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Synthesis and characterization of highly fluorinated diamines and benzoxazines derived therefrom

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ABSTRACT

A novel method for the synthesis of highly fluorinated benzoxazines in a high yield derived form a α,ω-diamine-polyfluoroalkane and α,ω-dianiline-polyfluoroalkane is described. The synthetic method increases the yield by 20% and reduces the reaction time by 90% in comparison to the currently known method, allowing synthesis of large quantity of highly fluorinated diamines. The diamines are used as the precursors for benzoxazine compounds. The diamines and benzoxazines are obtained in high yield and purity. The structures are characterized by nuclear resonance spectroscopy (NMR) and Fourier transform infrared spectroscopy (FT-IR).

1. Introduction

Fluorine-containing polymers have a number of unique properties [1]. The effect of the incorporation of fluorine into the polymer backbone for improving the thermal stability has been investigated [2–4]. The enhancement of thermal stability is a result of the strength of the C–F bond [5]. Other properties such as chemical stability, oxidative stability and melting point can also be improved by fluorine substitution [6,7]. The decrease in dielectric constant makes fluorocompounds very attractive to the electronics industry. The low moisture absorption due to the hydrophobicity of fluorine-contained polymers has also been reported [8,9]. The low moisture content of fluoropolymers is also favorable to dielectic constant reduction. In addition; fluorine incorporation can influence flammability, refractive index, friction coefficient, adhesion and crystallinity. A large variety of high performance fluorinated-polymers such as polyimides, polyether and polybenzoxazoles have been synthesized and characterized [10].

Benzoxazine chemistry of small compound has been known for more than 50 years [11]. However, the usefulness of benzoxazines as precursors for a class of thermosetting phenolic resins with excellent mechanical and thermal properties has not been recognized until recently [12]. Polybenzoxazines possess several outstanding properties such as near-zero shrinkage after curing, high thermal stability and low water absorption. Additionally, benzoxazines have high glass transition temperature [13].

Fluorinated benzoxazine monomers derived form pentafluoraniline and bisphenol-A had been obtained in high yield in an acid medium. It was found that the pH value of the reaction medium is the controlling factor in the yield for the compounds from very weak amines [14]. Another fluorinated benzoxazine was synthesized using bisphenol-AF and trifluoromethyl aniline (F-1). A copolybenzoxazine of F-1 and bisphenol-A/aniline (BA-a) showed a dielectric constant of 2.36 on 50/50% (w/w) blend [15]. The thermal properties of BA-a and bisphenol AF aniline (BAF-a) type benzoxazine were studied. It was found that, under the same curing conditions, the T_g of the polybenzoxazine derived from BAF-a was about 40–50 °C higher than the BA-a based polybenzoxazine. Thermogravimetric analysis showed an increase from 290 °C to 330 °C in the 1% weight loss temperature. The char yield, as defined by the residual weight obtained at 800 °C under inert environment, of the fluorinated benzoxazine was about 30% higher than the non-fluorinated counterpart [16]. Lin et al. showed that fluorinated aromatic amine component leads to higher thermal stability as well as lower dielectric constant in polybenzoxazine [17].

Commercial availability of highly fluorinated diamines is poor while their dialcohol counterparts that can be the precursor for the diamines are readily available. Scale-up of highly fluorinated diamines cannot be easily achieved using the known methods. We studied a novel approach to synthesize these diamines with high yield and ease of scale-up. Several methods have been used to synthesized amines from alcohol. The Mitsunobu reaction is one of the most common methods to obtain amines with the dehydration of alcohols when treated with diethyl azodicarboxylate and triphenylposphine on a mild to neutral condition in an anhydrous aprotic solvent at room temperature [18]. The most notable

