

UDC 541.64:541.68+546.171.1+547.539.1

Polyimides of AA/BB and AB Types Based on New Perfluorinated Monomers

E. V. MALYKHIN, T. A. VAGANOVA, I. K. SHUNDRINA, S. Z. KUSOV, V. I. RODIONOV and E. V. KARPOVA

Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, Pr. Akademika Lavrentyeva 9, Novosibirsk 630090 (Russia)

E-mail: malykhin@nioch.nsc.ru

Abstract

Convenient methods of the synthesis of new perfluoroaromatic monomers of BB and AB types and polyimides on their basis were developed. The effect of the structural factors (the nature of aromatic framework, substituents and bridges, isomerism) on the reactivity of monomers and major characteristics of polyimides was discussed. It was established that the obtained polyimides possess promising properties for optoelectronic applications.

Key words: polyfluoroarylenediamines, polyfluorohetarylenediamines, aminodefluorination, liquid ammonia, synthesis of fluoroaromatic polyimides, thermal stability, optical transparency

INTRODUCTION

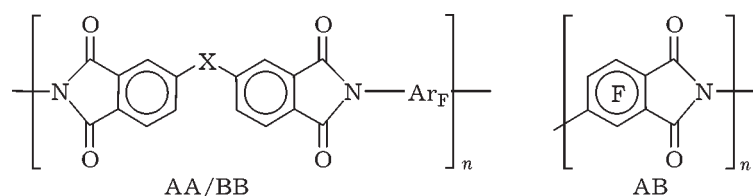
Fluorinated aromatic polyimides (PI) (Scheme 1) are used in modern optoelectronic applications [1] due to their unique transparency and low optical losses in the nearest IR, visible and UV spectral regions, good dielectric properties, high hydrophoby and thermal stability [2]. All the key properties that are required for the materials improve with an increase in fluorine content, but the synthesis of highly fluorinated PI is restricted by low availability and low reactivity of polyfluorinated diamine monomers.

In this connection, the goal of our work was to study the amination of highly fluorinated aromatic compounds with anhydrous (liquid) ammonia as the shortest way to obtain the monomers of AB and BB types; to develop

special methods for the synthesis of highly fluorinated PI on the basis of obtained monomers; to study the effect of structural factors (isomerism and the nature of aromatic framework, substituents and bridges) on the characteristics of PI.

AMINODEFLUORINATION OF POLYFLUOROAROMATIC COMPOUNDS WITH ANHYDROUS AMMONIA

Polyfluoroarylenediamines used as monomers to obtain PI materials for optoelectronic applications should be highly pure, that is, they should not contain impurities of either monoamines or hydrodefluorinated compounds. This is due to the fact that monoamines terminate the growth of PI chain, while hydrogen-containing fragments of molecules decrease the trans-

