



Synthesis and properties of organosoluble polyimides based on novel perfluorinated monomer hexafluoro-2,4-toluenediamine

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ABSTRACT

New highly fluorinated aromatic polyimides based on hexafluoro-2,4-toluenediamine and commercially available dianhydrides (6FDA and ODPa) were synthesized by one-pot high temperature polycondensation in benzoic acid melt. Owing to the CF_3 group and fluorine atoms in the meta-linked phenylenediamine fragment, these polyimides combine good solubility in organic solvents including such a low boiling point solvent as chloroform with high glass transition temperatures (330–345 °C), thermal and thermooxidative stability (T_5 is >500 °C). The highly fluorinated polyimide films (hydrogen content is $\leq 1\%$) exhibit good dielectric properties and low water absorption as well as excellent optical transparency in the UV–vis region (cut-off wavelength is 311 nm for 6FDA-based and 357 nm for ODPa-based polyimides), which is very important for optoelectronic materials.

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1. Introduction

The design of highly fluorinated aromatic polyimides (PIs) for optoelectronic applications aims at giving a complex of properties to polymeric materials, first of all, good optical and dielectric characteristics, hydrophobicity [1–3]. The replacement of hydrogen atoms in the PI structure by fluorines is of principal importance for high transparency and low optical transmission losses in the UV–vis and near-IR regions. These properties provide the application of fluorinated PIs as waveguides in optoelectronic integrated circuits, transmission medium for the most widely used lasers, multichip interconnections, and orientation films in liquid crystal display devices. Low water absorption of fluorinated PIs stabilizes the optical losses and improves the dielectric performance of materials at the wavelengths of optical communications. Good dielectric characteristics also hold promise for the use in high-speed microelectronic packaging devices. Along with these key features, PIs should have good thermal properties and solubility in relatively low boiling point organic solvents. High glass transition temperatures T_g , low thermal expansion coefficient, and high polymer decomposition temperatures T_d are needed both for manufacturing these devices (which includes short-term processes at temperatures of up to 300–400 °C) and maintaining their steady operation. The solubility of PIs in the fully

imidized form provides the necessary processability. As a rule, the listed properties are hardly compatible in the same material.

In most cases the incorporation of fluorine into PIs is carried out by the insertion of pendant CF_3 groups or hexafluoroisopropylidene linkages; this results in improvement of the essential properties, including the solubility in organic solvents [2–4]. The use of unsymmetrical CF_3 -containing diamines especially enhances processability of PIs [5]. An increase in the F/H ratio can be achieved by incorporation of bulky fluorinated pendant groups (oxaliphatic [6,7], aliphatic [7], and oxyaromatic [8]), as well as bridging perfluoroalkylene groups [9], which improve the solubility of PIs, but impairs the thermal properties. Contrastingly, replacement of hydrogen by fluorine in aromatic backbone does not affect the good thermal properties of aromatic PIs [1–4]. However, synthesis of highly fluorinated aromatic PIs is complicated by the marginal reactivity of polyfluorinated diamines, on the one hand, and the unavailability of commercial monomers, on the other. The known PIs containing the perfluoroaromatic fragments in the main chain were synthesized from tetrafluoro-*para*- [10] and *meta*-phenylenediamines [11], octafluorobenzidine [10], hexafluoro-2,6- and -2,7-naphthylenediamines [12], as well as 1,4-bis(3,4-dicarboxytrifluorophenoxy)tetrafluorobenzene dianhydride [11]. These PIs exhibit promising optical properties, low dielectric permittivity, good thermooxidative stability, but they are insufficiently soluble in organic solvents and poorly processable in fully imidized form. The insertion of CF_3 group into perfluoroaromatic fragments can enhance the PIs solubility.

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Recently we elaborated a convenient method of selective preparation and high purity isolation of polyfluorinated diamines, having various (het)aromatic frameworks and substituents, through direct amination of commercially available perfluoro (het)arenes with anhydrous ammonia [13,14]. This makes perfluoroaromatic diamines-monomers, including those containing CF_3 groups, accessible for designing new PIs. The aims of the present work are the synthesis and characterization of highly fluorinated aromatic PIs based on hexafluoro-2,4-toluenediamine (6FTDA), and 2,2-bis(3',4'-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) or 4,4'-oxydiphthalic dianhydride (ODPA). The combination of asymmetrically located CF_3 group with aromatic fluorine atoms in the *meta*-diamine structure is expected to provide an excellent balance of all PI properties. In this work special conditions needed for the polycondensation of perfluorinated diamines were found. The novel polyimides 6FTDA/6FDA (PI-1) and 6FTDA/ODPA (PI-2) were characterized by FTIR and ^{19}F NMR spectroscopy, inherent viscosity, and elemental analysis; also their thermal, dielectric, optical properties and solubility were studied.

2. Experimental

2.1. Materials

4,4'-Oxydiphthalic dianhydride (ODPA) was purified by double sublimation at 240–260 °C/5 Torr. 2,2-Bis(3',4'-dicarboxyphenyl)-hexafluoropropane dianhydride (6FDA) was dried in vacuum oven at 140 °C for 6 h. Tetrafluorophthalic anhydride (4FPA) was obtained by dehydration of tetrafluorophthalic acid prepared by analogy to the method [15]. Phthalic anhydride (PA) was purified by sublimation. N-methyl-2-pyrrolidinone (NMP) and N,N-dimethylacetamide (DMA) were purified by distillation over P_2O_5 under reduced pressure and stored over 3 Å molecular sieve; residual moisture <0.02%. Benzoic acid (BA) was purified by sublimation under reduced pressure.

Hexafluoro-2,4-toluenediamine (6FTDA, 2,5,6-trifluoro-4-trifluoromethyl-1,3-phenylenediamine) was prepared according to the data [13]. Octafluorotoluene (0.4 mol, 100 g) was placed into a steel autoclave and liquid NH_3 (300 mL) was added; then the autoclave was sealed. The reaction mixture was stirred, heated to 120 °C, and kept for 48 h. After completion of the reaction, the autoclave was cooled and gaseous NH_3 was slowly vented. The reaction mixture was extracted with CH_2Cl_2 (3 × 200 mL), the combined extract was dried over MgSO_4 , and the extractant was evaporated to give the crude product, which was purified by crystallization from pentane. Purity of 6FTDA 99%, mp 31.5–32.5 °C, spectral characteristics are given in [13].