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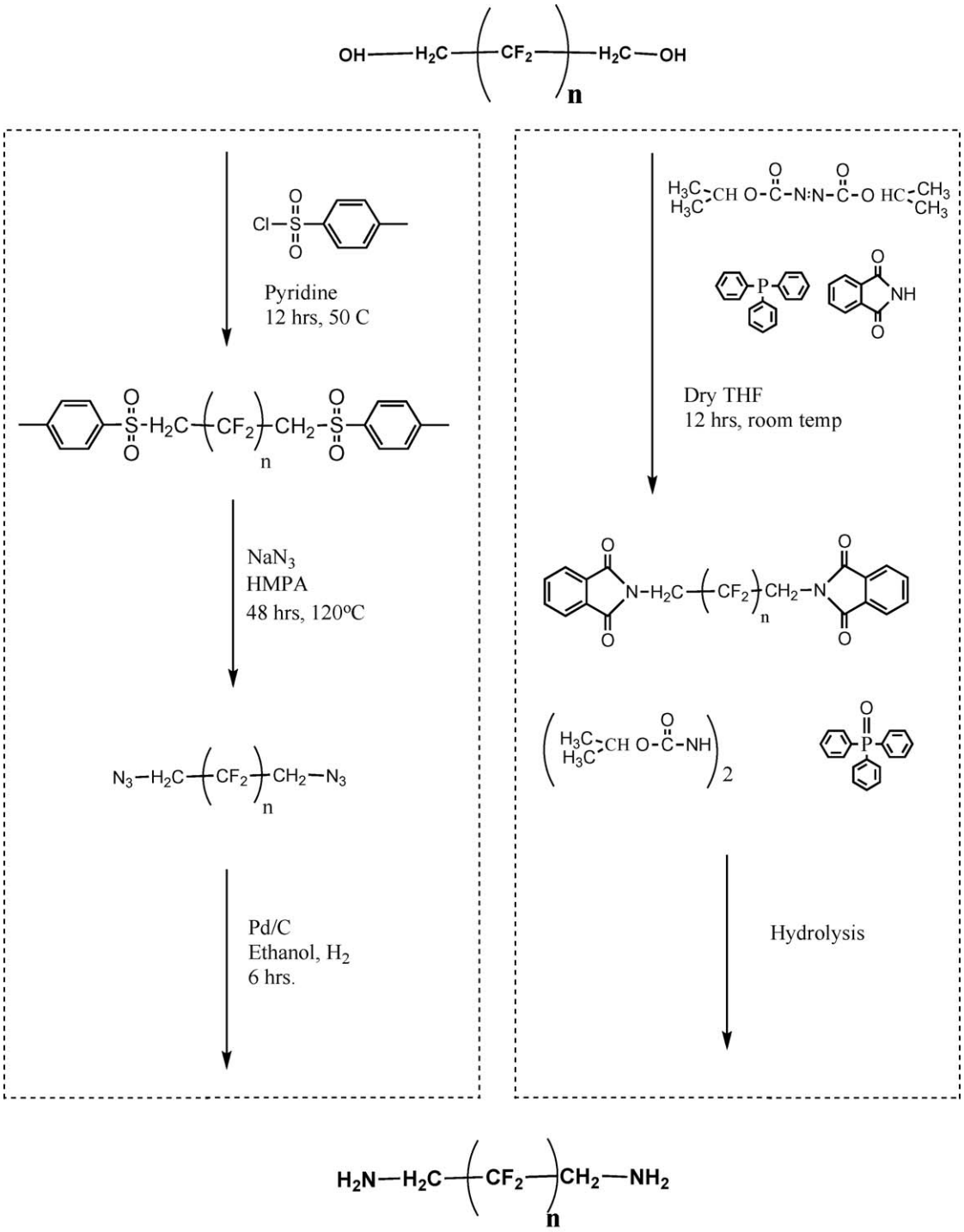
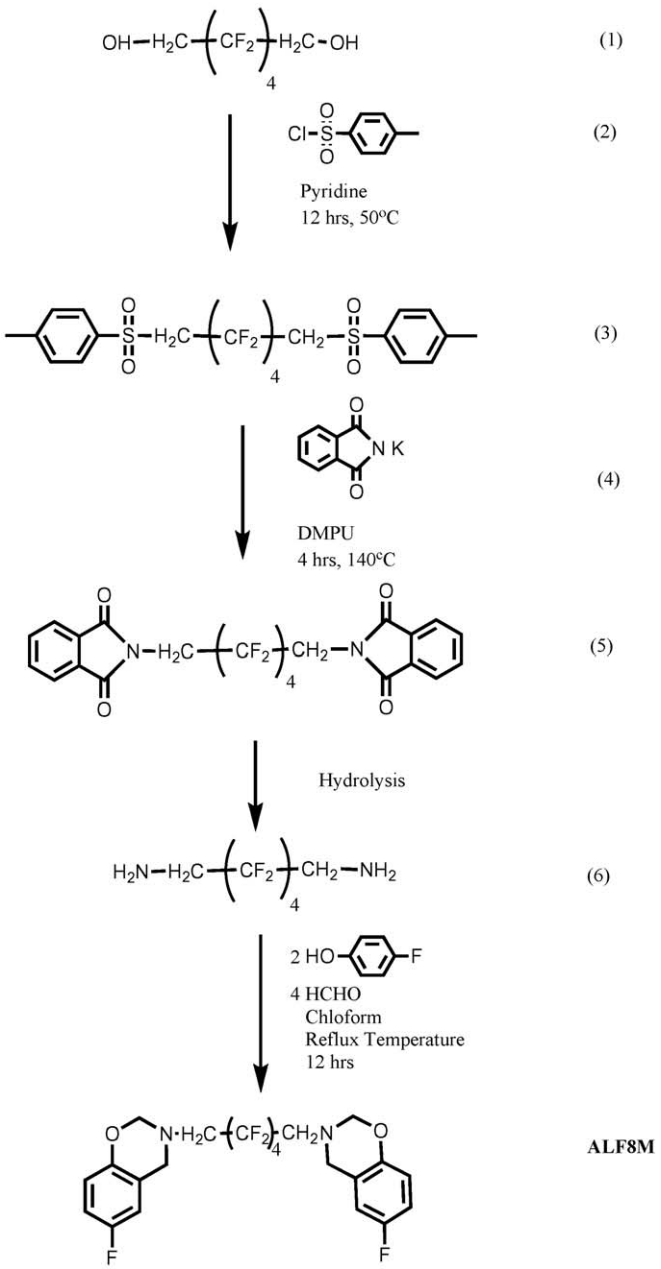
disadvantage of the Mitsunobu reaction is the difficulty in isolating the product from the unreactive materials and from the oxidized/reduced compounds. The purification method usually includes a chromatographic column, which makes it unsuitable for large quantity synthesis. In the preparation of *N*-alkylimides, general yield is close to 85%, whereas 40–60% is obtained when azides are used instead of imides. Scheme 1 shows the general procedure for the Mitsunobu reaction as well as the main products from the reaction.

Another popular method, shown in Scheme 1, first converts the alcohol into the alkyl halide or sulfonate, which is then reacted with metal azide to give an alkyl azide. This is reduced to the amine by one of a variety of reagents. In this case, the intermediates have to be isolated and problems associated with handling toxic and potentially explosive (alkyl azide) are encountered [19]. This method has been used to synthesize symmetric diamines in hexamethylphosphoramide (HMPA); however, this method requires isolation of the azide and the use of hydrogen, which are not the first choice for industrial process [20,21]. The method used in this paper is a novel combination of both. We replaced the sodium azide with a phthalamide potassium salt, which is more reactive than the phthalamide used in the Mitsunobu reaction, to



Scheme 1. Synthesis of the aliphatic amine from an alcohol. On the left side the synthesis with sodium azide; on the right Mitsunobu reaction.



