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Fabrication and characterization of novel high-performance fluorinated polyimides with xanthene pendent architecture: Study of thermal, photophysical, antibacterial and heavy metal ion adsorption behavior

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Two series of novel fluorinated aromatic polyimides derived from two new monomers with commercially available dianhydrides were successfully synthesized. Diamines and synthesized polyimides were fully characterized and their properties such solubility, thermal, photophysical, antibacterial activity and ability for removal of environmentally toxic heavy metal ions were investigated.

Highlight

- Fabrication and characterization of novel fluorinated polyimides was carried out.
- The effects of CF₃ polar group substitution on polyimides properties was studied.
- Bulky CF₃ and xanthene units in the polymer backbone improving polymers solubility.
- Extraction capability for heavy metal ions from aqueous solutions was investigated.
- Novel polyimides were also tested for antibacterial activity.

ABSTRACT

Two series of new fluorescent polyimides (PIs) with different functional groups such as flexible ether linkages, substituted imidazole, photoactive xanthene pendant, and electron withdrawing CF₃ groups were prepared using novel monomers and three commercially

available dianhydrides. The structures of two diamines and PIs were fully characterized by elemental analysis, FT-IR and ¹H NMR spectroscopy. The prepared polymers were amorphous with inherent viscosity ranged from 0.38 to 0.66 dL/g, they were readily soluble in a variety of organic solvents and tough transparent films were prepared by solution casting method. These polymers showed useful level of thermal stability having high glass transition (Tg) (235-303 °C) and 10% weight loss (402-498 °C) temperatures with more than 62% residue at 800 °C under N₂. They exhibited strong UV-vis absorption in solutions and in films. Photoluminescence efficiency was affected by the chemical structure of the polymers and their quantum yields ranged from 7 to 21%. The antibacterial activity of diamines and two polymers were investigated against Gram positive and Gram negative bacteria. Also, the prepared PIs were investigated for the removal of heavy metal ions such as Cr^{3+} , Pb^{2+} , Hg^{2+} , Cd^{2+} and Co^{2+} from aqueous solutions at pH 7-8.

Keywords: Fluorinated polyimides; Xanthene; Thermal stability, Antibacterial, Heavy metal ions.

1. Introduction

Aromatic polyimides (PIs) are an important class of polymeric materials with good mechanical, chemical and electrical properties and favorable balance of thermal and hydrolytic stability [1-3]. However, this class of polymers suffers from poor

processability due to limited solubility in common organic solvents, high glass-transition (T_g) and softening (T_s) temperatures. Therefore, an increasing number of researches have been directing towards the design and development of structurally modified aromatic PIs with increased solubility and better processability [4-10]. The most common approaches for increasing solubility and lowering T_g and T_s are the introduction of heterocyclic rings, -CF₃ groups, flexible linkages, and bulky pendant in the side or backbone chains of polymers [11-20]. In this respect, the introduction of both flexible ether linkages and -CF₃ groups into the aromatic polyimides backbone improves processability and solubility of polymers without much loss of good thermal and thermo-oxidative stability [21-25]. On the other hand, the incorporation of fluorinated substituents into the polymer backbone further decreases the regularity of polymer chains leading to the weakening of intermolecular hydrogen bonding and chain packing efficiency, resulting in a decrease in crystallinity and improvement in solubility in organic solvents [26-30]. Moreover, CF₃ and bulky heterocyclic groups along the polymer backbones are expected to give rise to restricted segmental mobility, leading overall to a high T_g and enhanced solubility at the same time. These groups make packing-disruptive moieties which hinder the chain packing [31-34]. The rigidity based on the aromaticity and polarity of the heteroaromatic rings contributes to the thermal and chemical stability and retention of mechanical properties of the resulting polymer at elevated temperatures [35-40]. However, the polarizability resulting from the heteroatoms such as nitrogen atoms in the imidazole ring improves the polymer's solubility in organic solvents [41-46]. Imidazole heterocyclic ring and its derivatives such as lophine (substituted imidazole) are useful n-type building blocks with high electron affinity and good thermal stability and have been successfully

incorporated in small molecules and polymers as an electron-transport component. Moreover, imidazole and its derivatives have been extensively studied for their applications in medicine as biologically active substances. However, the use of antimicrobial agent blended in a polymer matrix can give rise to the migration towards the surface, which decreases the antimicrobial activity during the lifetime of polymer application. For this reason, recently several research groups have tested the use of different antimicrobial agents covalently bonded to the polymer chains [47, 48].

Treatment of industrial wastewaters polluted with toxic heavy metal ions has been a great concern of environmental protection agencies all over the world. Among different technologies for removal of the heavy metal ions from aqueous solution, adsorption is a reliable and widely used method due to its simplicity and easy operational conditions [49]. Polymers containing heterocyclic functional groups such as imidazole group not only chelate cationic metal ions but can also adsorb anionic adsorbates through electrostatic interaction [50, 51].

In this work, synthesis and characterization of two series of novel organosoluble and thermostable PIs are reported based on diamines containing CF₃ polar groups, flexible ether linkages (-O-), and substituted imidazole and bulky xanthene pendants. The prepared PIs were characterized by FT-IR, ¹H NMR, and elemental analysis, and their properties including solubility, thermal stability, photophysical, antibacterial activity and adsorption of heavy metal ions such as Cr³⁺, Pb²⁺, Hg²⁺, Cd²⁺and Co²⁺ from water were investigated.

2. Results and discussion

2.1. Synthesis and characterization of diamines

Two new diamines were synthesized according to the synthetic route shown in **Scheme 1.** The purity of all compounds was checked by thin-layer chromatography (TLC) using ethyl acetate/hexane mixture. Compound 1 was successfully synthesized from 2-naphthol and terephthalaldehyde as starting materials in the presence of ptoluenesulfonic acid (*p*-TSA). The structure of compound 1 was identified by elemental analysis, FT-IR and ¹H NMR. The FT-IR spectrum showed absorption band at 1251 cm⁻¹ related to the C-O-C stretching vibration, and ¹H NMR spectrum showed signal at 9.75 ppm related to the C-H of aldehyde group. Compound 2 was synthesized by nucleophilic aromatic substitution reaction of 4,4'-dihydroxybenzil with 4-fluoronitrobenzene in the presence of K_2CO_3 in DMSO solution. The reaction between compounds 1 and 2 in ammonium acetate and glacial acetic acid, which is a well-known synthetic method for preparation of imidazole ring, was used to synthesize the dinitro compounds. The FT-IR spectrum of DNb (Fig. 1) showed the absorption bands at 1536 and 1340 cm⁻¹ due to asymmetric and symmetric stretching vibrations of -NO₂ group, and absorption band at 1240 cm⁻¹ was assigned to C-O-C stretching vibration. In the ¹H NMR spectrum of DNb, the signal at 10 ppm related to the aldehyde group disappeared and a new signal was observed in the region of 12-13 ppm due to the N-H of imidazole ring. The catalytic hydrogenation of the nitro groups into the corresponding amino groups were accomplished by using hydrazine hydrate in ethanol in the presence of a catalytic amount of Pd/C. The structure of intermediates and diamines were characterized by FT-IR, ¹H NMR, and elemental analysis, the extracted data have been given in the experimental section. After reduction, absorption bands at 1536 and 1340 cm⁻¹ related to NO₂ groups disappeared and new bands were observed at 3396 and 3372 cm⁻¹ due to N-H stretching.

Fig. 2 shows the ¹H NMR spectrum of DAb, signals in the region of 5.44, 5.50 and 6.79 ppm were related to the protons of amino group and those attached to the xanthene ring, respectively.