2.2. Measurements

^{19}F NMR spectra were recorded on NMR spectrometer Bruker AV-300 (282.36 MHz) using C_6F_6 ($\delta = -163$ ppm from CCl_3F) as internal standard; ^1H and ^{13}C NMR spectra were recorded on NMR spectrometer Bruker DRX-500 (500.13 and 125.76 MHz, respectively) using peaks of pyridine- d_5 ($\delta = 7.19$ ppm for ^1H and 123.5 for ^{13}C from tetramethylsilane) as internal standard; δ are given in ppm, J are given in Hz. Solid PI samples for registration of NMR spectra were dissolved to concentration ~5% in NMP. Signals in the spectra of PIs were assigned by using the spectral data of the model compounds. To estimate \bar{M}_n , the signals of CF_3 group in the range from $\delta -50$ to -65 ppm were used; signal/noise ratio ≥ 40 , relative error ~4%. Fourier transform infrared (FTIR) spectra were recorded on Bruker Vector-22 instrument for KBr disks. Ultraviolet–visible (UV–vis) spectra and color intensity of the polymer films were measured on Varian spectrophotometer Cary 5000. Color mea-

surements were performed with an observational angle 10° and a Commission International de l'Éclairage (CIE)-D50 illuminant. A CIE LAB color difference equation was used. Precise molecular weights of ions were determined by high resolution mass spectrometry on Thermo Scientific DFS instrument, ionizing energy of 70 eV. Thermogravimetric (TGA) and differential scanning calorimetry (DSC) analyses were performed on NETZSCH STA 409 instrument. The T_g s of the PIs were determined using DSC at a heating rate of 20 °C/min under He flow. The short-term thermal stability of PIs was estimated from the 5% and 10% weight loss temperatures T_d5 and T_d10 using TGA with a heating rate of 10 °C/min in an inert (He) or oxidative (He:O₂ = 80:20) atmosphere. To avoid the influence of absorbed water and residual solvents, the samples were preheated to 350 °C and cooled down to room temperature; the second heating scans were recorded. Dielectric constants and dissipation factors were measured on thin films (~35 μm) by the parallel-plate capacitor method using Instek LCR 816 Meter instrument at 23 °C at the frequency 1 kHz. Samples were preconditioned at 23 °C and 50% relative humidity or dried at 150 °C under reduced pressure for 12 h. Elemental analyses were determined by a Eurovector model EA 3000 CHN analyzer. Fluorine content was determined by spectrophotometric analysis [16]. The values of inherent viscosity (η_{inh}) were determined by an Ubbelohde viscosimeter at concentration 0.5 g dL⁻¹ in NMP at 25 °C.

Solubility was determined qualitatively as follows: 50 mg of PI was mixed with 0.5 mL of solvent and the mixture was mechanically stirred at room temperature or upon heating. Water uptake was determined by immersing the polyimide film (3 cm × 1 cm) in water at 25 °C for 24 h, which was then dried immediately by blotting with a paper towel and weighed.

2.3. Synthesis of model imide compounds (Scheme 1)

2.3.1. Mono- and diimide derivatives of 6FTDA

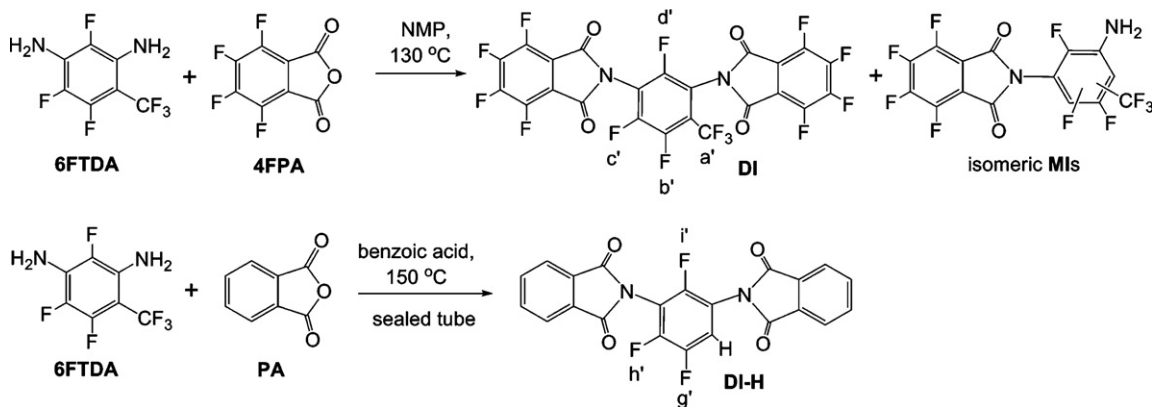
Hexafluoro-2,4-toluenediamine (1.3 mmol, 0.3 g) and tetrafluorophthalic anhydride (2.6 mmol, 0.57 g) were placed into a round-bottom flask and NMP (10 mL) was added upon stirring under an argon atmosphere. The solution was stirred for 30 h at 130 °C, and then solvent was removed at heating under the reduced pressure (30 Torr). Mixture of isomeric monoimides and individual diimide were isolated from the residue thus obtained using fractional sublimation.

The mixture of N-(3'-amino-2',5',6'-trifluoro-4'-trifluoromethylphenyl)-3,4,5,6-tetrafluorophthalimide and N-(3'-amino-2',4',5'-trifluoro-6'-trifluoromethylphenyl)-3,4,5,6-tetrafluorophthalimide (isomeric MIs), 2:1; ^{19}F NMR (acetone- d_6): the first set of signals (integrated intensity 1) $\delta -55.7$ (d, 3F, CF_3), -140.7 , -142.7 , -152.5 (all m, all 1F, aromatic fluorines of toluene fragment), -136.3 (m, 2F, F-3, F-6), -143.5 (m, 2F, F-4, F-5); the second set of signals (integrated intensity 2) $\delta -56.3$ (d, 3F, CF_3), -138.3 , -144.3 , -158.5 (all m, all 1F, aromatic fluorines of toluene fragment), -136.7 (m, 2F, F-3, F-6), -143.7 (m, 2F, F-4, F-5); HRMS calcd 450.1941, $\text{C}_{15}\text{H}_4\text{F}_{10}\text{N}_2\text{O}_3$, found 450.1937.

1,3-Bis(3',4',5',6'-tetrafluorophthalimido)-2,4,5-trifluoro-6-trifluoromethylbenzene (DI), mp 314–315 °C; IR (KBr): ν 1802 (C=O asym. stretching); 1747 (C=O sym. stretching); 724 (C=O bending) cm^{-1} ; ^{19}F NMR (acetone- d_6), letter symbols of fluorines are given in Scheme 1 and Fig. 1a: $\delta -56.9$ (d, 3F, $J = 22$, $\text{CF}_3(\text{a}')$), -119.0 (d, 1F, $J = 12$, F-2(d'')), -127.0 (d, 1F, $J = 22$, F-4(c'')), -135.7 (m, 1F, F-5(b'')), -135.2 , -136.0 (both m, both 2F, F-3', F-6'), -142.4 , -142.6 (both m, both 2F, F-4', F-5'); HRMS calcd 633.9629, $\text{C}_{23}\text{O}_4\text{N}_2\text{F}_{14}$, found 633.9336.

