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A Smart Latent Catalyst Containing *o*-Trifluoroacetamide Functional Benzoxazine: Precursor for Low Temperature Formation of Very High Performance Polybenzoxazole with Low Dielectric Constant and High Thermal Stability

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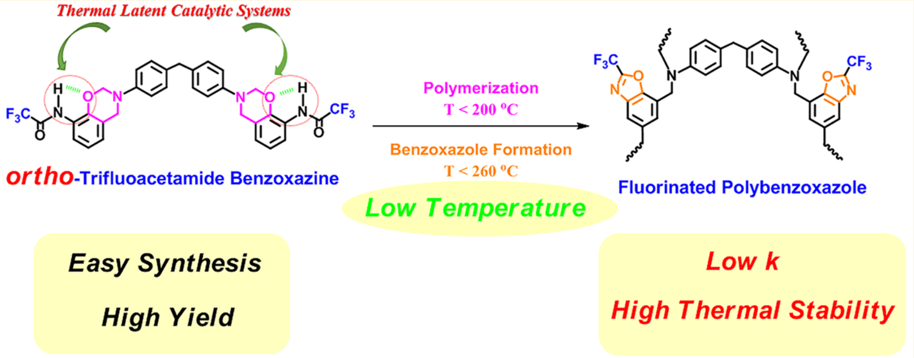

ABSTRACT: A novel difunctional benzoxazine with *o*-trifluoroacetamide functionality has been synthesized via Mannich condensation. The chemical structure of synthesized monomer has also been confirmed by ^{1}H, ^{13}C, and ^{19}F nuclear magnetic resonance (NMR) spectroscopy and Fourier transform infrared (FT-IR) spectroscopy. The ring-opening polymerization of the resin and the subsequent conversion of the freshly generated polybenzoxazine into polybenzoxazole are studied by FT-IR and differential scanning calorimetry (DSC). In addition to the advantage of low polymerization temperature as other reported *o*-amide benzoxazines, the *o*-trifluoroacetamide benzoxazine also exhibits an unexpected lower benzoxazole formation temperature. Furthermore, the resulting fluorinated polybenzoxazole derived from the benzoxazine monomer possesses the combined excellent properties of facile synthesis, easy processability, low dielectric constant, high thermal stability, and long shelf life, evidencing its potential applications in microelectronic industries, aerospace, and other high-performance areas.

■ INTRODUCTION

Multilevel interconnection technology has been well developed in recent years since it is the key way for the production of ultralarge scale integration (ULSI) circuits. However, the propagation delay and cross-talk are the primary problems, which have been the concern in ULSI circuits.[1] In order to reduce the resistance−capacitance (*RC*) delay, low dielectric constant (low *k*) materials are urgently required. In general, there are two approaches to scale down the *k* value of a dielectric layer: one is to reduce the polarizability by incorporating the least polarizable groups such as C−H, C−C, C−O, and C−F bonds in molecular design; the other is to decrease the density of the film by increasing the free volume.[2−5]

Benzoxazine resin has attracted strong attention in recent years because it possesses significant advantages compared with other traditional thermosets, such as high thermal stability, excellent mechanical properties, low surface energy, and near-zero shrinkage upon polymerization.[6−12] The most outstanding characteristic of this class of benzoxazine thermosets is their extraordinarily rich molecular design flexibility, which allows design of various molecular structures to tailor the desired properties.[13,14] Moreover, incorporation of functional group with benzoxazine structure is not only simple to prepare but also compatibility to other polymeric materials to improve their properties. By taking advantage of molecular design flexibility, fluorinated benzoxazines were synthesized and found to exhibit very low dielectric constant.[15−17] It is well-known that the incorporation of fluorinated substituents into a polymer can decrease its dielectric constant because of small dipole and the low polarizability of the C−F bond.[1] In addition, polymer free volume is also increased via replacing methyl groups by

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trifluoromethyl groups.[1,18] Additionally, increased hydrophobicity by the fluorinated groups helps to decrease the water content in the polymer. Since water has one of the highest dielectric constant of all materials, reducing even a small amount of water significantly contributes to the reduction of the dielectric constant.

Recently, unique superior mechanical and physical properties of *ortho*-functional benzoxazines to *para*-counterparts have been discovered.[19] The anomalous properties of the *o*-benzoxazine structure inspired us to develop highly thermally stable polybenzoxazole (PBO) structure via *o*-amide or *o*-imide functional benzoxazines.[20−22] Among these benzoxazines, *o*-amide functional benzoxazines polymerize at much lower temperature than ordinary benzoxazines without added initiators and/or catalysts to form polybenzoxazines.[20,23] A very detailed study on the existence of intramolecular hydrogen bonding in *o*-amide benzoxazines has recently been reported.[24] The importance of such study mainly lays on the fact that the intramolecular hydrogen bonding between an amide linkage and the adjacent oxazine ring of *o*-amide benzoxazine acts as an incentive to stimulate an acceleration effect on the ring-opening polymerization.[25]

Thermal conversion of *o*-hydroxylamides into benzoxazoles take place around 300 °C for *o*-amide benzoxazines, while similar benzoxazole formation from *o*-imide benzoxazines are at about 400 °C, bringing potential difficulties during their fabrication. Thus, a lower benzoxazole formation temperature is strongly desired for expanding the applications of such series of smart benzoxazines. On the other hand, however, the thermal conversion of *o*-hydroxyls, amides, and even imides into benzoxazole significantly reduces the polarizability, which is advantageous from the low-dielectric point of view. Therefore, if the benzoxazole conversion temperature can be reduced while the decreased dielectric constant can also be maintained, development of an attractive electronic material with significant processing advantage is possible. It is thus the goal of this paper to achieve the development and structural understanding of such a material.

