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Synthesis of new cross-linked copolymer from bisphenol A–aniline based benzoxazine and *meta*-linked fluorinated poly(arylene ether)

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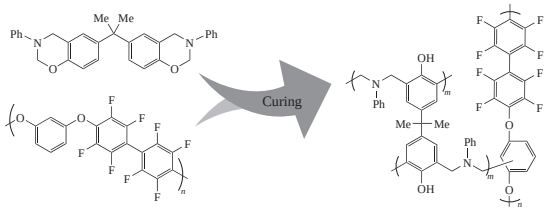
New fluorinated cross-linked polybenzoxazine-based copolymer was obtained as mechanically stable free-standing film from the reaction of bisphenol A–aniline based benzoxazine with *meta*-linked fluorinated poly(arylene ether).

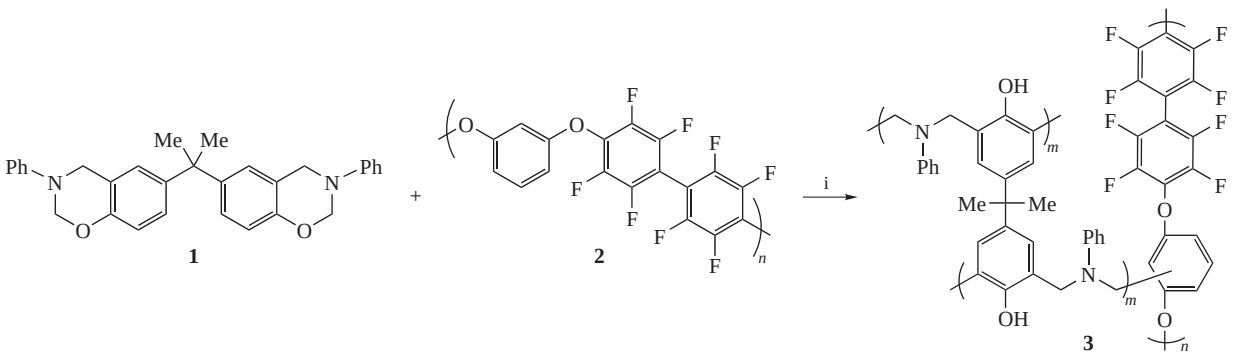


Polybenzoxazines (PBZ) have attracted attention due to their promising characteristics, such as thermal stability with 5% weight loss temperatures above 450 °C, glass transition temperatures exceeding 360 °C, char yields above 50% at 800 °C, low flammability with limiting oxygen index values higher than 27, improved hydrophobicity illustrated by water contact angles more than 90° and relative permittivity as low as ~2.5 at 1 MHz as well as negligible moisture absorption.[1,2]

Despite these properties, the application of PBZ in electronic and aerospace areas is hampered by their brittleness, typical of most thermosets. In particular, the low impact resistance of PBZ materials[1,2] complicates the production of so-called mechanically stable free-standing films, *i.e.* films capable of existing without support. Several ways to improve the mechanical properties of PBZ materials are known, such as their synthesis from oligomers or prepolymers bearing benzoxazine rings, from benzoxazine-based monomers with flexible aliphatic fragments or, alternatively, production of PBZ-based copolymers.[1,3]

The PBZ-based copolymers have been obtained by polymerization of benzoxazines with bismaleimides, cyanate esters, polycaprolactones, polyarylenesulfones, polyimides or epoxides.[1,4–9] However, the known approaches negatively affect the thermal and chemical stability as well as dielectric properties, water absorption and hydrophobicity of the final materials.[1] An alternative route to copolymer synthesis, namely the polymerization of PBZ with fluorinated polymers, seems to keep the useful properties and even exert a synergistic effect on them. It is known that incorporation of fluorine into PBZ copolymers improves their mechanical properties and thermal stability as well as reduces the relative permittivity.[1–3] Therefore, we supposed that core-fluorinated poly(arylene ether)s (FPAEs) might be promising for the PBZ copolymer synthesis. FPAEs demonstrate various useful properties, such as high thermal stability, improved mechanical characteristics and chemical resistance in combination with low relative permittivity, reduced friction coefficient, refractive index, optical losses and moisture absorption.[10] As well, the non-fluorinated aromatic moieties of FPAE may serve as additional cross-linking sites for benzoxazine curing to result in a cross-linked product. To our knowledge, published data on the PBZ-based copolymers with FPAE are lacking.

The purpose of this work was the preparation as a mechanically-stable free-standing film of a new core-fluorinated cross-linked benzoxazine-based copolymer from bisphenol A–aniline benzoxazine derivative **1**, as the most common monomer for benzoxazine polymers,[1] and *meta*-linked FPAE **2** bearing decafluorobiphenyl and resorcinol moieties. The benzoxazine derivative **1** and the polyether **2** were obtained according to the reported procedures.[11,12] The polyether **2** was chosen as a precursor due to its mechanical and thermal characteristics, namely the values of tensile strength and elongation at break of 54 MPa and 1%, respectively, as well as 5% weight loss temperature of 540 °C.[12] The core-fluorinated cross-linked copolymer **3** was prepared *via* the mixing of precursors **1** and **2** in DMF and thermal curing of the resulting mixture (Scheme 1).† The optimal conditions



1 **2** **3**

Scheme 1 *Reagents and conditions*: i, DMF, 150 °C, 2 h, then casting, then curing at 100–250 °C, 1–4 h (see Table 1).

Table 1 The curing conditions for different samples and their DSC data.