2.3.2. 1,3-Bis-phthalimido-2,4,5-trifluorobenzene (DI-H)

The mixture of hexafluoro-2,4-toluenediamine (1.3 mmol, 0.3 g), phthalic anhydride (2.6 mmol, 0.39 g), and benzoic acid



Scheme 1. Synthesis of model mono- and diimides.

(2 g) was heated at 150 °C in a sealed tube for 20 h. Benzoic acid was removed by sublimation and the crude product thus obtained was recrystallized from chloroform, yield 70%. Mp 292–293 °C; IR(KBr): ν 3103, 3074 (aromatic C–H stretching); 1789 (C=O asym. stretching); 1732 (C=O sym. stretching); 881 (C–H absorption in polyfluoroaromatic ring); 796, 768 (aromatic C–H absorption), 717 (C=O bending) cm^{-1} ; ^1H NMR (pyridine- d_5): δ 7.66, 7.69, 7.90, 7.93 (all m, 8H, 2H4', 2H5', 2H6', 2H7'), 7.99 (ddd, 1H, $J_{\text{HF}} = 10, J_{\text{HF}} = 8, J_{\text{HF}} = 7$, H6); ^{13}C NMR (pyridine- d_5): δ 167.5, 166.7 (C1', C3'), 152.4 (d, $^1J_{\text{CF}} = 257$, C2), 148.5, 147.9 (both dd [$^1J_{\text{CF}} = 258, ^2J_{\text{CF}} = 15$], [$^1J_{\text{CF}} = 247, ^2J_{\text{CF}} = 12$] C4, C5), 137.6, 137.1 (C4', C7'), 133.3, 133.1 (C8', C9'), 126.3, 125.9 (C5', C6'), 121.6 (d, $^2J_{\text{CF}} = 21$, C6), 118.2, 113.0 (both dd [$^2J_{\text{CF}} = 14, J_{\text{CF}} = 10$], [$^2J_{\text{CF}} = 17, J_{\text{CF}} = 14$], C1, C3); ^{19}F NMR (pyridine- d_5), letter symbols of fluorines are given in Scheme 1 and Fig. 1e: δ –123.2 (dd, 1F, $J_{\text{FF}} = 13, J_{\text{FH}} = 7$, F-2(i')), –136.0 (dd, 1F, $J_{\text{FF}} = 23, J_{\text{FH}} = 8$, F-4(h')), –138.9 (ddd, 1F, $J_{\text{FF}} = 13, 23, J_{\text{FH}} = 10$, F-5(g')); EIMS, 70 eV, m/z (rel. int.): 422 [M]⁺ (100), 378 [M–CO₂]⁺ (66), 334 [M–2CO₂]⁺ (10), 104 [C₆H₄CO]⁺ (35), 76 [C₆H₄]⁺ (51); HRMS calcd 422.0509, C₂₂H₉O₄F₃N₂, found 422.0508.

2.4. One-pot synthesis of polyimides and co-polyimides in benzoic acid melt (Scheme 2)

Variant A. A 100 mL round-bottomed flask equipped with a magnetic stirrer bar was charged with 5 mmol (1.15 g) of the diamine (6FTDA), equimolar amount of dianhydride (2.22 g of 6FDA or 1.55 g of ODPDA), and BA (20 g) under argon current. The flask was tightly closed; the mixture was kept upon stirring at 135 °C for 3 h. Then the reactor was equipped with an argon gas inlet tube and a short condenser with a calcium chloride outlet tube; reaction was kept on at stepped heating under an argon atmosphere: for 6 h at 150 °C and for 20 h at 190 °C. On completion of the reaction BA was extracted with EtOH (3 × 20 mL), polymer residue was washed with hot EtOH (20 mL). The polymer was dissolved in DMA and the solution obtained (10 wt%) was poured upon stirring into ethanol (10-fold excess) to form a precipitate. The precipitate was washed with ethanol and dried *in vacuo* at 150 °C for 6 h.

(6FTDA + 3FPDA)/6FDA co-polyimide (co-PI-1), portions of diamine fragments 85/15. IR spectrum is indistinguishable from those of the PI-1 (see below); ^{19}F NMR (NMP + acetone- d_6), letter symbols of fluorines are given in Fig. 1d, ratios of integrated intensities are given in Table 1: δ –54.8, –55.5 (CF₃-f), –57.0 (CF₃-a), –118.8 (F-d), –123.3 (F-i), –127.4 (F-c), –135.0 (F-h), –136.6 (F-b), –138.8 (F-g). Anal. calcd for (C_{25.5}H_{6.2}F_{11.3}N_{1.9}O₄)_n: C, 49.5; H, 0.99; F, 34.7; N, 4.30. Found: C, 48.4; H, 0.96; F, 33.5; N, 3.67.

(6FTDA + 3FPDA)/ODPA co-polyimide (co-PI-2), portions of diamine fragments 70/30. IR spectrum is indistinguishable from those of the PI-2 (see below); ^{19}F NMR (NMP + acetone- d_6), letter symbols of fluorines are similar to those of co-PI-1, ratios of integrated intensities are given in Table 1: δ –54.8, –55.4 (CF₃-f), –56.9 (CF₃-a), –120.3 (F-d), –124.2 (F-i), –128.9 (F-c), –135.99 (F-h), –136.8 (F-b), –139.5 (F-g). Anal. calcd for (C₂₂H_{6.3}F_{4.6}N_{1.8}O₅)_n: C, 57.0; H, 1.36; F, 18.9; N, 5.44. Found: C, 55.6; H, 2.05; F, 18.0; N, 5.04.

Variant A'. The reagents mentioned above were placed into a glass tube under an argon atmosphere, the tube was sealed and underwent a stepped heating for 50 h at 160 °C and for 20 h at 190 °C. On completion of the reaction polymer was isolated as described in the method A

(6FTDA + 3FPDA)/6FDA co-polyimide (co-PI-1'), portions of diamine fragments 40/60. IR spectrum is indistinguishable from those of the PI-1 (see below); ^{19}F NMR shifts are similar to those of co-PI-1, ratios of integrated intensities are given in Table 1. Anal. calcd for (C_{24.5}H_{6.5}F_{9.6}N_{1.7}O₄)_n: C, 51.4; H, 1.14; F, 31.9; N, 4.17. Found: C, 49.4; H, 1.02; F, 30.2; N, 4.33.