All previously described features motivated us to incorporate trifluoromethyl group into *o*-amide functional benzoxazine to decrease the dielectric constant of the resultant polymer. In this work, we prepared *o*-trifluoroacetamide difunctional benzoxazine from *o*-trifluoroacetamide functional phenol, 4,4′-diaminodiphenylmethane, and paraformaldehyde. Although benzoxazole formation through an intramolecular cyclization between neighboring hydroxyl and benzamide of *o*-amide polybenzoxazine has been well developed,[20,23] the thermal reaction between neighboring hydroxyl and acetamide has never been studied. Therefore, we reasonably expect this *o*-trifluoroacetamide difunctional benzoxazine to undergo a very interesting thermal behavior. The detailed synthetic strategy, the thermal behavior of benzoxazine monomer, and the properties of the resulting fluorinated polymers are discussed in this work.

EXPERIMENTAL SECTION

Materials. *o*-Aminophenol (>98%), trifluoroacetic anhydride (TFAA), and paraformaldehyde were used as received from Sigma-Aldrich. 4,4′-Diaminodiphenylmethane (DDM) (98%) was purchased from Aldrich. Hexane, ethyl acetate, xylenes, dimethylformamide (DMF), tetrahydrofuran (THF), sodium bicarbonate, and sodium sulfate were purchased from Fisher Scientific and used as received.

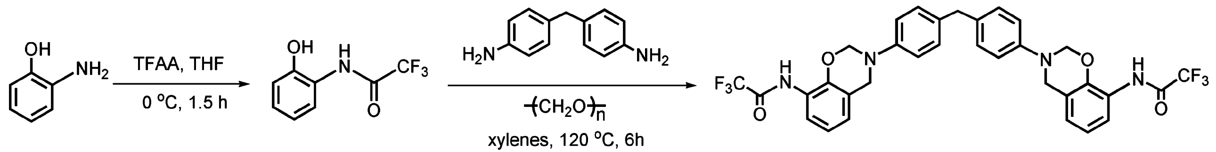
Characterization. ^{1}H, ^{13}C, and ^{19}F nuclear magnetic resonance (NMR) spectra were recorded on a Varian Oxford AS600 (600 MHz) using deuterated dimethyl sulfoxide (DMSO-d_6) and chloroform ($CDCl_3$) as solvents. Fourier transform infrared (FT-IR) spectra were measured by a Bomem Michelson MB100 FT-IR spectrometer, which was equipped with a deuterated triglycine sulfate (DTGS) detector and a dry air purge unit. Sixty-four scans were coadded to obtain a spectrum at a resolution of 4 cm^{-1}. All samples were finely ground with potassium bromide powder and pressed into disk, and the spectrum was taken as the transmission mode. Differential scanning calorimetric (DSC) measurements were made with a TA Instruments DSC Model 2920 under a nitrogen atmosphere at a purge rate of 60 mL/min and a heating rate of 10 °C/min. All samples (2.0 ± 0.5 mg) were sealed using hermetic aluminum pans and covered with lids. Dynamic mechanical analysis (DMA) was conducted on a TA Instruments Model Q800 DMA applying controlled strain tension mode with amplitude of 10 μm and a temperature ramp rate of 3 °C/min. Strain sweep was first performed to determine the linear viscoelastic limit. Dielectric constant and dielectric loss values were measured by a Concept 80 broadband dielectric spectrometer (Novocontrol) at room temperature. All samples were dried at 100 °C for 8 h under vacuum before the measurements. A sample with 20 mm diameter and 1−2 mm thickness was placed between the two copper electrodes to form a parallel plate capacitor. Thermogravimetric analysis (TGA) was performed by a TA Instruments Q500 TGA using nitrogen as a purge gas (40 mL/min) at a heating rate of 10 °C/min up to 800 °C.

Synthesis of 2,2,2-Trifluoro-*N*-(2-hydroxyphenyl)acetamide (Abbreviated as *o*TFA). Into a 250 mL round flask were added *o*-aminophenol (7.71 g, 0.07 mol) and THF (100 mL). Then the mixture was stirred and cooled in an ice bath for 15 min. Trifluoroacetic anhydride (19.6 mL, 0.14 mol) was charged dropwise with stirring for 30 min. Afterward, the reaction mixture was sequentially stirred in the ice bath for an additional 1.5 h. The product was concentrated using a vacuum rotary evaporator, followed by dissolution of the residue in ethyl acetate (200 mL). The solution was washed with saturated aqueous sodium bicarbonate solution and water three times, respectively. The solution was dried over sodium sulfate, filtered, and concentrated under vacuum. At last, the product was precipitated in 500 mL of hexanes, filtered, and dried under vacuum overnight to give cotton-like crystals (yield ca. 86%). ^{1}H NMR (600 MHz, DMSO-d_6), ppm: δ = 6.78−7.34 (4H, Ar), 9.93 (OH), 10.53 (s, NH). FT-IR spectra (KBr, cm^{-1}) = 3388 (N−H stretching), 3274 (O−H stretching), 1718 (C═O stretching), 1692 (amide I mode).

