge values (λ_0) obtained from their UV–vis curves were determined, and all the resulting polyimides films exhibited high optical transparency. Thermal stability of the polymers was investigated using TGA analyses. The T_g values of the polyimides obtained from their DSC plots were quantified. Solubility of the samples in a variety of organic solvents was also tested.

1. Introduction

Fluoro-containing polymers constitute a unique class of materials with a combination of interesting properties that have attracted significant attention of material chemists over the last few decades. In general, these polymers have high thermal stability, improved chemical resistance and lower surface energy when compared to their non-fluorinated counterparts [1–6]. On the other hand, for many applications, polymers need to have good film-forming ability, high chemical resistance, adequate organo-solubility and great thermo-stability. In order to answer these requirements, structural modifications of polymers often become essential. It has been observed that introduction of bulky substituents in preferably asymmetric backbones can impart many of these desirable properties to the polymers, making them suitable for a much wider range of applications [7–11]. Furthermore, aromatic ether linkages inserted in polymer main chains provide them with significantly lower energy of internal rotation. Such a structural modification leads to a lower glass-transition temperature (T_g) and crystalline melting temperature as well as a significant improvement in the solubility and process characteristics without greatly sacrificing thermal stability [12–16].

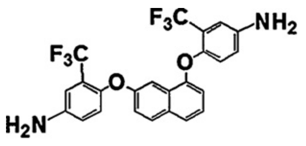
In 2004, a naphthalene-based bis(ether amine) monomer containing trifluoromethyl groups namely 1,5-bis(4-amino-2-trifluoromethylphenoxy)naphthalene (DA1542) was synthesized by Hsiao et al. [17]. In a continuation of this study, in 2009, the isomeric form of diamine DA1542 namely 1,7-bis(4-amino-2-trifluoromethylphenoxy)naphthalene (DA1742) was also synthesized by the same group [18]. Each of these monomers was then utilized to prepare the corresponding fluoro-containing polyimides. With due regard to noticeable role of polyimides in development of high performance materials, as well as their extensive application in advanced technologies, we decided to continue and modify the above interesting research area. Thereby, since it is well accepted that bond orientation and consequently macromolecular alignment has so much importance in good designing the structure of a new monomer, we thought that if 4-chloro-3-nitrobenzotrifluoride is used instead of its isomers, i.e. 2-chloro-5-nitrobenzotrifluoride in the reaction with dihydroxynaphthalene, the resultant monomer profit by more degree of asymmetry. In this case, both amino groups of the monomer were placed at the structure middles, not terminals. This could be surely resulted in the preparation of polyimides with high organo-solubility and better film quality. In addition, with a view to cost and availability, it seems likely that 1,5-dihydroxynaphthalene to be a better choice comparing its 1,7-isomer without noticeable lessening degree of asymmetry. Consequently, synthesis of 1,5-bis(2-amino-4-trifluoromethylphenoxy)naphthalene (DA1524) instead of diamines DA1542 and DA1742, as well as

---

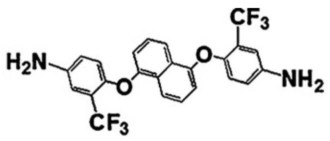
* Corresponding author.
E-mail address: h_behniafar@du.ac.ir (H. Behniafar).

0022-1139/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2011.06.017

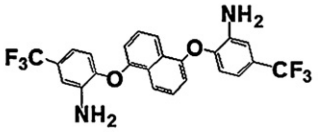
preparation of the related polyimides via the polycondensation reaction of diamine DA1524 and various commercially available tetracarboxylic dianhydrides could be a good goal in our path. Indeed, the CF_3-substituted monomer 1,5-bis(2-amino-4-trifluoromethylphenoxy)naphthalene (DA1524) has two well-oriented amino groups that can endow its derivative polymers some desired properties like enhanced organo-solubility.



DA1742



DA1542



DA1524

Accordingly, this work deals with the preparation of a series of new fluorinated polyimides derived from structurally well-designed diamine DA1524 and some dianhydride comonomers using a two-stage process with chemical imidization method. Optical and thermal behaviors of the obtained polymers are fully investigated and compared with those of previously reported counterparts. Film-forming ability and organo-solubility are the other topics that discussed in detail.