Variant B (with azeotropic removing of water). A 50 mL round-bottomed flask equipped with a magnetic stirrer bar, argon gas inlet tube and downtake condenser was charged with 5 mL toluene, 5 mmol (1.15 g) of the diamine (6FTDA), equimolar amounts of (2.22 g of 6FDA or 1.55 g of ODPDA) and BA (20 g). The reaction mixture was heated up to the boiling point of toluene and kept at this temperature until toluene was distilled off (~2 h). Then the reactor was equipped with a short air condenser with a calcium chloride outlet tube; reaction was kept on at stepped heating under an argon atmosphere for 4 h at 150 °C and for 10–20 h at 190 °C. On completion of the reaction polymers were isolated and purified as described in the method A.

6FTDA/6FDA polyimide (PI-1). IR (KBr): ν 3132, 3086 (aromatic C–H stretching); 1802 (C=O asym. stretching); 1749 (C=O sym. stretching); 782, 766 (aromatic C–H absorption); 720 (C=O bending) cm^{-1} ; ^{19}F NMR (NMP + acetone- d_6), letter symbols of fluorines are given in Fig. 1c, ratios of integrated intensities are given in Table 1: δ –54.8, –55.5 (CF₃-f), –57.0 (CF₃-a), –118.8 (F-d), –127.4 (F-c), –136.6 (F-b). Anal. calcd for (C₂₆H₆F₁₂N₂O₄)_n: C, 48.9; H, 0.94; F, 35.7; N, 4.39. Found: C, 49.8; H, 0.98; F, 35.6; N, 4.32.

6FTDA/ODPA polyimide (PI-2). IR(KBr): ν 3105, 3046 (aromatic C–H stretching); 1796 (C=O asym. stretching); 1742 (C=O sym. stretching); 773, 740, 700 (aromatic C–H absorption); 712 (C=O bending) cm^{-1} ; ^{19}F NMR (NMP + acetone- d_6), letter symbols of fluorines are given in Fig. 1b, ratios of integrated intensities are given in Table 1: δ –54.8, –55.4 (CF₃-f), –56.9 (CF₃-a), –120.3 (F-d), –128.9 (F-c), –136.8 (F-b). Anal. calcd for (C₂₃H₆F₆N₂O₅)_n: C,

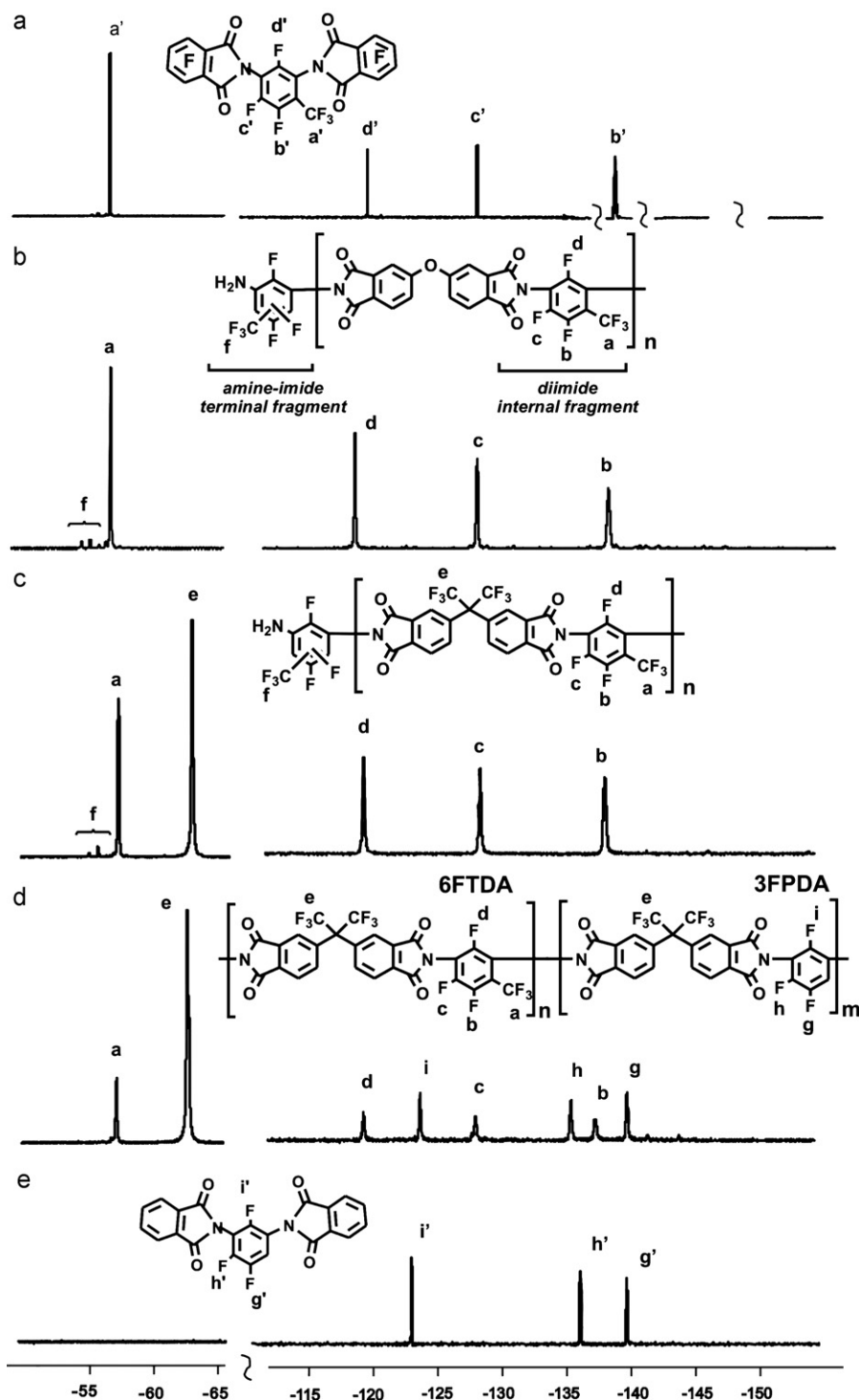


Fig. 1. ^{19}F NMR spectra of PIs and model compounds: (a) DI; (b) PI-2; (c) PI-1; (d) co-PI-1 and (e) DI-H.

