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Synthesis and characterization of polyimides based on novel isomeric perfluorinated naphthylenediamines

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ABSTRACT

Novel highly fluorinated polyimides containing hexafluoronaphthylene fragment in the main chain were prepared by the two-stage polymerization of 2,7- and 2,6-diaminohexafluoronaphthalenes with 4,4′-oxydiphthalic anhydride: polycondensation in a solution at 80 °C followed by high-temperature solid-state chain extension. The influence of hexafluoronaphthylene fragment isomerism on the key polyimide features – molecular weight, thermal stability, solubility, optical properties – was characterized. Polyimides based on 2,7-diaminohexafluoronaphthalene or easily accessible mixture of isomeric diamines formed the flexible, transparent, and thermostable films.

1. Introduction

Incorporation of fluorine into the framework of aromatic polyimides (PIs) is intensively explored with the purpose of improving the polymer properties that are of particular interest for optical and electronic applications [1–5]. Increase of fluorine content has been found to generally lower optical loss, dielectric constant and moisture absorption, to enhance solubility in organic solvents and thermal stability.

Most works were focused on the incorporation of trifluoromethyl group or hexafluoroisopropylidene moiety into dianhydride and diamine components [2,5–13]. This concentration of efforts was presumably due to a significant enhancement of PI properties. Other fluorinated monomers are hard to get because they are relatively difficult and expensive to synthesize. To our knowledge, only three perfluorinated aromatic diamines – tetrafluoro-*meta*- and -*para*-phenylenediamines and octafluorobenzidine – were used as monomers for preparing highly fluorinated PIs [1,2,14–16]. Recently we have elaborated [17] a method of selective preparation and high-purity isolation of new compounds, which can serve as potential monomers—2,7- and 2,6-diaminohexafluoronaphthalenes (2,7-DAHFN and 2,6-DAHFN), as well as an inexpensive short route to their 3:1 mixture through direct amination of commercially available octafluoronaphthalene by liquid ammonia used as a reagent/medium system (see also [18]).

The aims of the present work are: (i) to synthesize PIs from 4,4′-oxydiphthalic anhydride (ODPA) and isomeric hexafluoronaphthylene diamines or their mixture (Scheme 1) for investigating the diamines relative reactivity, and (ii) to study the influence of structural isomerism of hexafluoronaphthylene fragment in the main chain on the properties of the highly fluorinated PIs.

2. Results and discussion

2.1. Synthesis of polyimides

The replacement of all hydrogens in the aromatic ring by fluorines is known to decrease the reactivity of phenylenediamines for acylation by a factor of ~10^{-5} [1] because of the high electronegativity of fluorine. The resultant low nucleophilicity of polyfluoroaromatic diamines, as reported for benzene and biphenyl derivatives [1,2,15], impedes their interaction with dianhydride and the formation of poly(amic)acids. Indeed, solutions of equivalent amounts of 2,7-DAHFN or 2,6-DAHFN and ODPA in NMP at ambient temperature have a low viscosity (η_{inh} 0.06 dL g^{-1}), which remains unchanged for 24 h. Correspondingly, there occur no changes in ^{19}F NMR spectra of these solutions. Nevertheless, coating the solutions of monomers (method A, Scheme 1) onto a glass plate, drying them slowly to a constant

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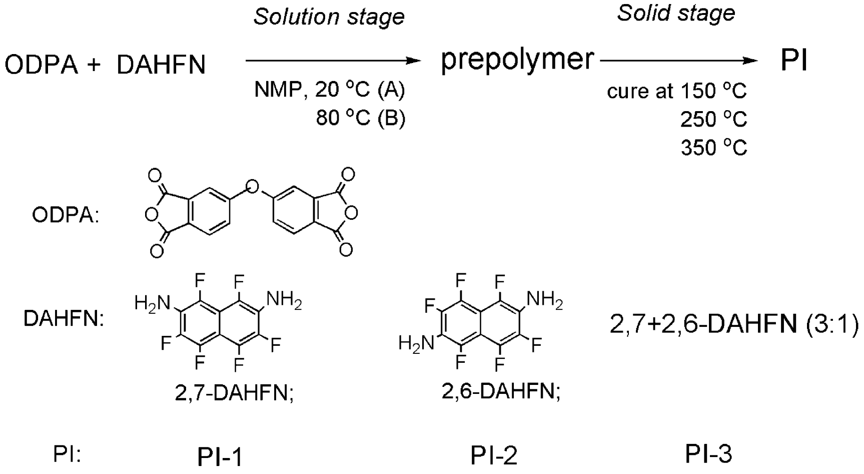


Scheme 1. Synthesis of PIs.

weight, and curing at 350 °C (rate of heating is 1 °C min^{-1}) provide the preparation of PI-1(A) and PI-2(A) films (Table 1). It should be noted that the yields of the samples thus obtained are far from quantitative (80–85%), which is evidently caused by partial loss of monomers during the thermal cure. Moreover, there is some absorption of residual anhydride groups in FTIR spectra of PI-1(A) and PI-2(A) (Fig. 1), which testifies to a relatively low polycondensation degree. Thus, slow high-temperature curing yields the samples of PIs due to the solid-state chain extension, but it does not provide a good quality of the films. As it was shown in the works [2,15], using the high-temperature solution stage for the process acceleration results in a higher polycondensation degree. For the synthesis of prepolymers from DAHFNs and ODPA we carried out the solution stage at 80 °C (method B, Scheme 1). Thermal cure of the samples provided the preparation of high-quality films (Table 1).

The polycondensation process has been investigated in detail by using ^{19}F NMR and FTIR spectroscopy, TGA/DSC, and MALDI-TOF MS (matrix-assisted laser desorption/ionization time-of-flight mass spectrometry) to control the extent and type of the occurring transformation and to get information on the molecular weight and structure of PIs. Table 2 contains quantitative characteristics of the polycondensation of ODPA with individual 2,7- or 2,6-DAHFN and their 3:1 mixture. Figs. 2–4 show the changes in ^{19}F NMR spectra of condensation solutions and PI samples obtained at different cure temperatures (T_c 150, 250 °C). The ratios of the different types of hexafluoronaphthylene units given in Table 2 were determined from the intensity ratios of α-fluorine signals located in the down-field area of ^{19}F NMR spectra (−120 to −125 ppm).