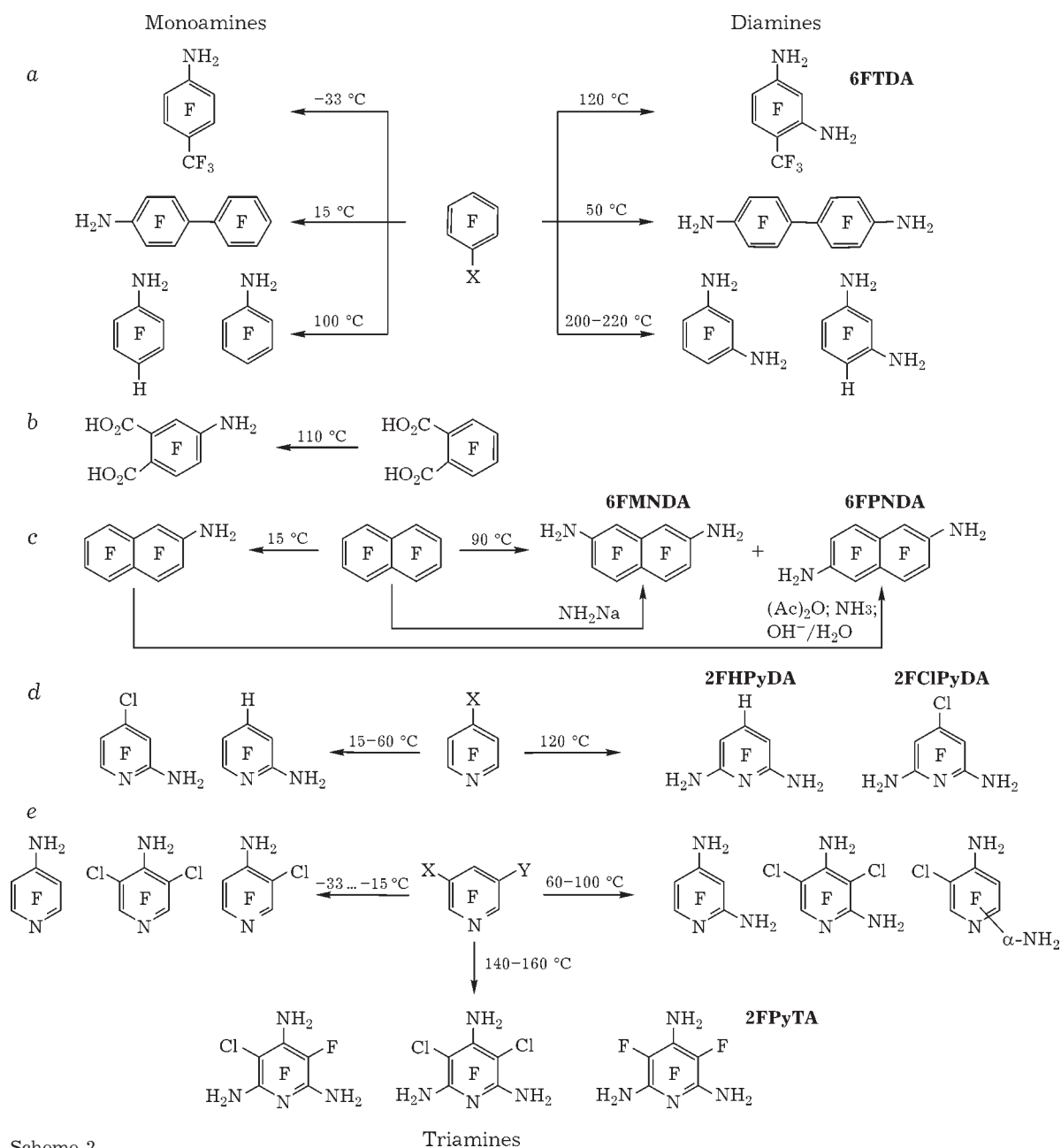


Scheme 1.

parency of PI at the working wavelengths of optical telecommunication devices (the near IR region).

It is known that aminodehalogenation of arenes in aqueous ammonia, which is usually carried out in steel autoclaves at high temperatures (up to 250 °C) is often accompanied by competing transformations, such as hydroxy- and/or hydrodehalogenation of arenes, proceeding with the participation of water and the material of autoclaves. For example, the action of aqueous ammonia on hexafluorobenzene

at 180–220 °C leads to the formation of a mixture of isomeric tetrafluorophenylene diamines and 2,4,5-trifluorophenylene-1,3-diamine. The concentration of the products of hydrodefluorination is essentially dependent on temperature and reaction time, as well as on the concentration of NH_4F (the accompanying product of aminodefluorination process) and Fe^{3+} ion (formed in the oxidation of the autoclave surface). Under rigid conditions, even the product of double defluorination (2,5-difluorophenylene-1,3-diamine) is formed [3].



Scheme 2.

The method of polyfluoroarene amination developed by us is based on the use of anhydrous liquid ammonia as the reagent and reaction medium at the same time. It was demonstrated that in anhydrous ammonia (or in its mixtures with aprotic solvents) in a steel autoclave mono- and bisamination of various polyfluoro(het)arenes proceeds selectively; the products of hydrodefluorination are not formed even at 220 °C.

Under these conditions, aminodefluorination of hexa- and pentafluorobenzenes, octafluorotoluene, decafluorobiphenyl was carried out (Scheme 2, *a*) [4], and also 2,3,5,6-tetrafluoro- and 3-chloro-2,4,6-trifluoropyridine (see Scheme 2, *d*), pentafluoro-, 3,5-dichlorotrifluoro- and 4-chlorotetrafluoropyridines (see Scheme 2, *e*) [5]. Temperature points at which the introduction of the first, second and third amino group into the aromatic ring are carried out vary substantially, which provides the conditions for selective synthesis of mono-, di- and triamino derivatives (using perhalogenopyridines as initial compounds) with high yield and purity.