2. Results and discussion

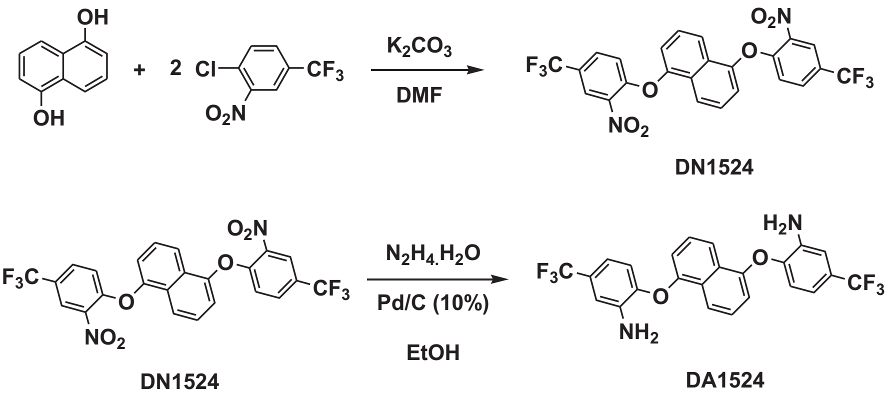
2.1. Synthesis processes

2.1.1. Dinitro DN1524 and monomer DA1524

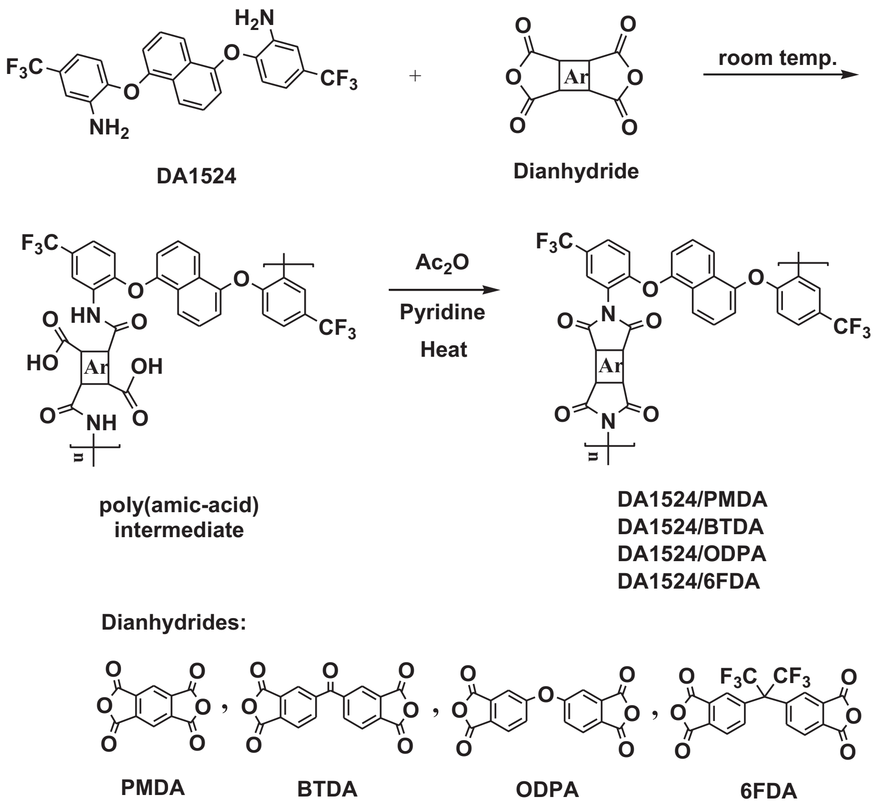
Scheme 1 shows the synthesis route used to prepare 1,5-bis(2-amino-4-trifluoromethylphenoxy)naphthalene (DA1524) by a two-step process. In the first step, aromatic nucleophilic displacement of 4-chloro-3-nitrobenzotrifluoride with 1,5-dihydroxynaphthalene in the presence of anhydrous K_2CO_3 in DMF solvent resulted in the dinitro DN1524 as a yellow solid. In the second step, this dinitro intermediate was reduced in ethanol in the presence of hydrazine hydrate and a catalytic amount of palladium on activated carbon at 80 °C to produce white fine crystals of the new fluorinated diamine DA1524. The structures of dinitro DN1524 and diamine DA1524 were confirmed by IR and NMR spectroscopic methods. In the IR spectrum of dinitro DN1524, the peaks attributed to the stretching vibrations of the bond Ar–O appeared at 1265 cm^{-1}. Moreover, absorptions appearing around 1322 and 1540 cm^{-1} are due to symmetric and asymmetric stretching of $-NO_2$ groups. In the ^1H NMR spectrum of DN1524 all the existing signals can be easily attributed to their appropriate hydrogens in the chemical formula. Furthermore, in the ^{13}C NMR spectrum, 12 peaks corresponding to the 12 kinds of carbons appeared in the range 117.9–153.7 ppm. In this spectrum, the quartets of the heteronuclear $^{13}C–^{19}F$ coupling appeared in the region of 119.0–125.6 ppm with coupling constant of about 230 Hz. Thereby all these spectral patterns are thoroughly in agreement with the proposed structure of dinitro DN1524. In the IR spectrum of monomer DA1524, the characteristic absorption of nitro groups disappeared and the characteristic bonds of amino groups at 3439 and 3366 cm^{-1} (N–H stretching) and 1595 cm^{-1} (N–H bending) appeared after reduction. In the ^1H NMR spectrum of diamine DA1524, the signals of aromatic protons appeared in the range of 6.70–8.00 ppm. The characteristic resonance signal at 5.56 ppm is due to hydrogens of the amino groups. In the ^{13}C NMR spectrum of diamine DA1524, the quartets of the heteronuclear $^{13}C–^{19}F$ coupling appeared in the region of 120.0–126.8 ppm. Here, the coupling constant of one-bond C–F was found to be about 280 Hz. The results obtained clearly confirm that the structure of diamine DA1524 is consistent with that of the proposed structure.