2.2. Polymer synthesis and characterization

The PIs were prepared from polycondensation reaction between the synthesized novel diamines, 2-(4-(14H-dibenzo[a,j]xanthen-14-yl)phenyl)-4,5-bis(4-(4aminophenoxy)phenyl)-1H-imidazole (DAa) and 2-(4-(14H-dibenzo[a,j]xanthen-14yl)phenyl)-4,5-bis(4-(4-amino-2-(trifluoromethyl)phenoxy)phenyl)-1H-imidazole (DAb) with aliphatic and aromatic dianhydrides, as illustrated in Scheme 2. The PIs were synthesized in one pot using two-step reactions; fabrication of poly(amic acid) (PAA) precursors followed by chemical imidization. The chemical imidization of PAA was carried out in acetic anhydride/pyridine mixture. The PIs were light brown powder and the yields were in the region of 85-92% after extraction with refluxing methanol for 24 h to remove low fraction oligomers. The inherent viscosity of PIs was in the range of 0.38-0.66 dL/g indicating medium molecular weights. The FT-IR spectrum of PIb2 (Fig. 1) showed the characteristic absorption bands at 1781 and 1727 cm⁻¹ corresponding to the asymmetric and symmetric C=O stretching, at 1376 cm⁻¹ related to C-N stretching, and at 1109 and 832 cm⁻¹ due to the imide ring deformation. Fig. 3 shows ¹H NMR spectrum of the representative PIa2. The hydrogen atoms in the repeating unit of this polymer were appeared as signals at 6.79, 6.99-8.71, and 12.42 ppm corresponding to the xanthenes ring, aromatic protons, and N-H of imidazole ring, respectively.

2.3. Solubility of PIs

The solubility of PIs was tested in different organic solvents at concentration of 5% (w/v), and the results were tabulated in Table 1. These polymers exhibited good solubility behavior in polar aprotic solvents such as NMP, N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and even in less polar solvents like pyridine and m-cresol. The good solubility of these PIs might be attributed to the flexible ether linkages, bulky groups such as xanthenes and polar hetroaromatic imidazole ring. The bulky groups prevent close chain-packing and allow the solvent molecules to diffuse into the polymer chains and interact with polar groups in the polymer backbone. The solubility of these polymers is higher or comparable with the solubility of previously reported PIs [52]. In addition, the solubility varies depending upon the dianhydride used. PIs synthesized from aliphatic dianhydride (PI3) exhibited good solubility behavior in Py and m-cresol in comparison with PIs prepared from aromatic dianhydride. Also the PIs prepared from diamine containing CF₃ group showed better solubility than PIs obtained from diamine without CF₃ group. The attachment of bulky CF_3 groups would decrease polymer interchain interactions such as hydrogen bonding and generally disturbs the co-planarity of aromatic units. This can reduce packing efficiency and crystallinity, which is expected to lead to the enhanced solubility. It should be noted that good solubility in low-boiling point solvents is critical for preparing objects at a relatively low processing temperature which is desirable for advanced microelectronics manufacturing applications. The water uptake determines the final application of high performance materials. The absorbed water diminishes Tg and

influence mechanical and electrical properties. However, in the membrane technology the greater water uptake implied better performance. The present PIs showed low water uptake in the range of 2.05-2.94% (**Table 1**). This could mainly be attributed to the polymer hydrophobicity due to the presence of trifluoromethyl groups. Among these PIs, the PIb exhibited the lowest water absorption which can be due to the highest fluorine content in its repeating unit. PIa2 obtained from dianhydride 2, showed the highest water uptake due to the presence of carbonyl linkage which forms hydrogen bonding with water molecules.

2.4. UV-vis absorption and fluorescence characteristics

The photoluminescence (PL) spectra of the diamines and PIs in dilute (0.2 g/dL) NMP solutions were shown in **Fig. 4**. The UV-vis spectra of dilute NMP solution of the diamines (2×10⁻⁵ M) and the corresponding PIs (0.2 g/dL) are shown in **Fig. 4A**. The absorption spectra of PIs in dilute NMP solution (0.2 g/dL) and in films were almost identical with maximum at λ_{ab} =308-322 nm, which is related to the π - π * transitions resulting from the conjugation between the aromatic rings and nitrogen atoms. The optical properties of these PIs could also be elucidated from cut-off wavelength observed in the UV-visible spectra and the results were listed in **Table 2**. **Fig. 4B** shows the PL emission spectra of the monomers and PIs in dilute NMP solution. The excitation wavelength used was 315 nm in all cases. The maximum emission wavelength (λ_{em}) of the diamines in NMP solution was observed at 422-427 nm. The PIs solutions and thin films showed broad fluorescent emission spectra with λ_{em} =422-467 nm and λ_{em} =423-470

nm, respectively. To measure the PL quantum yields (Φ_f) , dilute polymer solutions (0.2 g/dL) in NMP were prepared. A 0.1 N solution of quinine in H₂SO₄ (Φ_f = 0.53) was used as a standard [40]. The Φ_f values were 27-31% for the diamines, 19-21% for the aliphatic PIs, and 7-12% for the aromatic PIs. The lower quantum yield of PI2 can be attributed to dissipation of energy into heat as a result of facilitated bond rotation in the bridging carbonyl group between two phenyl rings. The blue shift and higher fluorescence quantum yield of the aliphatic PIs compared with the aromatic PIs were suggested to be attributed to reduced conjugation and capability of charge-transfer complex formation by the aliphatic dianhydrides with the electron-donating diamine moiety in comparison to the stronger electron-accepting aromatic dianhydrides [53]. Because of the lower capability of charge-transfer, the PI3 showed a light colour and high optical transparency. Intermolecular interaction between the xanthene and imidazole moieties in the polymer backbone is negligible, presumably because both chromophores have similar absorption and emission properties.

2.5. Thermal properties

DSC and TGA were applied to evaluate the thermal properties of the PIs. The DSC and TGA curves of the PIs were shown in **Fig. 5**, and thermal analysis data from the original curves are summarized in **Table 3**. The absence of melting peak in the DSC thermograms supported the generally amorphous nature of the PIs. The amorphous nature of these polymers can be attributed to bulky pendent group which decreased the intra and inter-chain interactions, resulting in loose polymer chain packaging and aggregates. The T_g values of PIs were in the range of 235-303 °C. As expected, T_g values depended on the structure of the dianhydride component; it decreased with increasing flexibility of the PI

backbone based on the structure of dianhydride. The bridging carbonyl group between two phenyl rings present in 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) facilitated bond rotation and reduced the T_g of PI2 in comparison with the T_g of PI1. Among the synthesized PIs, PI3 based on bicyclic aliphatic dianhydride showed the lowest T_g value because of the absence of rigid phenyl groups that inhibit molecular motion. Also, the results indicated that Tg values of the PIb containing -CF3 groups was lower than that of PIa without -CF₃ groups. This might be a result of increase in free volume caused by the introduction of the bulky $-CF_3$ substituents. Although the increased rotational barrier caused by the bulky aromatic pendent groups of diamines enhanced the Tg values, but the solubility and processability of these polymers improved significantly due to the presence of ether linkages in the main chain and amorphous nature of the polymer. Thermal stability of these polymers was evaluated by TGA under N_2 atmosphere and the curves were shown in Fig. 5B. All these polymers exhibited good thermal stability with insignificant weight loss up to 370 °C under N₂. TGA data in Table **3** show that the temperature of 10% weight loss was in the range of 402-498 °C, and the residual weights were in the range of 23-62% at 800 °C. Also, the results indicated that PIs containing $-CF_3$ groups had lower thermal stability. The Char yield can be used as criteria for evaluating limiting oxygen index (LOI) of the polymers in accordance with Van Krevelen and Hoftyzer equation [54]. LOI= 17.5 + 0.4 CR where CR= char yield. For all the polymers LOI values were calculated based on their char yield at 800 °C. PI1 had a better thermal stability than PI2 because the carbonyl-bridging group between the two phenyl rings in the backbone of PI2 increased the flexibility and decreased the thermal stability of polymer. According to **Table 3**, it is clear that aromatic PIs have

higher thermal stability and LOI values compared to the aliphatic PIs. This can be pertained to the rigid structure of aromatic dianhydrides compared to the flexible structure of aliphatic dianhydrides. Therefore, the PI1 and PI3 showed the highest and the lowest thermal stability due to the presence of rigid phenyl and flexible aliphatic units in the backbones, respectively.