The increase of temperature from ambient up to 80 °C provides an appreciable increase of the reaction rate: after 16 h no more than 30% of 2,7-DAHFN remains in the condensation solution prepared from equivalent amounts of 2,7-DAHFN and ODPA in NMP. The complete conversion of diamine takes 48 h (Fig. 2b; Table 2). After that the viscosity of the condensation solution noticeably increased, but did not achieve the values testifying to the formation of high-molecular weight compounds [2,9–13]. According to ^{19}F NMR data, the prepolymer formed at this stage consists of low molecular weight derivatives, because in the spectrum there are no signals of prevailing intensity which would indicate long, structurally uniform fragments. It is noteworthy that amic acid and imide fragments are contained in comparable quantities (determined from signal intensity ratio $(j + k)/(a + d)$, Fig. 2b). So, the formation of amic acid at 80 °C is accompanied by its substantial cyclodehydration. Released water can hydrolyze anhydride groups thereby interrupting the further growth of the

Table 1
Yield and characteristics of PIs obtained by A and B methods, T_c 350 °C.

PI	Method	Yield (%)	Film forming	The residual anhydride groups bond (1855 cm^{-1}) in FTIR spectrum
PI-1	A	85	Yes	+
	B	94	Yes	–
PI-2	A	81	Yes	+
	B	92	Yes	–
PI-3	B	94	Yes	–

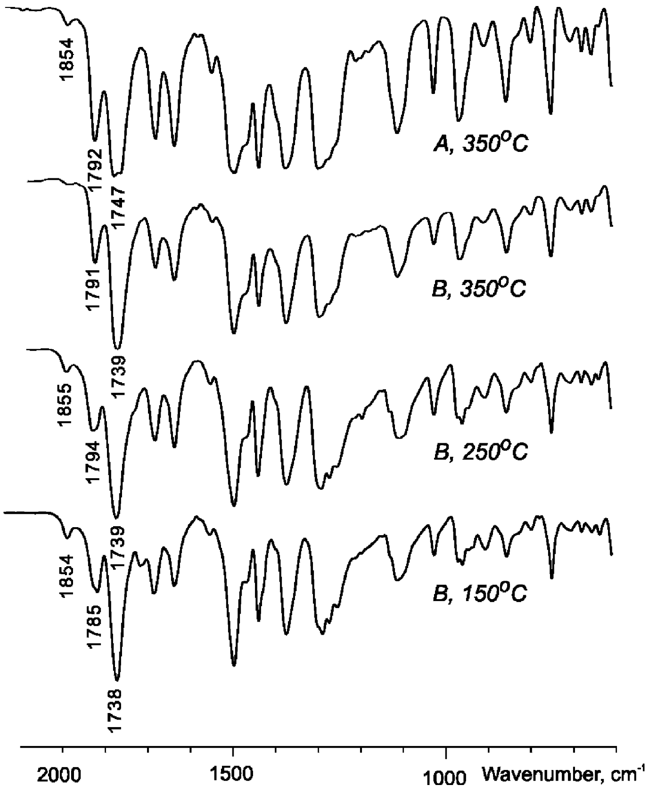


Fig. 1. FTIR spectra of PI-1 (2,7-DAHFN/ODPA) during polycondensation by methods A and B at different T_c (in KBr). The absorption at ~1790 and 1740 cm^{-1} is assigned to the stretching vibrations of imide group carbonyl, 1855 cm^{-1}—anhydride group carbonyl.

Table 2
Polyimidization of individual 2,7- and 2,6-DAHFN and their 3:1 mixture with ODPA (method B).

Diamine (polyimide)	Curing conditions	η_{inh} (dL g^{-1}), solution stage	Yield (%), solid stage	Content of structural hexafluoronaphthylene units[a] (%,^{19}F NMR)				Internal/terminal fragments ratio, ^{19}F NMR	M_{max} MALDI	Average molecular weights, method		
				DAHFN	Sum of non-identified fragments	Amine-terminal fragments	Imide-internal fragments			$\bar{M}_n$ NMR	$\bar{M}_n$ MALDI	$\bar{M}_w$ MALDI
2,7-DAHFN (PI-1)	Solution stage, 80 °C, 16 h	0.12		30	70							
	Solution stage, 80 °C, 48 h	0.21		3	57	30	10					
	Solid stage, 150 °C		99		2	15	83	5.5	5,958	3500	1970	2420
	Solid stage, 250 °C	0.38	95		4	8	88	11	8,410	6500	2600	3370
2,6-DAHFN (PI-2)	Solution stage, 80 °C, 48 h	0.14		2	49	48	1					
	Solid stage, 150 °C		99		1	30	69	2.3	3,550	1800	1690	1970
	Solid stage, 250 °C	0.29	93		1	20	79	4.0	4,338	2700	1730	2100
2,7 + 2,6-DAHFN (3:1) (PI-3)	Solution stage, 80 °C, 48 h	0.19		6	54	23 + 13	3 + 1					
	Solid stage, 150 °C		99		4	12 + 10	60 + 14	3.4	4,878	2400	1830	2220
	Solid stage, 250 °C	0.40	95		1	3 + 4	72 + 20	13	11,650	7500	3640	4980

[a] Different types of structural hexafluoronaphthylene units in samples of prepolymer and PIs; signals of fluorines used for evaluation of their content are given in Figs. 2–4.

polymer chain; for this reason prolongation of the solution stage is inexpedient. At the same time, carrying out the solid stage will not cause any loss of substance due to the absence of volatile monomers in the prepolymer.

Removing the solvent and curing at 150 °C give a sample of PI-1 with virtually quantitative yield (Table 2). According to the ^{19}F NMR data (Fig. 2c *vs* b), this cure results in a considerable growth of the polyimide chain due to the regeneration of anhydride groups, their interaction with amino groups, and full imidization of amic acid fragments. The averaged length of the polymer chain, estimated by the internal/terminal fragments ratio, amounts to 6–7 structural units. It corresponds to the value of number-averaged molecular weight $\bar{M}_n \sim 3500$. The end-groups content further decreases with increasing cure temperature. The sample obtained at 250 °C is characterized by the chain length ~12 units and $\bar{M}_n \sim 6500$. In accordance with the growth of polymer molecular weight the inherent viscosity also increased (Table 2). The observed value of η_{inh} is comparable to the characteristics of partially fluorinated film forming polyimides [9,12,13]. Curing at 350 °C yields an insoluble sample which has not been characterized by ^{19}F NMR.