2.1.2. Fluorinated polyimides

The ether-hinged fluorinated polyimides, i.e. DA1524/PMDA, DA1524/BTDA, DA1524/ODPA, and DA1524/6FDA were prepared by two-step polyimidization method involving ring-opening polyaddition of the reactants, leading to the appropriate poly(amic-acid) intermediate and subsequent cyclodehydration [19,20]. Scheme 2 outlines the synthesis route to the above polymers. In general, the cyclodehydration step can be done both thermally by heating an appropriate solution of the previously separated poly(amic-acid) and chemically by addition of some dehydrating agents such as a mixture of acetic anhydride and pyridine to the reaction system [21–23]. It is noticeable that thermal imidization method is not suitable for preparing polymers with high molecular weights since the chains may break in some points at high temperatures needed for thermal cyclodehydration step. This leads to lower values of solution viscosity. Therefore if possible (if a clear solution and not a suspension create during the polymerization reaction) chemical polyimidization using a dehydrating agent is better than the former method. Accordingly, in the current work, chemical cyclodehydration has been utilized to prepare the polymers. All the polycondensations were homogeneously throughout the reactions and afforded highly viscous polymer solutions with up to 95% yield. Intrinsic viscosity [η] values of the resulting polyimides in DMAc at 30 °C as well as the results of GPC analyses are tabulated in Table 1. Intrinsic viscosity values of the



Scheme 1. Synthesis of new monomer DA1524.



Scheme 2. Preparation of the resulting polyimides.

solutions were measured at concentrations 0.10, 0.25, and 0.50 g dL^{-1} in DMAc at 30 °C. These values for all polymeric solutions were determined by the extrapolation of their viscosity numbers till zero concentration [24]. The obtained polymers had intrinsic viscosities in the range of 0.73–1.10 dL g^{-1}. Furthermore, the weight and number average molecular weights of the resulting polyimides were found to be about 25,000 and 12,000, respectively. Therefore, the ratios of $\bar{M}_w/\bar{M}_n$ are conformed to polydispersity index (PDI) values of about 2.0. Hence, as is expectable, the molecular weights of these two representative polymers were high enough to obtain flexible and tough thin films by casting from their DMF solutions. The average molecular weight of the other two polyimide (DA1524/PMDA) was not detectable because of their low solubility in THF eluent.

IR spectra of the fluoro-containing polyimides exhibited characteristic absorption bands of the imide rings at about 1780 and 1730 (asymmetric and symmetric C=O stretching vibration), 1370 (C–N stretching vibration) and 1120 and 725 cm^{-1} (imide ring deformation). The lack of absorption in the region 2500–3500 cm^{-1} (O–H and N–H stretch) and around 1680 cm^{-1} (amide C=O stretch) indicates that the imidization of the polymers were fully done. ^{1}H NMR spectra of the resultant polymers showed a number of peaks in the region of about 6.90–8.20 ppm due to the aromatic protons. In all spectra, the hydrogens incoming from the structure of dianhydrides gave absorption peaks above 8 ppm. In all cases, chemical shifts and integral values of the peaks are thoroughly compatible with the type and the number of attributed hydrogens. For example, Fig. 1 shows representative IR (top) and ^{1}H NMR (bottom) spectra of the polyimide DA1524/BTDA.

2.1.3. Film characteristics and optical properties

As said earlier, to prepare a pliant and equable thin film, 10% (w/v) solutions of the polyimides were made by dissolving of about 0.20 g of the samples in 2.0 ml of DMF. These solutions were poured into a 3-cm glass Petri dish, which was heated appropriately to evaporate the solvent slowly. By being soaked in distilled

Table 1
Some characteristics of the resulting fluorinated polyimides.

Polymer	Formula	$[\eta]$[a] (dL g^{-1})	$\bar{M}_w \times 10^{-3}$ (g mol^{-1})[b]	$\bar{M}_n \times 10^{-3}$ (g mol^{-1})[b]	PDI
DA1524/PMDA	$(C_{34}H_{14}F_6N_2O_6)_n(660.482)_n$	[c]	[d]	[d]	[d]
DA1524/BTDA	$(C_{41}H_{18}F_6N_2O_7)_n(764.590)_n$	0.86	18.9	10.5	1.80
DA1524/ODPA	$(C_{40}H_{18}F_6N_2O_7)_n(752.579)_n$	0.73	25.3	11.5	2.20
DA1524/6FDA	$(C_{43}H_{18}F_{12}N_2O_6)_n(886.601)_n$	1.10	24.6	12.9	1.91
DA1542/BTDA[e]	$(C_{41}H_{18}F_6N_2O_7)_n(764.590)_n$	0.60[f]	57.0	35.0	1.63
DA1742/BTDA[g]	$(C_{41}H_{18}F_6N_2O_7)_n(764.590)_n$	0.52[f]	43.0	25.5	1.70

[a] Measured in DMAc at 30 °C.

[b] Measured by GPC in THF with polystyrene as a standard.

[c] Was not dissolved in DMAc adequately.

[d] Appropriate concentration in THF could not be prepared.

[e] Data obtained from Ref. [17].

[f] Inherent viscosity measured in DMAc at a concentration of 0.5 g dL^{-1} at 30 °C.

[g] Data obtained from Ref. [18].