2.6. Antibacterial activity

The antibacterial properties of the diamines and polymers (PIa1 and PIb1) were evaluated by using two Gram-positive bacteria S. aureus and B. subtilis and two Gram-negative bacteria E. coli and P. aeruginosa. In addition, the finding towards inhibition of microorganisms was correlated with a standard antibiotic tetracycline. The obtained results were summarized in **Table 4** and screened in **Fig. 6**. The antibacterial screening revealed that all the tested compounds, DAs and PIs, showed moderate to good inhibition. The antibacterial activity seemed to be dependent on the heterocyclic moiety as well as on the nature of substituent. The imidazole containing compounds are antibacterial activity can be further enhanced by the presence of electron withdrawing groups on the imidazole moiety [48]. The polymers DAb and PIb containing –CF₃ groups have shown good activity against all tested bacteria which can be due to the strong electronegativity of F atom and the high polarity of -CF₃ group. The results also indicated that electrondonating groups such as -NH₂ decreased the antibacterial effect of the imidazole-containing compounds. Also, PIa and PIb had good inhibitory effect

against the tested bacteria due to the presence of imidazole moieties and were comparable with antibiotic tetracycline.

2.7. Adsorption of heavy metal ions

In these polymers, the presence of imidazole rings and ether linkages in the backbone can act as proper hosts for the adsorption and formation of complex with the target metal ions. 5 mg PIa2 and PIb2 was added to the separate 25 mL metal ion solution with initial concentration of 10 mg L⁻¹. The solutions were stirred for 3 days at room temperature. After separation by centrifuge, the amount of adsorbed ions was calculated using equations given in the experimental section and the respective adsorption data. As the results were summarized in **Table 5**, the order for the adsorption was: $Hg^{2+} > Cr^{3+} > Cd^{2+} > Co^{2+} > Pb^{2+}$. It is observed that the adsorption order of metal ions by the polymers is inversely proportional with the radius of metal ions. These results show that there might be not enough large free space between the polymer chains in the solid state to accommodate large radius metal ions. Also, the adsorption of metal ions by PIa was higher than adsorption by PIb. This can be due to the strong electron withdrawing effect of -CF₃ groups and as a result of attractive force with the metal ions.

3. Conclusions

Two series of novel polyimides were prepared from new diamines and commercially available dianhydrides. These polymers had inherent viscosities ranging from 0.38 to 0.66 dL/g and exhibited solubility in a wide range of organic solvents. The results showed that presence of different functional groups such as ether linkage and bulky

groups such as -CF₃, substituted imidazole and xanthene in the polymers backbones improve the solubility while maintaining thermal stability. The thermal stability of these polymers were verified by measuring Tg (235-303 °C), temperature of 10% weight loss (402-498 °C), and char yields (31-62 wt%). The antibacterial study of these polymers showed that those containing electron withdrawing groups had higher activity against gram-positive and gram negative bacteria. Therefore, these polymers containing combination of different functional groups in their structures showed acceptable properties of thermal, solubility, antibacterial, and metal ions adsorption and can be suitable for varieties of applications.

4. Experimental

4.1. Materials

All chemicals were purchased from Fluka and Merck Chemical Co. (Germany) through a local agency and were used as received without further purification. *N*-methyl-2-pyrrolidone (NMP), *N*,*N*-dimethylacetamide (DMAc), and pyridine (Py) were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Dianhydrides such as pyromellitic dianhydride (PMDA), 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and bicycle-[2.2.2]-oct-7-ene-2,3,5,6 tetracarboxylic dianhydride (BCDA) were dried in a vacuum oven at 110 °C for 5 h.

4.2. Characterization

Proton nuclear magnetic resonance (¹H NMR) spectra were recorded on a 400 MHz Bruker Avance DRX (Germany) instrument using DMSO- d_6 as solvent and tetramethyl

silane as an internal standard. Proton resonances are designated as singlet (s), doublet (d), and multiplet (m). FT-IR spectra were recorded using a Bruker Tensor 27 spectrometer on KBr pellets over the range of 400-4000 cm⁻¹. Elemental analyses performed by a CHN-600 Leco elemental analyzer. Melting point (uncorrected) was measured with a Barnstead Electrothermal engineering LTD 9200 apparatus. Inherent viscosities (at a concentration of 0.5 g/dL) were measured with an Ubbelohde suspended-level viscometer at 25 °C using NMP as solvent. Quantitative solubility was determined using 0.05 g of the polymer in 0.5 mL of solvent. Thermogravimetric analysis (TGA) was performed with the DuPont Instruments (TGA 951) analyzer well equipped with a PC at a heating rate of 10 °C/min under nitrogen atmosphere (20 cm³/min) and in the temperature range of 30-800 °C. Calorimetry curves were recorded on a Perkin Elmer pyris 6 DSC under nitrogen atmosphere (20 cm³/min) at a heating rate of 10 °C/min. Glass-transition temperatures (T_g) values were read at the middle of the transition in heat capacity and were taken from the second heating scan after cooling from 350 °C at a cooling rate of 20 °Cmin⁻¹. Ultraviolet-visible and fluorescence emission spectra were recorded on a Cecil 5503 (Cecil Instruments, Cambridge, UK) and Perkin-Elmer LS-3B spectrophotometers (Norwalk, CT, USA) (slit width= 2 nm), respectively, using a dilute polymer solution (0.20 g/dL) in NMP. The metal ion concentrations in the supernatants were determined using atomic absorption spectrophotometer (BRAICWFX-130 AA). PIs films were prepared by dissolving 0.5 g PI in 5 mL NMP and the homogeneous solution was poured into a 9 cm-diameter glass culture dish, heated under vacuum at 50 °C for 2 h, 100 °C for 5 h, and 150 °C for 3 h to evaporate the solvent slowly. Polymer films were self-stripped off from the glass surface by soaking in water and then dried in a vacuum oven at 170 $^{\circ}C$

for 10 h. To determine water uptake of the polymers, the dried films were immersed in deionized water at 25 °C. After 24 h, the films were removed from water and then they were quickly placed between sheets of filter paper to remove the excess water and films were weighed immediately.