Scheme 2. Synthesis of the fluorinated aliphatic amine-based benzoxazine monomer proposed in this work.

obtain the same product with high purity and without chromatographic column separation, as shown in Scheme 2. We also have replaced the HMPA that is a carcinogenic solvent with 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU).

The Ullmann coupling has been used to produce fluroalkyl substituted aromatic compound. This reaction has been previously applied to the synthesis of α,ω-diarylperfluroalkenes from α,ω-diiodofluroalkanes and iodoaromatic compound with copper in polar aprotic solvent [22].

In this paper, two highly fluorinated diamines have been synthesized in high yield and purity. Since highly fluorinated diamines are not commercially available, the emphasis of this paper is placed on the easier preparation method than the existing methods of such amines as precursors to many compounds. The newly adopted approach will allow easy scale-up in production. The diamines were used to obtain novel benzoxazine monomers with 4-flurophenol and paraformaldehyde in chloroform. Thus, discussing polymerization of benzoxazines is beyond the scope of this paper. However, application examples of using highly fluorinated diamines for preparation of polymerizable benzoxazine monomers are shown. Using these newly developed diamines, polybenzoxazines with oxazine rings in the polymer main chain have been developed and reported elsewhere [23]. The crosslinked polybenzoxazines with dielectric constant as low as 2.2 has been prepared.

2. Experimental

2.1. Materials

Reagents used for syntheses are commercially available. 2,2,3,3,4,4,5,5-Octafluro-1-6-hexanodiol (96%) and 1,6-diiodoperfluorohexane were obtained from Oakwood Products Inc. *p*-toluenesulfonyl chloride (98%), phthalimide potassium salt (98%), paraformaldehyde (95%), 4-iodoaniline (97%), 4-fluorophenol (99%), 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) (98%), pyridine (98%), and hydrazine hydrate (50–60%) were purchased from Aldrich. Except for the 4-iodoaniline all of these were used without further purification. 4-Iodoaniline was purified by dissolving it in ethyl ether and stirring with activated charcoal for 8 h, filtered out and evaporated under vacuum.

2.2. Equipment

The structure of the compound was verified by proton (^{1}H), carbon (^{13}C) and fluorine (^{19}F) nuclear magnetic resonance spectroscopy (NMR) using Varian Inova NMR spectrometer at proton frequency of 600 MHz as well as the corresponding carbon and fluorine frequencies at room temperature using deuterated chloroform as solvent. Signals were averaged from 256 transients for ^{1}H NMR and ^{19}F NMR, and 1024 transients for ^{13}C NMR to yield spectra with sufficient signal-to-noise ratio. A relaxation time of 10 s was used for the integrated intensity determination. ^{19}F-decoupled NMR spectra were recorded using the waltz16 composite pulse decoupling.

Infrared spectra were recorded using a Bomem Michelson MB100 Fourier transform infrared (FT-IR) spectrometer with deuterated triglycine sulfate (DTGS) detector under dry air purge. Co-addition of 32 scans at a 4 cm^{-1} resolution was used.

2.3. Synthesis

The synthetic routes are shown is Schemes 2 and 3.

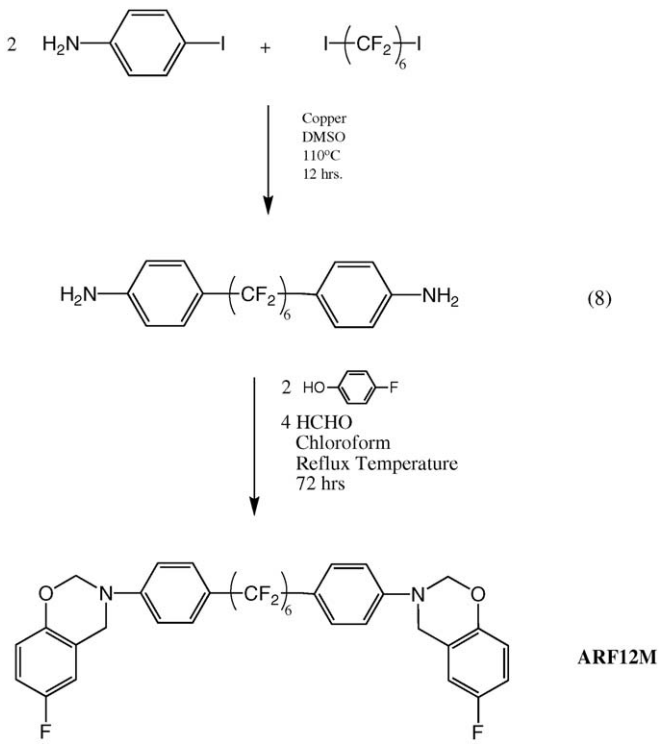
2.3.1. Synthesis of 2,2,3,3,4,4,5,5-octafluorohexane-1,6-ditosyl (3)

A solution of 2,2,3,3,4,4,5,5-octafluoro-1,6-hexanediol (**1**) (25.0 g, 95.4 mmol) in pyridine (20 ml) was added to a solution of *p*-toluenesulfonyl chloride (**2**) (43.0 g, 225 mmol) in pyridine (30 ml) and stirred overnight at 50 °C. Cold water was added and the precipitates were filtered out and recrystallized twice from methanol. White crystals were obtained in 87% yield (44.2 g, 82 mmol).

^{1}H NMR (Chloroform-d): δ = 7.78 (d, Ar, 4H), 7.36 (d, Ar, 4H); 4.41 (t, S–CH_2–CF_2, 4H), 2.45 (s, CH_3–Ar, 6H). ^{19}F NMR (Chloroform-d) δ = −119.79 (s, CH_2–CF_2–CF_2, 4F), −123.65 (s, CH_2–CF_2–CF_2, 4F).