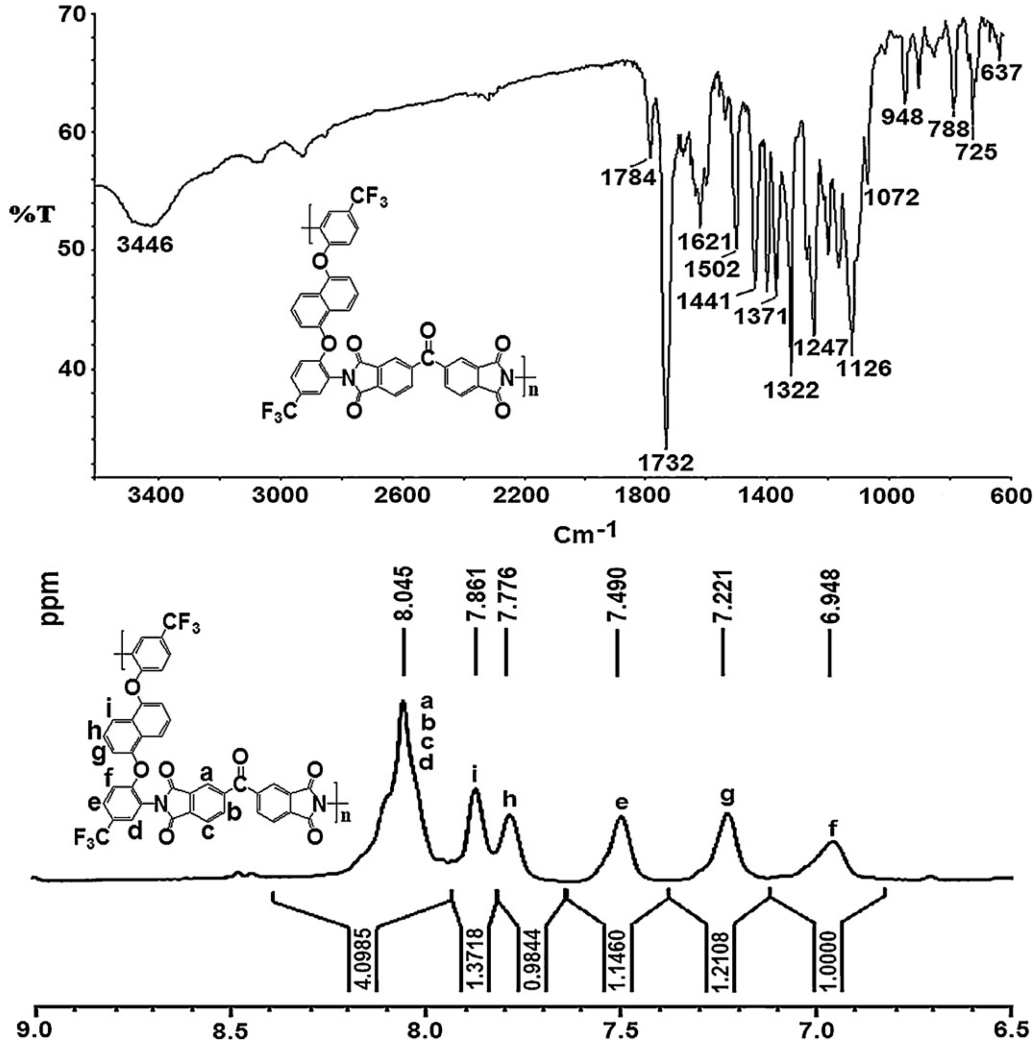


Fig. 1. IR (top) and ^{1}H NMR (bottom) spectra of polyimide DA1524/BTDA.

water, the flexible and transparent thin films with almost no color was self-stripped off from the glass surface. All new fluoro-containing polyimides were noticeably flexible. A part of this flexibility might be attributed to the presence of flexible ether linkages that play the role of hinge along the macromolecular chains. The obtained films were then used to investigate the optical properties of the polyimides. Table 2 lists the characteristics of the resulting polymeric films along with some important optical data obtained from both these films and diluted solutions of the polymers in DMSO. The value of λ_{80} is defined as the point at which the light transmittance from the prepared thin films becomes less than 80%. This point sits at the left side of plateau region in the UV–vis absorption spectrum. Furthermore, λ_0 (absorption edge or cut-off wavelength) is defined as the point at which the transmittance becomes below 1%. For example, the transmission spectra of polymer DA1524/6FDA film are shown in Fig. 2 (top). The values of

Table 2
Film characteristics and optical behavior of the resulting polyimides.

Polymer	Film characteristics[a]	λ_{80}[b] (nm)	λ_0[c] (nm)	λ_{max}[d] (nm)
DA1524/PMDA	[e]	[e]	[e]	269
DA1524/BTDA	Colorless, transparent, flexible	604	354	271
DA1524/ODPA	Colorless, transparent, flexible	598	347	290
DA1524/6FDA	Colorless, transparent, flexible	608	340	267
DA1542/PMDA[f]	Transparent, flexible[g]	[h]	[h]	[h]
DA1742/PMDA[i]	Colorless, transparent, flexible	[h]	421	[h]

[a] Film thickness: about 50 μm.
[b] This wavelength is defined as the point at which the light transmittance from the prepared thin films became below 80%.
[c] Cut-off wavelength is defined as the point at which the light transmittance from the prepared thin films becomes less than 1%.
[d] Obtained from the diluted solutions with polymer concentration of 10^{-5} mol L^{-1} in DMSO.
[e] Film of this polymer could not be prepared.
[f] Data obtained from Ref. [17].
[g] Color of the film was not reported.
[h] Not reported.
[i] Data obtained from Ref. [18].