Synthesis of *N,N*′-((Methylenebis(4,1-phenylene))bis(3,4-dihydro-2*H*-benzo[*e*][1,3]oxazine-3,8-diyl)bis(2,2,2-trifluoroacetamide) (Abbreviated as *o*TFA-ddm). 30 mL of xylenes, 4,4′-diaminodiphenylmethane (1.93 g, 9.75 mmol), *o*TFA (4 g, 19.50 mmol), and excess paraformaldehyde (1.46 g, 48.75 mmol) were mixed in a 100 mL round-bottom flask equipped with a reflux condenser. The mixture was heated and refluxed at 120 °C for 6 h. Then the reaction solution was cooled to room temperature and poured into 150 mL of hexane to precipitate the reaction product. Then, the crude product was dissolved in 200 mL of ethyl acetate, followed by washing with deionized water three times. The solution was dried over sodium sulfate anhydrous, followed by evaporation of solvent under vacuum to afford a light yellow solid (yield ca. 90%). ^{1}H NMR (600 MHz, DMSO-d_6), ppm: δ = 3.71 (s, CH_2), 4.63 (s, Ar−CH_2−N, oxazine), 5.45 (s, O−CH_2−N, oxazine), 6.84−7.20 (14H, Ar), 10.58 (s, NH). FT-IR spectra (KBr), cm^{-1}: 3403 (N−H stretching), 1731 (carbonyl stretching), 1495 (stretching of trisubstituted benzene ring), 1223 (C−O−C asymmetric stretching), 1164 (C−F stretching), and 918 (benzoxazine related band).

Preparation of Polybenzoxazine (Poly(*o*TFA-ddm)) and Cross-Linked Polybenzoxazole (CFPBO). A solution of 30% solid content of *o*TFA-ddm in DMF was prepared. Then, the solution was cast on a dichlorodimethylsilane-pretreated glass plate. The film was dried in an air-circulating oven at 100 °C for 2 days to remove the solvent. The film as coated on a glass plate was polymerized stepwise

Scheme 1. Preparation of *o*-Trifluoroacetamide Difunctional Benzoxazine



*o*TFA

*o*TFA-ddm

at 140, 160, 180, and 200 °C for 2 h each to obtain poly(*o*TFA-ddm). Poly(*o*TFA-ddm) can be further treated at 260 °C for 1 h and then obtain cFPBO.

■ RESULTS AND DISCUSSION

Synthesis of *o*-Trifluoroacetamide-Functional Benzoxazine. Prior to this study, *p*-trifluoroacetamide monofunctional and difunctional benzoxazines were prepared in good yields and short reaction time by using a solvent system of mixture of chlorobenzene/xylene (1:1 v/v) at 130 °C.[26] However, in that study, the trifluoroacetamide functional benzoxazines were just the intermediate for obtaining amino-functional benzoxazines, and the synthesis and understanding of the function of trifluoroacetamide-containing benzoxazine as a precursor for polybenzoxazole were not intended. In the current study, the pathway adopted for obtaining cross-linked polybenzoxazole (cFPBO) was started from *o*-trifluoroacetamide functional phenol (*o*TFA) for preparation of benzoxazine monomer as a precursor and then by ring-opening polymerization and benzoxazole formation to obtain cFPBO. *o*-Trifluoroacetamide difunctional benzoxazine (*o*TFA-ddm) was simply synthesized from the Mannich condensation of *o*TFA, paraformaldehyde, and DDM as shown in Scheme 1.

The structures of *o*TFA-ddm were confirmed by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, and FT-IR analyses. As shown in Figure 1, the characteristic proton resonances attributed to the benzoxazine structure, Ar−CH_2−N− and −O−CH_2−N−, are observed at 4.60 and 5.42 ppm, respectively. Also, the ^{1}H NMR spectra confirm the presence of the methylene group and amide group as observed by the presence of the resonances of −CH_2− and −N*H*− at 3.71 and 10.58 ppm, respectively. It must be noted the unusually high acidic character exhibited by this −NH−, whose signal in the ^{1}H NMR spectrum falls into the typical region ascribed for ordinary organic acids (normally from 10 to 14 ppm approximately).

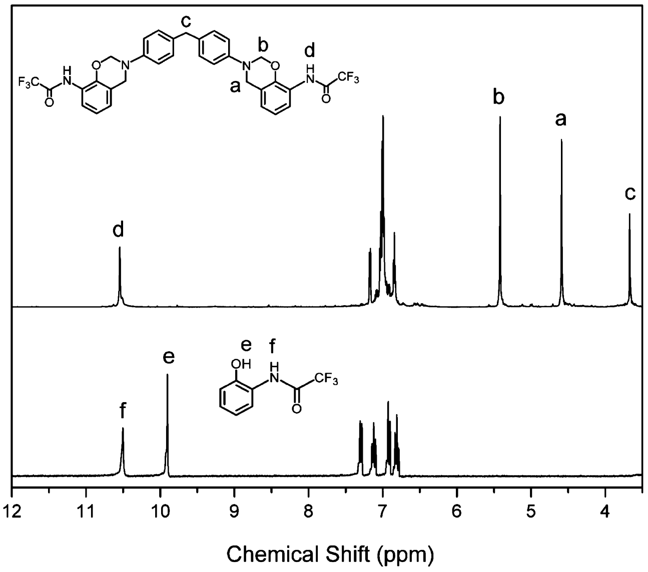


Figure 1. ^{1}H NMR spectra of *o*TFA and *o*TFA-ddm.

