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Synthesis and characterization of the first perfluoroaromatic polyimide of the AB-type

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ABSTRACT

Aminodefluorination of tetrafluorophthalic acid by anhydrous ammonia was shown to give 4-amino-3,5,6-trifluorophthalic acid selectively and in a high yield. Under the action of dicyclohexylcarbodiimide this acid was quantitatively converted into 4-amino-3,5,6-trifluorophthalic anhydride, which is the simplest monomer of the AB-type. The first perfluoroaromatic AB-type polyimide was prepared by the one-step high-temperature polycondensation in a benzoic acid melt and characterized using FTIR, NMR, UV–vis, MALDI TOF MS, and TG/DSC methods. The near-IR spectrum of the polyimide exhibits no absorption of C–H and O–H bond harmonic vibrations, which testifies to considerable promise of AB-type perfluorinated polyimides for optical communication systems.

1. Introduction

Fluorinated aromatic polyimides (PIs) are used as optical materials for modern telecommunication systems due to the excellent transparency and low optical transmission losses, as well as good dielectric properties and hydrophobicity [1]. These properties improve as fluorine content increases [1,2]. However, possibilities of preparing completely fluorinated aromatic PIs are limited by the low availability of hydrogen-free monomers. Up to the present the only perfluorinated PI was synthesized via polymerization of 1,4-bis(3,4-dicarboxytrifluorophenoxy)tetrafluorobenzene dianhydride (AA-monomer) and tetrafluoro-*m*-phenylene diamine (BB-monomer) [3]. In addition, a series of promising highly fluorinated PIs was obtained using other perfluoroaromatic diamines [3–6]. No synthesis of fluorinated aromatic PIs from AB-monomers (the anhydride and amine groups are both contained in one molecule) was reported. At the same time, from a synthetic point of view, by using AB-monomers one can avoid the strict stoichiometric control, which is required in AA/BB polycondensation systems. The peculiarities of the structure of AB-type aromatic PIs (the arrangement of imide cycles, the combination of cyclic fragments and linkage groups) reduce the interchain interaction in macromolecules as compared with AA/BB-type PIs, thereby increasing the processability of PIs. Besides, on the basis of heterofunctional compounds of AB_x-type hyperbranched (dendritic) polymers can be obtained (see [7] and Refs. herein).

Combining the processing advantages of AB-based PIs with the called-for properties (optical, dielectric, thermal) of the known highly fluorinated PIs appears to be an advanced task. Thereupon, the present work aims at (i) the development of a convenient method for synthesis of the perfluorinated AB-type monomer – 4-amino-3,5,6-trifluorophthalic anhydride (**1**), (ii) investigation of its polymerization, and (iii) characterization of the primary perfluorinated polyimide of the AB-type (PI-AB).

2. Results and discussion

2.1. Synthesis of AB-monomer 1 (4-amino-3,5,6-trifluorophthalic anhydride)

Preparation of 4-amino-3,5,6-trifluorophthalic acid (**2**) mixed with isomeric 3-amino-4,5,6-trifluorophthalic acid (9:1) by the action of aqueous ammonia upon commercially available tetrafluorophthalic acid (**3**) in the presence of alkaline or alkaline earth metal salts at 150–170 °C was reported in the patent [8]. However, no method for isolation of the main product was suggested. Besides, in aqueous ammonia, at high temperatures (>100 °C), partially hydrodefluorinated compounds are known to be formed along with desired products [9]. These by-products are practically inseparable from perfluorinated compounds, but their presence in monomers impairs the optical characteristics of polymers [1,3]. In the previous works [10] we developed an effective and selective method for aminodefluorination of electrophilic polyfluoroarenes

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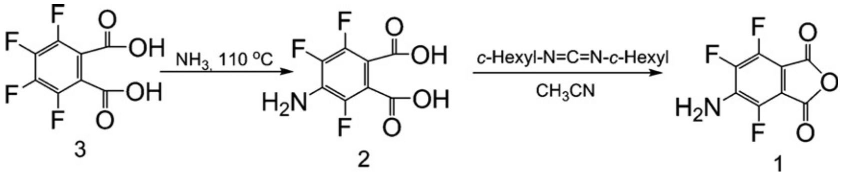


Scheme 1. Synthesis of aminotrifluorophthalic anhydride **1**.

in anhydrous ammonia applied as a reagent and a solvent simultaneously, which ensures the absence of hydrodefluorination products. In this manner acid **2** is selectively prepared (Scheme 1) in a high yield (95%) and purity (98%).

Acid **2** is a direct precursor of the AB-type monomer **1**. However, non-fluorinated compounds of this type undergo rapid oligomerization even under slight heating, which complicates their preparation and isolation. For this reason, the synthesis of AB-monomers should be carried out under the mildest conditions. We applied *N,N′*-dicyclohexylcarbodiimide (DCC) as a mild cyclodehydrating agent; this compound is widely used for the condensation of amino acids in peptide synthesis [11]. DCC interacts with acid **2** to form anhydride **1** in a high yield and without by-products (Scheme 1); after a single crystallization, it was used as a monomer.