54.8; H, 1.19; F, 22.6; N, 5.56. Found: C, 54.6; H, 1.22; F, 22.1; N, 5.52.

2.5. Preparation of PI films

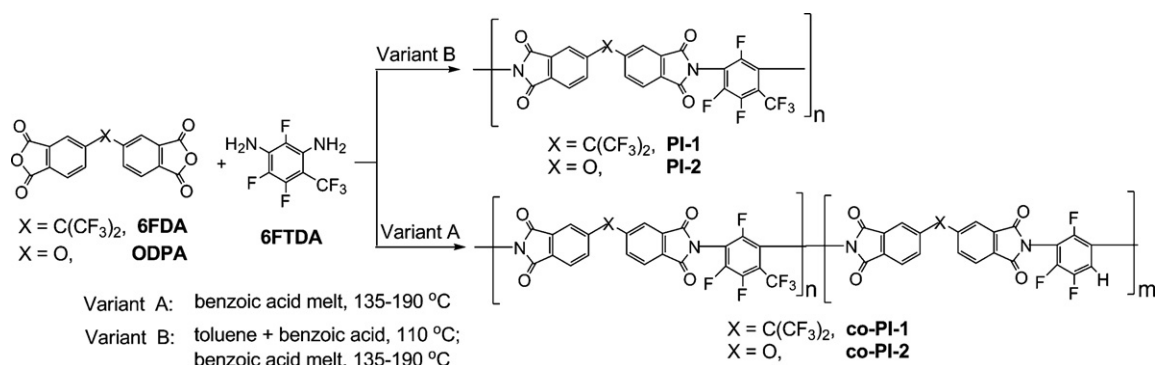
PI samples were dissolved in DMA at concentrations of 20–50 wt%. The solutions were filtered through a 0.5 μm Teflon membrane filter. The filtered solutions were spin-coated on glass wafer substrates. After coating, the substrates were placed on a hot plate and kept at 70 $^{\circ}\text{C}$ for 4 h to gently evaporate the solvent. The semidried films were placed into a vacuum oven and dried at

150 $^{\circ}\text{C}$ for 12–24 h up to constant weight. The thickness of the obtained films (10–100 μm) was controlled by adjusting concentration of the polymer solution.

3. Results and discussion

3.1. Synthesis of polyimides

Exhaustive fluorination of the benzene ring is known to decrease the reactivity of phenylenediamines for acylation by a factor of $\sim 10^{-5}$ [1] because of the total effect of high



Scheme 2. Synthesis of PIs.

electronegative fluorines. The resulting low nucleophilicity of polyfluoroaromatic diamines impedes their effective interaction with dianhydride and the formation of high-molecular weight poly(amic acid)s. To prepare PIs based on highly fluorinated diamines [10,12], the condensation in a solution at 80–130 °C with the formation of low-weight oligomers and subsequent high-temperature solid-state chain extension up to 250 °C were used. Under these conditions the formation of amic acid fragments is accompanied by their cyclodehydration and polymer chain growth proceeds via polyaddition of completely cyclized PI oligomers having amino and anhydride end groups. In the case of the least reactive monomers, the solid-state cure was carried out using a cyclic procedure [10] (2–3-fold redissolving of the already cured soluble material, redrying, and recurring). PIs with perfluoroaromatic fragments thus obtained had molecular weight less than 10,000.

We tested the possibility to use the cyclic chain extension procedure for synthesis of PIs based on 6FTDA. Control of the process was carried out by using ^{19}F NMR. This method is valuable in providing the needed information [17] on the extent and type of the occurring transformations, purity and structural regularity of the growing polymer, \bar{M}_n value, and presence of active end groups. Signals in ^{19}F NMR spectra of oligo- and polyimides were assigned using the spectral characteristics of specially synthesized model compounds (Scheme 1, Section 2.3).

It was found that 6FTDA interacts with 6FDA and ODPA rather slowly: condensation solutions prepared at 80 °C for 75 h contain the initial diamine (up to 15%) and 6FTDA derivatives comprising one modified amino group, i.e. isomeric monoamic acids and monoimides. No molecules containing two modified amino groups

practically form at the solution stage. In addition, water, which forms during cyclodehydration of amic acids, hydrolyses anhydride groups thus interrupting the acylation of amino groups. Carrying out the cyclic solid-state chain extension procedure (3 cycles) at the final curing temperature T_c 250–300 °C results in the formation of macromolecules having $\bar{M}_n \sim 10,000$ for 6FDA-based PI and ~ 3500 for ODPA-based PI. Increase in the number of cycles brings to a loss of solubility, which does not make it possible to use this method for obtaining polymers with higher molecular weights.

Method of one-step high-temperature polycondensation in high boiling point solvents (*o*-dichlorobenzene, *m*-cresol and chlorinated phenols) at 150–200 °C with using catalytic additives of organic and mineral acids is considered more practical for polymerization of low reactive monomers [18]. In the works [19–21] the melt of aromatic carboxylic acid–benzoic or salicylic was used as an effective catalytic medium for the one-step preparation of completely cyclized PIs. The rates of polymerization of low-reactive diamines in this medium are higher than in amide solvents [20]. Besides, melts of these acids are a non-toxic medium as compared with dichlorobenzene and chlorinated phenols and they can be easily separated from polymer on completion of the reaction. As to our knowledge, there are no examples of using this method to prepare polymers based on perfluoroaromatic diamines. In the present work reactivity of 6FTDA in these conditions was studied and special technique for synthesis of 6FTDA-based PIs in the benzoic acid (BA) melt was developed.

Two techniques of PI synthesis in the carboxylic acid melt were reported [19–21]: in open and closed vessels without removing water. Taking into account a relatively high volatility of 6FTDA, the initial stage of the polycondensation in BA melt (up to the complete

Table 1
Characteristics of 6FTDA-based polyimides and copolyimides.

Dianhydride	Polyimide	Yield (%)	Content of F (% elemental analysis)	Structural characteristics (^{19}F NMR ^a)				η_{inh} (dL g ⁻¹)	The residual anhydride groups bond in FTIR spectrum
				Ratio of diamine/dianhydride fragments ^b	Portions of 6FTDA/3FPDA internal fragments ^c	Ratio of internal/terminal PI units ^d	Number average molecular weight \bar{M}_n		
6FDA	co-PI-1	86	33.3	0.95	85/15			+	
	co-PI-1'	80	30.1	0.85	40/60		0.16	–	
	PI-1	85	35.5	1	100/–	29	19,000	–	
ODPA	co-PI-2	84	18		70/30		0.25	+	
	PI-2	87	22.1		100/–	28	14,500	–	

^a Signals of fluorines used for an evaluation are showed in Fig. 1.

