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Low dielectric material from novel core-fluorinated polybenzoxazine

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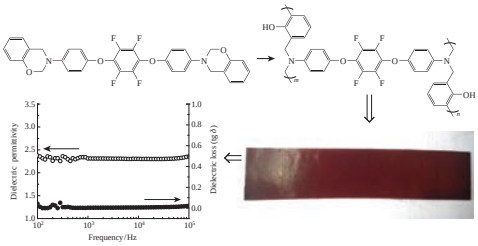
Cross-linked polybenzoxazine with substantially reduced dielectric constant and loss factor (2.3 and 0.0041 at 10 kHz, respectively) based on a novel core-fluorinated bis(benzoxazine)-containing monomer with 1,4-tetrafluorobenzene dioxyphenylene central unit was prepared. Herewith, this fluorinated polybenzoxazine possesses low water absorption (0.5%) and high degree of cross-linking (98.5%).



Readily available polybenzoxazines (PBOs) show excellent properties such as high thermal stability, glass transition temperature, char yields, low flammability, moisture absorption and excellent electrical insulation properties.[1–9] These characteristics make PBOs suitable for the preparation of flame-resistant film materials, coatings, adhesives and composites for a variety of applications, for example, in electronics and aerospace industries.[3] It is known that incorporation of fluorinated fragments into a polymeric structure, and in particular into PBOs, can enhance its performance on various properties simultaneously.[10–12] Fluorine-containing PBOs (FPBOs) possess reduced surface free energy and dielectric constants and some other improved properties.[3,13] This makes FPBOs attractive as materials with the low dielectric constant (k < 3.0) for electronic and microelectronic industries.[3] The fluorine atoms are introduced into the PBOs using monomers containing perfluorinated aliphatic fragments (CF_3 groups, hexa- or tetrafluoromethylene units), alicyclic (octafluorocyclopentene unit), partially fluorinated (mono-, di- and trifluorophenylene units) or perfluorinated (pentafluorophenylene or octafluorobiphenylene) aromatic moieties.[1,3,14,15]

It is important to note that the high brittleness is a major drawback associated with either aromatic non-fluorinated PBOs or fluorinated PBOs.[1] Generally, there are several ways to improve their mechanical properties, such as the use of oligomers[16,17] or prepolymers[18,19] containing 1,3-benzoxazine rings or benzoxazine-based monomers containing flexible aliphatic moieties for PBO synthesis.[1,16] However, incorporation of the flexible aliphatic fragments into the PBO structures decreases their thermal stability,[1,16] whereas employment of benzoxazine-containing oligomers[16,17] or prepolymers[18,19] for obtaining PBOs is typically tedious and time-consuming.[16] The incorporation of the flexible ether linkages along with core-fluorinated fragments into the polymer chains is one of the ways to improve their mechanical properties without impairing the other properties.[10] Meanwhile, the FPBOs containing the ether linkages along with core-fluorinated fragments still lacks in the literature. Furthermore, the introduction of low polarization C–O bonds can reduce the dielectric constants of polybenzoxazine materials.[3]

Here we report on the synthesis of aromatic core-fluorinated FPBO prepared from newly synthesized bis(1,3-benzoxazine)-containing monomer with 1,4-tetrafluorobenzene (TFB) dioxyphenylene central unit. Properties of the synthesized polymer, such as dielectric characteristics and water absorption, were thoroughly investigated.