2.3.2. Synthesis of 2,2′-(2,2,3,3,4,4,5,5-octafluorohexane-1,6-diyl)diisoindoline-1,3-dione (5)

Phthalimide potassium salt (**4**) (20.0 g, 108 mmol) was added to a solution of **3** (25 g, 46.5 mmol) in 25 ml of DMPU and the temperature was increased from room temperature to 140–150 °C, the mixture was stirred for 3–4 h under nitrogen. The reaction was characterized by the formation of yellow foam. The reaction was stopped when no more foam was produced. The reaction products



Scheme 3. Synthesis of the fluorinated aromatic-amine based benzoxazine monomer proposed in this work.

were cooled to room temperature and brine (300 ml) was added. The solids were filtered out. A light brown powder was obtained at a yield of 90%; however, according to the ^{1}H NMR spectra, the compound was obtained in 90–95% purity for the repeat trials as shown in Fig. 1. The compound was used on the next step without any further purification (21.7 g, 41.7 mmol).

^{1}H NMR (Chloroform-d): δ = 7.91 (s, Ar, 4H), 7.24 (s, Ar, 4H); 4.37 (t, S–CH_2–CF_2, 4H). ^{19}F NMR (Chloroform-d) δ = −116.14 (s, CH_2–CF_2–CF_2, 4F), −123.44 (s, CH_2–CF_2–CF_2, 4F).

2.3.3. Synthesis of 2,2,3,3,4,4,5,5-octafluorohexane-1,6-diamine (6)

5 (25 g, 48.0 mmol) was treated with hydrazine hydrate in 50 ml of pure ethanol under reflux for 4 h. The solvent was evaporated under vacuum. The pure product was obtained as a clear liquid by vacuum distillation. After several days at room temperature, crystals are formed. White crystals; 72% yield (9.0 g, 34.5 mmol).

^{1}H NMR (Chloroform-d): δ = 3.26 (t, N–CH_2–CF_2, 4H). ^{19}F NMR (Chloroform-d) δ = −122.29 (s, CH_2–CF_2–CF_2, 4F), −124.39 (s, CH_2–CF_2–CF_2, 4F).

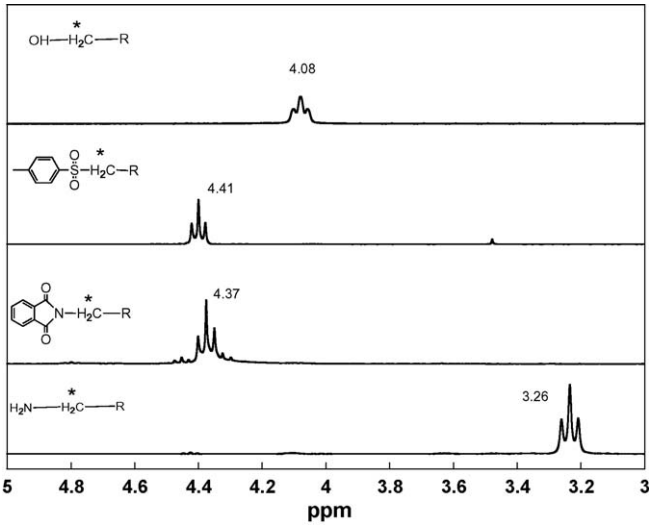


Fig. 1. ^{1}H NMR spectra in $CDCl_3$ of the fingerprint region for the methylene group of the compounds **1**, **3**, **5** and **6**.

2.3.4. Synthesis of 3,3′-(2,2,3,3,4,4,5,5-octafluorohexane-1,6-diyl)bis(6-fluoro-3,4-dihydro-2H-benzooxazine) (ALF8M)

Paraformaldehyde (2.3 g, 77 mmol) and 4-fluorophenol (4.3 g, 38.5 mmol) were added to a solution of **6** (5 g, 19.2 mmol) in chloroform (50 ml) and catalytic amount of triethylamine. The mixture was stirred for 8 h at reflux temperature. The solvent was evaporated under vacuum. The solids were redissolved in ethyl ether and washed with an aqueous solution of 0.1N NaOH, dried over sodium sulfate, filtered out, and evaporated under vacuum, and recrystallized twice from 1-butanol. 80% yield (5.72 g, 10.7 mmol).

Anal. Calcd: C, 49.63; H, 3.41; N, 5.26. Found: C, 49.13; H, 3.70; N, 5.21.

^{1}H NMR (Chloroform-d): δ = 6.86 (td, Ar, 2H), 6.77 (dd, Ar, 2H), 6.69 (dd, Ar, 2H), 4.81 (s, O–CH_2–N<, 4H), 4.09 (s, >N–CH_2–Ar, 4H), 3.38 (t, >N–CH_2–CF_2, 4H). ^{19}F NMR (Chloroform-d) δ = −118.59 (s, CH_2–CF_2–CF_2–, 4F), −122.64 (s, Ar–F, 2F), −123.67 (s, CH_2–CF_2–CF_2–, 4F),

2.3.5. Synthesis of 4,4′-(perfluorohexane-1,6-diyl) dibenzeneamine (8)

Copper–bronze was activated as reported elsewhere [24]. 4-Iodoaniline (7.5 g, 34.3 mmol) and copper–bronze (10 g) were stirred in 20 ml of degasified DMSO at about 110 °C under argon. A solution of diiodoperfluorohexane (10 g, 18.0 mmol) in 10 ml of degassed DMSO was added slowly below the surface of the solution and the mixture was stirred for 12 h. The product was isolated by treating the mixture with water and ethyl ether, and filtered out to remove the cuprous salts. The organic phase was washed with brine until free of DMSO. The solution was dried over sodium sulfate with activated charcoal, filtered out, and evaporated under vacuum. Recrystallization from hexane yielded yellowish crystals in 91% yield (7.5 g, 15.6 mmol).