4.3. Antibacterial assay

The antibacterial activities of the synthesized compounds were tested onto LB (Luria-Bertani) medium. The LB medium included: BactoTM tryptone, 10.0 g L⁻¹; yeast extract, 5.0 g L⁻¹; sodium chloride, 5.0 g L⁻¹; and glucose, 1.0 g L⁻¹. The medium was dispensed into universal bottles and sterilized at 121 °C for 15 min. 0.04 g of diamines and PI1(a,b) were dissolved separately in 20 mL DMSO to produce 2 mg/mL solutions which were filter sterilized using a 0.22 µm Ministart (Sartorius). The sterilized solutions were added into LB medium to give a final concentration of 1-300 µg/mL as required. The antibacterial activities of the compounds were compared with known antibiotic tetracycline at the same concentration. The minimum inhibitory concentration (MIC) test of the newly synthesized compounds were determined in vitro against microorganisms including the two Gram-positive bacteria Staphylococcus aureus ATCC 25923 and Bacillus subtilis PTCC 1156 and two Gram-negative bacteria Escherichia coli PTCC1533 and Pseudomonas aeruginosa PTCC 1707. 1% (v/v) inoculums of each culture was inoculated into the LB medium containing different concentrations of the synthesized compounds and incubated on the orbital shaker at 37 °C and 100 rpm. Before using the cultures, they were standardized with a final cell density of approximately 108 cfu mL⁻

¹.The synthesized compounds sensitivity of the strains were determined for positive or negative growth after 24h.

4.4. Adsorption studies

For solid-liquid extraction of Cr^{3+} , Pb^{2+} , Hg^{2+} , Cd^{2+} and Co^{2+} , 5 mg of the appropriate polymer powder was shaken with 25 mL of aqueous solution of the metal salt with initial concentration of 10 mg L⁻¹ for 3 days at 25 °C and pH 7-8. After centrifugal separation, the metal ion concentrations in the supernatants were determined by atomic absorption spectrophotometer. The removal percentage (R%) of each metal ion and the adsorption capacity that represents the amount of adsorbed ions (mg g⁻¹) were calculated using the following equations, respectively:

(%)
$$R = [(C_o - C_A)/C_o] \times 100$$
 (1)

$$Q_t = [(C_o - C_A)] \times V/W$$
(2)

where C_0 and C_A are the concentrations of metal ions in the initial solution and in the aqueous phase after adsorption, respectively (mg L⁻¹), Q_t is the amount of metal ions adsorbed into the unit of the composites (mg g⁻¹), V is the volume of the aqueous phase (mL) and W is the weight of the polymer (g).

4.5. Monomer synthesis

The following synthetic methods led to the synthesis of target diamines are also outlined in Scheme 1.

4.5.1. Synthesis of 4,4'-dihydroxybenzil

Into a 100 mL round-bottomed two-necked flask equipped with a magnetic stir bar and a reflux condenser, 4,4'-dimethoxy benzil (2 g, 0.0075 mol), aqueous HBr (15 mL, 48%) and glacial acetic acid (15 mL) were placed. The reaction mixture was refluxed for 24 h, and then poured in 100 mL water after cooling to room temperature. Ethyl acetate was added to the mixture to give two phases of which the organic phase containing the product was separated and dried over magnesium sulfate for 12 h. The solvent was removed under reduced pressure and the obtained yellow precipitate was washed thoroughly with water and then dried in a vacuum oven at 80 °C. Yield: 94% (1.7 g), and melting point: 229-231 °C. FT-IR (KBr) at cm⁻¹: 3400 (OH phenol), 3045 (C-H aromatic), 1646 (C=O), 1576 (C=C), 1223 (C-O). ¹H NMR (400 MHz, DMSO-*d*₆,): δ 6.91-6.95 (d, 4H, *J*= 8.0 Hz), 7.73-7.77 (d, 4H, *J*= 8.0 Hz), 10.84 (s, 2H).

4.5.2. Synthesis of 4-(14H-dibenzo[a,j]xanthen-14-yl)benzaldehyde (1)

Into a 100 mL round-bottomed two-necked flask equipped with a condenser and a magnetic stir bar, a mixture of 2-naphthol (1.44 g, 0.01 mol), terephthalaldehyde (0.67 g, 0.005 mol), and *p*-toluenesulfonic acid as catalyst were added. The mixture was stirred for 2 h in CHCl₃ at 60-65 °C. After completion of the reaction (as indicated by TLC), the reaction mixture was poured into the ice water and the solid was collected by filtration, washed with water and then dried. The obtained solid was recrystallised from hot ethanol and dried in a vacuum oven at 80 °C. Yield: 95% (1.83 g), and melting point: 310-312 °C.

FT-IR (KBr) at cm⁻¹: 3060 (aromatic C-H); 2929 (aliphatic C-H); 2738 (aldehyde C-H); 1690 (C=O); 1591 (C=C); 1251 (C-O-C). ¹H NMR (400 MHz, DMSO-*d*₆,): δ 6.85 (s, 1H, CH), 7.46 (t, 2H, Ar-H, *J*= 8.0 Hz), 7.58 (d, 2H, Ar-H, *J*= 8.0 Hz), 7.63 (t, 2H, Ar-H, *J*= 8.0 Hz), 7.68 (d, 2H, Ar-H, *J*= 8.0 Hz), 7.87 (d, 2H, Ar-H, *J*= 8.0 Hz), 7.94 (t, 4H,

Ar-H, J= 8.0 Hz), 8.68 (d, 2H, Ar-H, J= 8.0 Hz), 9.75 (s, 1H, C-H aldehyde) (For the ¹H NMR spectrum, see Fig. S1 in Supporting Information). Anal. Calcd. for C₂₈H₁₈O₂ (386 g/mol): C, 87.05%; H, 4.66%. Found: C, 87.01%; H, 4.73%.

4.5.3. Synthesis of 1,2-bis(4-(4-nitrophenoxy)phenyl)ethane-1,2-dione (2a)

Into a 100 mL round-bottomed two-necked flask equipped with a magnetic stir bar and a reflux condenser, 4,4'-dihydroxybenzil (1.21 g, 0.005 mol) and 4fluoronitrobenzene (1.41 g, 0.01 mol) were dissolved in 10 mL DMSO, and then potassium carbonate (1.38 g, 0.01 mol) was added and the mixture was stirred for 30 min at room temperature. The reaction mixture was heated at 110 °C for 6 h and then poured in 100 mL water. The yellow precipitate was filtered off and dried in a vacuum oven at 80 °C. Yield: 91% (2.2 g), and melting point: 150-153 °C.

FT-IR (KBr) at cm⁻¹: 3070 (aromatic C-H); 1690 (C=O); 1585 (C=C); 1532, 1342 (NO₂); 1241 (C-O) stretching. ¹H NMR (400 MHz, DMSO- d_6 ,): δ 7.34 (d, 8H, Ar-H, J= 8.0 Hz), 8.04 (d, 4H, Ar-H, J= 8.0 Hz), 8.31 (d, 4H, Ar-H, J= 8.0 Hz) (For the ¹H NMR spectrum, see Fig. S2 in Supporting Information). Anal. Calcd. for C₂₆H₁₆N₂O₈ (484 g/mol): C, 64.46%; H, 3.31%; N, 5.79%. Found: C, 64.41%; H, 3.40%; N, 5.77%. 4.5.4. Synthesis of 1,2-bis(4-(4-nitro-2-(trifluoromethyl)phenoxy)phenyl)ethane-1,2-dione

(2b)

Into a 100 mL round-bottomed two-necked flask equipped with a magnetic stir bar and a reflux condenser, 4,4'-dihydroxybenzil (1.21 g, 0.005 mol) and 1-chloro-4-nitro-2-(trifluoromethyl) benzene (2.25 g, 0.01 mol) were dissolved in 10 mL DMSO, then potassium carbonate (1.38 g, 0.01 mol) was added and the mixture was stirred for 30 min at room temperature. The reaction mixture was heated at 110 °C for 6 h and then poured

in 100 mL water. The yellow precipitate was filtered off and dried in a vacuum oven at 80 °C. Yield: 93% (2.9 g), and melting point: 157-160 °C.