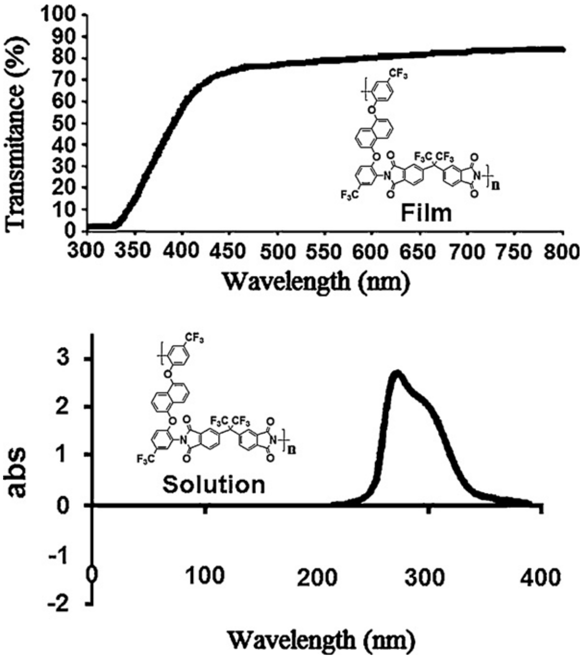


Fig. 2. UV–vis transmission spectrum of polyimide DA1524/6FDA film (top) and molar absorptivity spectrum of the same polymer solution (bottom).

λ_{80} and λ_0 were determined at about 600 and 350 nm, respectively. It could be clearly resulted that these polymers have good optical transparency in the visible light region. This behavior should be related to the position of amino groups in the structure of monomer DA1524 that affects on the alignment of the polymeric chains growth. The amount of charge transfers between the macromolecular chains might be lowered by this kind of chain orientation, which naturally affects on color intensity and pellucidity of the final films. In addition to study on optical behavior of polymeric films, the light absorption of the samples solutions was also evaluated. The maximum absorption wavelength (λ_{max}) of all solutions with concentration of 10^{-5} mol L^{-1} in DMSO appeared at about 270 nm, which shows a relatively small energy band gap for $\pi \rightarrow \pi^*$ transition. Reasonably, this could be attributed to the long length of conjugation in these naphthalene-based aromatic structures. Fig. 2 (bottom) shows a representative molar absorptivity spectrum for solution of polyimide DA1524/6FDA.

2.1.4. Thermal behavior

Thermal behavior of the resulting polyimides were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under nitrogen atmosphere at a heating rate of 10 °C min^{-1}, and corresponding initial decomposition temperatures (IDT) as well as weight loss temperatures of 5% and 10% ($T_{5\%}$ and $T_{10\%}$) were all determined from original TGA curves. All of them exhibited good thermal stability with insignificant weight loss up to 450 °C in nitrogen. The $T_{5\%}$ and $T_{10\%}$ values of the polyimides in nitrogen were up to 520 and 530 °C, respectively. The amount of carbonized residue (char yield) of these polymers in nitrogen atmosphere was about 80% at 600 °C. The high char yields of these polymers can be ascribed to their high aromatic content. The results obtained from these analyses are entirely tabulated in Table 3. DSC analysis was used to determine the glass-transition temperature values (T_g's) of the samples obtained with a heating rate of 10 °C min^{-1} under nitrogen flow. Hereby, T_o (the onset temperature, defines the point at which the first deviation from the base line on the low temperature side of a DSC curve is observed) and T_g ($T_{0.5}$, the midpoint temperature of baseline shift, which is temperature of 50% transition) values of the resulting polyimides were determined. The marked difference between T_o and T_g values of the resulting polymers indicates that neither of them showed discernible glass transitions on the DSC traces, probably due to the rigid nature of their backbones. Thereby, the T_g values were read at the middle of the transition taken from the DSC plots, and found to be in the range of 280–306 °C. In general, molecular packing and chain rigidity are among the main factors influencing on T_g values. Therefore, the increased rotational barrier caused by the macromolecular arrangement type enhanced T_g values. Accordingly, T_g of polyimide DA1524/BTDA was about 20 °C and 40 °C greater than its counterparts namely DA1542/BTDA and DA1742/BTDA. In addition to DA1524, the values of T_g were normally affected by dianhydride moieties too, which shows the order PMDA > 6F-6FDA > BTDA > ODPA as illustrated in Table 3.

2.1.5. Organo-solubility

The solubility behavior of the resulting fluorinated polyimides were tested in various solvents and compared with their preceding counterparts (Table 4). DA1524-derived polyimides could be easily dissolved in polar organic solvents such as DMF, DMAc, DMSO, NMP, pyridine, and THF at room temperature. All members of this class of polymers except for DA1524/PMDA were nearly dissolved even in toluene as a less polar solvent upon heating. The inflexible structure of comonomer PMDA might be participated in this low solubility of DA1524/PMDA. The presence of CF_3 groups in these

Table 3
Thermal properties the resulting fluorinated polyimides.