Aminodefluorination of tetrafluorophthalic acid with anhydrous ammonia leads to the selective synthesis of 4-amino-3,5,6-trifluorophthalic acid with the high yield (see Scheme 2, *b*); isomeric 3-amino acid is not formed [6]. Under the action of dicyclohexylcarbodiimide, aminophthalic acid gets transformed quantitatively into 4-amino-3,5,6-trifluorophthalic anhydride which is the simplest aromatic monomer of AB type.

Monoamination of octafluoronaphthalene with anhydrous ammonia leads to the formation of 2-aminoheptafluoronaphthalene as the major product (preparative yield is 85–90 %), while diamination gives a mixture of isomeric 1,6-, 1,7-, 2,6- and 2,7-diaminonaphthalenes with substantial predominance of the 2,7-isomer (about 70 %) (see Scheme 2, *c*) [7]. For the selective synthesis of perfluorinated diaminonaphthalenes, a method based on reversible modification of amino group was developed. It was shown that the ratio of 2,7/2,5 isomers for amination of 2-X-heptafluoronaphthalenes ($X = \text{NH}$, NH_2 and NHAc) increases with an increase in the electron-donor effect of substituent X. For instance, 2,7-diaminoheptafluoronaphthalene is formed in the reactions of 2-

aminoheptafluoro- or octafluoronaphthalene with excess NaNH_2 in anhydrous ammonia; under these conditions, the amino group in the aromatic ring gets ionised through proton elimination. 2,6-Diaminoheptafluoronaphthalene is formed in the interaction of 2-acetylamidoheptafluoronaphthalene with anhydrous ammonia, followed by hydrolysis of acetylamido group.

In some cases high purity monomers of BB type were isolated using reversible selective complexing with 18-crown-6. The developed procedure allows one to separate target products from the trace amounts of monoamines and to separate the mixtures of isomeric polyfluoroarylenediamines. The selectivity of the formation of crystal associates depends on the enthalpy of melting of the crystal phase: associates possessing higher heat of melting are selectively crystallized from the solutions of the mixtures of isomeric diamines with the lack of the crown ether [4, 7, 8].

Thus, a combination of aminodefluorination of perfluoroarenes by anhydrous ammonia (the amount of the introduced amino groups depends on process temperature) and co-crystallization of arylenediamines with the crown ether (selectivity depends on the relations between the heats of melting of isomeric associates) is an efficient and convenient method to obtain new perfluorinated monomers of BB and AB types.

SYNTHESIS OF NEW POLYIMIDES BASED ON PERFLUORINATED MONOMERS WITH LOW REACTIVITY

The features and regularities of polycondensation of perfluoroarylenediamines possessing low reactivity were studied with the help of ^{19}F NMR spectroscopy and modelling of the internal and end fragments of the polymeric chain. On this basis, special experimental procedures were developed for obtaining highly fluorinated PI (Scheme 3): high temperature solid-phase growth of the polymer chain (method *a*) and a single-reactor synthesis of PI in the melt of benzoic acid (methods *b*, *c*). PI based on new monomers of BB type and the first aromatic PI of AB type containing no hydrogen atoms were synthesized. The structure of polymers was characterized by spectral meth-



Scheme 3.

ods (NMR, IR, and MALDI TOF) and elemental analysis.

Highly fluorinated PI containing hexafluoronaphthylene fragment in the main chain were obtained through two-stage polycondensation of hexafluoronaphthylene-2,6- and hexafluoronaphthylene-2,7-diamines (6FPNDA and 6FMNDA, respectively) or their mixture with 4,4'-oxydiphthalic dianhydride (ODPA) [9] (see Scheme 3, method *a* and Table 1). Reaction conducted in amide solvents at 80 °C for 40–50 h leads to the formation of low molecular mass prepolymers containing amino acid and imide fragments inside the chain; the anhydride end groups in these molecules are hydrolysed to a substantial extent. Solvent removal followed by slow heating of prepolymer mass from 150 to 250 °C provides the growth of the polymer chain. Soluble PI with the number mean molecular mass $\bar{M}_n = 3500\text{--}7500$ were obtained using this operation. The mass spectra of PI contain a repeating fragment with the period m/z 540 amu, equal to the molecular mass of the structural unit of $\text{C}_{26}\text{H}_6\text{F}_6\text{N}_2\text{O}_5$ polymer. So, fragmentation and destruction of macromolecules do not occur during solid-phase polycondensation. Subsequent heating of PI to 350 °C causes further increase in the molecular mass of the polymer and allows obtaining insoluble polyimide films. Increased ability of 6FMNDA (in comparison with 6FPNDA) to undergo polycondensation is due to the absence of conjugation of amino groups, as conjugation prevents the formation of high molecular mass PI. It should be stressed that the use of available and cheap mixture of monomers 6FMNDA + 6FPNDA (at a ratio of 3 : 1) provides the formation of PI with the molecular mass and properties comparable with those of structurally uniform polymer ODPA/6FMNDA.