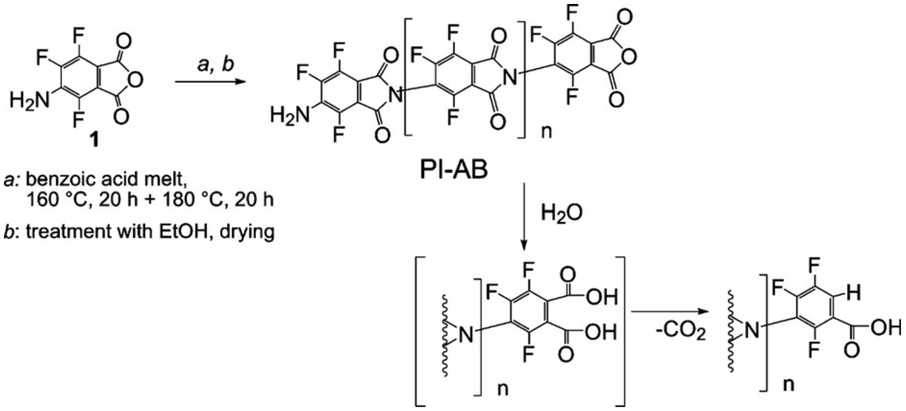
2.2. Synthesis and structural characterization of PI-AB

Synthesis of AB-type PIs from fluorine-free aminophthalic and aminophenoxyphthalic anhydride was realized in amide solvents or pyridine [12,13], including the use of condensing agents [14,15], and in solid phase [16]. Electrophilicity of fluorinated anhydrides increases as compared with non-fluorinated compounds owing to the high electronegative effect of fluorines in an aromatic ring. On the contrary, nucleophilicity of the amino group decreases greatly because of the same effect [1]. Thus, the reactivity of perfluorinated compound **1** is determined by a balance of these opposite factors. We tested the behavior of monomer **1** in amide solvents in the temperature range from 20 to 130 °C. Monitoring the process was carried out using ^{19}F NMR spectroscopy; this method provides an essential information on the chemical transformations taking place during polycondensation of fluorine containing monomers [1,4,6,17]. Under these conditions no reaction was found to occur between amine and anhydride fragments of compound **1**.

For this reason, to prepare the perfluorinated PI-AB method of one-pot high-temperature polycondensation in a benzoic acid melt [18] was chosen (Scheme 2). For less reactive diamines, this method possesses an advantage over the synthesis in high boiling point solvents owing to the acid catalysis of the condensation; and it was successfully applied for obtaining polyimides based on hexafluoro-2,4-toluenediamine [4].

AB-type monomer **1** was kept in a benzoic acid melt upon stirring for 20 h at 160 °C and, further, for 20 h at 180 °C, whereupon the reaction mixture split into two phases. During the process there appeared three new signals in the ^{19}F NMR spectrum (Fig. 1a, signals *a*, *b*, and *c*), whose intensity became predominant with time. According to the known substituent shielding parameters [17], these signals correspond to the fluorine atoms of the internal fragment of PI-AB. In the resulted spectrum along with the aforementioned signals *a*–*c* there is a set of signals of a substantially lower intensity (Fig. 1a, signals *d*–*i*), which can be ascribed to fluorines of the terminal amine and anhydride fragments of PI; there are also low-intensity signals of the uncertain origin (*j*, *k*, *m*).

To identify the structural fragments and end groups in the polymer and to determine the repeated unit weight, the obtained PI-AB was analyzed by the MALDI-TOF MS, which is used for such purposes [6,19]. The negative-ion MALDI spectrum of PI-AB contains repeated fragments (groups of signals) with the period *m/z* 199 Da equal to the weight of the polymer structural unit ($C_8F_3NO_2$). Fig. 2 shows a fragment of the spectrum in the range *n* from 4 to 8; Table 1 presents tentative peak mass assignments. Besides the peaks of PI-AB radical anions (Entry 3, Table 1), there are peaks of adducts of PI-AB radical anions with two molecules of NaOH (Entry 4, Table 1), as well as peaks of the anions of decarboxylated PI-AB molecules (Entry 1 and 2, Table 1). The latter particles can be formed during both the MS analysis and the polycondensation process. As a rule, preparation of the PI samples for analysis is carried out using water–organic solvents and is followed by the hydrolysis of some of the anhydride end groups [6,19]. The electron withdrawing effect of the aromatic fluorines is known to facilitate CO_2-elimination from *ortho*-dicarboxylic fragments [20], so even a moderate voltage drop can cause the destruction of the molecule (cf. [21]). On the other hand, during high-temperature one-step polycondensation a part of the anhydride end groups is hydrolyzed by the released water, which can be accompanied by their decarboxylation (e.g. see [22]). Taking



Scheme 2. Synthesis of the perfluorinated polyimide of AB-type.