^{1}H NMR (Chloroform-d): δ = 7.33 (d, Ar, 4H), 6.69 (d, Ar, 4H), 3.95 (s, –NH_2, 4H). ^{19}F NMR (Chloroform-d) δ = −109.85 (s, Ar–CF_2–CF_2, 4F), −121.85 (s, Ar–CF_2–CF_2–, 4F), −122.54 (s, Ar–$(CF_2)_2$–CF_2–, 4F).

2.3.6. Synthesis of 3,3′-(4,4′-(perfluorohexane-1,6-diyl)bis(4,1-phenylene))bis(6-fluoro-3,4-dihydro-2H-benzoxazine) (ARF12M)

A 20% (w/w) solution of paraformaldehyde (1.24 g, 41.2 mmol), 4-fluorophenol (2.31 g, 20.6 mmol), and **8** (5 g, 10.3 mmol) in chloroform was prepared. The mixture was stirred for 72 h at reflux temperature. The solvent was evaporated under vacuum. The solids were redissolved in ethyl ether and washed with an aqueous solution of 0.1N of NaOH, dried over sodium sulfate, filtered out and evaporated under vacuum. The solids were washed with 1-butanol and dried. A powder in 79% yield was obtained (6 g, 8.0 mmol).

Anal. Calcd: C, 53.98; H, 2.93; N, 3.70. Found: C, 52.95; H, 3.05; N, 3.53.

^{1}H NMR (Chloroform-d): δ = 7.48 (d, Ar, 4H), 7.11 (d, Ar, 4H), 6.86 (td, Ar, 2H), 6.77 (dd, Ar, 2H), 6.69 (dd, Ar, 2H), 5.34 (s, O–CH_2–N<, 4H), 4.65(s, >N–CH_2–Ar, 4H). ^{19}F NMR (Chloroform-d) δ = −110.34 (s, Ar–CF_2–CF_2, 4F), −121.81 (s, Ar–CF_2–CF_2–, 4F), −122.35 (s, Ar–$(CF_2)_2$–CF_2–, 4F), −122.65 (s, Ar–F, 2F).

3. Results

The synthesis of two new highly fluorinated benzoxazine monomers has been performed using **6** and **8** as flexible diamines.

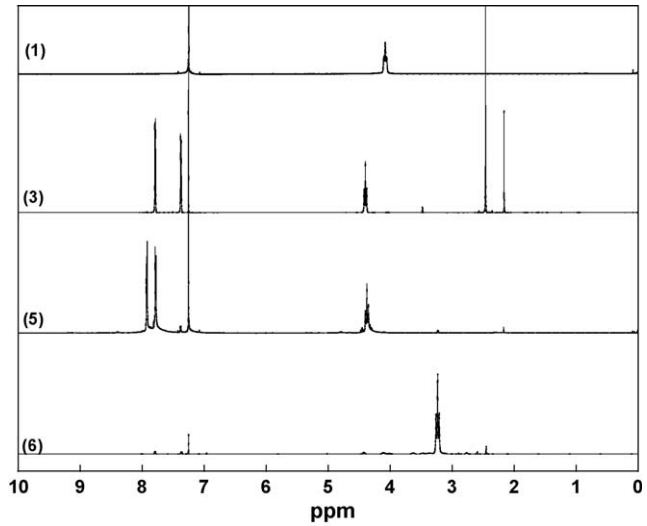


Fig. 2. ^{1}H NMR spectra in $CDCl_3$ of the compounds **1**, **3**, **5** and **6**.

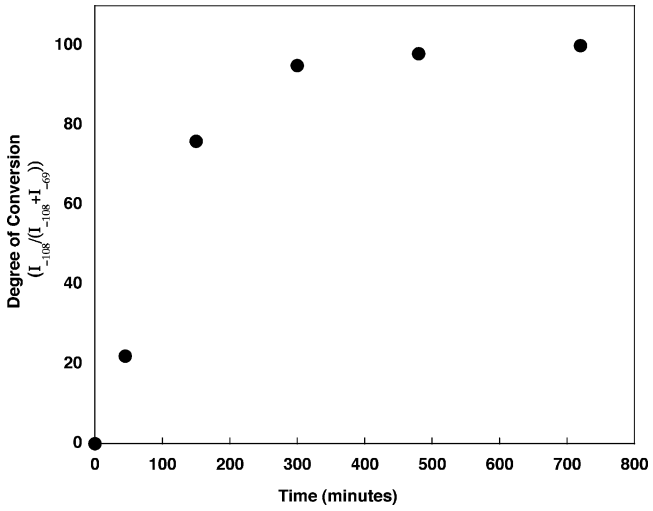


Fig. 4. Degree of conversion of 1-6-diiodoperflurohexane in DMSO at 120 °C with copper–bronze.

3.1. Synthesis and characterization of the fluorinated diamines

For the synthesis of the 1,6-di-aniline-polyflurohexane, Scheme 2, a novel synthetic method was developed in this paper. The method presents several advantages over the previously reported methods. The first step consists of the substitution of the OH group for the tosyl leaving group that will be used for the nucleophilic substitution. This method has been performed before and the results obtain in this paper were similar to those reported [21,23]. The key element of our new method comes from the second step that involves the substitution of the tosyl group with the imide group. The use of phthalamide potassium salt instead of sodium azide eliminated the problems associated with the handling of toxic and potentially explosive azide compounds and produced the α,ω-di-imide-polyfluoroalkane that is the same compound obtained with the Mitsunobu reaction. By exchanging these two nucleophiles, the reaction time decreased into one-tenth from 48 h to 3–4 h while the yield increased by 13% from 77% to 90% [21]. This reaction was characterized by the formation of a yellow foam that started producing at 140 °C. Once the production of the foam stops, the substitution seems to slow down drastically. The integrated intensity ratio of the ^{1}H NMR spectra of the methylene group at 4.41 ppm for compounds **3** and 4.37 ppm for compound **5** indicated that most of the product is formed during the first 3 h. The use of longer reaction times, 12–36 h produced a black insoluble compound with a decrease in the overall yield. A black insoluble compound is also produced if the temperature of the reaction is higher than 160 °C. Once the reaction products were cooled to room temperature, brine was added and brown solids were precipitated out. The solids were mostly 1,6-di-imide-polyfluorohexane (**5**) and small amount of the unreacted 1,6-di-tosyl-polyfluorohexane (**3**). This can be seen in Fig. 1 where most of the triplet at 4.41 ppm had disappeared and a new triplet at 4.37 ppm appeared, indicating that the reaction was successful. Additionally, Fig. 2 shows two doublets at 7.91 ppm and 7.24 ppm in the aromatic region, indicating the absence of unreacted phthalamide. The ^{1}H NMR spectrum of compound **5** in Fig. 2 shows two small resonances around 2 ppm and 3 ppm; these frequencies come from the remaining DMPU. Unlike the Mitsunobu reaction, only the water-soluble phthalamide salt was used as a reactive material having a yield higher than 90%. No further purification was needed.