^b $\Sigma(b, c, d, g, h, i)/e$

^c $\Sigma(b, c, d)/\Sigma(g, h, i)$

^d $a/\Sigma f$.

conversion of monomers into non-volatile oligomers) was performed in a closed reactor, then the reactor was equipped with a short condenser and the process was continued in an argon atmosphere with gradually rising temperature up to 190 °C (variant A, Scheme 2).

¹⁹F NMR characteristics of polymers obtained by the variant A testify to the presence in their structure of two types of polyfluoroaromatic fragments (Fig. 1d). The first type contains CF₃ group and has signals *a*, *b*, *c*, and *d*, which are similar to the signals of the model DI (Fig. 1a). Three additional signals of aromatic fluorine atoms (*g*, *h*, and *i*) belong to the second type of internal fragments, which have no CF₃ group. This follows from the smaller integrated intensity of the CF₃ group signal *a* in comparison with the total intensity of aromatic fluorine atom signals (*b*, *c*, *d*, *g*, *h*, *i*) (Table 1). Appearance of the modified fragments in the polymers can be caused by hydrolysis of CF₃ group and subsequent decarboxylation, occurring at a high temperature under the action of water onto monomer, oligomer or polymer. Examples of such a transformation of CF₃ group in polyfluoroaromatic compounds are known [22]. Realization of this process during the polycondensation results in the formation of co-polyimides containing two types of diimide fragments, derived from 6FTDA and 2,4,5-trifluorophenylenediamine (3FPDA) (Fig. 1d). Judging by the ¹⁹F NMR data, co-PI-1 contains 85% of internal 6FTDA fragments, and co-PI-2 – only 70% (Table 1).

A model reaction of 6FTDA with phthalic anhydride (PA) in BA melt at 150 °C, which was carried out in a sealed glass tube (Scheme 1, Section 2.3), confirms the possibility of CF₃ group hydrolysis and subsequent decarboxylation in these conditions. The ¹⁹F NMR spectral characteristics of DI-H (Fig. 1e) correspond to those of the modified co-PI fragments, derived from 3FPDA (Fig. 1d).

Accordingly, composition of co-PIs depends on the reaction conditions. The polymerization of 6FTDA and 6FDA carried out in a sealed tube (variant A') caused a considerable decrease in the portion of the internal 6FTDA fragments in co-PI-1' – down to 40%. The elemental analysis data agree with the assumed way of structural modification: the fluorine content in copolymers reduces in going from co-PI-1 to co-PI-1' (Table 1). Besides, the NMR data indicate a distortion in the stoichiometry of the diamine and dianhydride fragments in copolymers in favor of the latter. Apparently, at the first stage of polymerization a part of perfluorinated diamine decomposes under the action of water at the high temperature.

To prevent the undesirable destruction, polycondensation was carried out in the open reactor with the addition of toluene (variant B). Owing to this modification of the reaction conditions, the water, which formed intensively at the initial stage, was effectively removed by means of azeotropic distillation. After all toluene was distilled off, the process was kept on under the conditions similar to those provided for the variant A. The synthesis of 6FDA-based PI-1 was stopped after the reaction mixture split into two phases; and the synthesis of PI-2, based on the less reactive ODPA – after the growth of macromolecules stopped. The elemental analysis data and ¹⁹F NMR characteristics of PI-1 and PI-2 thus obtained (Table 1,

Fig. 1b and c, Section 2) testify to the homogeneous structure of the macromolecules. In particular, the fluorine content fits its calculated value, which confirms the retention of CF₃ group. Judging by these results, the variant B makes it possible to retain the stoichiometric ratio of monomers and to prepare PIs with relatively high molecular weight. As to co-PIs prepared by the variants A and A', in their ¹⁹F NMR spectra there are no signals of the terminal 6FTDA and 3FPDA fragments excepting low-intensity CF₃ group signal, and stoichiometry of the diamine and dianhydride fragments of macromolecules is distorted. For these reasons, the \bar{M}_n values of co-PIs cannot be evaluated using ¹⁹F NMR. Judging by the inherent viscosity values (η_{inh}) (Table 1), co-PIs have lower molecular weights than PIs 1 and 2.

Thus, the results obtained demonstrate the possibility of the 6FTDA-based PIs preparation by one-step high temperature polycondensation in BA melt. This method is practically feasible and effective mode of preparing PIs based on low reactive perfluorinated diamines.

3.2. Polyimide properties

The solubility of PIs was investigated qualitatively in different organic solvents at room temperature or upon heating. The results are reported in Table 2.

All PIs obtained at 190 °C are soluble in amide-type solvents, *m*-cresol, DMSO, and *c*-hexanone. Besides, they show the good solubility in such a low boiling point organic solvent as chloroform; this is a distinctive feature improving the processability of polymers. Films cast from solutions of PI-1 and PI-2 and cured at 350 °C for an hour do lose solubility. Only 6FDA-based PI-1 remains partially soluble due to the joint influence of the structural hexafluoroisopropylidene (6F) fragment. Co-PIs are less soluble because of the lower content of 6FTDA fragments in their structure.

The glass transition temperatures of the PIs were determined using differential scanning calorimetry. All PIs exhibit no crystallization or melting transition in DSC measurements. The T_g values of PIs and co-PIs (Table 3) depend on the structure of both dianhydride and diamine fragments. ODPA-based PI-2 has a lower T_g value than 6FDA-based PI-1 (328 vs. 346 °C) due to the presence of a flexible ether linkage in the PI backbone. The same T_g s ratio was reported for PIs prepared from these dianhydrides and various diamines [25–28].

Both PI-1 and PI-2 have higher T_g s than PIs prepared from unsubstituted *meta*-phenylenediamine (MPDA, Table 3) and from phenylenediamines containing long side polyfluorinated aliphatic or oxyaliphatic groups (the range of T_g s for 6FDA-based polyimides is 190–270 °C [6,7]). There are two structural factors, which distinguish 6FTDA from MPDA: aromatic fluorine atoms and CF₃ group. It was shown [10] that incorporation of either one or four fluorine atoms into *para*-linked phenylenediamine fragment does not change the T_g . If this is also true for *meta*-linked fragments, CF₃ group should be regarded as a factor responsible for the relatively high T_g s of 6FTDA-based PIs. Judging by the data [2], CH₃ and CF₃ groups have a similar effect upon the T_g of PIs, direction and size of which depend strongly on the isomerism of the phenylenediamine

Table 2
Solubility of polyimides^a.