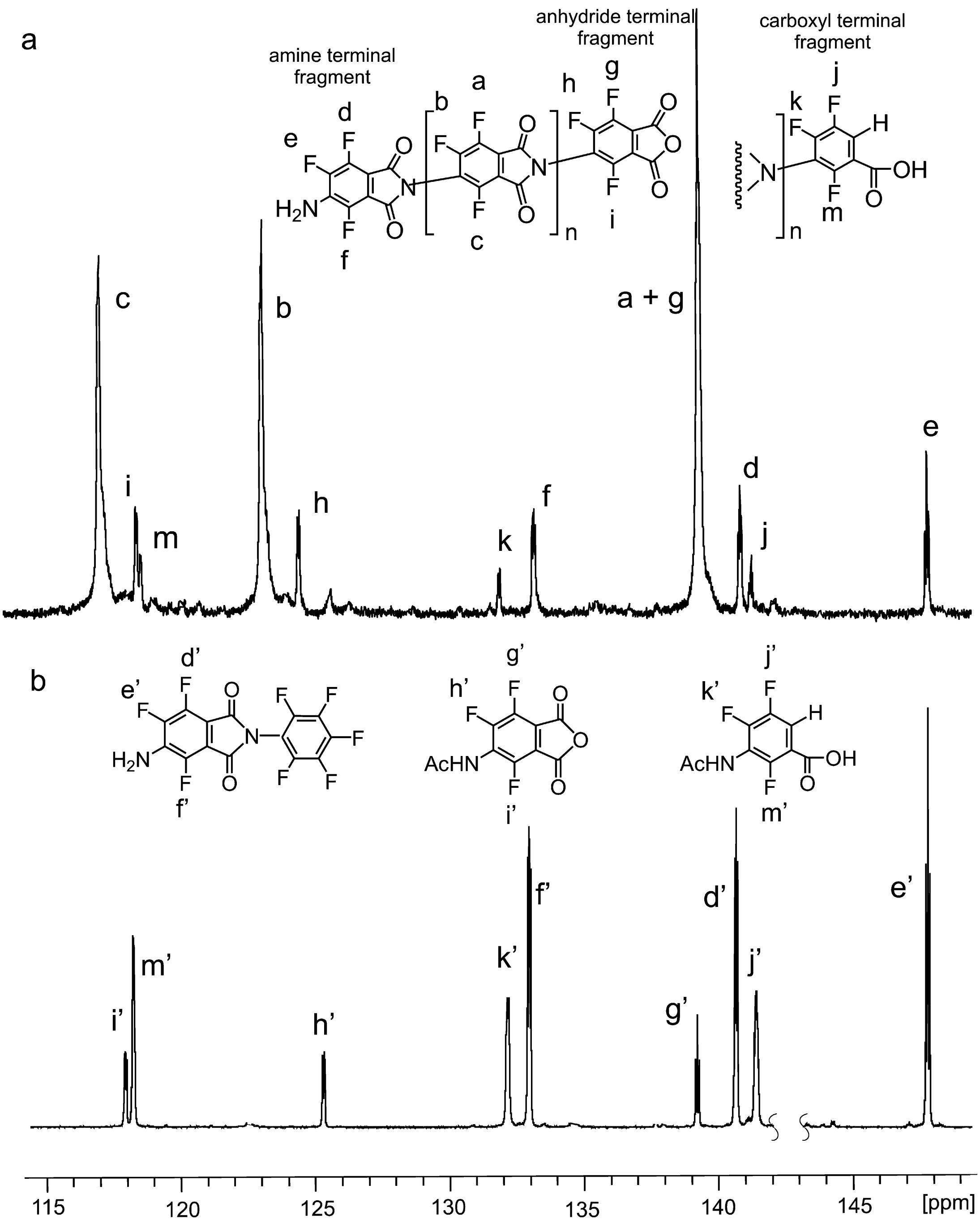
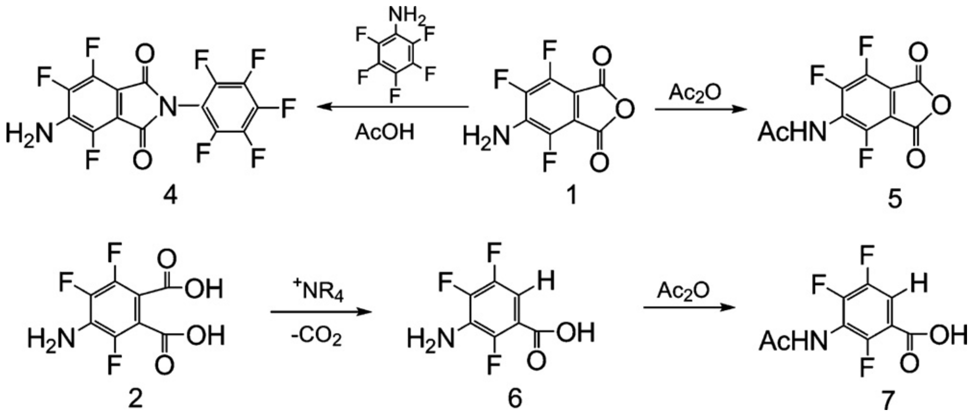


Fig. 1. ^{19}F NMR spectra of PI-AB (a) and model compounds (b).

into consideration the presence of three additional signals *j*, *k*, and *m* in the ^{19}F NMR spectrum of PI-AB (Fig. 1a), the latter variant appears to be more probable.

The reliable identification of the terminal fragments in PI-AB was carried out by ^{19}F NMR spectroscopy using data on the model compounds, i.e. *N*-pentafluorophenyl-4-amino-3,5,6-trifluorophthalimide (**4**), 4-acetamido-3,5,6-trifluorophthalic anhydride (**5**) and 3-acetamido-2,4,5-trifluorobenzoic acid (**7**). These compounds were synthesized for the first time (Scheme 3); comprehensive spectral data on them are given in Sections 4.3.3–4.3.6. The signals in ^{19}F NMR spectra of compounds **4**, **5**, and **7** are presented in Fig. 1b.

Differences in the chemical shifts of signals in the spectra of PI-AB and of model compounds (Fig. 1) amount to 0.1–1.5 ppm. The amine terminal fragment of PI has the signals *d*, *e*, and *f*; anhydride terminal fragment has the signals *h*, *i*, and signal *g*, which coincides with the signal *a* that belongs to the imide internal fragment. Apart from these the spectrum contains the signals of lower intensity – *j*, *k*, *m* – that apparently belong to the carboxyl terminal fragment. The ratio of anhydride/carboxyl terminal fragments in PI-AB molecules, evaluated by the ratio of the integrated intensities of the signals *h* and *k*, is ~4/1. The total intensity of the signals *g*–*m* approximates to the intensity of the signals *d*–*f* belonging to the amine terminal fragment. The averaged length of the polymer chain, evaluated by the number of the internal and terminal fragments, comes to ~9 structural units. This corresponds to the value of number-averaged molecular weight of PI-AB $\bar{M}_n \sim 1800$. The low value of the inherent viscosity of PI-AB ($\eta_{\mathrm{inh}} \sim 0.1$) conforms to this evaluation of the molecular weight. The results of the elemental analysis of PI-AB are satisfactory; this is in



Scheme 3. Synthesis of the model compounds.