^{13}C NMR analysis was performed and a representative spectrum of *o*TFA-ddm is shown in Figure 2. The characteristic carbon resonances of the oxazine ring appear at 49.55 and 79.32 ppm for Ar−CH$_2$−N− and −O−CH$_2$−N−, respectively. The characteristic carbon resonance of the methylene group was not easily observed because it is overlapped with the DMSO-d_6 signal, used as deuterated solvent. In addition, the ^{19}F NMR spectrum of *o*TFA-ddm (Figure 3) shows the characteristic resonance at −74 ppm corresponding to the fluorine atom of −CF_3 in a symmetrical motif.

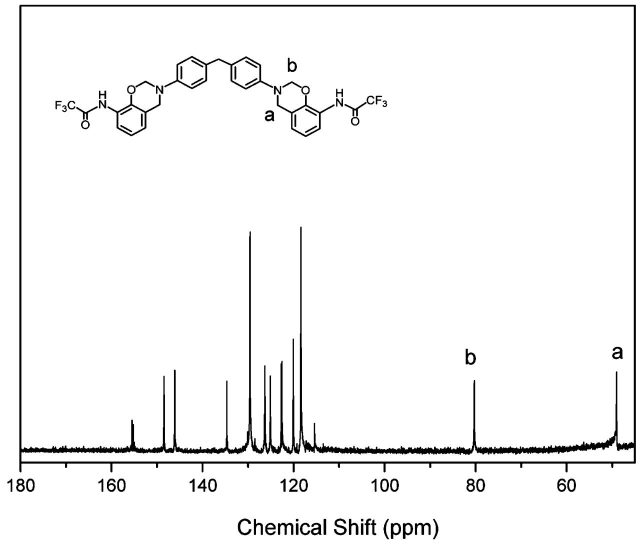


Figure 2. ^{13}C NMR spectrum of *o*TFA-ddm.

The structure of benzoxazine monomer was also confirmed by FT-IR. There are a number of infrared absorption bands, highlighted in Figure 4, that are used to verify the formation of trifluoroacetamide and oxazine ring in *o*TFA-ddm. The band of NH stretching mode at 3403 cm^{-1} and the carbonyl absorption band at 1731 cm^{-1} support the formation of amide group. Band for trisubstituted benzene that appears at 1495 cm^{-1} indicates the incorporation of amide group into benzoxazine monomer. Furthermore, the band at 1164 cm^{-1} corresponds to the C−F bond absorption. The presence of the benzoxazine ring aromatic ether in the monomer is indicated by the band centered at 1223 cm^{-1}, which is due to the C−O−C antisymmetric stretching modes.[27] The characteristic benzoxazine related mode is located at 918 cm^{-1}.[28] All the above information is consistent with the successful synthesis of the target compound.

Ring-Opening Polymerization, and Thermal Cyclization Behavior of *o*-Trifluoroacetamide Difunctional Benzoxazine. It is well-known that *o*-amide polybenzoxazines

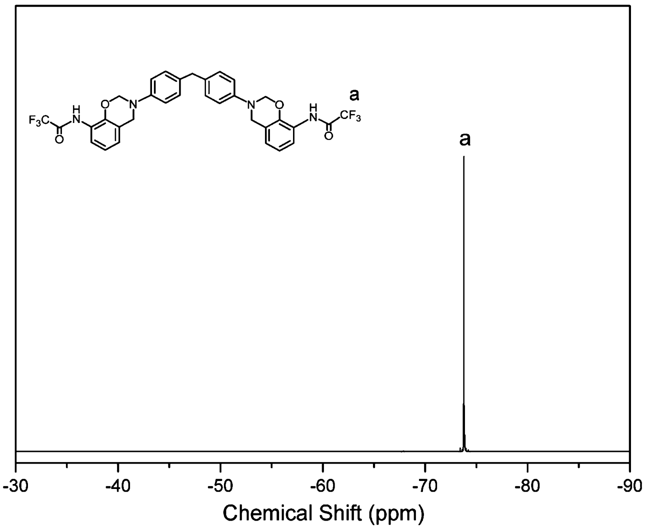


Figure 3. ^{19}F NMR spectrum of *o*TFA-ddm.