FT-IR (KBr) at cm⁻¹: 3074 (aromatic C-H); 1695 (C=O); 1586 (C=C); 1534, 1353 (NO₂); 1268 (C-O) stretching. ¹H NMR (400 MHz, DMSO- d_6 ,): δ 7.41 (d, 4H, Ar-H, J= 8.0 Hz), 7.46 (d, 2H, Ar-H, J= 8.0 Hz), 8.08 (d, 4H, Ar-H, J= 8.0 Hz), 8.54 (dd, 2H, Ar-H, J= 8.0 Hz), 8.57 (d, 2H, Ar-H, J= 2.8 Hz) (For the ¹H NMR spectrum, see Fig. S3 in Supporting Information). Anal. Calcd. for C₂₈H₁₄F₆N₂O₈ (620 g/mol): C, 54.19%; H, 2.26%; N, 4.52%. Found: C, 54.15%; H, 2.32%; N, 4.48%.

4.5.5. Synthesis of 2-(4-(14H-dibenzo[a,j]xanthen-14-yl)phenyl)-4,5-bis(4-(4nitrophenoxy)phenyl)-1H-imidazole (DNa)

Into a 100 mL round-bottomed two-necked flask equipped with a condenser, a magnetic stir bar and a nitrogen gas inlet tube, a mixture of compound 1 (1.93 g, 0.005 mol), compound 2a (2.42 g, 0.005 mol), ammonium acetate (2.7 g, 0.035 mol), and glacial acetic acid (25 mL) was refluxed for 14 h. Upon cooling, the yellow precipitate was collected by filtration, washed with a mixture of C₂H₅OH/H₂O (50/50, v/v), and dried in a vacuum oven at 80 °C. Yield: 93% (3.95 g), and melting point: 205-207 °C.

FT-IR (KBr) at cm⁻¹: 3351 (NH, imidazole ring); 3068 (aromatic C-H); 2927 (aliphatic C-H); 1590 (C=C); 1546, 1340 (NO₂); 1243 (C-O-C). ¹H NMR (400 MHz, DMSO- d_6 ,): δ 6.74 (s, 1H, CH), 7.11 (d, 4H, Ar-H, J= 8.0 Hz), 7.13 (d, 4H, Ar-H, J= 8.0 Hz), 7.46 (t, 2H, Ar-H, J= 8.0 Hz), 7.56 (d, 4H, Ar-H, J= 8.0 Hz), 7.58 (d, 2H, Ar-H, J= 8.0 Hz), 7.63 (t, 2H, Ar-H, J= 8.0 Hz), 7.70 (d, 2H, Ar-H, J= 8.0 Hz), 7.87 (d, 2H, Ar-H, J= 8.0 Hz), 7.93 (d, 4H, Ar-H, J= 8.0 Hz), 8.22 (d, 4H, Ar-H, J= 8.0 Hz), 8.69 (d, 2H, Ar-H, J= 8.0 Hz), 12.97 (s, 1H, N-H imidazole ring) (For the ¹H NMR spectrum, see Fig.

S4 in Supporting Information). Anal. Calcd. for C₅₄H₃₄N₄O₇ (850 g/mol): C, 76.23%; H, 4.00%; N, 6.59%. Found: C, 76.18%; H, 4.10%; N, 6.56%.

4.5.6. Synthesis of 2-(4-(14H-dibenzo[a,j]xanthen-14-yl)phenyl)-4,5-bis(4-(4-nitro-2-(trifluoromethyl)phenoxy)phenyl)-1H-imidazole (DNb)

In a 100 mL round-bottomed two-necked flask equipped with a condenser, a magnetic stir bar and a nitrogen gas inlet tube, a mixture of compound 1 (1.93 g, 0.005 mol), compound 2b (3.1 g, 0.005 mol), ammonium acetate (2.7 g, 0.035 mol), and glacial acetic acid (25 mL) was refluxed for 14 h. Upon cooling, the yellow precipitate was collected by filtration, washed with a mixture of C₂H₅OH/H₂O (50/50, v/v), and dried in a vacuum oven at 80 °C. Yield: 95% (4.68 g), and melting point: 209-211 °C.

FT-IR (KBr) at cm⁻¹: 3390 (NH, imidazole ring); 3064 (aromatic C-H); 2929 (aliphatic C-H); 1590 (C=C); 1536, 1340 (NO₂); 1246 (C-O-C). ¹H NMR (400 MHz, DMSO-*d*₆,): δ 6.78 (s, 1H, CH), 7.11 (dd, 2H, Ar-H, *J*= 8.0 Hz), 7.16 (d, 2H, Ar-H, *J*= 8.0 Hz), 7.29 (d, 2H, Ar-H, *J*= 8.0 Hz), 7.47 (t, 2H, Ar-H, *J*= 8.0 Hz), 7.58 (d, 4H, Ar-H, *J*= 8.0 Hz), 7.65 (d, 2H, Ar-H, *J*= 8.0 Hz), 7.75 (d, 2H, Ar-H, *J*= 8.0 Hz), 7.84 (d, 2H, Ar-H, *J*= 8.0 Hz), 7.95 (d, 4H, Ar-H, *J*= 8.0 Hz), 8.40 (dd, 2H, Ar-H, *J*= 8.0 Hz), 8.48 (d, 2H, Ar-H, *J*= 2.8 Hz), 8.51 (dd, 2H, Ar-H, *J*= 8.0 Hz), 8.71 (d, 2H, Ar-H, *J*= 8.0 Hz), 12.58 (s, 1H, N-H imidazole ring) (For the ¹H NMR spectrum, see Fig. S5 in Supporting Information). Anal. Calcd. for C₅₆H₃₂F₆N₄O₇ (986 g/mol): C, 68.15%; H, 3.25%; N, 5.68%. Found: C, 68.10%; H, 3.33%; N, 5.65%.

4.5.7. Synthesis of 2-(4-(14H-dibenzo[a,j]xanthen-14-yl)phenyl)-4,5-bis(4-(4aminophenoxy)phenyl)-1H-imidazole (DAa)

In a 100 mL round-bottomed two-necked flask equipped with a magnetic stir bar, a mixture of compound DNa (4.25 g, 0.005 mol) and Pd/C (0.1 g, 10%) was dispersed in 50 mL ethanol. The suspension was heated to reflux, and then 6 mL hydrazine monohydrate was added slowly to the mixture. After a further 8 h of reflux, the solution was filtered hot to remove Pd/C, and the filtrate was cooled until white crystals were formed. The product was collected by filtration and dried in a vacuum oven at 80 °C. Yield: 88% (3.48 g), and melting point: 179-182 °C.

FT-IR (KBr) at cm⁻¹: 3453 (N-H imidazole ring); 3382, 3372 (NH₂); 3048 (C-H aromatic); 2916 (aliphatic C-H); 1616 (C=N); 1582 (C=C); 1236 (C-O-C). ¹H NMR (400 MHz, DMSO- d_6 ,): δ 4.99 (s, 4H, NH₂), 6.60 (d, 4H, Ar-H, J= 8.0 Hz), 6.75 (s, 1H, CH), 6.79 (d, 4H, Ar-H, Ar-H, J= 8.0 Hz), 6.86 (d, 4H, Ar-H, Ar-H, J= 8.0 Hz), 7.32 (d, 2H, Ar-H, J= 8.0 Hz), 7.37 (d, 2H, Ar-H, J= 8.0 Hz), 7.46 (t, 2H, Ar-H, J= 8.0 Hz), 7.58 (d, 2H, Ar-H, J= 8.0 Hz), 7.65 (t, 2H, Ar-H, J= 8.0 Hz), 7.70 (d, 2H, Ar-H, J= 8.0 Hz), 7.78 (d, 2H, Ar-H, J= 8.0 Hz), 7.95 (d, 4H, Ar-H, J= 8.0 Hz), 8.70 (d, 2H, Ar-H, J= 8.0 Hz), 12.30 (s, 1H, N-H imidazole ring) (For the ¹H NMR spectrum, see Fig. S6 in Supporting Information).