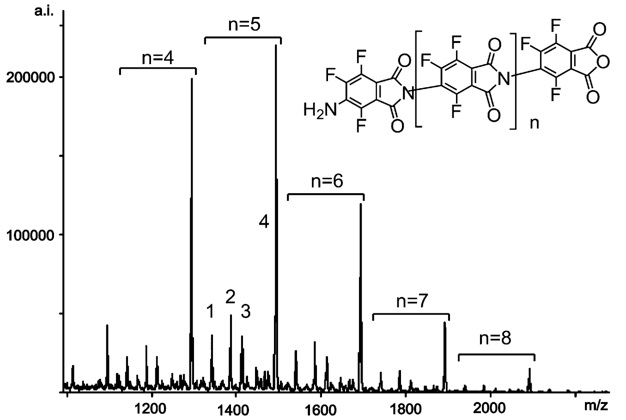


Fig. 2. MALDI-TOF mass spectrum of PI-AB, repeated fragments in the range *n* from 4 to 8; peak assignment is given in Table 1.

accordance with the above conclusion that the fragmentation of PI is insignificant.

The FTIR spectral data on PI-AB conform to the imide structure and show characteristic absorptions at 1747 and 1801 cm^{-1} (asymmetrical and symmetrical stretching of carbonyl group in the imide cycle). No absorptions of the anhydride and amino end groups have been recorded in the spectrum. Fig. 3 shows the FTIR spectra of PI-AB and the initial anhydride **1**.

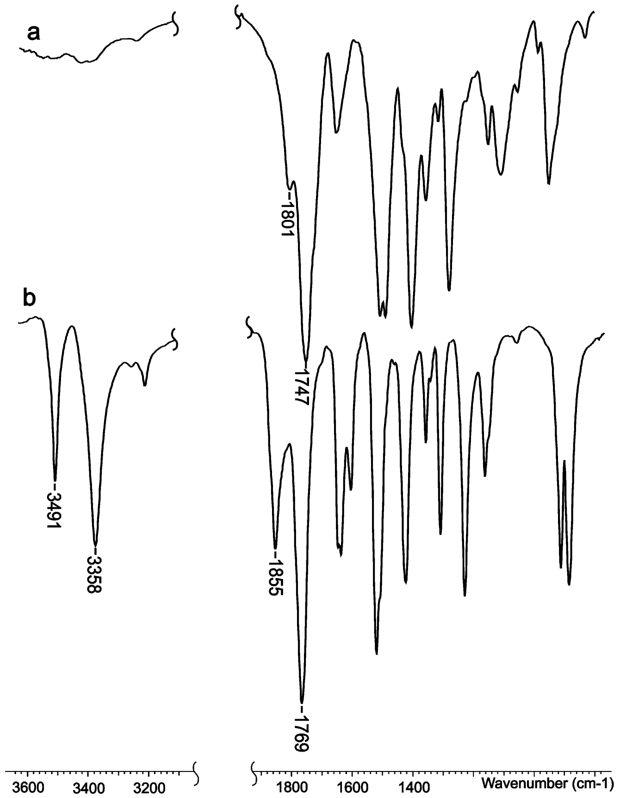


Fig. 3. FTIR spectra of PI-AB (a) and aminotrifluorophthalic anhydride **1** (b).

On account of a minor extent of the fragmentation of the anhydride end groups by CO_2-elimination (~20% according to the ^{19}F NMR data), this process is not the only reason retarding the growth of the PI chain. The polymerization degree is significantly affected by the chain and end group mobility along with the end group reactivity. In the case of the rigid perfluorinated PI-AB both of these factors are unfavorable for preparing a high-molecular polymer. Judging by the data [12,13,16], the simplest non-fluorinated AB-type PI obtained from aminophthalic anhydride also has a low molecular weight, whereas the use of aminophenoxyphthalic anhydrides as monomers enables to prepare PIs with higher molecular weights and better film-forming properties. This is caused by the effect of the oxygen linkage, which imparts more flexibility to the polymer chain and higher mobility to the end groups, as well as enlarges the amino group reactivity due to the electron donating effect of the oxygen atom. This way of the

Table 1
Mass assignments of the peaks displayed in the MALDI-TOF mass spectrum of PI-AB (see also Fig. 2).

Structure	Monoisotopic mass (Da)						
	n = 2	*n* = 3	*n* = 4	*n* = 5	*n* = 6	*n* = 7	*n* = 8
$[AB+H_2O-2CO_2-H]^-$		941.82	1140.76	1339.58			
$[AB+H_2O-CO_2-H]^-$		985.77	1184.71	1383.63	1582.51	1781.36	
$AB^{\bullet -}$		1012.72	1211.74	1410.59	1609.51	1808.32	
$[AB+2NaOH]^{\bullet -}$	893.86	1092.83	1291.77	1490.66	1689.52	1888.36	2087.28

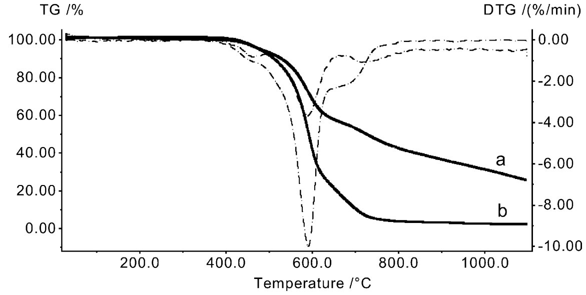


Fig. 4. TG and DTG diagrams of PI-AB, inert (a) and oxidative (b) atmosphere.

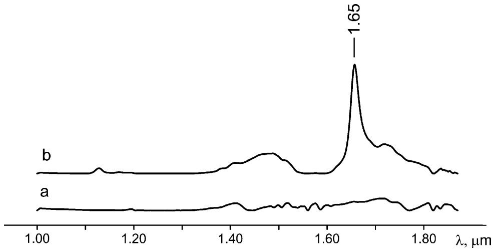


Fig. 5. Near-IR absorption spectra of PI-AB (a) and 6FTDA/ODPA (b) dissolved in acetone-d_6.

structural modification appears to be promising for the perfluorinated AB-type monomer as well.