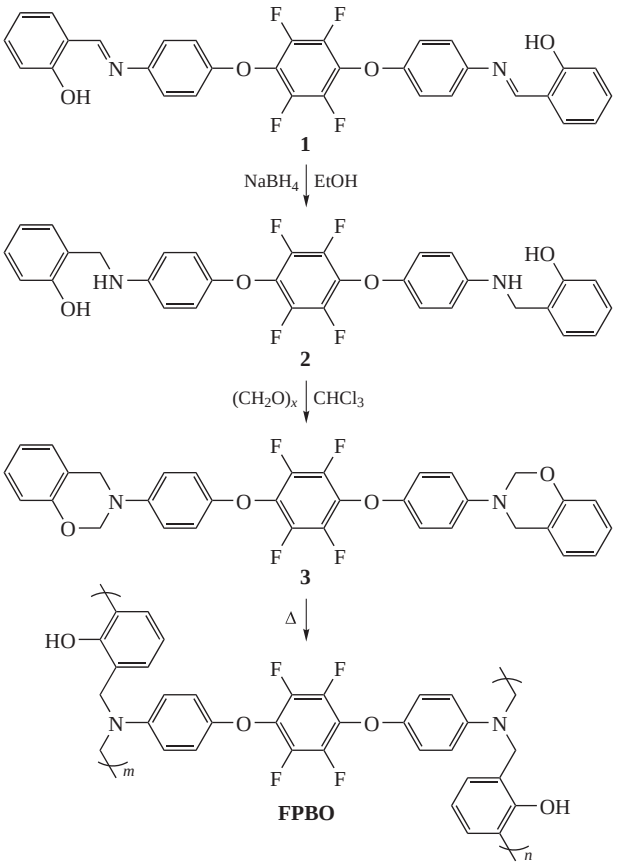
In order to prepare FPBO (Scheme 1), the core-fluorinated bis(1,3-benzoxazine)-containing monomer **3** was synthesized in two steps.† In the first step, compound **2** with TFB dioxyphenylene central unit was obtained by reductive amination of the previously prepared azomethine-containing bisphenol **1**.[20] In the second step, 1,3-benzoxazine moieties of monomer **3** were formed *via* cyclization of CH and NH groups by paraformaldehyde (see Scheme 1).

The structures of the synthesized compounds were determined by FTIR, ^{1}H, ^{13}C and ^{19}F NMR spectroscopy techniques (Figures S1–S4, Online Supplementary Materials). Thus, for example, the appearance of characteristic peaks in ^{1}H NMR spectrum of compound **2** at 6.05 and 4.14 ppm, attributed to NH and CH_2

† Fourier transform infrared (FTIR) spectra of synthesized compounds were recorded with a TENSOR 37 spectrometer in the absorption region of 600–4000 cm^{-1}. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker Avance DRX 500 MHz and Bruker Avance 250 MHz spectrometers at room temperature with DMSO-d_6 as a standard. Fluorotrichloromethane was used as the internal standard for ^{19}F NMR.

Starting 2,2′-{(2,3,5,6-tetrafluoro-1,4-phenylene)bis[oxy-4,1-phenylene-nitrilo-(*E*)-methylylidene]}diphenol **1** was synthesized as reported.[20]

2,2′-[(2,3,5,6-Tetrafluoro-1,4-phenylene)bis(oxy-4,1-phenyleneimino-methylene)]diphenol **2**. $NaBH_4$ (0.211 g, 5.59 mmol) was added in three portions with 2-h intervals to a stirred solution of compound **1** (1 g, 1.747 mmol) in 50 ml of absolute ethanol. The reaction mixture was further stirred at room temperature for 10 h and then poured into water with stirring. The obtained precipitate was collected by filtration and dried *in vacuo* at 80 °C. Yield 0.941 g (93%), mp 201–204 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 9.51 (s, 2H, OH), 7.18 (d, 2H, Ph, J 7.16 Hz), 7.03 (t, 2H, Ph, J 7.16 Hz), 6.90 (d, 4H, Ph, J 8.41 Hz), 6.81 (d, 2H, Ph, J 7.47 Hz), 6.71 (t, 2H, Ph, J 7.47 Hz), 6.56 (d, 4H, Ph, J 8.09 Hz), 6.05 (s, 2H, NH), 4.14 (s, 4H, CH_2). ^{13}C NMR (125.73 MHz, DMSO-d_6) δ: 155.54, 148.83, 145.82, 143.54, 141.08, 130.69, 128.79, 128.01, 125.98, 119.26, 116.74, 115.39, 113.48, 42.45. ^{19}F NMR (188.14 MHz, DMSO-d_6) δ: –154.28 (s, 4F, Ph). FTIR (ν/cm^{-1}): 3400–3200 (OH), 3263 (NH), 2956–2867 (CH), 1510–1492 (Ph), 1249 (C–N), 1203 (Ph–O–Ph), 1008–998 (C–F).



Scheme 1

groups, confirms reduction of imine linkage of compound **1**. Simultaneously, the presence of characteristic peaks in ^{1}H NMR spectrum of compound **3** at 5.39 and 4.61 ppm, standing for the O–CH_2–N and Ph–CH_2–N groups of oxazine ring, respectively, verifies the formation of benzoxazine rings. Two singlets at 79.77 and 49.86 ppm in its ^{13}C NMR spectrum correspond to carbon methylene groups of the oxazine ring. As expected, compounds **2** and **3** containing TFB fragments show a singlet peak in their ^{19}F NMR spectra from four equivalent fluorine atoms.