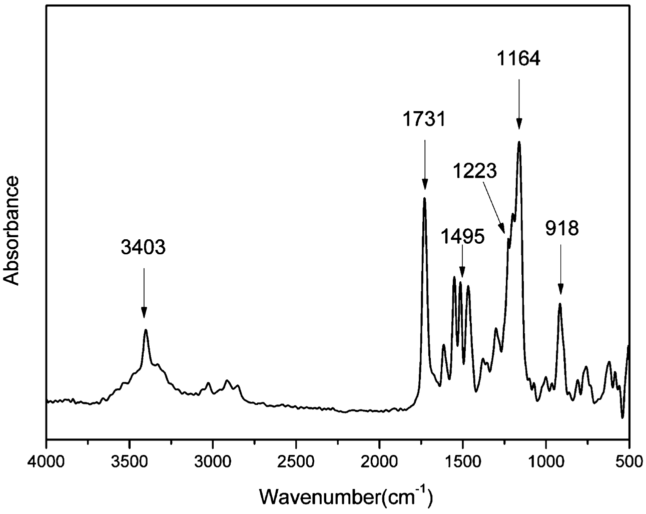


Figure 4. FT-IR spectrum of *o*TFA-ddm.

undergo structural transformation by further thermal treatment into another class of polymer, specifically, cross-linked polybenzoxazole. Taking advantage of the remarkable flexibility in the molecular design of *o*-amide benzoxazine resins, a large variety of *o*-amide functional benzoxazines have been developed for obtaining polybenzoxazoles through an intramolecular cyclization between neighboring hydroxyl and benzamide;[20,23−25] however, the thermal reaction between neighboring hydroxyl and acetamide has never been reported.

In order to qualitatively study the structural evolution of *o*TFA-ddm during heating, FT-IR analyses were carried out. As shown in Figure 5, the characteristic absorption bands at 1223 cm^{-1} (C−O−C antisymmetric stretching mode) and 918 cm^{-1} (benzoxazine related mode) can be used to study the ring-opening polymerization of the benzoxazine resin by observing the gradually decrease as a function of the temperature and finally complete disappearance at 220 °C. This result suggests the polymerization of *o*TFA-ddm can be completed at the temperature as low as 220 °C to form polybenzoxazine. However, the characteristic bands for carbonyl absorption at 1731 cm^{-1} gradually decreases when heated from 220 to 260 °C, and meanwhile two bands at 1618 cm^{-1} (C=N stretching) and 1055 cm^{-1} (−O−C stretching) gradually increase.[29,30] The FT-IR spectrum of this novel *o*-trifluoroacetamide-functional polybenzoxazine is practically identical to those reported for cross-linked polybenzoxazoles synthesized through the cyclization between neighboring hydroxyl and benzamide of *o*-amide benzoxazines, indicating that benzoxazole formation has been completed after the final thermal treatment at 260 °C for 1 h.

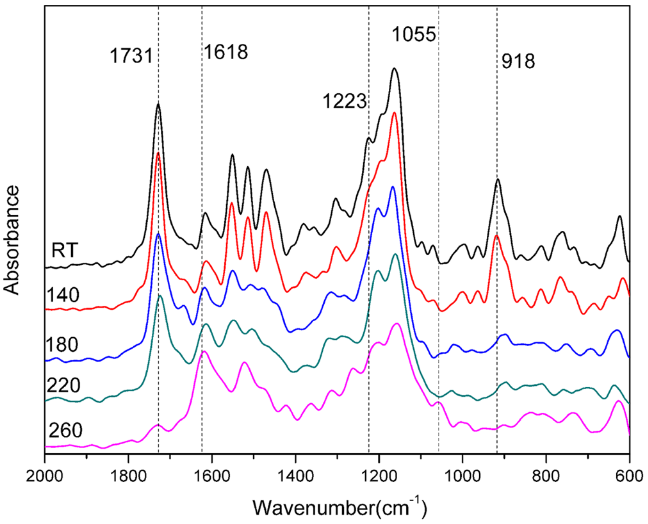


Figure 5. FT-IR spectra of *o*TFA-ddm after various thermal treatments at the designated temperature for 1 h.

In order to further support the benzoxazole formation, thermogravimentric analysis (TGA) with the isothermal condition at 260 °C for 1 h of poly(*o*TFA-ddm) has also been studied. As shown in Figure 6, a weight loss of 5.54 wt % is observed after thermal treatment at 260 °C. The weight loss for this stage is nearly identical to the theoretically expected value of 5.49% from the loss of water, through a direct dehydration reaction, implying that no significant additional degradation mechanism exists. The previous approaches for obtaining PBO precursors that are soluble in organic solvents were developed by incorporating flexible groups, such as *tert*-butyldimethylsilyl, methyl, and isopropyl.[31,32] As a result, the degradation of those flexible groups occurred during thermally