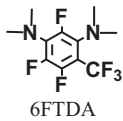
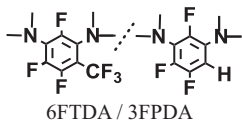
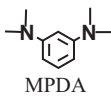
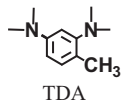
PI (dianhydride)	T_{max}^b (°C)	<i>m</i> -Cresol	NMP	DMAA	DMF	DMSO	<i>c</i> -Hexanone	Acetone	CHCl ₃	EtOH
PI-1 (6FDA)	190	+	+	+	+	+	+	+–h	+	–h
	350 ^c	+–h	+–h	+–h	+–h	–h	–h	–h	+–h	–h
PI-2 (ODPA)	190	+	+	+	+	+	+	+–h	+	–h
	350 ^c	–h	–h	–h	–h	–h	–h	–h	–h	–h

^a Qualitative solubility was determined visually as: completely soluble (+), partially soluble (+–), insoluble (–), heating (h).

^b The maximal curing temperature.

^c PI films.

Table 3
Glass transition temperatures ($^{\circ}\text{C}$) of polyfluorinated polyimides and their H-analogs.

Dianhydride	Diamine			
				
	6FTDA	6FTDA/3FPDA	MPDA	TDA
6FDA	346	332 (85/15) 327 (40/60)	285 [23]	342 [23]
ODPA	328	318 (70/30)	260 [24]	278 [24]

fragment. The replacement of MPDA fragment by 2,4-toluenediamine (TDA) fragment, which is a structural analog of 6FDA, increases T_g s of both 6FDA- and ODPA-based PIs by 57 and 18 $^{\circ}\text{C}$, respectively (Table 3). The same tendency, even more pronounced ($>60^{\circ}\text{C}$ for both PIs), occurs in going from MPDA-based PIs to 6FTDA-based PI-1 and PI-2. Accordingly, the co-PI samples, containing 3FPDA fragments along with 6FTDA fragments, have lower T_g values. The data of Table 3 show the decrease of T_g s with a diminution in the portion of the CF_3 containing fragments.

The considered tendencies confirm the presence of CF_3 group at position 4 of *meta*-linked phenylenediamine fragment to be an important factor increasing T_g of PIs. Thereby, 6FTDA is a prospective monomer for the synthesis of highly fluorinated PIs with high T_g s.

The short-term thermal stability of the PIs in inert and oxidative atmospheres was studied using thermogravimetric analysis. The decomposition temperatures are summarized in Table 4. The polymers obtained show a high thermal stability intrinsic to aromatic polyimides: there is no obvious weight loss before the scanning temperature reaches to 500 $^{\circ}\text{C}$. Temperatures of 5 and 10% weight losses of ODPA-based PI-2 exceed the same characteristics of 6FDA-based PI-1 by 20–30 $^{\circ}\text{C}$ both in inert and oxidative atmosphere. This tendency for T_d changes is known to realize for pair of ODPA/6FDA-based PIs prepared using various diamines [25,27–29]; it is caused by a lower thermal stability of the 6F linkage as compared with the oxygen linkage.

Incorporation of fluorine atoms and CF_3 group in phenylenediamine fragment influences the PIs thermal stability ambiguously [2]. According to the data [10] the complete replacement of hydrogen atoms by fluorines slightly increases the thermal stability of PIs, whereas incorporation of CF_3 group slightly decreases the thermal and thermooxidative characteristics. The presence of the both structural factors evidently compensates for these opposite tendencies. As a result, the thermal properties of 6FTDA-based PIs 1 and 2 are close to those of PIs containing non-fluorinated diamine fragments, and exceed the characteristics of PIs containing the long fluorinated side chain by 40–50 $^{\circ}\text{C}$ [2].

These observations can be of importance for the design of new PI materials.

Co-Pis 1, 1', and 2 have worse thermal and especially thermooxidative stability. It can be caused by the distortion of macromolecules stoichiometry resulting in excess of the lower thermostable anhydride end groups.

The dielectric constants, dissipation factors and water absorption of PI-1 and PI-2 were measured on thin films (35 μm). The films were preconditioned at 50% relative humidity (r.h.) or dried *in vacuo* (dry). The data obtained are presented in Table 5.

The PI films exhibit low water absorption, low relative permittivity as well as low differences between dielectric constants under dry and ambient conditions (humidity-induced change in the dielectric constant). All these characteristics improve as fluorine content increases in going from ODPA-based PI-2 to 6FDA-based PI-1. These facts agree with the known data that the fluorine-containing PIs have lower dielectric constants and higher hydrophobicity as compared with fluorine-free PIs [2].

The fluorine atoms and CF_3 group affect the PIs relative permittivity by several ways. The hydrophobic effect of fluorine atoms and the increase of the fractional free volume, which reduce the number of polarizable groups in a unit volume, decrease the dielectric constant [10,30]. Accordingly, the insertion of the bulky fluorine atoms and CF_3 group instead of the hydrogen atoms, as well as the 6F fragment instead of the oxygen linkage impedes a close packing of the polymer chains, thus decreasing the relative permittivity of PIs. In addition, the interchain electronic interaction and, as a result, the efficiency of the chain packing diminish due to the decrease in the donating effect of phenylenediamine fragment under the action of the strong electron withdrawing fluorine atoms and CF_3 group. The last way is changing polarizability [31]. Fluorines and CF_3 groups in the PI framework decrease the electronic polarizability due to their electronegative nature. The same effect can enlarge the dipole moment of the chain fragment, thus increasing the orientation polarizability at low frequencies. These factors act on the total polarizability in the opposite directions, but the contribution of the second factor depends on the

Table 4
Thermal degradation properties of 6FTDA-based polyimides and copolyimides.

Dianhydride	Polyimide	In inert atmosphere				In oxidative atmosphere		
		T_5^a ($^{\circ}\text{C}$)	T_{10}^a ($^{\circ}\text{C}$)	R_{700}^b (%)	R_{900}^b (%)	T_5^a ($^{\circ}\text{C}$)	T_{10}^a ($^{\circ}\text{C}$)	R_{600}^b (%)
6FDA	PI-1	528	554	55	42	515	526	17
	co-PI-1	523	550	55	44	506	522	15
	co-PI-1'	511	538	47	40	492	513	5
ODPA	PI-2	549	574	52	44	534	555	16
	co-PI-2	524	562	52	43	474	495	1

^a T_5 , T_{10} , temperature at 5% and 10% weight loss.

^b R_{600} , R_{700} , and R_{900} , residual weight retention at 600, 700, and 900 $^{\circ}\text{C}$.