The FTIR spectrum of compound **2** (Figure 1) contains characteristic absorption bands at 3400–3200, 3263, 2956–2867, 1510–1492, 1249, 1203 and 1008–998 cm^{-1}, corresponding to vibrations of OH, NH, CH, C=C_{arom}, C–N, Ph–O–Ph and C–F groups, respectively (Figure 1). The absorption bands in the FTIR spectrum of compound **3** at 1365, 1201, 1043, 1010–991 and 945 cm^{-1} correspond to C–N, Ar–O–C, Ar–O–C, C–F and N–C–O groups, respectively (Figure 1).[3,21,22] Therefore, according to spectral measurements no extraction or purification is required

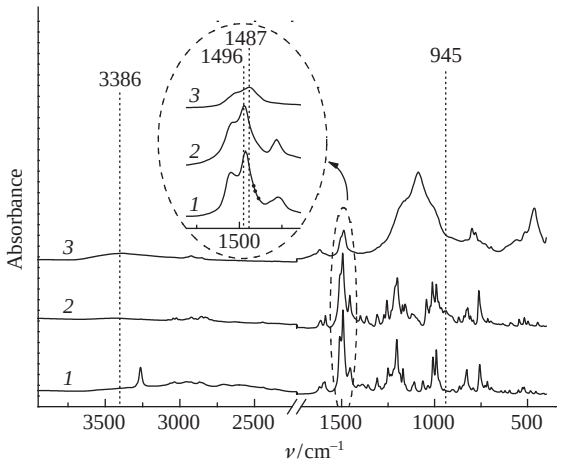


Figure 1 FTIR spectra of monomers (*1*) **2**, (*2*) **3** and (*3*) polymer FPBO.

to yield high-purity benzoxazine-based monomer **3**. Note that Mannich synthesis of benzoxazines (one-step procedure) often requires additional extraction operations to remove insoluble oligomers and unreacted monomers.[23]

The melting and curing behavior of the novel bis(benzoxazine) monomer **3** was studied by differential scanning calorimetry (DSC).‡ The value of melting point of monomer **3** is 205 °C. There is one exothermic peak on the DSC thermogram of the monomer **3**, which is associated with the ring-opening polymerization of benzoxazine fragments.[3] The DSC data show that the onset of the exothermic process begins at 265 °C and reaches its maximum at 279 °C. Thus, our studies showed that the synthesized monomer **3** has wide processing temperature and can be effectively polymerized by a melting method.

Consequently, we used the melting method to obtain FPBO (Scheme 1).§ The FPBO was synthesized by the thermal ring-opening polymerization reaction of the bis(benzoxazine) monomer **3** in air without addition of any extra catalysts and solvents.

The FTIR spectrum of FPBO after polymerization of monomer **3** (see Figure 1) deprives the characteristic absorption band at 945 cm^{-1} of the benzene ring fused with oxazine one. The band at 1496 cm^{-1} of the trisubstituted benzene ring reduced its intensity. On the other hand, new absorption bands at 3386 cm^{-1} of the phenolic hydroxyl group and at 1487 cm^{-1} of the tetrasubstituted benzene ring appeared, suggesting that the polymerization of compound **3** occurred and afforded cross-linked FPBO.[3,21,22] The gel content of FPBO is 98.5% that confirms its densely cross-linked structure.

Thermal stability of FPBO was evaluated by thermogravimetric analysis (TGA) under air conditions. The resulting polymer exhibited good thermal stability and high char yield. A 5% weight loss of the polymer was found to occur at 390 °C. The char yield at 800 °C of FPBO was 43 wt%.