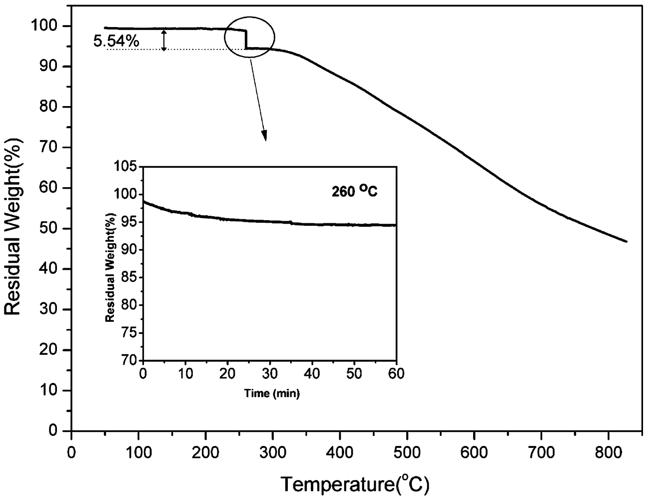
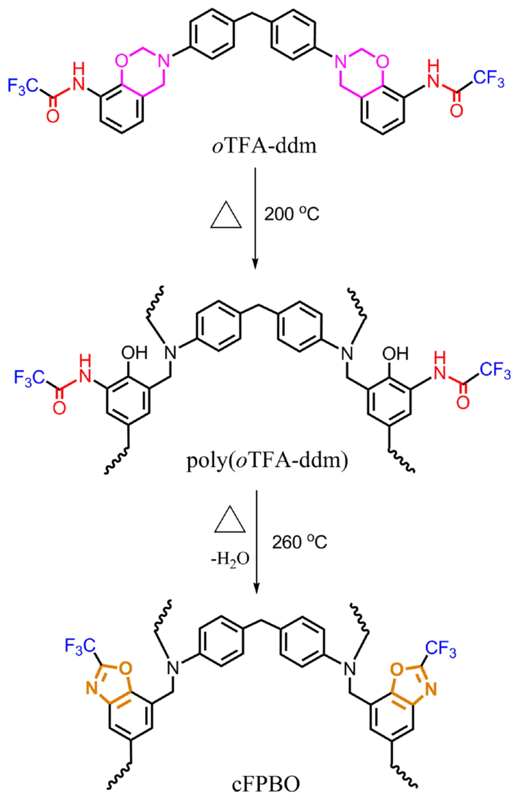


Figure 6. Thermogravimetric analysis of poly(*o*TFA-ddm). At 260 °C, isothermal heating was applied for 1 h.

induced ring closure reaction, thus leading to benzoxazole formation, which results in a weight loss as high as 33−36 wt %. Generally, a trade-off exists between processability and thermal stability for the polybenzoxazole precursors. However, only a 5.54 wt % of total weight loss was observed in this study, which is much lower compared with other methods for obtaining cross-linked PBOs with weight losses of 14−20 wt % via *o*-amide functional benzoxazines.[20,23] The proposed structural transformation mechanism of *o*TFA-ddm is shown in Scheme 2.

Scheme 2. Polymerization of *o*TFA-ddm Generating Polybenzoxazine and Subsequent Structural Conversion into Polybenzoxazole



DSC Thermograms of Benzoxazine. The polymerization profile of *o*TFA-ddm was studied by DSC as depicted in Figure 7. The thermogram exhibits an endotherm at 91 °C associated with the melting of the resins and an exotherm between 170 and 230 °C, approximately, showing somewhat multiple complex events related to the polymerization of *o*TFA-ddm.

The *o*-trifluoroacetamide functional benzoxazine is shown to polymerize at much lower temperature than ordinary benzoxazines without added initiators and or/catalysts. This result is similar as the previously reported *o*-amide functional benzoxazines,[20,23] although in a greater magnitude for the *o*TFA-ddm. Thus, the presence of a five-membered-ring hydrogen-bonding system involving the amide linkage and the adjacent oxazine belonging to the oxazine ring might be acting as a "reinforced incentive" to stimulate the ring-opening polymerization.

As in other examples reported in the literature,[24,25] *o*TFA-ddm presents as a constitutive portion of its formula a structural array possibly forming a five-membered ring hydrogen-bonding system at each side of the symmetric molecule. Although this kind of array has been demonstrated to stimulate an acceleration effect on the ring-opening polymerization of benzoxazines, the magnitude of such effect has never been as impressive as when polymerizing *o*TFA-ddm (as shown by DSC in Figure 7). Therefore, we developed an interest in understanding the nature of the possible hydrogen-bonding system enhancing the polymerization rate of this resin, and the results are shown in Figure 8.

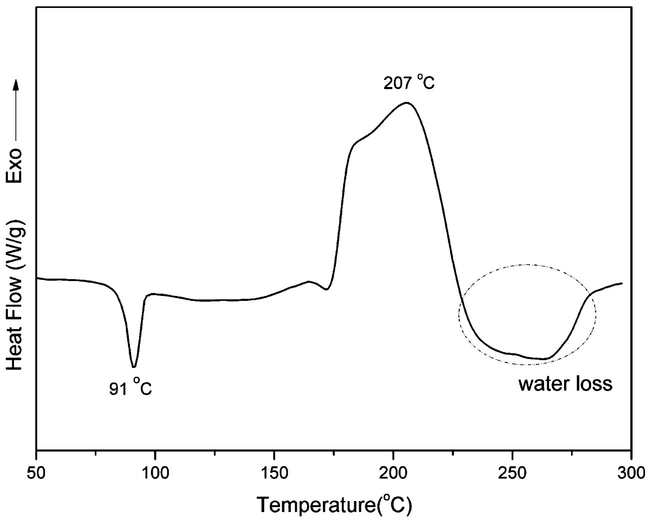


Figure 7. DSC thermogram of *o*TFA-ddm.