MALDI-TOF MS is used for the determination of molecular and repeated unit weights and the identification of end-groups in synthetic polymers, in particular, polyimides [19,20]. The spectra of PI-1 samples irrespective of T_c contain repeated fragments (groups of signals) with the period m/z 540 Da equal to the molecular weight of the polymer structural unit $C_{26}H_6F_6N_2O_5$ (Fig. 5 shows a representative spectrum). All fragments have a similar intensity ratio of peaks corresponding to PI molecules with different charge agent cations. The relative intensities of the main signals decrease with increase of m/z. Table 3 presents tentative peak mass assignments in the representative fragment ($n = 5$) of the spectrum of PI-1 cured at 250 °C (Fig. 5b). The fragment contains peaks of molecules with three different end-group combinations (Scheme 2) labeled AA (two anhydride groups), AB (one anhydride group and one amino group) and BB (two amino groups). The AA and AB series can include one or two hydrolyzed anhydride groups in acid and salt forms. The above species are cationized in different ways. The MALDI MS data obtained are well correlated with the assumed polymer structure and evidence that no fragmentation or destruction has occurred during polyimidization.

Maximal molecular weights (M_{max}) detected in PI-1 samples by MALDI MS increase with rising cure temperature and achieve ~8400 Da (Table 2). Calculation of number ($\bar{M}_n$) and weight ($\bar{M}_w$) averaged molecular weights of synthetic polymers by MALDI MS data is known to give understated values, as compared with those obtained by NMR and SEC methods [20]. This is caused by the discrimination of high-molecular masses in samples. For this reason, $\bar{M}_n$ values obtained by MALDI MS are lower than $\bar{M}_n$ derived from NMR (Table 2). However, MALDI data confirm that PI-1 molecular weight increases with increasing T_c.

Comparison of polycondensation degree of PI-1 samples obtained by method B at different T_c values and by method A at 350 °C has been done by means of FTIR spectral data (Table 1; Fig. 1). During the polycondensation by method B, amine and anhydride end-group absorptions in PI-1, which remain after high-temperature solution stage, are still present after 150 °C solid-state cure, are partially consumed by 250 °C cure, and are fully consumed by 350 °C cure. On the contrary, much more anhydride end-groups remain in PI-1(A) cured at 350 °C. Thus, carrying out the high-temperature solution stage provides a high-polycondensation degree. It is noteworthy that the yield of polymer obtained from the condensation solution B is satisfactory.

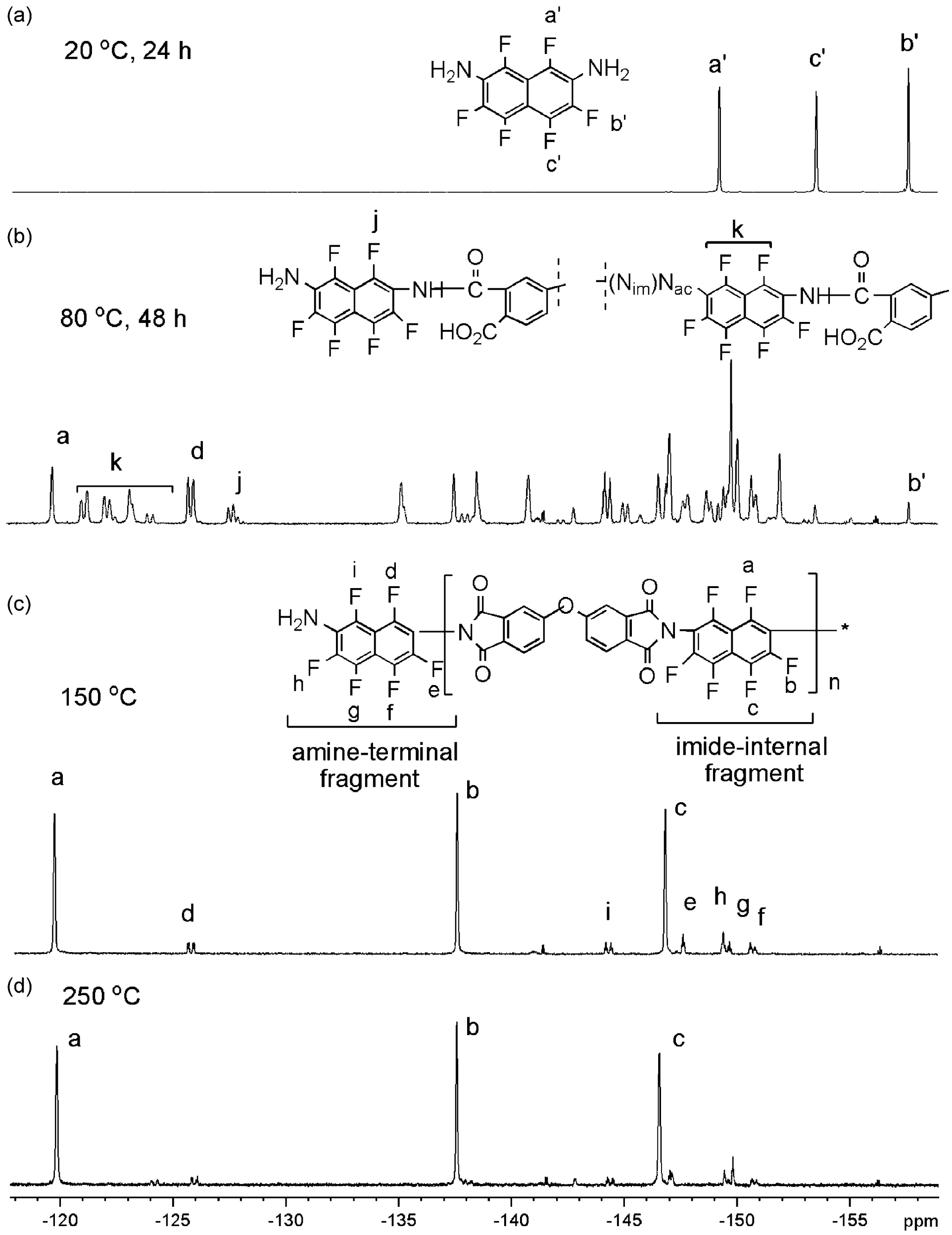


Fig. 2. ^{19}F NMR spectra of PI-1 (2,7-DAHFN/ODPA) during polycondensation by method B (solution in NMP): a and b, solution stage; c and d, solid stage.