2.3. Properties of the PI-AB

In spite of the low values of molecular weight and inherent viscosity (see Section 2.2) the perfluorinated PI-AB obtained has a satisfactory thermal and thermooxidative stability appropriate to high molecular weight PIs [2]. PI-AB exhibits no crystallization or melting transition in DSC measurements. Glass transition was not detected by DSC either, which is caused by the rigid structure of the PI chain; this is typical of rod-like PIs containing no flexible linkages. The short-term thermal stability of PI-AB was estimated from the temperatures of 10% weight loss (T_d10) using TGA (Fig. 4). T_d10 is 528 °C in an inert and 512 °C in an oxidative atmosphere. The residual weight retention at 700 °C amounts to 57% and 12% in inert and oxidative atmospheres, respectively. The maximal rate of degradation in both atmospheres was fixed at 592 °C.

The perfluoroaromatic PI-AB, in spite of the absence of flexible linkages and pendant groups, displays good solubility in acetone, cyclohexanone, DMSO, DMF, DMA, and NMP, which is provided by the presence of fluorines in the PI backbone. PI-AB film is transparent, glassy and yellow colored. When heated up to 300 °C, the film becomes yellowish brown and does lose solubility.

The key property providing the application of polyfluorinated PIs as materials for optical waveguides is their transparency at the wavelengths of 1.3 and 1.5 µm referred to as telecommunication windows [1]. Fig. 5a presents the near-IR absorption spectrum of PI-AB dissolved in acetone-d_6. For comparison, Fig. 5b shows the spectrum of PI, which is prepared from hexafluoro-2,4-toluenediamine and 4,4′-oxydiphthalic dianhydride (6FTDA/ODPA) [4] and contains 22.6% of F and only 1.19% of H. This PI exhibits rather an intensive absorption at 1.65 µm due to the second harmonic of the stretching vibration of the C–H bond in non-fluorinated aromatic rings. On the contrary, perfluorinated PI-AB has a transparency window throughout the investigated range (Fig. 5a). Within the UV–vis range the PI-AB films exhibit a cut-off wavelength λ_0 of 400 nm. The transmittance at 450 nm is equal to 73% for the film of the 40 µm in thicknesses. The λ_0 value of PI-AB is shifted to the long-wave area as compared with the λ_0 values of highly fluorinated CF_3-containing PIs, whose cut-off wavelengths lie between 340 and 360 nm [1]. This shift appears to be caused by the conjugation of chromophore groups in the PI-AB chain resulting in the formation of an intramolecular charge-transfer complex [23].

3. Conclusions

Convenient conditions were found for aminodefluorination of tetrafluorophthalic acid **3** (anhydrous ammonia, 110 °C), which provide a high efficiency and isomeric selectivity of the reaction. Owing to the use of a mild dehydrating agent (dicyclohexylcarbodiimide), 4-aminotrifluorophthalic acid **2** was quantitatively converted into 4-aminotrifluorophthalic anhydride **1**, which is the simplest monomer of the AB-type. The first perfluorinated PI-AB was prepared by the one-step high-temperature polycondensation in a benzoic acid melt. The growth of the macromolecules seems to be limited by low reactivity of the amino group, partial destruction of the anhydride end groups, and restricted mobility of the end groups in a rigid polymer chain. The PI-AB structure was characterized by FTIR, NMR, MALDI-TOF MS and elemental analysis. The properties of perfluorinated PI-AB were studied: absorbance and transmittance in the UV–vis and near-IR regions, solubility, and thermal stability. Note that this polymer exhibits no absorption of harmonic vibrations of C–H and O–H bonds in the near-IR region (1.0–1.7 µm), which defines AB-type perfluorinated PIs as promising materials for optical telecommunication systems.

4. Experimental

4.1. Materials

The following commercial products were used: pentafluoroaniline (99%), anhydrous NH_3, *N,N*′-dicyclohexylcarbodiimide (DCC, 99%), acetic anhydride (95%). Benzoic acid was purified by sublimation under reduced pressure. Tetrafluorophthalic acid (**3**) was prepared by analogy to the method [24].

4.2. Methods

^1H and ^{19}F NMR spectra were recorded on NMR spectrometer Bruker AV-300 (300.13 MHz and 282.36 MHz for ^1H and ^{19}F, respectively) using residual proton signals of the deuterated solvent and C_6F_6 ($\delta = -163$ ppm from CCl_3F) as internal standard; δ are given in ppm relative to TMS and CCl_3F, *J* are given in Hz. PI-AB samples for registration of NMR spectra were dissolved to concentration ~5% in DMA; signal/noise ratio ≥ 40, integration error ≤ 4%. FTIR spectra were recorded on Bruker Vector-22 instrument for KBr disks. UV–visible spectra of the polymer films, spin-coated from cyclohexanone solutions on a quartz substrate, were measured on Varian spectrophotometer Cary 5000. Purity of compounds was performed on HP 5890 Series II gas chromatograph (thermo conductivity detector); HP5 column (5% of biphenyl and 95% of dimethylsiloxane), 30 m × 0.22 mm × 2.6 µm; with helium as carrier gas, flow rate 1 mL min^{-1}; column temperature programming from 90 °C (2 min) at an increment of 10 °C min^{-1} to 330 °C (5 min); injector temperature 300 °C; detector temperature 320 °C. Precise molecular weights of ions were determined by HRMS on Thermo Scientific DFS instrument, ionizing energy of 70 eV. Mass spectra were recorded using autoflex III MALDI-TOF mass spectrometer (Bruker Daltonics, Germany) equipped with a pulsed N_2 laser (337 nm) in a negative reflectron mode. Ions formed by a laser beam were accelerated to 20 keV kinetic energy. The final spectra were obtained by accumulating 2500 single laser shot spectra. The saturated solution of 2,5-dihydroxybenzoic acid (DHB) in 50% aqueous acetonitrile was used as a matrix. A sample of polymer solution (10% in DMAA) was mixed with the same volume of matrix solution. About 1 μL of the resulting solution was deposited on the 384 ground steel target plate and allowed to dry before being introduced into the mass spectrometer. External calibration in positive mode was done using Peptide Calibration Standard II (Part No. 222570, Bruker Daltonics, Germany). Spectra obtained were processed using flexAnalysis 2.4 software package (Bruker Daltonics, Germany). Mass accuracy about 0.1% was usually achieved. TG and DSC analyses were performed on NETZSCH STA 409 instrument. The phase transitions of the PI were examined using DSC at a heating rate of 20 °C min^{-1} 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^{-1} in an inert (He) or oxidative (He:O_2 = 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. Elemental analyses were determined on Eurovector model EA 3000 CHN analyzer. Fluorine content was determined by spectrophotometric analysis [25]. The values of inherent viscosity (η_{inh}) were determined by 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.