It is well-known that protons are more deshielded than usual if participating in hydrogen bonds and that stronger hydrogen bonds cause stronger deshielding effects, producing greater downfield shiftings. Therefore, the solvent of choice for this kind of study is crucial since it as well can compete with or break existing hydrogen bonds and even form new ones.

Figure 8a shows the temperature-dependent experiment carried out using ^{1}H NMR spectroscopy. Experiments were designed by using two different solvents, deuterated chloroform ($CDCl_3$) and dimethyl sulfoxide (DMSO-d_6), presenting medium-to-low and high polarity, respectively. Moreover, $CDCl_3$ is a weak hydrogen-bonding donor and acceptor, while DMSO-d_6 is a strong hydrogen-bonding acceptor only. Thus, chloroform would help providing insights and understanding on how *o*TFA-ddm might behave under storing conditions (relatively low polar environment at low (room) temperature), while dimethyl sulfoxide under polymerization conditions (high temperature). Results obtained in both solvents show linear response against temperature with linear regression coefficients equal to and greater than 0.999. Therefore, the temperature coefficients ($\Delta\delta/\Delta T$) are straightforwardly obtained from the slope on each plot.

As shown in Figure 8a, and mentioned earlier (see also Figure 1), the −NH− signal belonging to the amide group is observed downfield shifted far beyond the amide region and within the ordinary organic acids region of the ^{1}H NMR spectrum when using DMSO-d_6. Moreover, the calculated temperature coefficient obtained (−5.40 ppb/K) is more negative than −5.0 ppb/K, denoting that no hydrogen bonding is detected in this condition. Instead, the unusually high mobility of this amide proton clearly evidences its high acidic character in dimethyl sulfoxide. Keeping into consideration that benzoxazine polymerization is acid-catalyzed, result easy to predict that under this condition, or similar ones, *o*TFA-ddm must be highly reactive. Figure 8b depicts the chemical

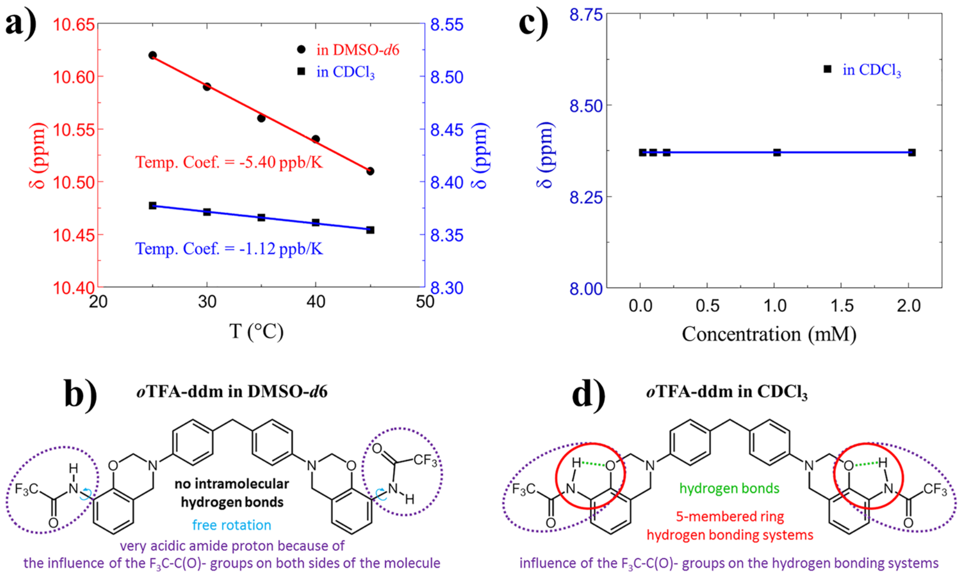


Figure 8. Temperature dependence (a) and concentration dependence (b) experiments carried out by ^{1}H NMR for *o*TFA-ddm. Simplified molecular structures of *o*TFA-ddm showing no hydrogen bonds in its structure when solubilized in dimethyl sulfoxide (c) and exhibiting a five-membered-ring hydrogen-bonding system at each side of the symmetric resin in chloroform (d).

structure of the resin where no hydrogen bonds are present. The very acidic character of the amide protons present in the molecule is straightforwardly understood by making simple electronic considerations. The very strong electron withdrawing trifluoroacetyl group is directly bonded to the nitrogen atom of the amide function, thus leaving this nitrogen with a relatively high positive density, which in turn repels the naturally positive proton. Combination of all these effects explains the unusually high acidic character for these amide protons in *o*TFA-ddm. Conversely, the results obtained in chloroform indicate the presence of strong five-membered-ring hydrogen-bonding systems at both sides of the molecular structure of *o*TFA-ddm. The strong character of the hydrogen bonds present in the resin is calculated from Figure 8a, where the calculated temperature coefficient (−1.12 ppb/K) is less negative than −3.0 ppb/K, while the intramolecular array is confirmed by the no variation of the chemical shift as a function of the concentration of *o*TFA-ddm solutions, shown in Figure 8c. Figure 8d depicts the chemical structure of *o*TFA-ddm in chloroform where hydrogen bonds are denoted in green dotted lines, the five-membered-ring hydrogen-bonding arrays within the red circles, and the influence of the trifluoroacetyl groups with a purple dotted ellipse. The lower acidic character of the same amide proton in chloroform compared when solubilized in dimethyl sulfoxide is due to the solvents themselves. For instance, dimethyl sulfoxide is a relatively high polar solvent in which electron motion and polarized electronic densities are not only possible but favored and even stabilized by the polar solvent. This is why studying a system in dimethyl sulfoxide might help to get an insight into how that same system may behave at high temperature, where the high energy would play the role of allowing those electron motion and polarization of electronic densities to occur. Nevertheless, chloroform is a medium-to-low polar solvent where all those electron and electronic distributions are much hindered.