Evolution of thermal characteristics of PI-1 samples obtained at different T_c values (Table 4) indicates the growth of polycondensation degree and agrees with the NMR data. The glass transition temperature (T_g) as well as the thermal stability (weight loss temperatures) of PIs increases with rising T_c. A considerable change of these characteristics occurs in going from T_c 250 to 350 °C, which testifies to the increase of the polymer molecular weight.

Polycondensation of 2,6-DAHFN, containing pseudo-*para*-located amino groups, with ODPA and characteristics of PI-2 samples differ from those of PI-1. In both cases the complete conversion of diamine-monomer takes 48 h at 80 °C, i.e. the isomeric 2,7- and 2,6-DAHFN have comparable rates of first acylation. However, according to the ^{19}F NMR data, at the end of solution stage only one amino group in 2,6-DAHFN has modified into acylamido or imido group (Fig. 3b, signals *j* and *d* of α-fluorines, respectively, cf. PI-1, Fig. 2b), whereas second amino group has not changed; thus, the naphthalene units with two modified amino groups (signals *a* and *k*, cf. PI-1) are practically absent. It is caused by a considerable decrease of nucleophilicity of the amino group in 2,6-DAHFN monoacyl derivative under the action of the electron-withdrawing acylamido or imido group at the resonance position. The electronic effect of the modified amino group on the reactivity of monoacyl derivatives controls the possibility of high-molecular weight polymer synthesis. This effect has been characterized quantitatively in the works [1,21] for perfluorinated phenylenediamines. The first acylation of tetrafluoro-*p*-phenylenediamine provokes decrease of the second acylation rate constant by a factor of $>10^3$. On the contrast, the reactivity of the residual amino group in tetrafluoro-*m*-phenylenediamine derivative is shown to be little affected by the first acylation. Similarly, in the perfluoronaphthalene framework the pseudo-*para*-located acylamido or imido group appreciably decelerates the polymeric chain growth (in the case

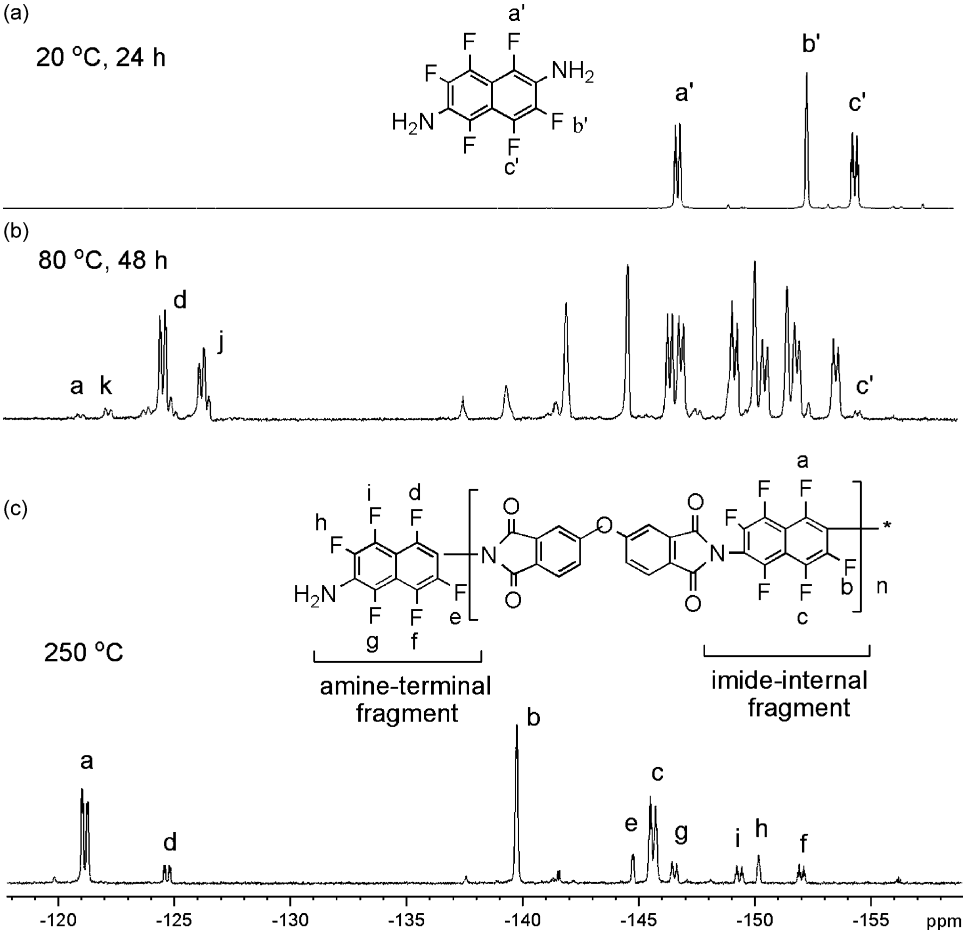


Fig. 3. ^{19}F NMR spectra of PI-2 (2,6-DAHFN/ODPA) during polycondensation by method B (solution in NMP): a and b, solution stage; c, solid stage. Assignment of signals *j* and *k* is similar to that in PI-1 spectra, see structures in Fig. 2b.

of 2,6-DAHFN), as compared with pseudo-*meta*-located substituent (in the case 2,7-DAHFN). For this reason, PI-2 samples obtained at T_c 150 and 250 °C have the chain lengths half as long and the $\bar{M}_n$ values less than those of PI-1 (^{19}F NMR and MALDI MS data, Table 2). Nevertheless, the absorption of residual anhydride groups in FTIR spectrum of PI-2 obtained by method B (Table 1) is practically absent, and its yield is above 90%. Thermal characteristics of PI-2 are worse only in the case of the sample obtained at T_c 150 °C (Table 4).