4.3. Synthesis of the monomer and model compounds

4.3.1. 4-Amino-3,5,6-trifluorophthalic acid (2)

Tetrafluorophthalic acid (**3**) (4.76 g, 20 mmol) was placed into an autoclave, anhydrous NH_3 (30 mL) was added through a measuring funnel with back pressure and the autoclave was sealed. The reaction mixture was heated up to 110 °C upon stirring by rotation of the autoclave and kept under these conditions for 100 h. On completion, the autoclave was cooled and NH_3 was slowly vented. The solid residue was dissolved in water, the solution obtained was acidified with dilute HCl to pH ~ 2, and product was extracted with CH_2Cl_2 (3 × 70 mL). The extract was dried over $CaCl_2$ and solvent was evaporated to give 4.5 g of acid **2**, yield 95%, purity 98%. Mp 150–151 °C; FTIR (KBr): ν 3497, 3398 (NH_2), 3000 (OH, broad), 1712 (C=O), 1637 (NH_2) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 4.52 (br.s, NH_2); ^{19}F NMR ($CDCl_3$): δ −138.9 (dd, 1F, $J_{F,F}$ = 15 Hz, $J_{F,F}$ = 11 Hz, F-3), −140.0 (dd, 1F, $J_{F,F}$ = 20 Hz, $J_{F,F}$ = 11 Hz, F-6), −155.0 (dd, 1F, $J_{F,F}$ = 20 Hz, $J_{F,F}$ = 15 Hz, F-5) (cf. [13]); EIMS, 70 eV, *m/z* (rel. int.): 235 $[M]^+$ (64), 217 $[M–H_2O]^+$ (62), 191 $[M–CO_2]^+$ (61); 174 $[M–CO_2–H_2O]^+$ (63); 145 $[M–2CO_2H]^+$ (100); HRMS calcd for $C_8H_4O_4F_3N$: 235.0092, found: 235.0096.

4.3.2. 4-Amino-3,5,6-trifluorophthalic anhydride (1)

Solution of DCC (3.5 g, 17 mmol) in CH_3CN (10 mL) was added to the solution of acid **2** (4.0 g, 17 mmol) in CH_3CN (20 mL) upon stirring. The mixture obtained was kept under these conditions for 1 h. The precipitate of *N,N′*-dicyclohexylurea was filtered off and washed with CH_3CN. Solvent from the combined filtrate was evaporated and the crude product (3.6 g) was crystallized from a benzene:CH_3CN mixture (3:1) to give 3.3 g of anhydride **1**, yield 90%, purity 99%, spectral characteristics were identical to those reported in [26].

4.3.3. N-pentafluorophenyl-4-amino-3,5,6-trifluorophthalimide (4) (cf. [27])

Solution of anhydride **1** (0.42 g, 1.94 mmol) and pentafluoroaniline (0.34 g, 1.94 mmol) in acetic acid (5 mL) was stirred at 100–110 °C for 45 h. The reaction mixture was diluted with aqueous solution of $NaHCO_3$; the precipitate formed was filtered off, washed with water, and crystallized from aqueous EtOH to give imide **4**, yield 81%. Mp 181–182 °C; FTIR (KBr): ν 3493, 3350 (NH_2), 1788, 1734 (C=O), 1640 (NH_2); ^{1}H NMR (acetone-d_6): δ 6.64 (br.s, NH_2); ^{19}F NMR (acetone-d_6): δ −133.7 (dd, 1F, $J_{F,F}$ = 21 Hz, $J_{F,F}$ = 14 Hz, F-3), −140.2 (dd, 1F, $J_{F,F}$ = 20 Hz, $J_{F,F}$ = 14 Hz, F-6), −142.9 (m, 2F, F-2′, F-6′), −147.7 (dd, 1F, $J_{F,F}$ = 21 Hz, $J_{F,F}$ = 20 Hz, F-5), −151.9 (tt, 1F, $J_{F,F}$ = 21 Hz, $J_{F,F}$ = 3 Hz, F-4′), −162.0 (m, 2F, F-3′, F-5′); EIMS, 70 eV, *m/z* (rel. int.): 382 $[M]^+$ (93), 338 $[M–CO_2]^+$ (54), 173 $[M–CO–NC_6F_5]^+$ (16), 145 $[M–2CO–NC_6F_5]^+$ (100); HRMS calcd for $C_{14}H_2O_2F_8N_2$: 381.9983, found: 381.9978.