Aromatic monomers with electron-deficient framework or substituents, such as 2,4-diaminohexafluorotoluene (6FTDA), diamines of polyfluorinated pyridines and AB type monomer, are substantially less reactive than the derivatives of perfluoronaphthalene. These diamines interact with ODPA or 4,4'-hexafluoroisopropylidenediphthalic anhydride (6FDA) very slowly: the condensation solution obtained in amide solvents at 80 °C for 75 h contains the initial diamine (up to 15 %) and compounds with

one modified amino group. Molecules with two modified amino groups practically are not formed at the liquid-phase stage. The solid-phase chain growth procedure, even in the cyclic mode (repeated dissolution of PI followed by heating) results only in the formation of low molecular mass PI. For this reason, high temperature polycondensation in high boiling solvents with the addition of acid catalysts appears to be more practical for polycondensation of monomers with low reactivity. In particular, the melt of benzoic acid, which is not toxic in comparison with high boiling chlorine-containing solvents and can be easily separated from the product, may be used as efficient catalytic medium for a single-stage synthesis of fully imidized PI.

Highly fluorinated PI based on 6FDTA and ODPA were synthesized by polycondensation in the melt of benzoic acid with azeotropic distillation of water at the initial stage [10] (see Scheme 3, method *b*). Synthesis without water removal leads to the formation of co-polyimide co-PI) which contains two types of polyfluoroaromatic fragments originating from 6FTDA and 2,4,5-trifluorophenylene-1,3-diamine (3FPDA) (see Scheme 3, method *c*, Table 1). The appearance of modified fragment in the PI chain is due to hydrolysis of CF_3 group and subsequent decarboxylation, both proceeding at high temperature under the action of water on the monomer, oligomer or polymer. The composition of co-PI depends on polycondensation conditions. For instance, the fraction of the 3FPDA fragment increases when the reaction is performed in a sealed ampoule.

Polyimides containing the pyridine fragment with variable γ -substituent in the main chain were synthesized using method *c* from 6FDA and 3,5-difluoropyridylene-2,6-diamines: $\gamma\text{-X} = \text{H}$ (2FHPyDA), Cl (2FCIPyDA), NH_2 (2FPyTA) [11] (see Scheme 3). The molecular masses of these PI depend on the electron effect of γ -substituent and the solubility of the polymer. It was established that exclusively α -amino groups participate in the polycondensation of 2FPyTA. This most reactive monomer gives the PI with $\bar{M}_n = 17\,000$ within 3 h at 135 °C, after which the reaction mixture gets separated into two phases, and polycondensation stops. For polyimide based on less reactive 2FHPyDA,

TABLE 1

Characteristics of polyimides based on highly fluorinated monomers of BB and AB types

Parameters	ODPA /6FMNDA [9]	ODPA /6FPNDA [9]	ODPA /6FMNDA + 6FPNDA (75 + 25) [9]	6FDA /6FTDA [10]	6FDA /6FTDA + 3FPDA (85 + 15) [10]	6FDA /6FTDA + 3FPDA (40 + 60) [10]	ODPA /6FTDA [10]	ODPA /6FTDA + 3FPDA (70 + 30) [10]	6FDA /2FHPyDA [11]	6FDA /2FCIPyDA [11]	6FDA /2FPyTA [11]	PI-AB [6]
\overline{M}_n	(>10 000)	(≤10 000)	(>10 000)	19 000	<15 000	<15 000	15 000	<15 000	30 000	12 000	17 000	1800
Concentration of F, %:												
found	20.3	20.2	20.3	35.5	33.5	30.1	22.1	18.0	26.5	25.0	25.8	26.6
calculated	21.1	21.1	21.1	35.7	34.7	31.9	22.6	18.9	27.5	25.9	26.8	28.6
Solubility:												
amide solvents	–	–	–	+	+	+	+	+	+	+	gel	+
CHCl ₃ , Me ₂ CO	–	–	–	+	–	–	+	–	–	–	–	+
Vitrifying temperature (T_v), °C	abs.	abs.	abs.	346	332	327	328	318	342	324	abs.	abs.
Temperature of 5 % mass loss, °C:												
inert atmosphere	562	549	570	528	523	511	549	524	519	504	511	476
oxidative atmosphere	527	504	511	515	506	492	534	474	512	496	511	478
Film quality	T, F	O, C	T, F	T, F	–	–	T, F	–	–	–	–	T, C
Transmission cut-off ($\lambda_{\text{cut-off}}$), nm	362	–	371	311	–	–	360	–	–	–	–	400
Transmission at 450 nm, %	88/20	–	83/20	98/10	–	–	94/10	–	–	–	–	73/40
Dehumidification, %	0.30	–	0.35	0.35	–	–	0.54	–	–	–	–	–
Dielectric constant (ϵ)**	–	–	–	2.86/2.92	–	–	2.87/3.27	–	–	–	–	–
Dielectric loss (tg δ)**	–	–	–	0.008/0.0013	–	–	0.008/0.0016	–	–	–	–	–