Polycondensation of diamine monomers mixture – 2,7- and 2,6-DAHFN (3:1) – with ODPA at T_c 80, 150 °C occurs with minor complications, but after curing at 250 °C the averaged molecular weight of PI-3 sample achieves the value, which is even higher than that of PI-1 (Fig. 4; Table 2). Curing at 350 °C gives film forming polymer PI-3 (Table 1) whose thermal properties are comparable with the characteristics of the structurally uniform PI-1 (Table 4).

2.2. Polyimide properties

Solubility of PIs in different organic solvents has been investigated at room temperature (Table 4). All PI samples cured at 150 °C exhibit solubility in polar organic solvents such as NMP, DMA, and DMF. PI-1 and PI-3 are also soluble in less polar acetone. Solubility of PIs decreases with increasing T_c: all the samples obtained at 350 °C are insoluble, and PI-2 cured at 250 °C is partially soluble. The better solubility of PIs obtained from individual 2,7-DAHFN and its mixture with 2,6-isomer, in comparison with the samples obtained from individual 2,6-DAHFN, seems to result from asymmetric arrangement of pseudo-*meta*-disubstituted hexafluoronaphthalene framework relative to the polyimide chain, which increases the polymer backbone flexibility and free volume [10,22].

Data of elemental analysis of PIs 1–3 (T_c 350 °C, Table 5) agree with the calculated values. Therefore, polycondensation and imidization reactions are completed without by-products. The high fluorination degree (fluorine content in PIs is ~20%) provides a high hydrophobicity of the PIs. Water uptake of PIs 1–3 (not more than 0.36%, Table 5) is comparable with the known characteristics of partially fluorinated polyimides [10,11].

PI-1 and PI-3 give flexible and transparent films upon curing at 350 °C (Table 5). Unlike this, the film obtained from PI-2 is cracked, which agrees with its relatively low molecular weight. Besides, this film is opaque; it becomes opaque during solid-state chain extension (at ~180 °C), which can be caused by the formation of a specific crystalline structure [23,24]. DSC of PI 1–3 films cured at 350 °C detect no obvious melting and crystallization transition up to the temperature of 10% weight loss (see below). However, the POM data show differences in the morphology of PI-1 and PI-2 films (Fig. 6). It appears that the grainy texture of PI-2 film is responsible for its opaqueness [23]. Optical properties of PI-1 and PI-3 films have been investigated using UV–vis spectroscopy (Table 5; Fig. 7). PI-1 exhibits a rather low cut-off wavelength (λ_0 362 nm). The λ_0 of PI-3 is slightly higher because of the presence of 2,6-isomer, but its influence worsens the optical properties of the

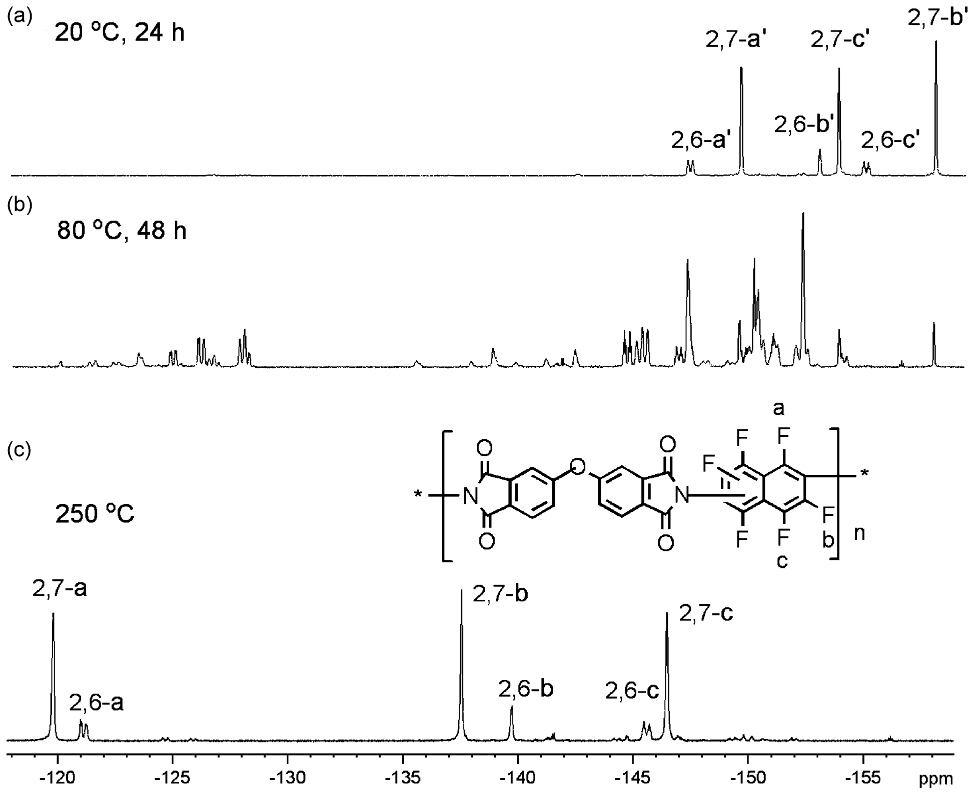


Fig. 4. ^{19}F NMR spectra of PI-3 (2,7 + 2,6-DAHFN/ODPA) during polycondensation by method B (solution in NMP): a and b, solution stage; c, solid stage.