4.3.4. 4-Acetamido-3,5,6-trifluorophthalic anhydride (5)

It was prepared in 85% yield through acylation of anhydride **1** by acetic anhydride in a benzene:acetonitrile mixture (10:1). Mp 217–218 °C; FTIR (KBr): ν 3248, 3211 (NHAc), 2991, 2956 (CH_3), 1871, 1788 ($C=O_{anhydride}$) 1695 ($C=O_{amide}$), 1553 (NHAc), 1485 (CH_3), 1223 cm^{-1} (C–O–C); ^{1}H NMR (acetone-d_6): δ 2.24 (s, 3H, CH_3), 9.68 (br.s, 1H, NH); ^{19}F NMR (acetone-d_6): δ −116.6 (dd, 1F, $J_{F,F}$ = 19 Hz, $J_{F,F}$ = 9 Hz, F-3), −124.0 (dd, 1F, $J_{F,F}$ = 20 Hz, $J_{F,F}$ = 9 Hz, F-5), −138.0 (dd, 1F, $J_{F,F}$ = 20 Hz, $J_{F,F}$ = 19 Hz, F-6); EIMS, 70 eV, *m/z* (rel. int.): 259 $[M]^+$ (2), 217 $[M–COCH_2]^+$ (92), 173 $[M–COCH_2–CO_2]^+$ (25), 145 $[M–COCH_2–CO_2–CO]^+$ (42); HRMS calcd for $C_{10}H_4O_4F_3N$: 259.0087, found: 259.0087.

4.3.5. 3-Amino-2,4,5-trifluorobenzoic acid (6) (cf. [8])

Acid **2** (0.54 g, 2.3 mmol), NEt_3 (1.01 g, 10 mmol), and NH_4Cl (0.44 g, 10 mmol) were solved in water (10 mL) and the necessary amount of H_2SO_4 was added to reduce the pH of the mixture to 2. The solution obtained was heated at 130 °C in a sealed tube for 170 h. The crude product was extracted with diethyl ether and crystallized from benzene in yield 80%. Mp 140–141 °C; FTIR (KBr): ν 3472, 3416, 3333, 3201 (NH_2), 3094, 3002 ($C_{ar}H$), 2400–2700 (OH), 1698 (C=O), 1641 (NH_2) cm^{-1}; ^{1}H NMR (acetone-d_6): δ 7.04 (ddd, 1H, $J_{H,F}$ = 11 Hz, $J_{H,F}$ = 9 Hz, $J_{H,F}$ = 6 Hz, H_6), 5.29 (br.s, 2H, NH_2); ^{19}F NMR (acetone-d_6) δ: −131.2 (ddd, 1F, $J_{F,F}$ = 18 Hz, $J_{F,F}$ = 13 Hz, $J_{H,F}$ = 6 Hz, F-2), −143.3 (ddd, 1F, $J_{F,F}$ = 21 Hz, $J_{F,F}$ = 13 Hz, $J_{H,F}$ = 11 Hz, F-5), −149.4 (ddd, 1F, $J_{F,F}$ = 21 Hz, $J_{F,F}$ = 18 Hz, $J_{H,F}$ = 9 Hz, F-4); EIMS, 70 eV, *m/z* (rel. int.): 191 $[M]^+$ (100), 174 $[M–OH]^+$ (43), 146 $[M–CO_2H]^+$ (35); HRMS calcd for $C_7H_4O_2F_3N$: 191.0187, found: 191.0192.

4.3.6. 3-Acetamido-2,4,5-trifluorobenzoic acid (7)

It was prepared through acylation of acid **6** by acetic anhydride in benzene and crystallized from a benzene:CH_3CN mixture (5:1), yield 85%. Mp 203–204 °C; FTIR (KBr): ν 3432, 3309 (NH), 3089 ($C_{ar}H$), 2912, 2854 (CH_3), 2460–2700 (OH), 1695, 1668 (C=O) cm^{-1}; ^{1}H NMR (acetone-d_6): δ 2.18 (s, 3H, CH_3), 7.76 (ddd, 1H, $J_{H,F}$ = 11 Hz, $J_{H,F}$ = 9 Hz, $J_{H,F}$ = 7 Hz, H_6), 9.12 (br.s, 1H, NH); ^{19}F NMR (acetone-d_6) δ: −117.5 (ddd, 1F, $J_{F,F}$ = 14 Hz, $J_{F,F}$ = 7 Hz, $J_{H,F}$ = 7 Hz, F-2), −131.0 (ddd, 1F, $J_{F,F}$ = 23 Hz, $J_{H,F}$ = 9 Hz, $J_{F,F}$ = 7 Hz, F-4), −141.2 (ddd, 1F, $J_{F,F}$ = 23 Hz, $J_{F,F}$ = 14 Hz, $J_{H,F}$ = 11 Hz, F-5); EIMS, 70 eV, *m/z* (rel. int.): 233 $[M]^+$ (1), 191 $[M–COCH_2]^+$ (100), 174 $[M–COCH_2–OH]^+$ (21); HRMS calcd for $C_9H_6O_3F_3N$: 233.0294, found: 233.0296.