Notes. 1. \overline{M}_n is numerical average molecular mass established as the relation between internal and end fragments (¹⁹F NMR data); for PI based on 6FMNDA and 6FPNDA, this value was estimated by extrapolation of the value for soluble samples. 2. Qualitative solubility was determined visually as dissolved completely (+), insoluble (–). 3. T – transparent, O – opaque, F – flexible, C – fragile. 4. Abs. – absent, dash – no data.

* The second value is film thickness, μm .

** The first value is for dry film, the second value is for the film kept at relative humidity 50 %.

$\overline{M}_n = 30\,000$ is achieved within 24 h under step-wise heating to 190 °C; PI remains soluble in the melt of benzoic acid. Perhalogenated 2FCIPyDA forms PI having relatively low molecular mass because of the minimal nucleophilic properties of amino groups (see Table 1).

Polycondensation in the melt of benzoic acid was used to obtain the first perfluorinated aromatic PI of AB type with 10–12 links in the chain [6] (see Scheme 3, method c). Further growth of macromolecules is limited by the low reactivity of amino group, limited mobility of the end groups of the rigid polymer chain, and partial destruction of anhydride fragments – about 30 % of macromolecules have decarboxylated end fragments. The MALDI TOF mass spectrum of this PI contains the groups of signals with the period m/z 199 (the mass of the structural unit $C_8F_3NO_2$) corresponding to the molecules of PI and its monodecarboxylated analogue.

CHARACTERISTICS OF POLYFLUOROAROMATIC POLYIMIDES

The data on the thermal and thermooxidative stability of PI, hydrophobicity, optical and dielectric properties are presented in Table 1. The data obtained demonstrate the effect of structural factors (aromatic framework, isomerism, substituents and bridges) on the properties of PI.

It was established that the isomerism of hexafluoronaphthylene fragment affects the quality of PI film. The ODPa/6FPNDA film is fragile, which is likely to be due to relatively low molecular mass. In addition, this film is not transparent because of the formation of specific crystal structure that is characteristic of PI with *para*-substituted fragments of the framework. Quite contrary, the asymmetric position of the *meta*-substituted fragments in the PI chain of ODPa/6FMNDA enhances its flexibility and free volume. As a result, this PI forms a flexible and transparent film characterized by the low value of transmission cut-off ($\lambda_{\text{cut-off}}$). It should be noted that the presence of *para*-substituted fragments in the ODPa/(6FMNDA + 6FPNDA) co-PI at the ratio of 3 : 1 insignificantly worsens the optical characteristics of the film.

It was established that the combination of asymmetric pendant CF_3 group and fluorine atoms (a fragment of 6FTDA) is extremely favourable for the characteristics under investigation. Polyimides based on 6FTDA demonstrate good solubility in organic solvents including such a low-boiling solvent as chloroform, and have high vitrifying temperature, thermal and thermooxidative stability. Due to the high fluorine content, flexible PI films have low dielectric constant and dehumidification. All these characteristics get improved with the substitution of the oxygen bridge by hexafluoroisopropylidene passing from ODPa/6FTDA to 6FDA/6FTDA. In addition, due to the electron and steric effects, CF_3 groups decrease the formation of inter- and intrachain charge-transfer complexes, which provides the characteristics that are extremely important for optoelectronic materials: colourless 6FDA/6FTDA films, excellent transparency in the UV and visible spectral regions, and very low $\lambda_{\text{cut-off}}$ value.