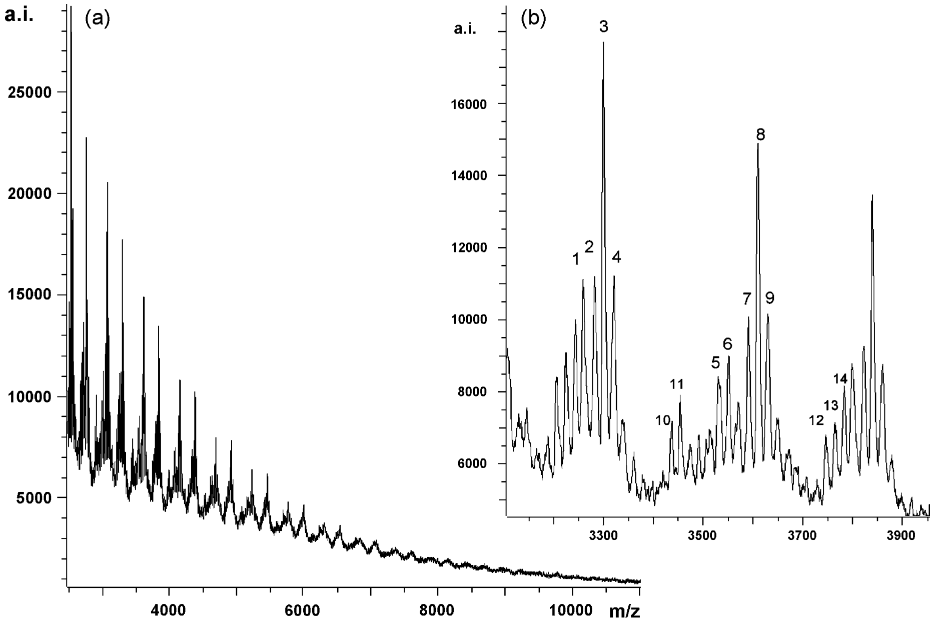


Fig. 5. MALDI-TOF mass spectrum of PI-1, T_c 250 °C: a, the whole spectrum; b, representative repeated fragment, $n = 5$ (Scheme 2), peak assignment is given in Table 3.

film to an insignificant degree. The PI-1 and PI-3 films exhibit an excellent transparency at 450 nm (transmittance is ~85%) that is an inherent attribute of fluorinated PIs [1,3,10,11,25].

Thermal stability properties of final PIs have been evaluated by TGA/DSC and the results are summarized in Table 6. In inert atmosphere there are no considerable differences in the thermal stability of PIs obtained both from individual isomeric diamines and their mixture (PI-1, PI-2, and PI-3), as well as from different condensation solutions (A and B). All PIs exhibit a good thermal stability: there is no obvious weight loss before the scanning temperature reaches to 540 °C. The temperatures at 5% and 10% weight loss in inert atmosphere (T_5 and T_{10}) are above 540 and

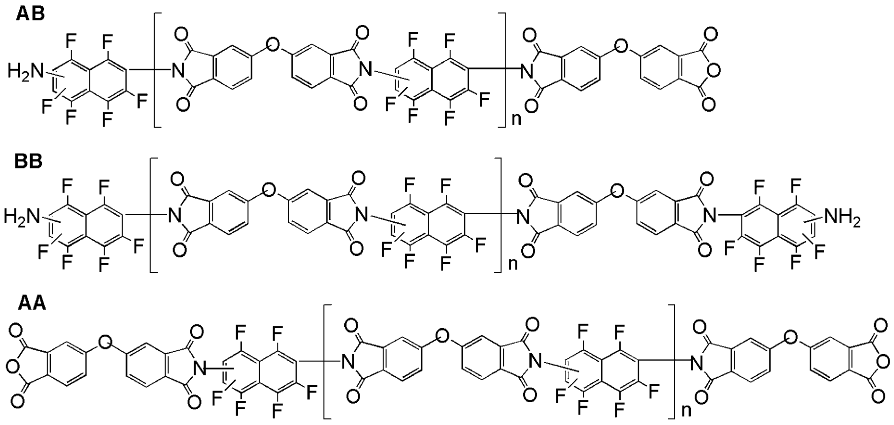
570 °C, respectively. The residual weight retention R_w at 700 °C is not less than 56%, which practically coincides with the carbon content. Further heating of the samples up to 900 °C in inert atmosphere is not accompanied by appreciable R_w changes. In oxidative atmosphere PI-2 is less thermostable, as compared to PI-1 (Table 6), which can be caused by a greater oxidation susceptibility of the conjugate imide cycles. The total weight loss temperatures (T_{100}) in oxidative atmosphere for all PIs are in the range of 650–700 °C. Note that PIs cured at 250 °C exhibit high T_g values (Table 4) (cf. [2,11,15]); for the final PI samples T_g have not been detected.

Thus, thermal stability properties of PIs 1–3 are slightly higher than those of the known PIs, which contain CF_3 groups [2,5–13] and aromatic fluorines (based on tetrafluoro-*meta*- and -*para*-phenylenediamines, octafluorobenzidine) [1,2,15].

Table 3
Mass assignments of the peaks displayed in the fragment ($n = 5$) of MALDI-TOF mass spectrum of PI-1, T_c 250 °C (Fig. 5b; Scheme 2).

Peak number[a]	M (Da)	Structure
1	3259.81	$AB + H^+$
2	3281.87	$AB + Na^+$
3	3299.44	$AB + H_2O + Na^+$
4	3320.94	$AB + H_2O + (Na^+–H^+) + Na^+$
5	3530.24	$BB + Na^+$
6	3551.01	$AA + H^+$
7	3591.26	$AA + H_2O + Na^+$
8	3610.00	$AA + 2H_2O + Na^+$
9	3630.26	$AA + 2H_2O + (Na^+–H^+) + Na^+$

[a] Peaks 10, 11 (M 3435.91, 3453.16) and 12, 13, 14 (M 3746.28, 3764.67, 3782.73) can be assigned to adducts consisting of AB and AA molecules correspondingly with DHB (used as a matrix, cf. [19]), water and charge agent cations.



Scheme 2. PI structures having the three possible end-group combinations.

Table 4
Influence of cure temperature (T_c) on thermal properties and solubility of PIs (method B).

PI	T_c (°C)	T_g (°C)	T_2[a] (°C)	R_{580}[b] (%)	Solubility in organic solvents[c]			
					NMP	DMA	DMF	Acetone
PI-1	150	310	224	83	++	++	++	++
	250	352	396	88	++	++	++	–
	350	None detected	477	89	–	–	–	–
PI-2	150	295	168	80	++	++	++	–
	250	324	425	87	+–	+–	+–	–
	350	None detected	505	88	–	–	–	–
PI-3	150	315	184	76	++	++	++	++
	250	320	411	88	++	++	++	–
	350	None detected	501	91	–	–	–	–

[a] T_2—temperature at 2% weight loss.
[b] R_{580}—residual weight retention at 580 °C.
[c] Qualitative solubility was determined visually as: completely soluble (++), partially soluble (+–), and insoluble (–). The complete solubility is defined as a visibly transparent and homogenous solution.