Generally, the dielectric constant of PBOs is approximately 3.0−3.5 at 1 MHz, which is slightly higher than that of typical low dielectric constant materials (k < 3.0).[3] The dependence of the dielectric constants of the FPBO on the frequency of the

*3,3'-[(2,3,5,6-Tetrafluoro-1,4-phenylene)bis(oxy-4,1-phenylene)]bis-3,4-dihydro-2*H*-1,3-benzoxazine* **3**. Compound **2** (1.000 g, 1.734 mmol) and 50 ml of chloroform were introduced into a 100 ml round bottom glass flask equipped with a condenser and a magnetic stirrer. Then 0.110 g (3.470 mmol) of paraformaldehyde was added. The mixture was stirred at room temperature for 6 h and then refluxed for 24 h. After drying with $MgSO_4$, chloroform was evaporated. The residue was dried *in vacuo* at 40 °C. Yield 0.990 g (95%), mp 205 °C (DSC) and an exothermic peak temperature of 280 °C was obtained. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.06–7.10 (m, 12 H, Ph), 6.85 (m, 2 H, Ph), 6.74 (d, 2 H, Ph, J 6.02 Hz), 5.39 (s, 4 H, CH_2), 4.61 (s, 4 H, CH_2). ^{13}C NMR (125.73 MHz, DMSO-d_6) δ: 154.36, 151.71, 144.74, 143.73, 141.27, 130.47, 128.16, 127.64, 121.60, 120.96, 119.73, 116.67, 116.49, 79.77, 49.86. ^{19}F NMR (188.14 MHz, DMSO-d_6) δ: –154.96 (s, 4 F, Ph). FTIR (ν/cm^{-1}): 1365 (C–N), 1201 (Ar–O–C, asym.), 1043 (Ar–O–C, sym.), 1010–991 (C–F), 945 (N–C–O).

‡ For DSC thermogram of monomer **3**, see Online Supplementary Materials.

§ *Preparation of FPBO film*. The monomer **3** was casted into teflon petri, melted, and subjected to a step-curing procedure at 50, 100, 150, 200, 250 °C in an air-circulating oven. The sample was annealed for 1 h at each temperature and then for 30 min at 300 °C for final polymerization. After that, the FPBO film was slowly cooled to room temperature within several hours to obtain their thermosets. After curing, stiff brown film was obtained. FTIR (ν/cm^{-1}): 3400–3200 (OH), 1487 (trisubstituted benzene ring stretching), 1244–929 (C–O–C, C–O–C, C–F), 798 (C–H).

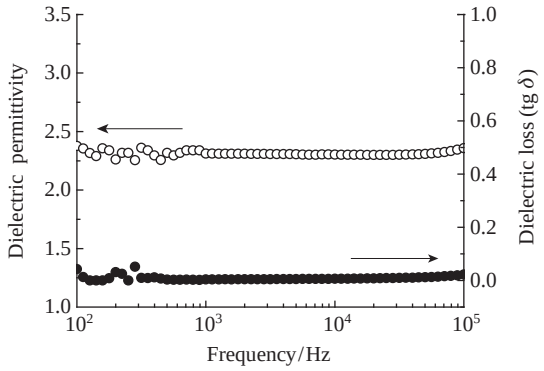


Figure 2 Frequency dependencies of the dielectric constant and loss factor of FPBO.

applied field was studied at room temperature (25 °C) with the frequency range of 0.1 to 100 kHz (Figure 2).¶

It is important that dielectric constant and loss factor of the polymer remain almost constant in the frequency range. The dielectric constant for the polymer FPBO is 2.3 at 10 kHz. The loss factor is also an essential feature of interlevel dielectric materials for microelectronic applications. Thus, FPBO film has low loss factor (0.0041 at 10 kHz) (see Figure 2). Note that the dielectric constant of the obtained FPBO is fairly low, which indicates that this fluorinated polybenzoxazine system can be used as microelectronic packaging material.[3]

The water absorption, an important characteristic of materials with the low dielectric constant, is required to be below 1% since the water possesses large dielectric constant value (78.5 at 25 °C).[13] The obtained FPBO has low water absorption (0.51%) ability due to its hydrophobic nature.††

In conclusion, core-fluorinated bis(benzoxazine) monomer **3** with TFB dioxyphenylene central unit was successfully prepared in two steps. Novel cross-linked polymer based on this new core-fluorinated compound was obtained by thermal ring-opening polymerization. The FPBO film has the low dielectric constant and loss factor (2.3 and 0.0041 at 10 kHz, respectively) at room temperature. In addition, the obtained cross-linked polymer with the high level of hydrophobicity displayed excellent frequency stability of the dielectric properties.

¶ For more detail, see Online Supplementary Materials.

†† The percentage of water absorption is $[(W_2 - W_1)/W_1] \times 100\%$, where W_1 and W_2 are the weight (in grams) of the sample before and after immersion in water, respectively.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2017.01.012.

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