Polymer	T_{IDT}[a] (°C)	$T_{d5\%}$[b] (°C)	$T_{d10\%}$[c] (°C)	CY[d] (%)	T_o[e] (°C)	T_g[f] (°C)
DA1524/PMDA	458	520	526	81	298	306
DA1524/BTDA	442	515	531	78	276	283
DA1524/ODPA	449	518	528	75	271	280
DA1524/6FDA	436	482	502	79	292	301
DA1542/BTDA[g]	[h]	593	624	61[i]	[h]	266
DA1742/BTDA[j]	[h]	559	585	56[i]	[h]	240

[a] Initial decomposition temperature, determined by TGA in N_2 at a heating rate of 10 °C min^{-1}.
[b] Temperature at which 5% weight loss was recorded by TGA.
[c] Temperature at which 10% weight loss was recorded by TGA.
[d] Char yield: residual weight percentages at 600 °C.
[e] Onset temperature, from DSC measurements, defines the point at which the first deviation from the base line on the low temperature side is observed.
[f] Glass-transition temperatures were read at the middle of the transition taken from the DSC traces.
[g] Data obtained from Ref. [17].
[h] Not reported.
[i] Data was determined at 800 °C.
[j] Data obtained from Ref. [18].

Table 4
Solubility of the resulting fluorinated polyimides.[a]

Solvent[a]	DA1524/PMDA	DA1524/BTDA	DA1524/ODPA	DA1524/6FDA	DA1542/BTDA[b]	DA1742/BTDA[c]
DMF	±	++	++	++	++	++
DMAc	±	++	++	++	++	++
DMSO	±	++	++	++	+	++
NMP	±	++	++	++	++	++
Pyridine	±	++	++	++	[d]	[d]
THF	±	++	++	++	++	++
Toluene	–	+	+	+	[d]	[d]

[a] Qualitative solubility was tested with 10 mg of polymer in 1 mL of solvent. ++, soluble at room temperature; +, soluble on heating; ±, partially soluble; –, insoluble even on heating.
[b] Chemical polyimidization, data obtained from Ref. [17].
[c] Chemical polyimidization, data obtained from Ref. [18].
[d] Not reported.

polyimides surely plays the main role in their high solubility. The effects of the chains alignments caused by orientation of copulative imide groups as the second influencing factor in high solubility of the resulting polymers is easily revealed when comparing the solubility results of these polymers with those of previously prepared ones i.e. DA1542/BTDA and DA1742/BTDA. An indirect alignment for macromolecular extension results in asymmetry enhancement in their chains because of endowing the chains a large amount of polarity, and thereby these fluoropolymers show good organo-solubility, particularly in polar solvents.

3. Conclusions

A series of suitably arranged fluoro-containing macromolecules was successfully synthesized by two-step chemical polyimidization reaction of the new diamine DA1524 with four commercially available dianhydride comonomers. The flexible thin films of the resulting polymers were entirely transparent and colorless. The resulting well-oriented macromolecules were almost soluble in all the organic solvents tested in this study at room temperature. In sum, these polymers displayed good film-forming capability, excellent solubility, low crystallinity, high thermal stability, and high T_g values suitable for thermoforming processing. These desired characteristics indicate that the prepared polyimides are promising materials for optical communication applications.

4. Experimental

4.1. Materials

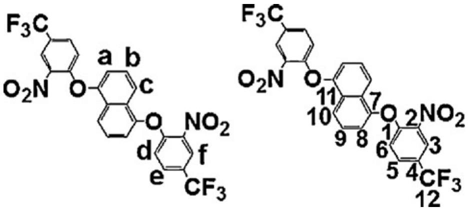
1,5-Dihydroxynaphthalene (from MERCK, m.p. 259–261 °C), 4-chloro-3-nitrobenzotrifluoride (from MERCK, m.p. 108–109 °C), potassium carbonate (from MERCK), 10% palladium on charcoal (Pd/C) (FLUKA), and hydrazine monohydrate (from MERCK) were used as received. Commercially available aromatic tetracarboxylic dianhydrides including pyromellitic dianhydride (PMDA) (from MERCK, m.p. 284–287 °C) and 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) (from MERCK, m.p. 220–223 °C) were purified by recrystallization from acetic anhydride. 4,4′-Oxydiphthalic dianhydride (ODPA) (from ALDRICH, m.p. 225–229 °C) and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) (from ALDRICH, m.p. 244–247 °C) were heated at 250 °C under vacuum for 3 h before use. Solvents used including *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), *N*-methyl-2-pyrrolidone (NMP), and pyridine were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Tetrahydrofuran (THF) and toluene were dried by sodium before use.

4.2. Measurements

Intrinsic viscosity data were measured using an Ubbelohde viscometer with polymer solutions in DMAc at 30 °C. Melting points were determined in open capillaries with IA 9200 Series Digital Melting Point apparatus. FT-IR spectra were recorded on a PERKIN ELMER RX I FT-IR spectrometer. The spectra of solids were obtained using KBr pellets. ^1H NMR and ^{13}C NMR spectra were recorded with a Bruker AVANCE 500 NMR operated at 500 MHz for proton and 125 MHz for carbon using $CDCl_3$ and tetramethylsilane was used as an internal standard. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on a Mettler TA 5000 system (Columbus, OH) under nitrogen atmosphere at a heating rate of 10 °C min^{-1}. Weight- and number-average molecular weights of the resulting poly(amide–imide)s were determined by gel-permeation chromatography (GPC). This chromatography was performed on a Waters 150-C instrument using Styragel columns and a differential refractometer detector. The molecular weight calibration was carried out using polystyrene standards. Calibration and measurements were made at a flow rate of 1 mL min^{-1} with tetrahydrofuran (THF) as the eluent. Ultraviolet maximum wavelength (λ_{max}) values were determined with a GBC model 916 ultraviolet–visible (UV–vis) instrument (GBC Scientific Equipment, Australia) in DMSO at a concentration of 0.1 mg/ml. Cut-off wavelength (absorption edge) values (λ_0) were determined with a Perkin Elmer PTP-1 Peltier System Lambda 25 UV/VIS Spectrometer.