Table 5
Characteristics of PI films cured at 350 °C (method B).

PI		Elemental analysis (%)				Film quality[a]	Water uptake (%)	λ_0[b] (nm)	Transmittance at 450 nm (%)[c]
		C	H	N	F				
	Calcd.	57.78	1.11	5.19	21.11				
PI-1	Found	58.08	1.19	5.22	20.28	T, F	0.30	362	88
PI-2	Found	57.41	1.15	5.31	20.20	O, C			
PI-3	Found	57.67	1.16	5.44	20.34	T, F	0.35	371	83

[a] T, Transparent; O, opaque; F, flexible; C, cracked.
[b] λ_0—the cut-off wavelength.
[c] Film thickness ~20 μm.

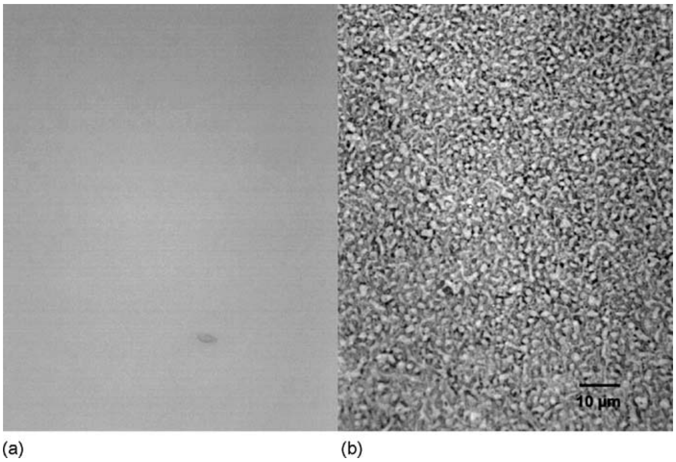


Fig. 6. Optical micrographs of polyimide films, T_c 350 °C, PI-1 (a) and PI-2 (b) (bar = 10 μm).

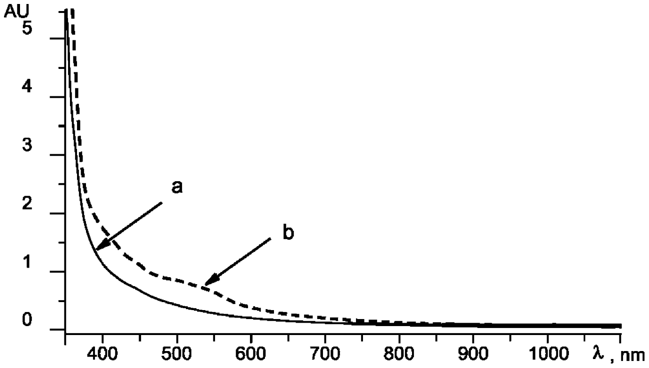


Fig. 7. UV–vis spectra of PI-1 (a) and PI-3 (b), T_c 350 °C.

Table 6
Thermal degradation properties of PIs obtained by A and B methods, T_c 350 °C.

PI	Method	In inert atmosphere				In oxidative atmosphere		
		T_5[a] (°C)	T_{10}[a] (°C)	R_{700}[b] (%)	R_{900}[b] (%)	T_5[a] (°C)	T_{10}[a] (°C)	T_{100}[a] (°C)
PI-1	A	546	570	56	48			
	B	562	581	58	52	527	554	703
PI-2	A	549	571	57	52			
	B	553	575	56	52	504	536	662
PI-3	B	570	586	59	52	511	544	655

[a] T_5, T_{10}, and T_{100}—temperature at 5%, 10%, and 100% weight loss.
[b] R_{700} and R_{900}—residual weight retention at 700 and 900 °C.

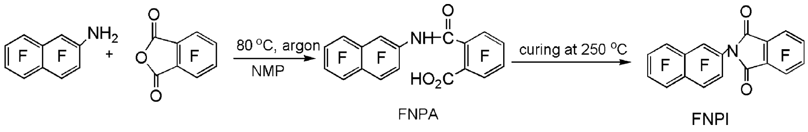
3. Conclusions

New polyimides containing isomeric hexafluoronaphthylene fragments in the main chain have been successfully synthesized by the two-step method. The low reactivity of perfluoroaromatic diamine monomers has been overcome by carrying out high-temperature solution stage followed by high-temperature solid-state chain extension. 2,7-DAHFN exhibits a higher reactivity than 2,6-DAHFN, and PI-1 (2,7-DAHFN/ODPA) forms a film with good thermal and optical properties. The ability of 2,6-DAHFN to polymerize is weakened by substituents conjugation, which reduces the reactivity of the amino group in monoacyl derivatives and impedes the synthesis of high-molecular weight polymer. For this reason PI-2 (2,6-DAHFN/ODPA) has a lower molecular weight than PI-1 and forms a cracked and opaque film. It is noteworthy that using inexpensive mixture of isomeric diamines (2,7- + 2,6-DAHFN, 3:1) provides the preparation of PI-3, which has molecular weight, thermal and optical characteristics comparable with those of the structurally uniform PI-1. The new highly fluorinated aromatic polyimides seem to be promising materials for optic and optoelectronic applications.