Anal. Calcd. for C₅₄H₃₈N₄O₃ (790 g/mol): C, 82.02%; H, 4.81%; N, 7.09%. Found: C, 81.98%; H, 4.87%; N, 7.08%.

4.5.8. Synthesis of 2-(4-(14H-dibenzo[a,j]xanthen-14-yl)phenyl)-4,5-bis(4-(4-amino-2-(trifluoromethyl)phenoxy)phenyl)-1H-imidazole (DAb)

In a 100 mL round-bottomed two-necked flask equipped with a magnetic stir bar, a mixture of compound DNb (4.93 g, 0.005 mol) and Pd/C (0.1 g, 10%) was dispersed in 50 mL ethanol. The suspension was heated to reflux, and then 6 mL hydrazine

monohydrate was added slowly to the mixture. After a further 8 h of reflux, the solution was filtered hot to remove Pd/C, and the filtrate was cooled until white crystals were formed. The product was collected by filtration and dried in a vacuum oven at 80 $^{\circ}$ C. Yield: 86% (3.98 g), and melting point: 171-173 $^{\circ}$ C.

FT-IR (KBr) at cm⁻¹: 3462 (N-H imidazole ring), 3396, 3376 (NH₂), 3058 (C-H aromatic); 2921 (aliphatic C-H); 1625 (C=N); 1596 (C=C); 1238 (C-O-C). ¹H NMR (400 MHz, DMSO- d_6 ,): δ 5.44 (s, 2H, NH₂), 5.50 (s, 2H, NH₂), 6.76 (d, 2H, Ar-H, J= 2.0 Hz), 6.79 (s, 1H, CH), 6.83 (d, 2H, Ar-H, J= 8.0 Hz), 6.87 (d, 4H, Ar-H, J= 8.0 Hz), 6.92 (dd, 2H, Ar-H, J_1 = 8.0 Hz and J_2 = 2.0 Hz), 7.36 (d, 2H, Ar-H, J= 8.0 Hz), 7.41 (d, 2H, Ar-H, J= 8.0 Hz), 7.46 (t, 2H, Ar-H, J= 8.0 Hz), 7.58 (d, 2H, Ar-H, J= 8.0 Hz), 7.64 (t, 2H, Ar-H, J= 8.0 Hz), 7.71 (d, 2H, Ar-H, J= 8.0 Hz), 7.79 (d, 2H, Ar-H, J= 8.0 Hz), 7.94 (d, 4H, Ar-H, J= 8.0 Hz), 8.70 (d, 2H, Ar-H, J= 8.0 Hz), 12.35 (s, 1H, N-H imidazole ring). Anal. Calcd. for C₅₆H₃₆F₆N₄O₃ (926 g/mol): C, 72.57%; H, 3.89%; N, 6.05%. Found: C, 72.52%; H, 3.94%; N, 6.06%.

4.6. Polymer synthesis

The following general procedure was used for the preparation of two series of PIs from the prepared diamines DAa and Dab with aliphatic and aromatic commercial dianhydrides. A 100 mL three-necked round-bottomed flask equipped with a condenser, a magnetic stir bar, a nitrogen gas inlet tube, and a calcium chloride drying tube was charged with 1 mmol diamine and 10 mL dry NMP. This mixture was stirred at room temperature for 0.5 h, then 1 mmol dried dianhydride was added and stirred at room temperature for 24 h to obtain a viscous solution of poly(amic acid) (PAA) in NMP. The chemical imidization of PAA was carried out by adding 3 mL of a mixture of acetic

anhydride/pyridine (6/4, V/V) into the solution while stirring at room temperature for 1 h. The mixture was then stirred at 130 $^{\circ}$ C for 12 h to yield a homogeneous polymer solution, which was poured slowly into methanol to give a precipitate that was collected by filtration, washed thoroughly with hot water, and then was further purified by washing with refluxing methanol for 24 h in a Soxhlet apparatus to remove the low molecular weight oligomers. The yields were in the range of 85%-92%. The inherent viscosities of the polymers measured at a concentration of 0.5 g/dL in NMP (at 25 $^{\circ}$ C) were in the range of 0.38-0.66 dL/g.

4.6.1. *PIa1*: Yield = 90%, and η_{inh} (dL/g) = 0.46. FT-IR (KBr) at cm⁻¹: 3421 (N-H imidazole ring); 3037 (aromatic C-H); 2931 (aliphatic C-H); 1783 and 1720 (C=O imide); 1594 (C=N); 1509 (C=C); 1377 (C-N); 1242 (C-O-C). ¹H NMR (400 MHz, DMSO-*d*₆): δ 6.76 (s, 1H, CH), 6.91-8.71 (m, 34H, Ar-H), 12.49 (s, 1H, N-H, imidazole ring). Anal. Calcd. for (C₆₄H₃₆N₄O₇)_n (972 g/mol): C, 79.01%; H, 3.70%; N, 5.76%. Found: C, 78.99%; H, 3.76%; N, 5.74%.

4.6.2. *PIb1*: Yield = 92%, and η_{inh} (dL/g)= 0.52. FT-IR (KBr) at cm⁻¹: 3420 (N-H imidazole ring); 3042 (aromatic C-H); 2937 (aliphatic C-H); 1782 and 1722 (C=O imide); 1597 (C=N); 1512 (C=C); 1378 (C-N); 1245 (C-O-C). ¹H NMR (400 MHz, DMSO-*d*₆): δ 6.77 (s, 1H, CH), 7.93-8.72 (m, 32H, Ar-H), 12.50 (s, 1H, N-H, imidazole ring). Anal. Calcd. for (C₆₆H₃₄F₆N₄O₇)_n (1108 g/mol): C, 71.48%; H, 3.07%; N, 5.05%. Found: C, 71.39%; H, 3.12%; N, 5.06%.

4.6.3. *PIa2*: Yield = 89%, and η_{inh} (dL/g)= 0.61. FT-IR (KBr) at cm⁻¹: 3392 (N-H imidazole ring); 3060 (aromatic C-H); 2924 (aliphatic C-H); 1778 and 1722 (C=O imide); 1598 (C=N); 1501 (C=C); 1376 (C-N); 1241 (C-O-C). ¹H NMR (400 MHz,

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DMSO-*d*₆): δ 6.76 (s, 1H, CH), 6.99-8.71 (m, 38H, Ar-H), 12.42 (s, 1H, N-H, imidazole ring). Anal. Calcd. for (C₇₁H₄₀N₄O₈)_n (1076 g/mol): C, 79.18%; H, 3.72%; N, 5.20%. Found: C, 79.11%; H, 3.77%; N, 5.22%.