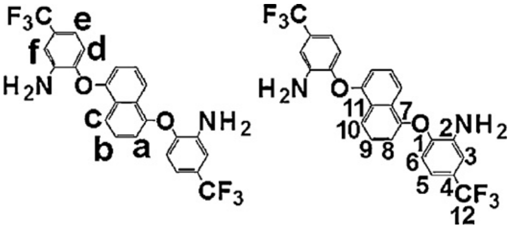
4.3. Synthesis of 1,5-bis(2-nitro-4-trifluoromethylphenoxy)naphthalene (DN1524)

A round-bottomed 50 mL flask equipped with magnetic stirrer and reflux condenser was charged with 1,5-dihydroxynaphthalene (1.6001 g, 10 mmol), 4-chloro-3-nitrobenzotrifluoride (3.2 mL, 22 mmol), anhydrous potassium carbonate (3.4502 g, 25 mmol), and dried DMF (17 mL). The resulting heterogeneous mixture was then refluxed for 18 h. Next, the reaction mixture was allowed to cool and then poured into 200 mL of H_2O/CH_3OH (3:1) to yield a precipitate, which was filtered, washed with water, and dried. The obtained crude product was repeatedly recrystallized from DMF/H_2O (1:1), and then dried to afford 4.7 g (86%) of dinitro DN1524 as yellow solid, m.p. 242–244 °C. FT-IR (KBr): 3088 (w, sh), 1627 (m, sh), 1584 (w, sh), 1540 (s, sh), 1505 (w, sh), 1489 (w, sh), 1398 (m, sh), 1348 (m, sh), 1322 (s, sh), 1265 (s, sh), 1251 (s, sh), 1182 (m, sh), 1137 (s, sh), 1090 (s, sh), 942 (m, sh), 891 (m, sh), 834 (m, sh), 788(s, sh), 709 (w, sh), 685 (w, sh). ^1H NMR (DMSO-d_6): δ (ppm) = 8.57 (s, 2H, H_f), 8.00 (d, J = 7.5 Hz, 2H, H_e), 7.97 (d, J = 8 Hz, 2H, H_c), 7.66 (t, J = 8 Hz, 2H, H_b), 7.46 (d, J = 7.5 Hz, 2H, H_d), 7.20 (d, J = 8 Hz, 2H, H_a). ^{13}C NMR (DMSO-d_6): δ (ppm) = 153.73 (C_1), 150.76 (C_7), 140.97 (C_2), 132.64 (C_5), 128.40 (C_9), 128.33 (C_{11}), 124.84 (C_{12}), 124.68 (q, $^2J_{C\text{-}F} \approx 30$ Hz, C_4), 124.44 (C_3), 123.04 (C_{12}), 121.20 (C_{12}), 120.80 (C_6), 119.73 (C_{10}), 119.34 (C_{12}), 117.92 (C_8).



4.4. Synthesis of 1,5-bis(2-amino-4-trifluoromethylphenoxy)naphthalene (DA1524)

To a suspension of dinitro DN1524 (5.0411 g, 8 mmol) and 10% Pd/C (0.0532 g) in ethanol (18 mL), a solution of hydrazine monohydrate (8.8 mL) and ethanol (12 mL) was added dropwise at reflux temperature over a period of 30 min, while stirring. After complete addition, the mixture was heated at reflux temperature for another 24 h. The hot reaction mixture was filtered to remove Pd/C, and the filtrate was then cooled and filtered again to give a dirty yellow precipitate. This crude product was finally purified by recrystallization from ethanol, and dried to give 2.80 g (54%) of diamine DA1524 as white crystals; m.p. 147–150 °C. FT-IR (KBr): 3502 (m, sh), 3439 (m, sh), 3366 (m, sh), 1633 (s, sh), 1595 (m, sh), 1515 (m, sh), 1504 (s, sh), 1446 (s, sh), 1402 (s, sh), 1334 (s, sh), 1281 (w, sh), 1248 (s, sh), 1199 (s, sh), 1171 (s, sh), 1139 (s, sh), 1122 (s, sh), 1081 (m, sh), 953 (w, sh), 909 (m, sh), 868 (m, sh), 835 (w, sh), 775 (s, sh), 668 (w, sh) cm^{-1}. ^1H NMR (DMSO-d_6): δ (ppm) = 7.92 (d, J = 8.0 Hz, 2H, H_c), 7.51 (t, J = 8.0 Hz, 2H, H_b), 7.18 (s, 2H, H_f), 7.01 (d, J = 7.5 Hz, 2H, H_e), 6.78 (d, J = 8.0 Hz, 2H, H_a), 6.80 (d, J = 7.5 Hz, 2H, H_d), 5.56 (s, 4H, NH_2). ^{13}C NMR (DMSO-d_6): δ (ppm) = 154.37 (C_1), 146.83 (C_2), 140.60 (C_7), 128.72 (C_9), 127.01 (C_3), 126.79 (C_{12}), 126.53 (q, $^2J_{C-F} \approx 30$ Hz, C_4), 124.55 (C_{12}), 122.23 (C_{12}), 119.98 (C_{12}), 119.12 (C_6), 118.05 (C_5), 114.35 (C_{10}), 113.55 (C_8), 112.39 (C_{11}).