4.4. Synthesis of the AB-type polyimide (PI-AB)

A 50 mL round-bottomed flask equipped with a magnetic stirrer bar was charged with 10 mmol (2.3 g) of the compound **1** and benzoic acid (10 g) under argon current. The flask was tightly closed; the mixture was kept upon stirring at 160 °C for 20 h up to complete conversion of monomer into non-volatile oligomers. Then the reactor was equipped with an argon gas inlet tube and a short condenser with a calcium chloride outlet tube; reaction was kept at 180 °C for 20 h under an argon atmosphere. On completion of the reaction benzoic acid was extracted with EtOH (3 × 60 mL), polymer residue was washed with hot EtOH and dried *in vacuo* at

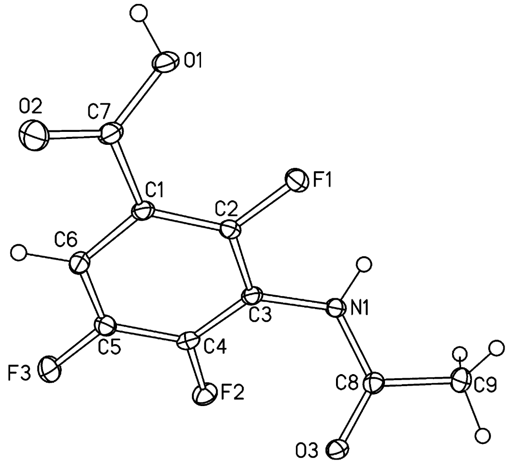


Fig. 6. X-ray structure of compound **7** with non-hydrogen atoms numbering.

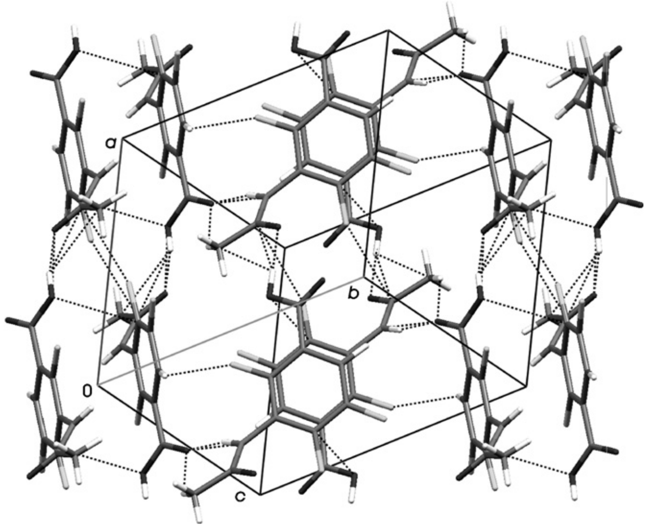


Fig. 7. Crystal packing of compound **7**.

150 °C for 6 h to prepare PI-AB, yield 75%. FTIR spectrum is given in Fig. 3a. ^{19}F NMR (DMA+acetone-d$_6$), letter symbols of fluorines are given in Fig. 1a: δ −115.9 (6.8F, F-c), −117.3 (0.8F, F-i), −117.5 (0.3F, F-m), −122.0 (6.9F, F-b), −123.4 (0.8F, F-h), −131.2 (0.2F, F-k), −132.8 (1F, F-f), −139.1 (7.7F, F-a, F-g), −140.7 (1.0F, F-d), −141.0 (0.2F, F-j), −147.8 (1F, F-e). Anal. calcd for $C_8O_2F_3N$: C, 48.2; N, 7.04; F, 28.6. Found: C, 49.3; N, 7.89; F, 26.4.

4.5. X-ray diffraction experiment and results

To confirm the molecular structure of compound **7** single crystal X-ray diffraction was performed at 150 K on a Bruker Kappa Apex II diffractometer equipped with a two-dimensional CCD-detector (monochromated Mo Kα radiation, λ = 1.54178 Å, ω–φ scans, $2\theta < 55°$). Crystallographic data for compound **7**: $C_9H_6O_3F_3N$, MW = 233.03, crystal system monoclinic, space group $P2_1/c$, a = 9.4199(9), b = 12.1657(11), c = 7.8719(8) Å, β = 92.820(4), V = 901.03(15) Å^3, Z = 4, d_{calc} = 1.719 mg mm^{-3}, μ = 0.168 mm^{-1}, crystal size 0.25 mm × 0.35 mm × 0.35 mm. Absorption correction was applied using the SADABS program [28] (transmission 0.68–0.75). The structure was solved by the direct methods (SHELXS97 [29]) and refined by a full matrix least-squares anisotropic–isotropic (for atom H) procedure using SHELXL97 program [29]. The hydrogen atom positions were located from difference Fourier map. The final indexes are wR_2 = 0.1066, S = 1.08 for all 2048 F^2 and R_1 = 0.0397 for 1955 $F^2 > 4\sigma$ (F), number of the refinement parameters is 169. CCDC-817812 contains the crystallographic data for compound **7**.

Table 2
The geometry of the hydrogen bonds in the crystal of compound **7**.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
O(1)–H(1)···O(3)	0.89(3)	1.73(3)	2.600(1)	169(2)
N(1)–H(1B)···O(2)	0.87(2)	2.02(2)	2.867(2)	168(2)
C(6)···H(6A)···F(1)	1.01(2)	2.53(2)	3.212(2)	125(1)
C(9)···H(9C)···O(2)	0.95(3)	2.54(3)	3.335(2)	141(2)

Molecular structure of compound 7 is shown in Fig. 6. The bond lengths and bond angles are typical (cf. [30]). It should be noted that the atom N1 has the planar configuration, its deviation from the plane of C3, C8 and H atoms is only 0.028(8) Å. According to the X-ray diffraction the crystal packing of **7** (Fig. 7) can be described as 3D supramolecular motif sustained by intermolecular H-bonds (Table 2) and π-stacking of the polyfluoroarene–polyfluoroarene type with an interplanar separation of 3.55 Å (the corresponding intercentroid distance is 3.732(1) Å). The packing of molecules in crystalline organic solid by means of intermolecular interactions such as O–H···O and N–H···O is well studied [31]. Interactions C–H···F and $\pi_F \cdots \pi_F$ are extensively studied in recent years; they are weaker, but are considered to play a significant role in forming the molecular assemblies [32].

Supplementary material

Crystallographic data for compound **7** have been deposited with CCDC No. 817812. Copies of the data may be obtained, free of charge, from: www.ccdc.cam.ac.uk/data_request/cif.

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