4.6.4. *PIb2*: Yield = 92%, and η_{inh} (dL/g)= 0.66. FT-IR (KBr) at cm⁻¹: 3416 (N-H imidazole ring); 3063 (aromatic C-H); 2926 (aliphatic C-H); 1781 and 1727 (C=O imide); 1607 (C=N); 1494 (C=C); 1376 (C-N); 1245 (C-O-C). ¹H NMR (400 MHz, DMSO-*d*₆): δ 6.77 (s, 1H, CH), 6.99-8.72 (m, 36H, Ar-H), 12.50 (s, 1H, N-H, imidazole ring). Anal. Calcd. for (C₇₃H₃₈F₆N₄O₈)_n (1212 g/mol): C, 72.28%; H, 3.14%; N, 4.62%. Found: C, 72.19%; H, 3.18%; N, 4.64%.

4.6.5. *PIa3*: Yield = 87%, and η_{inh} (dL/g)= 0.38. FT-IR (KBr) at cm⁻¹: 3407 (N-H imidazole ring); 3058 (aromatic C-H); 2922 (aliphatic C-H); 1778 and 1719 (C=O imide); 1608 (C=N); 1501 (C=C); 1380 (C-N); 1241 (C-O-C). ¹H NMR (400 MHz, DMSO-*d*₆): δ 2.18 (m, 2H, CH), 2.57 (m, 2H, CH), 6.33 (m, 2H, CH) 6.74 (s, 1H, CH), 6.87-8.68 (m, 32H, Ar-H), 12.42 (s, 1H, N-H, imidazole ring). Anal. Calcd. for (C₆₆H₄₂N₄O₇)_n (1002 g/mol): C, 79.04%; H, 4.19%; N, 5.59%. Found: C, 78.98%; H, 4.26%; N, 5.57%.

4.6.6. *PIb3*: Yield = 85%, and η_{inh} (dL/g)= 0.42. FT-IR (KBr) at cm⁻¹: 3420 (N-H imidazole ring); 3064 (aromatic C-H); 2919 (aliphatic C-H); 1779 and 1714 (C=O imide); 1611 (C=N); 1505 (C=C); 1381 (C-N); 1244 (C-O-C). ¹H NMR (400 MHz, DMSO-*d*₆,): δ 2.20 (m, 2H, CH), 2.65 (m, 2H, CH), 6.35(m, 2H, CH) 6.76 (s, 1H, CH), 6.91-8.72 (m, 30H, Ar-H), 12.43 (s, 1H, N-H, imidazole ring). Anal. Calcd. for (C₆₈H₄₀F₆N₄O₇)_n (1138 g/mol): C, 71.70%; H, 3.51%; N, 4.92%. Found: C, 71.61%; H, 3.61%; N, 4.91%.

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References

- [1] P.E. Cassidy, Thermally stable polymers. Marcel Dekker, New York, 1980.
- [2] D. Wilson, H.D. Stenzenberger, P.M. Hergenrother, Polyimides. Chapman and Hall, New York, 1990.
- [3] M.K. Ghosh, K.L. Mittal, Polyimides fundamentals and applications. Marcel Decker, New York, 1996.
- [4] M. Ree, Macromol. Res. 14 (2006) 1-33.
- [5] Y.J. Cho, H.B. Park, Macromol. Rapid. Comm. 32 (2011) 579-586.
- [6] D. X. Yin, Y.F. Li, H.X. Yang, S.Y. Yang, Polymer 46 (2005) 3119-3127.
- [7] G. Maier, Prog. Polym. Sci. 26 (2001) 3-65.
- [8] S.H. Hsiao, T.L. Huang, J. Polym. Res. 11 (2004) 9-21.
- [9] S. Zhang, Y. Li, D. Yin, Eur. Polym. J. 41 (2005) 1097-1107.
- [10] A.H. Frazer, High temperature resistant polymers. New York: Wiley Inter Science, 1968.
- [11] A.T. Vaganova, I.K. Shundrina, S.Z. Kusov, E.V. Karpova, I.Y. Bagryanskaya, E.V. Malykhin, J. Fluorine Chem. 135 (2012) 129-136.

- [12] S.Z. Zhu, J.W. Zhao, Y.X. Zhang, J. Fluorine Chem. 123 (2003) 221-225.
- [13] Q. Jin, T. Yamashita, K. Horie, R. Yokota, I. Mita, J. Polym. Sci. Part A: Polym. Chem. 31 (1993) 2345-2351.
- [14] I.K. Shundrina, T.A. Vaganova, S.Z. Kusov, V.I. Rodionov, E.V. Karpova, E.V. Malykhin, J. Fluorine Chem. 132 (2011) 207-215.
- [15] M. Yamada, M. Kusama, T. Matsumoto, T. Kurosaki, Macromolecules 26 (1993) 4961-4963.
- [16] S. Chen, Y. Yin, H. Kita, K.I. Okamoto, J. Polym. Sci. Part A: Polym. Chem. 45 (2007) 2797-2811.
- [17] Y. Tsuda, M. Kojima, T. Matsuda, J.M. Oh, Polym. J. 40, (2008) 354-366.
- [18] D. Yin, Y. Li, Y. Shao, X. Zhao, S. Yang, L. Fan, J. Fluorine Chem. 126 (2005) 819-823.
- [19] J. G. Liu, Y. Nakamura, Y. Shibasaki, S. Ando, Polym. J. 39 (2007) 543-550.
- [20] Y. Shao, Y. Li, X. Zhao, T. Ma, C. Gong, F. Yang, Eur. Polym. J. 43 (2007) 4389-4397.
- [21] I.K. Shundrina, T.A. Vaganova, S.Z. Kusov, V.I. Rodionov, E.V. Karpova, V.V. Koval, Y.V. Gerasimova, E.V. Malykhin, J. Fluorine Chem. 130 (2009) 733-741.
- [22] M. Ghaemy, R. Alizadeh, Eur. Polym. J. 45 (2009) 1681-1688.
- [23] Y.C. Kung, G.S. Liou, S.H. Hsiao, J. Polym. Sci., Part A: Polym. Chem. 47 (2009) 1740-1755.
- [24] Q. Zhang, S. Li, W. Li, S. Zhang, Polymer 48 (2007) 6246-6253.
- [25] M. Taghavi, M. Ghaemy, M. Hassanzadeh, S. M. Amini Nasab, Chinese. J. Polym. Sci. 31 (2013) 679-690.

- [26] D.D. Guo, J.W. Jiang, Y.J. Liu, X.L. Liu, S.R. Sheng, J. Fluorine. Chem. 175 (2015) 169-175.
- [27] S.H. Hsiao, J.Y. Lin, J. Fluorine Chem. 178 (2015) 115-130.
- [28] A.I. Wozniak, A.S. Yegorov, V.S. Ivanov, S.M. Igumnov, K.V. Tcarkova, J. Fluorine Chem. 180 (2015) 45-54.
- [29] X. Wanga, F. Liu, J. Lai, Z. Fu, X. You, J. Fluorine Chem. 164 (2014) 27-37.
- [30] F. Yang, Y. Li, T. Ma, Q. Bu, S. Zhang, J. Fluorine Chem. 131 (2010) 767-775.
- [31] T.A. Vaganova, I.K. Shundrina, S.Z. Kusov, V.I. Rodionov, E.V. Malykhin, J. Fluorine Chem. 149 (2013) 57-64.
- [32] M. Ghaemy, S. Sharifi, S.M. Amini Nasab, M. Taghavi, J. Macromol. Sci., Pure Appl. Chem. 50 (2013) 487-497.
- [33] M. Ghaemy, M. Hassanzadeh, M. Taghavi, S.M. Amini Nasab, J. Fluorine Chem. 142 (2012) 29-40.
- [34] T. Ma, S. Zhang, Y. Li, F. Yang, C. Gong, J. Zhao, J. Fluorine Chem. 131 (2010) 724-730.
- [35] M. Ghaemy, M. Bazzar, J. Appl. Polym. Sci. 116 (2010) 64-71
- [36] S.H. Hsiao, G.S. Liou, Y.C. Kung, H.Y. Pan, C.H. Kuo, Eur. Polym. J. 45 (2009) 2234-2248
- [37] X.L.Wang, Y.F. Li, C.L. Gong, T. Ma, F.C. Yang, J. Fluorine Chem. 129 (2008) 56-63.
- [38] C.Y. Wang, G. Li, J.M. Jiang, Polymer 50 (2009) 1709-1716.
- [39] M. Ghaemy, R. Alizadeh, Eur. Polym. J. 45 (2009) 1681-1688.
- [40] M. Ghaemy, R. Alizadeh, H. Behmadi, Eur. Polym. J. 45 (2009) 3108-3115.