4.5. Preparation of the polyimides

A typical example of polyimidization reactions is as follows: a three-necked flask was charged with DA1524 (0.6280 g, 1.25 mmol) and CaH_2-dried DMAc (5 mL). The solution was magnetically stirred until the diamine dissolved completely, and then BTDA (0.4032 g, 1.25 mmol) was added to the reaction mixture in one portion. The mixture was stirred for 24 h to form poly(amic-acid) precursor. An extra-DMAc (3 mL) was then poured into the reaction flask. *In situ*-chemical cyclodehydration was carried out by adding an equimolar mixture of acetic anhydride (1 mL) and pyridine (0.5 mL) into the poly(amic-acid) solution with stirring at room temperature under a nitrogen flow. The solution was then heated at 120 °C for 3 h to perform a complete imidization. Next, the reaction mixture was coldly poured into methanol. The resulted precipitate was filtered, washed thoroughly with methanol and hot water, and dried at 100 °C under vacuum to yield DA1524/PMDA. DA1524/ODPA, and DA1524/6FDA were also prepared in a similar manner. The limited viscosity number values in DMAc at 30 °C as well as the number and weight average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) will be reported and discussed in Section 2.

In order to form a crack-free thin film of the polymeric samples, a homogeneous solution of polymer (0.2 g) in DMF (2 mL) was prepared and poured into an appropriate glass Petri dish (θ = 3 cm). This dish was then placed in an ordinary oven at 90 °C for 10 h to evaporate the main part of the solvent. The semi-dried film was sequentially heated in a vacuum oven at 80 °C for 12 h to remove the residual solvent. By being soaked in distilled water, the film with about 100 μm in thickness was self-stripped off from the glass surface.

Acknowledgements

The authors wish to express their gratitude to the Engineering Research Center for running the GPC analyses. The authors are also grateful to the Sharif University of Technology for running the NMR spectra, as well as Amir-Kabir University of Technology for running the TGA and DSC analyses.

References

[1] M.G. Dhara, S. Banerjee, Prog. Polym. Sci. 35 (2010) 1022–1077.
[2] R. Souzy, B. Ameduri, Prog. Polym. Sci. 30 (2005) 644–687.
[3] B. Chu, X. Zhou, K. Ren, B. Neese, M. Lin, Q. Wang, Science 313 (2006) 334–336.
[4] L. Kun, L. Siwei, L. Yingying, W. Qing, Macromolecules 40 (2007) 4121–4123.
[5] B. Ameduri, Chem. Rev. 109 (2009) 6632–6686.
[6] X.L. Wang, Y.F. Li, C.L. Gong, T. Ma, F.C. Yang, J. Fluorine Chem. 129 (2008) 56–63.
[7] F. Yang, Y. Li, Q. Bu, S. Zhang, T. Ma, J. Zhao, Polym. Degrad. Stab. 95 (2010) 1950–1958.
[8] T. Ma, S. Zhang, Y. Li, F. Yang, C. Gong, J. Zhao, J. Fluorine Chem. 131 (2010) 724–730.
[9] P.S. Patil, R.R. Pal, M.M. Salunkhe, N.N. Maldar, P.P. Wadgaonkar, Eur. Polym. J. 43 (2007) 5047–5054.
[10] M. Ding, Prog. Polym. Sci. 32 (2007) 623–668.
[11] M. Hasegawa, K. Horie, Prog. Polym. Sci. 26 (2001) 259–335.
[12] G. Maier, Prog. Polym. Sci. 26 (2001) 3–65.
[13] A. Ghosh, S. Banerjee, High Perform. Polym. 21 (2009) 173–186.
[14] S.K. Sen, S. Maji, B. Dasgupta, S. Chatterjee, S. Banerjee, J. Appl. Polym. Sci. 113 (2009) 1550–1559.
[15] S. Mehdipour-Ataei, M.H. Mosslemin, M. Shafieezadeh, React. Funct. Polym. 66 (2006) 403–412.
[16] L.Y. Jiang, Y. Wang, T.S. Chung, X.Y. Qiao, J.Y. Lai, Prog. Polym. Sci. 34 (2009) 1135–1160.
[17] S.H. Hsiao, C.P. Yang, S.C. Huang, Eur. Polym. J. 40 (2004) 1063–1074.
[18] C.L. Chung, W.F. Lee, C.H. Lin, S.H. Hsiao, J. Polym. Sci. Polym. Chem. 47 (2009) 1756–1770.
[19] K.L. Mittal, Polyimide: Synthesis, Characterization and Application, Plenum, New York, 1984.
[20] C.E. Sroog, Prog. Polym. Sci. 16 (1991) 561–694.
[21] M.I. Bessonov, M.M. Koton, V.V. Kudryavtsev, L.A. Laius, Polyimides, Consultants Bureau, New York, 1987.
[22] B. Sillion, R. Mercier, D. Picq, in: M.E. Rogers, T.E. Long (Eds.), Synthetic Methods in Step-Growth Polymers, Wiley, 2003, pp. 265–326.
[23] C. Feger, M.M. Khojasteh, M.S. Htoo, Advances in Polyimide Science and Technology, Ellenville, New York, 1991.
[24] D. Braun, H. Cherdron, M. Rehahn, H. Ritter, B. Voit, Polymer Synthesis: Theory and Practice, Springer, 2005, pp. 104–112.