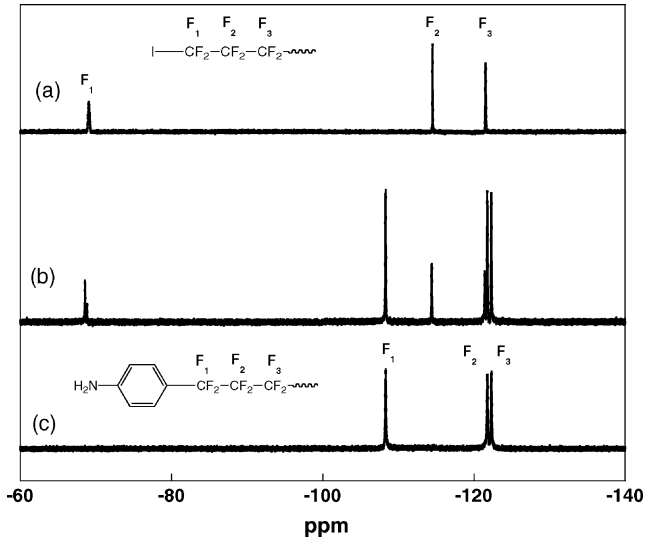


Fig. 3. ^{19}F NMR spectra in DMSO of the reaction of the 1-6-diiodoperflurohexane and 4-iodoaniline in DMSO at 120 °C with copper–bronze at different times. (a) At 0 min; (b) at 2.5 h and (c) 12 h.

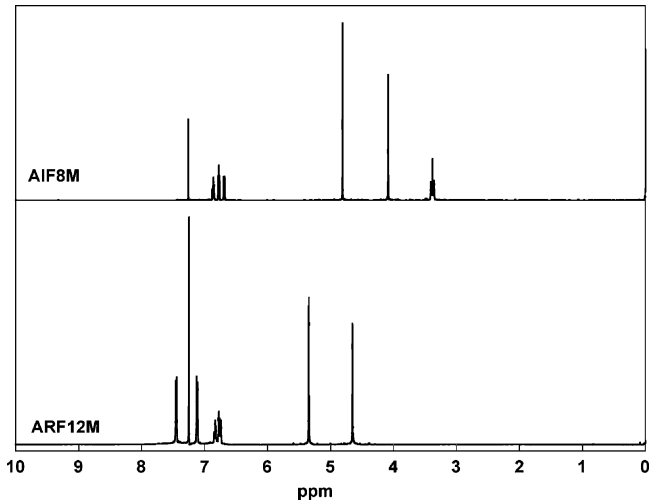


Fig. 5. ^{1}H NMR spectra in $CDCl_3$ of the benzoxazine monomers derived from fluorinated diamines.

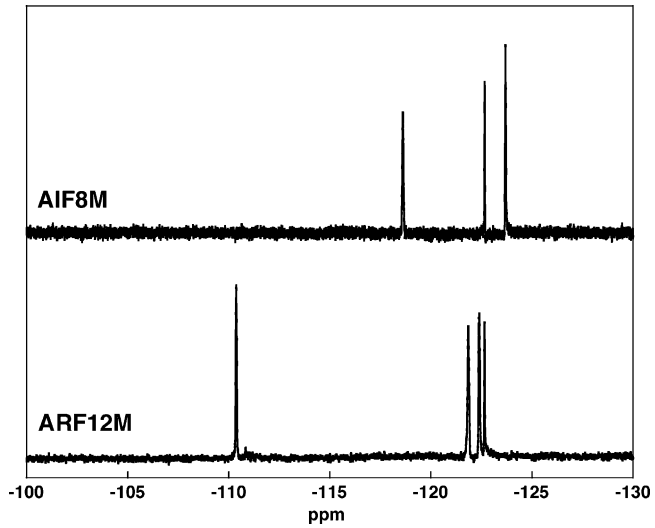


Fig. 6. ^{19}F NMR spectra in $CDCl_3$ of the benzoxazine monomers derived from fluorinated diamines.