Table 5
Dielectric properties and water absorption of PI-1 and PI-2 films.

Polyimide (dianhydride)	ϵ^a , 1 kHz		$\text{tg } \delta^b$, 1 kHz		Water absorption (%)	Fluorine content (%)
	Dry	r.h.	dry	r.h.		
PI-1 (6FDA)	2.68	2.92	0.0008	0.0013	0.35	35.5
PI-2 (ODPA)	2.87	3.27	0.0009	0.0016	0.54	22.1

^a ϵ , dielectric constant.

^b $\text{tg } \delta$, dissipation factor.

Table 6
Optical properties and color coordinates of PI-1 and PI-2 films.

Polyimide (dianhydride)	λ_0^a (nm)	Film thickness (μm)	Color coordinates ^b			Transmittance at 450 nm, films thickness 10 μm (%)
			b^*	a^*	L^*	
PI-1 (6FDA)	311	30	1.2	0.2	96.4	98
PI-2 (ODPA)	357	100	11.9	2.1	86.4	94
CF ₃ -containing PI ^c	358	60	11.3	-3.1	90.7	
Kapton	444	40	83.8	5.0	88.1	

^a λ_0 , the cut-off wavelength.

^b The color parameters were calculated according to a CIE LAB equation. L^* is lightness, 100 means white, and 0 means black. A positive a^* indicates red color, a negative a^* indicates green color. A positive b^* indicates yellow color, and a negative b^* indicates blue color.

^c 1,7-Bis(4-amino-2-trifluoromethylphenoxy)-naphthalene/6FDA polyimide, date on Ref. [26].

fragment symmetry. Due to the asymmetrical location of CF₃ group in *meta*-linked 6FTDA the orientation polarizability should increase [31], however, the presence of fluorine atoms in the aromatic ring compensates partially for the dipole of CF₃ group. Moreover, the contribution of the dipole orientation part into the total polarizability is low for polyimides with a high T_g [2]. As a result, fluorine-induced change of the polarizability and, consequently, of the relative permittivity of PIs 1 and 2 appear to be insignificant. This is confirmed by the low dissipation factors of the PIs at 1 kHz (Table 5). Thereby, owing to the first two ways, the 6FTDA fragment provides a reduction of the PI dielectric constants.

The optical properties of the PI films were investigated using UV–vis spectroscopy. The values of cut-off wavelength (λ_0), transmittance at 450 nm, and color intensity of the PI films are summarized in Table 6 and Fig. 2. For comparison, Table 6 presents the same characteristics of Kapton and of the known PI containing CF₃ groups in amine and anhydride fragments [26].

The PI films exhibit low λ_0 values, high transparency, and have color from pale fawny to colorless. The characteristics of the PIs, especially the cut-off wavelength, depend on the anhydride structure. The λ_0 value of 6FDA-based PI-1 is less than that of ODPA-based PI-2 by 45 nm.

The PI optical properties are considered to depend on the intra- and intermolecular charge-transfer complex (CTC) formation [32]. Accordingly, structural features of macromolecules, which reduce the CTC formation, improve the optical characteristics [1,26,28,33]. The 6F fragment and *meta*-linked diamine fragment disturb the conjugation within the PI chains, thereby preventing the intrachain CTC formation. The electron-withdrawing fluorine atoms and CF₃ group reduce the donating effect of diamine fragment to impede the interchain CTC formation. In addition, the interaction between PI chains is hindered by the bulky CF₃ groups. All these effects reduce the absorption at the UV–visible wavelengths and the λ_0 values. As a result, the obtained highly fluorinated PI films, especially 6FDA-based PI-1, exhibit the excellent optical transparency.

4. Conclusions

New highly fluorinated aromatic polyimides based on hexafluoro-2,4-toluenediamine (6FTDA) and 6FDA or ODPA were synthesized and their properties were investigated. It was found that presence of water in the reaction mixture causes partial destruction of CF₃ groups during the one-step high temperature polycondensation. It results in the formation of co-Pis containing trifluorophenylene fragments along with hexafluorotoluene fragments. To prevent the undesirable process and prepare 6FTDA-based PIs, special technique was developed for the one-step polycondensation in benzoic acid melt.

Owing to CF₃ group and fluorine atoms in the phenylenediamine fragment the PIs obtained have a good solubility in organic solvents including such a low boiling point solvent as chloroform, high glass transition temperatures, thermal and thermooxidative

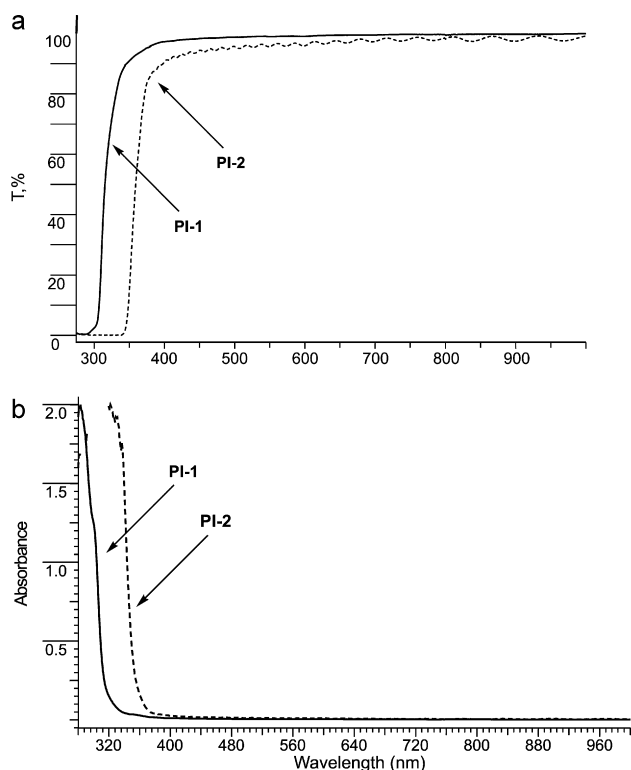


Fig. 2. UV–vis spectra of PI films: (a) transmittance and (b) absorbance.

stability. High fluorine content provides good dielectric properties and low water absorption of 6FTDA-based PI films. Their excellent optical transparency in the UV–vis region is achieved due to the presence of *meta*-linked diamine moiety containing bulky electron-withdrawing CF₃ group and fluorine atoms.

Thereby, highly fluorinated 6FTDA-based PIs have a complex of required properties. Owing to the low hydrogen content ($H \leq 1\%$) and the high hydrophobicity 6FTDA-based PIs are expected to reveal low optical transmission losses in the near-infrared region and to be promising materials for optical communications.

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