Sample	Precursors **1**:**2** ratio (w/w)	Curing conditions	DSC polymerization exotherm		
			T_{max}/°C[a]	T_{onset}/°C[b]	ΔH/J g^{-1} [c]
1	100:0	No heating	226.27	181.59	178.00
2	50:50	No heating	229.23	189.04	74.17
3	50:50	100 °C, 1 h	233.31	199.04	59.66
4	50:50	100 °C, 1 h, then 150 °C, 1 h	237.57	202.12	52.43
5	50:50	100 °C, 1 h, then 150 °C, 1 h, then 200 °C, 1h	241.23	198.99	27.11
6	50:50	100 °C, 1 h, then 150 °C, 1 h, then 200 °C, 2 h	269.06	239.97	3.66
7	50:50	100 °C, 1 h, then 150 °C, 1 h, then 200 °C, 1 h, then 250 °C, 1 h	–	–	–

[a] Peak maximum. [b] Onset of polymerization. [c] Enthalpy value from the exothermic peak.

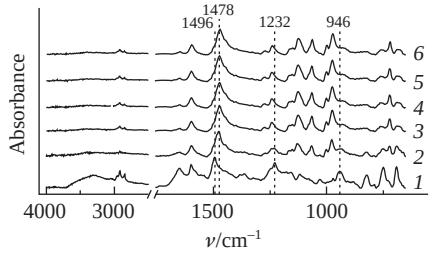


Figure 1 FTIR spectra of the samples after curing: (*1*) sample 2, (*2*) sample 3, (*3*) sample 4, (*4*) sample 5, (*5*) sample 6 and (*6*) sample 7 (see Table 1).

were found by varying the temperature and the duration of curing for different samples (Table 1). The samples were analyzed by FTIR spectroscopy (Figure 1) and DSC (Figure 2).

According to Figure 1, there is a small change in the FTIR spectrum of sample 4 compared to sample 2, while significant changes occur in the spectrum for sample 5 after thermal curing (curves *3* and *4*). The process is nearly complete for sample 6 and fully accomplished for sample 7 (curves *5* and *6*). The spectrum of the initial mixture exhibits the characteristic peaks of compound **1**, namely those at 1232 cm^{-1} for the anti-symmetric stretching of the C–O–C bond in the oxazine ring, at 1496 and 946 cm^{-1} for the trisubstituted benzene ring and the peaks in the ranges 990–1050 and 700–800 cm^{-1} for out-of-plane bending vibrations and in-plane vibrations of the C–H bond.[13–15] With the increase of temperature and curing time, the peaks of the precursors gradually disappear or become shifted. For example, a new peak attributed to the tetra-substituted aromatic ring occurs at 1478 cm^{-1}.[13,14]

The DSC thermograms of samples 1–6 demonstrate the decrease in ΔH values for the exothermic peak and the disappearance of this peak with elevation of temperature due to the ring-opening polymerization of precursor **1** (see Table 1 and Figure 2). The complete absence of the exothermic peak is observed after the

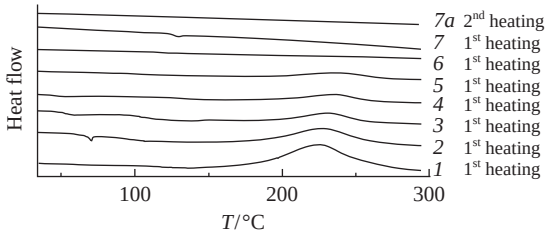


Figure 2 DSC thermograms of the samples after curing: (*1*) sample 1, (*2*) sample 2, (*3*) sample 3, (*4*) sample 4, (*5*) sample 5, (*6*) sample 6, (*7*) and (*7a*) sample 7 (see Table 1 for conditions).

treatment of sample 7 at 100–250 °C for 3 h, which indicates the end of curing. The flexible brown-colored polymer film was obtained as a result of the process (Figure S1, see Online Supplementary Materials), therefore this sample was further investigated by DSC.

The copolymer **3** is insoluble in water, concentrated or diluted acids and alkalis as well as in organic solvents at room temperature or under heating. The gel content of the synthesized product is 84.5%, which confirms its cross-linked structure. The DSC thermogram of copolymer **3** exhibits only one glass transition event with T_g value of 128.23 °C (see Figure 2, curve *7a*), implying its homogeneity.

The film was investigated using scanning electron microscopy (SEM) (Figure S2, see Online Supplementary Materials). As follows from the SEM images, the film looks smooth and homogeneous at the resolution of 20 μm. However, at the resolution 2–10 μm the holes or voids appear on the surface, which can be attributed to the solvent evaporation from the surface in the curing process.

In summary, a new core-fluorinated cross-linked copolymer **3** was prepared by thermal ring-opening polymerization. Compound **3** seems promising as a material with high thermal stability and as a candidate for further study of its relative permittivity, loss factor, water absorption, hydrophobicity and adhesion properties.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.05.022.

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† *Poly(oxy-1,3-phenyloxy-2,2',3,3',5,5',6,6'-octafluoro-1,1'-biphenyl-4,4'-diyl) polymer with 6,6'-isopropylidenebis(3-phenyl-1,3-benzoxazine)* **3**. The mixture of compounds **1** (0.05 g) and **2** (0.05 g) in DMF (1.5 ml) was stirred in a 50 ml two-neck round-bottomed flask equipped with condenser and nitrogen inlet at 150 °C for 2 h. Following the typical solution casting technique, the mixture was cast into Teflon Petri dish (75×10 mm) and heated stepwise in an air-circulating oven at 100, 150, 200 and/or 250 °C for 1 h at each temperature. The product was slowly cooled to room temperature for several hours to give the brown thermoset film with the thickness ranged from 80 to 120 μm. FTIR (ν/cm^{-1}): 1600 (Ph), 1478 (trisubstituted benzene ring stretching), 1244 (C–O–C), 977 (C–F), 760 (C–H).