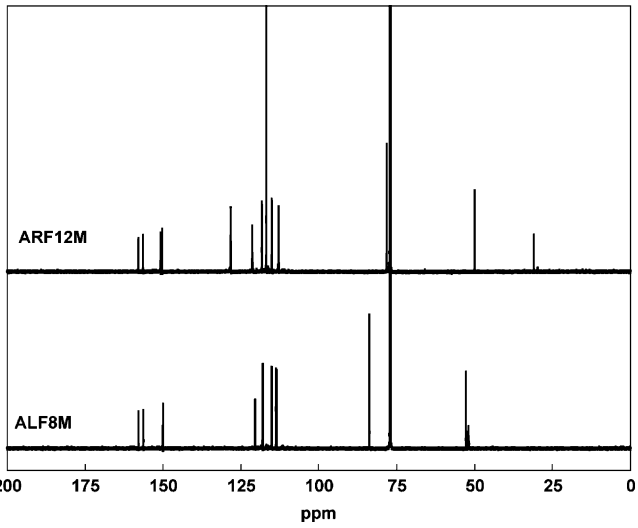
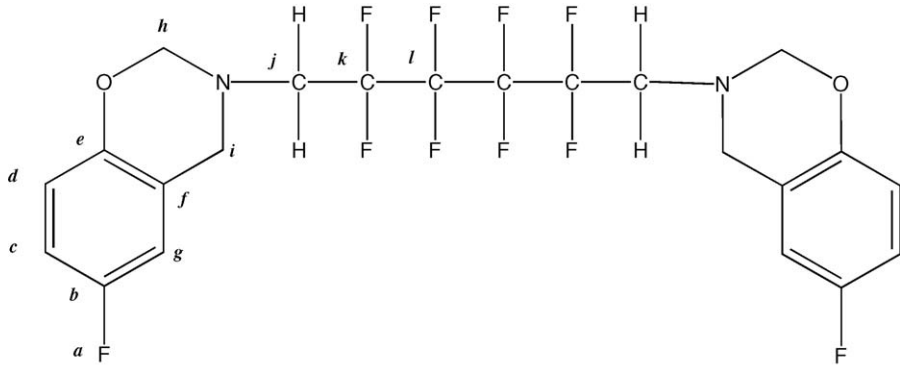


Fig. 7. ^{13}C NMR spectra in $CDCl_3$ of the benzoxazine monomers derived from fluorinated diamines.

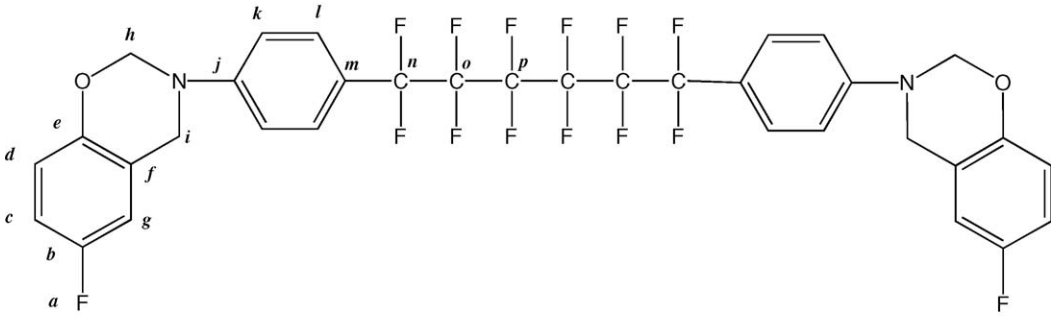
Once the 1,6-di-imide-polyfluorohexane was obtained, it was hydrolyzed with hydrazine hydrate in ethanol to obtain the 1,6-di-amine-polyfluorohexane on a quantitative yield, but other hydrolysis methods can also be used [25]. With the hydrolysis process used, there was no need for the reduction with hydrogen and palladium. The ^1H NMR spectra of the compounds obtained in each step of Scheme 2 are shown in Fig. 2.

The synthesis of 1,6-di-amine-polyfluorohexane (**8**), Scheme 3, was followed by ^{19}F NMR spectroscopy and the results indicate that, when the reaction temperature is below 120 °C, the structure of the fluoroalkyl group remains unchanged and biaryls are absent. But, if the temperature is higher than 120 °C the biaryls are formed and the dehalogenation of the fluoroalkyl occurs with the formation of allyl compounds. The reaction was followed by the



	^1H	^{13}C	^{19}F
a	-	-	-122.64
b	-	157.88	-
c	6.86	113.77	-
d	6.77	120.51	-
e	-	156.29	-
f	-	150.10	-
g	6.69	115.22	-
h	4.81	83.79	-
i	4.09	52.77	-
j	3.38	52.04	-
k	-	118.10	-118.59
l	-	116.90	-123.67

Fig. 8. Chemical shift for the ^1H, ^{13}C and ^{19}F analysis of the benzoxazine monomer in $CDCl_3$ at room temperature.



	^{1}H	^{13}C	^{19}F
a	-	-	-122.64
b	-	158.01	-
c	6.83	115.03	-
d	6.78	116.19	-
e	-	150.82	-
f	-	121.47	-
g	6.74	115.18	-
h	5.34	78.27	-
i	4.65	50.07	-
j	-	156.42	-
k	7.48	116.88	-
l	7.11	128.36	-
m	-	150.28	-
n	-	118.35	-110.34
o	-	113.06	-121.81
p	-	112.91	-122.35

Fig. 9. Chemical Shifts for the ^{1}H, ^{13}C and ^{19}F analysis of the benzoxazine monomer in $CDCl_3$ at room temperature.

decrease of the intensity and frequency change of the terminal –CF_2– resonance. This resonance is observed at −69.03 ppm when it is located next to an iodine group and −108.33 ppm when aniline is the contiguous group, as shown in Fig. 3. After 45 min, the conversion to **8** is 22% and 10% of unreacted diiodofluoroalkyl had shifted its resonance from −69 ppm to −67 ppm. This is due to the formation of the fluoroalkylcoper solvated complex that is an intermediate. This complex then coordinates with the aromatic halide followed by an exchange of ligands at copper [22]. At 2.5 h, almost all unreacted diiodofluoroalky is on the form of the metallocomplex, and the degree of conversion is 75%. After 12 h, there is no evidence of any unreacted or solvated complex left in the mixture. The degree of conversion is shown in Fig. 4. Although ^{19}F NMR shows 100% conversion within the detection limit of the spectrum obtained, the overall yield was close to 90% due to the fact that it was not possible to recover the entire product with solvent extraction.