4. Experimental

4.1. Measurements

^{19}F NMR spectra were recorded on Bruker AV-300 (282.36 MHz) spectrometer using C_6F_6 ($\delta = -163$ ppm from CCl_3F) as internal standard; δ are given in ppm relative to CCl_3F, J are given in Hz. Solid PI samples, prepared at the different cure temperatures, were dissolved to concentration ~5% in NMP for registration of spectra. Signals in the spectra were assigned by using substituent shielding parameters determined from the monomers [17], octafluoronaphthalene [26], 2-aminoheptafluoronaphthalene [27] and model compounds—N-(1,3,4,5,6,7,8-Heptafluoro-2-naphthyl)-3,4,5,6-tetrafluorophthalamic acid (FNPA) and N-(1,3,4,5,6,7,8-heptafluoro-2-naphthyl)-3,4,5,6-tetrafluorophthalimide (FNPI). Fourier transform infrared (FTIR) spectra were measured on Bruker Vector-22 instrument for KBr disks. Ultraviolet–visible (UV–vis) spectra of polymer films were recorded on Varian spectrophotometer Cary 5000. PI films for the transmittance determination were prepared by spin-coating 10% solution on a glass plate. Precise molecular weights of ions were determined by high-resolution mass spectrometry on Finnigan MAT-8200 instrument. Thermogravimetric (TGA) and differential scanning calorimetry (DSC) analyses were performed on NETZSCH STA 409 instrument. Experiments were carried out at the followed conditions: (a) Al crucible, heating from 25 to 580 °C with rate 10 °C min^{-1} under flowing He at 27 mL min^{-1}. (b) Pt/Rh crucible, heating from 25 to 1000 °C with rate 10 °C min^{-1} under flowing He or He/O_2 mixture (8:2, v/v) at 27 mL min^{-1}. Mass spectra were recorded using an AutoFlex MALDI-TOF mass spectrometer (Bruker Daltonics, Germany) equipped with a pulsed N_2 laser (337 nm) in a positive linear or reflectron mode. Ions formed by a laser beam were accelerated to 20 or 19 keV kinetic energy in the case of linear or reflectron mode, respectively. The final spectra were obtained by accumulating 1000–3000 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 0.7 μL of the resulting solution was deposited on the stainless steel multiprobe and allowed to dry before being introduced into the mass spectrometer. Mass spectra were obtained by averaging 3000 laser shots. External calibration was provided by $[M+H]^+$ ions of bradykinin fragments 1–7, human angiotensin II, human ACTH fragments 18–39, oxidized bovine insulin β-chain, bovine insulin and equine cytochrome *c* *m/z* 757.4, 1046.54, 2465.2, 3494.65, 5734.51 and 12361.96, respectively. Mass accuracy in the range 0.1–0.5% was usually achieved. $\bar{M}_w$ and $\bar{M}_n$ values were calculated with software supplied by the manufacturer of the spectrometer. Elemental analyses were performed by a Eurovector model EA 3000 CHN analyzer. Fluorine content was determined by spectrophotometric analysis [28]. 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. Polarized optical microscopy (POM) observation was performed



Scheme 3.

on an Olympus BX51 optical microscope equipped with a digital camera.

Solubility was determined as follows: 100 mg of PI was mixed with 900 mg of solvent at 25 °C and the mixture was mechanically stirred for 24 h. Water uptake was determined by immersing the polyimide film (3 cm × 1 cm × 0.01 cm) in water at 25 °C for 24 h, which was then dried immediately by blotting with a paper towel and subsequently weighed.

4.2. Materials

4,4′-Oxydiphthalic anhydride (ODPA) was purified by double vacuum sublimation at 240–260 °C/5 Torr. 2,7-Diaminohexafluoronaphthalene (2,7-DAHFN), 2,6-diaminohexafluoronaphthalene (2,6-DAHFN), their mixture in the ratio 3:1 (2,7 + 2,6-DAHFN), and 2-aminoheptafluoronaphthalene were synthesized and purified according to the data [17]. N-methyl-2-pyrrolidone (NMP, Aldrich) was purified by distillation over P_2O_5 under reduced pressure and stored over 3E molecular sieve; residual moisture <0.02%.

N-(1,3,4,5,6,7,8-Heptafluoro-2-naphthyl)-3,4,5,6-tetrafluorophthalamic acid (FNPA) and N-(1,3,4,5,6,7,8-heptafluoro-2-naphthyl)-3,4,5,6-tetrafluorophthalimide (FNPI) were prepared by method shown in Scheme 3.

Solution of tetrafluorophthalic anhydride and 2-aminoheptafluoronaphthalene in NMP was kept under stirring in argon atmosphere at 80 °C for 36 h to the formation of FNPA; ^{19}F NMR (NMP): δ −156.3 (m, 1 F, $F_{7'}$), −154.9 (t, 1 F, J = 18, $F_{6'}$), −152.9 and −151.5 (both t, both 1 F, J = 20, F_3 and F_6), −148.8 (dt, 1 F, J = 58, J = 17, $F_{4'}$), −147.0 (dt, 1 F, J = 58, J = 16, $F_{5'}$), −145.7 (dt, 1 F, J = 65, J = 16, $F_{8'}$), −138.9 (m, 1 F, $F_{3'}$), −139.4 and −138.0 (both m, both 1 F, F_4 and F_5), −123.9 (dd, 1 F, J = 65, J = 17, $F_{1'}$).

Thermal imidization of FNPA and sublimation of the product at 200 °C/5 Torr gave FNPI, mp 201.5–202.5 °C. ^{19}F NMR (acetone-d_6): δ −154.8 (m, 1 F, $F_{7'}$), −151.9 (t, 1 F, J = 16, $F_{6'}$), −146.9 (dt, 1 F, J = 60, J = 17, $F_{4'}$), −145.8 (dt, 1 F, J = 60, J = 16, $F_{5'}$), −143.9 (dt, 1 F, J = 67, J = 16, $F_{8'}$), −140.2 (m, 1 F, $F_{3'}$), −143.0 and −136.1 (both q, 2 F, J = 10, $F_{3,6}$ and $F_{4,5}$), −120.9 (dd, 1 F, J = 67, J = 17, $F_{1'}$). HRMS calcd. for $C_{18}F_{11}NO_2$: 470.9748, found: 470.9744.

4.3. A typical two-step synthesis of ODPA/DAHFN polyimides

4.3.1. Solution stage

Equimolar amounts (5 mmol) of ODPA (1.5511 g) and DAHFN (1.3307 g) were added to NMP (15 mL) in round-bottom flask to 15% concentration by weight and the solution was stirred at room temperature for 24 h (method A) or at 80 °C for 48 h (method B). All procedures were performed under argon atmosphere.

4.3.2. Solid stage

Condensation solution (A or B) was cast onto a glass plate and kept in vacuum oven at 80 °C for 12 h to constant weight. Polymer resin thus obtained was cured at the final temperature (variants 150, 250, 350 °C) for 1 h. The rate of heating to the cure temperature was 1 °C min^{-1}

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