- [41] M. Taghavi, M. Ghaemy, M. Hassanzadeh, High. Perform. Polym. 24 (2012) 305-318.
- [42] W. Li, S. Li, Q. Zgang, S. Zhang, Macromolecules 40 (2007) 8205-8211.
- [43] M. Ghaemy, R. Alizadeh, F.H. Nasr, J. Akbari, High. Perform. Polym. (2012) 262-273.
- [44] S.M. Amini Nasab, M. Ghaemy, J. Polym.Res. 18 (2011) 1575-1586.
- [45] M. Ghaemy, F. Rahimi Berenjestanaki, M. Bazzar, Des. Monomers Polym. 17 (2014) 101-110
- [46] M. Ghaemy, S.M. Amini Nasab, Polym. J. 42 (2010) 648-656.
- [47] E.B. Anderson, T.E. Long, Polymer. 51 (2010) 2447-2454.
- [48] M. Ghaemy, B. Aghakhani, M. Taghavi, S.M. Amini Nasab, M. Mohseni, React. Funct. Polym. 73 (2013) 555-563.
- [49] A. Masoumi, M. Ghaemy, eXPRESS Polym. Lett. 8 (2014) 187-196.
- [50] M.V. Dinu, E.S. Dragan, React. Funct. Polym. 68 (2008) 1346-1354.
- [51] A.S. Ozcan, O. Gok, A. Ozcan, J. Hazard. Mater. 161 (2009) 499-509.
- [52] S.M. Amini Nasab, R. Alizadeh, M. Ghaemy, Polym. Sci. Ser. B, 54 (2012) 30-40.
- [53] G.S. Liou, C.W. Chang, Macromolecules 41 (2008) 1667-1674.
- [54] D.W. Van Krevelen, P.J. Hoftyzer, Properties of polymers. 4th ed. Amsterdam: Elsevier Scientific Publishing, 2008.



Fig. 1. FT-IR spectra of the DNb, DAb and PIb2.



Fig. 2. ¹H NMR spectrum of diamine (**DAb**) in DMSO-*d*₆.



Fig. 3. ¹H NMR spectrum of **PIa2** in DMSO- d_6 .



Fig. 4. UV-vis and Fluorescence spectra of PIs.



Fig. 5. DSC (A) and TGA (B) curves of PIs under N_2 at a heating rate of 10 $^{\rm o}C/min.$



Fig. 6. Minimum inhibitory concentration of diamines and PIs against some bacteria.



Scheme 1. Synthesis of target diamines.



Scheme 2. Polycondensation reactions of the diamines with different dianhydrides.

	Solvent											
Code	Yield (%)	$\begin{array}{l} \eta_{inh} \\ (dL/g)^a \end{array}$	DMAc	DMF	NMP	DMSO	Ру	THF	CH ₂ Cl ₂	CH ₃ CN	m-cresol	Water uptake ^b (%)
PIa1	90	0.46	++	++	++	++	-	-	-	-	-	2.53
PIb1	92	0.52	++	++	++	++	±	±	-	-	±	2.05
PIa2	89	0.61	++	++	++	++	±	±	-	-	±	2.94
PIb2	92	0.66	++	++	++	++	+	±	±	±	+	2.46
PIa3	87	0.38	++	++	++	++	++	+	±	±	+	2.65
PIb3	85	0.42	++	++	++	++	++	+	+	+	++	2.11

Table 1.Solubility of synthesized PIs.

++, soluble at room temperature; +, soluble on heating at 60 °C; \pm , partially soluble on heating at 60 °C; -, insoluble on heating at 60 °C.

 $^{\rm a}$ Measured at a polymer concentration of 0.5 g/dL in NMP at 25 $^{\circ}\text{C}.$

^b The dried films were immersed in deionized water at 25 °C. After 24 h, the films were removed from water and then they were quickly placed between sheets of filter paper to remove the excess water and films were weighed immediately.

Polymer	$\lambda_{abs} (nm)^a$	$\lambda_{em}(nm)^a$	$\lambda_{abs} (nm)^b$	$\lambda_{em} \left(nm ight)^b$	$\Phi_f^{\mathfrak{c}}(0)$
DAa	302	427	-	-	31
DAb	299	422	-	-	27
PIa1	319	467	322	470	12
PIb1	317	464	318	467	10
PIa2	316	457	319	458	9
PIb2	314	453	316	456	7
PIa3	310	425	311	429	21
PIb3	308	422	310	423	19
PIa3 PIb3	310 308	425 422	311 310	429 423	21 19

Table 2.Optical properties data of PIs.

Polymer concentration of 0.20 g/dL in NMP.

^{a,b}UV-visible absorption and fluorescence emission data of the PIs in solution (a) and in films (b), respectively.

^c Fluorescence quantum yield relative to 10^{-5} M quinine sulfate in 1 N H₂SO₄ (aq) ($\Phi_f=0.55$) as a standard.

Polymer	$T_g (^oC)^a$	T ₁₀ (°C) ^b	Char yield ^c	LOI (%) ^d
PIa1	303	491	56	40
PIb1	296	498	62	42
PIa2	287	449	43	35
PIb2	273	472	52	38
PIa3	241	402	23	27
PIb3	235	420	31	30

Table 3. Thermal Properties of PIs.

^a Glass transition temperature was recorded at a heating rate of 10 $^{\circ}C/min$ under N₂.

^b Temperature at which 10% weight loss was recorded by TGA under N₂. ° C.Y.= Char yield, weight% of material left at 800 °C under N₂. ^d Limiting oxygen index percent evaluating at char yield 800 °C.

Strain —		Minimur	n inhibito	ry concentra	tion (µg.mL ⁻¹)
	DAa	DAb	PIa1	PIb1	Tetracycline
E. coli	150	100	100	50	25
P. aeruginosa	200	100	100	50	50
S. aureus	150	100	50	50	10
B. subtilis	200	150	100	50	25

Table 4. Minimum inhibitory concentration (MIC) of the compounds $(\mu g.mL^{-1})$ against some bacteria.

Table 5

The amount of metal ions adsorbed (Q_t) , removal percentage (R%) and remaining ions concentration (ppm) in polymers.

Metal ions	Q _t (mg/g)	Removal percentage (R%)	Re. ion conc.(ppm)	Q _t (mg/g)	Removal percentage (R%)	Re. ion conc.(ppm)
	PIa2			PIb2		
Hg^{2+}	37.90	75.80	2.42	35.20	70.40	2.96
Cr^{3+}	32.65	65.30	3.47	29.95	59.90	4.01
Cd^{2+}	28.60	57.20	4.28	26.75	53.50	4.65
Co^{2+}	21.15	42.30	5.77	19.90	39.80	6.02
Pb ²⁺	19.80	39.60	6.04	17.75	35.50	6.45