3.2. Synthesis and characterization of the fluorinated diamine-based benzoxazine monomers

3.2.1. Nuclear magnetic resonance spectroscopy

All benzoxazine monomers were obtained in satisfactory yields and high purity. The ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra are shown in Figs. 5–7. The assigned resonances are listed in Figs. 8 and 9.

The synthesis of the **ALF8M** was carried out in chloroform. During this step the concentration was an important factor. If the concentration was higher than 20% (w/w) an insoluble gel was formed after 30 min of reaction. This gel, characterized by a ^{1}H NMR resonance at 4.46 ppm, is very likely to be an infinite network of 1,3,5-triaza compound that is an intermediate in the benzox-

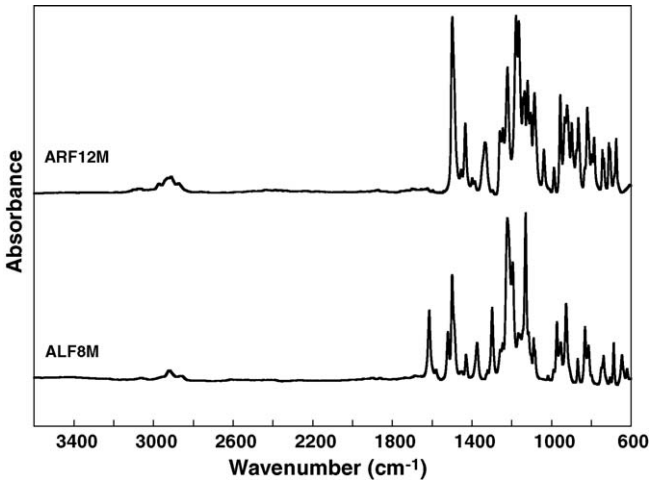


Fig. 10. Fourier transform infrared spectra of the benzoxazine monomers.

azine synthesis [26]. Once this gel is formed, it is not possible to break the triaza ring and the formation of the oxazine ring does not proceed. On the other hand, if the concentration is lower than 10%, only a small amount of solids are observed and the reaction is almost complete after 48 h.

The synthesis of **ARF12M** was carried out in chloroform. During this step the concentration was again an important factor. After 2 h of reaction a swollen-insoluble compound was formed and a ^{1}H NMR resonance at 4.91 ppm was found. This resonance value corresponds to the 1,3,5-triaza structure that is an intermediate on the benzoxazine synthesis [26]. Unlike the triaza compound formed with the aliphatic amine (**6**), this can be broken by decreasing the pH of the solution to 1 or 2 or by increasing the concentration of the solution [14]. If the concentration is 30% (w/w) or higher, the resonance at 4.91 ppm decreases while, at the same time, two new resonances at 5.3 ppm and 4.6 ppm start to appear. After 48 h of reaction, most of the resonance at 4.91 ppm has despaired.

The difference in the stability of the 1,3,5-triazas formed from compound **6** and compound **8** is because 1,3,5-triaza compound from aliphatic amines are extremely weak base and only very small quantities of monoprotonated cations are sufficient to inhibit further base hydrolysis. They are, therefore, exceptionally stable and can be hydrolyzed only after several days under very acidic conditions using an aqueous solution of HCl. On the other hand 1,3,5-triaza compound from aromatic amines can be hydrolyzed due to the fact that the aromatic ring allows the stabilization of the amino-carbonium ion with its resonance structure the iminium ion [26,27].

The ^{1}H NMR spectra, Fig. 5, suggest that the hydrogenated group next to the amine, either methylene or phenyl, has a greater influence in the chemical shift than the fluorinated portion of the amine. The typical characteristic chemical shift for the oxazine methylene groups in **ALF8M** are 4.09 ppm and 4.81 ppm that are very close to the aliphatic-diamine based benzoxazine, whose two peaks appear at approximately 4.0 ppm and 4.9 ppm [28]. For compound **ARF12M**, the typical peaks are located at 4.65 ppm and 5.34 ppm and are similar to BA-a benzoxazine, which is characterized for the peaks at 4.6 ppm and 5.3 ppm [26]. The absence of any proton resonances between the two frequencies indicates the absence of a 1,3,5-triaza type compound. This fact indicates that the purification was successful at separating any intermediate compounds. Furthermore the absence of any Mannich bridge protons of open oxazine ring around 3.7 ppm indicates the absence of oligomeric species. The integration analysis of the proton resonances shows the closed-ring content of each compound better than 99%.

3.2.2. Infrared spectroscopy

The infrared spectra of the benzoxazine monomers are presented in Fig. 10. There are a number of infrared bands that are common to both spectra. The presence of the benzoxazine ring aromatic ether is confirmed by the absorbance peak at 1223 cm^{-1} and 1038 cm^{-1}, due to the C–O–C antisymmetric and symmetric stretching modes, respectively [29]. The absorbance at 932 cm^{-1} and 926 cm^{-1} are characteristic modes of benzene with an attached oxazine ring. The band at 1501 cm^{-1} is characteristic of asymmetric trisubstituted benzene. The bands between 1200 and 1100 are assigned to the CF_2 stretching [30]. The absence of hydroxyl groups is confirmed by the lack of intermolecular hydrogen bonded group, which appears between 3600 cm^{-1} and 3200 cm^{-1} [31]. This further confirms that the purification has successfully eliminated any unreacted phenol and oligomers. Compound **9** shows a strong band at 1615 cm^{-1} which is related to the –C=C– "quadrant stretching" of the para-substitued benzene ring.

4. Conclusions

Two novel, highly fluorinated benzoxazine monomers have been successfully synthesized and characterized. A new synthetic method that leads to high yield with shorter reaction time and allows synthesis of large quantity of highly fluorinated diamines has been proposed. These diamines were used as the precursors for the newly developed benzoxazine compounds. The structure of these diamine-based benzoxazine monomers has been verified by ^{1}H, ^{13}C and ^{19}F NMR and infrared spectroscopy.

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