Perfluorinated aromatic PI of AB type does not have flexible bridges and pendant groups in the structure but demonstrates good solubility in various organic solvents. In spite of relatively low molecular mass, this PI possesses satisfactory thermal and thermooxidative stability. The $\lambda_{\text{cut-off}}$ value for this compound is shifted to longer wavelengths in comparison with that for highly fluorinated CF_3 -containing PI. One cannot exclude that this effect is due to the conjugation of chromophore groups. In the spectrum of PI in the near IR region, absorption of the harmonics related to C–H and O–H bonds is absent, which characterizes perfluorinated PI of AB type as promising materials for optoelectronic systems.

It was established that PI 6FDA/2FHPyDA, 6FDA/2FCIPyDA and 6FGA/2FPyTA are close in thermal and thermooxidative stability to PI based on polyfluoroarylenediamines. Other properties of PI containing pyridine fragment are still under investigation. The presence of potentially modifiable fragments, such as nitrogen atom in the aromatic framework and a substituent (H, Cl, NH_2) in *g* position, in the structure of these polymers provides the possibility of chemical transformations directed at rendering promising properties to these polymers.

CONCLUSION

The shortest cheap method of selective synthesis of new perfluorinated aromatic monomers of BB and AB types through direct amination of polyfluorinated derivatives of benzene, naphthalene and pyridine with anhydrous ammonia used as the reagent–medium system was developed. Practically reasonable and efficient methods of obtaining PI based on diamines with low reactivity were developed. New highly fluorinated PI were developed, possessing a set of valuable key (optical and dielectric) and technological (solubility in organic solvents and thermal stability) properties, which characterizes them as promising materials for high-technological applications.

REFERENCES

- 1 EP Pat. No. 1275679; *Chem. Abstrs.*, 138 (2003) 90676; Kobayashi J., Matsuura T., Sasaki S., Maruno T., *Appl. Opt.*, 37 (1998) 1032.
- 2 Hougham G., in G. Hougham (Ed.), *Fluoropolymers 2: Properties*, Kluwer Acad./Plenum Publ., New York, 1999, p. 233; Ando S., Matsuura T., Sasaki S., *Ibid.*, pp. 277–303.
- 3 Vaganova T. A., Kusov S. Z., Rodionov V. I., Shundrina I. K., Malykhin E. V., *Russ. Chem. Bull., Int. Ed.*, 58 (2009) 823.
- 4 Vaganova T. A., Kusov S. Z., Rodionov V. I., Shundrina I. K., Malykhin E. V., *Russ. Chem. Bull., Int. Ed.*, 56 (2007) 2239.
- 5 Kusov S. Z., Rodionov V. I., Vaganova T. A., Shundrina I. K., Malykhin E. V., *J. Fluorine Chem.*, 130 (2009) 461.
- 6 Vaganova T. A., Shundrina I. K., Kusov S. Z., Karpova E. V., Bagryanskaya I. Yu., Malykhin E. V., *J. Fluorine Chem.*, 135 (2012) 129.
- 7 Vaganova T. A., Kusov S. Z., Rodionov V. I., Shundrina I. K., Sal'nikov G. E., Mamatyuk V. I., Malykhin E. V., *J. Fluorine Chem.*, 129 (2008) 253.
- 8 Kusov S. Z., Gatilov Yu. V., Bagryanskaya I. Yu., Romanenko G. V., Vaganova T. A., Shundrina I. K., Malykhin E. V., *Russ. Chem. Bull. Int. Ed.*, 59 (2010) 382; Vaganova T. A., Kusov S. Z., Shundrina I. K., Gatilov Yu. V., Malykhin E. V., *J. Mol. Struct.*, 995 (2011) 109.
- 9 Shundrina I. K., Vaganova T. A., Kusov S. Z., Rodionov V. I., Karpova E. V., Koval V. V., Gerasimova Yu. I., Malykhin E. V., *J. Fluorine Chem.*, 130 (2009) 733.
- 10 Shundrina I. K., Vaganova T. A., Kusov S. Z., Rodionov V. I., Karpova E. V., Malykhin E. V., *J. Fluorine Chem.*, 132 (2011) 207.
- 11 Vaganova T. A., Shundrina I. K., Kusov S. Z., Rodionov V. I., Malykhin E. V., *preliminary data*.