The high stability at low temperatures combined with the high reactivity under polymerization conditions evidences the important latent-catalyst role played by the hydrogen bonds in this resin. It can be considered that at room temperature each hydrogen-bonding system acts as a protecting group holding the acidic proton within the five-membered-ring hydrogen-bonding arrays. However, only when the resin is submitted to the polymerization conditions do the hydrogen bonds easily break permitting the acidic amide proton to react, thus acting as a traditional acidic catalyst accelerating the polymerization rate of the benzoxazine.

An additional very interesting result obtained upon the spectroscopic studies is that *o*TFA-ddm has been demonstrated to exhibit high stability at room temperature, thus offering a very long shelf life. For instance, this resin has been proven to be completely unaltered for a period longer than one and a half years when simply stored in a vial without extra protection against light, moisture, and even oxygen.

It is worth noting that the DSC results of *o*TFA-ddm shown in Figure 7 exhibit a different thermal behavior compared with traditional benzoxazines. The thermogram not only shows the typical endothermic melting and exothermic ring-opening polymerization of benzoxazine but also an extra endothermic event assigned to a cyclodehydration reaction of *o*-hydroxyacetamide to yield polybenzoxazole. Importantly, the cyclodehydration toward benzoxazole formation seems to be completed at around 280 °C, which is much lower than the previously studied *o*-amide benzoxazines at around 330 °C.[20,23] Thus, benzoxazine polymerization as well as the chemical conversion of the polybenzoxazine to polybenzoxazole can take place at even lower temperatures if an isothermal polymerization condition is used as is typically the case for composite manufacturing. This aspect of low-temperature conversion leads to a processing advantage. The low temperature for the benzoxazole formation by reacting the neighboring hydroxyl and trifluoroacetamide groups implies that a certain role of the trifluoroacetamide dominated the cyclodehydration over possible steric factors.

Thermal behavior of products obtained by thermally activated cross-linking polymerization of *o*TFA-ddm was also studied by DSC as shown in Figure 9 after cumulative thermal treatments at 140, 180, 220, and 260 °C for 1 h at each temperature. It is observed that the exothermic peak gradually

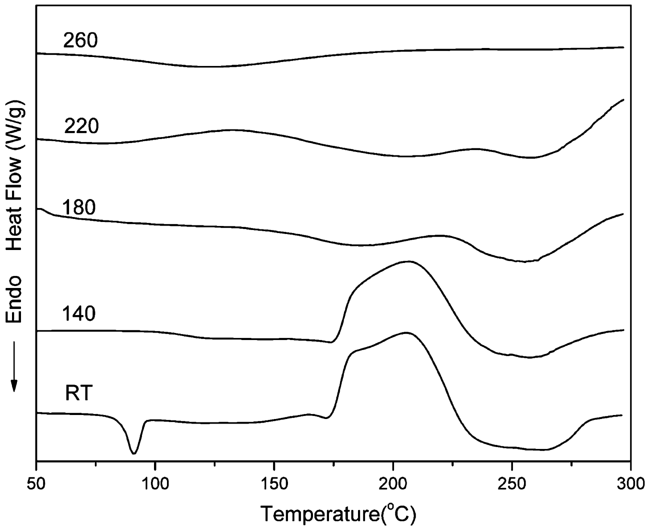


Figure 9. DSC thermograms of *o*TFA-ddm after various thermal treatments.

decreases after each treatment temperature. The exotherm and endotherm peaks practically disappeared even below 200 °C as previously discussed. After the treatment at 260 °C, completion of the ring-opening and cyclodehydration reactions has been observed. This remarkable reduction of the oxazole formation temperature might be in part due to the hydrophobicity of the fluorinated polybenzoxazine, driving off the water produced, thereby forcing the equilibrium in favor of the benzoxazole formation direction. It is also possible the coexistence or influence of other mechanisms based on electronic properties of those groups involved. For example, there is a possibility that N-alkylation of −NH is partially taking place due to the electrophilic $-CH_2$ that is formed after ring-opening of benzoxazine structure. Further detailed study is needed before understanding the molecular mechanism of this temperature reduction. Nevertheless, the DSC result is a strong support of the proposed benzoxazole formation in *o*-trifluoroacetamide functional benzoxazine and in accordance with other aforementioned evidence by FT-IR and TGA analyses. No T_g was observed under 300 °C after the thermal treatment at 260 °C of *o*TFA-ddm, which indicates the excellent thermal property of cFPBO.

Dielectric Properties of Poly(*o*TFA-ddm) and Cross-Linked CFPBO. The dependence of dielectric constant and dielectric loss (tan δ) of poly(*o*TFA-ddm) and cFPBO on the frequency of the applied field was investigated at room temperature. As shown in Figure 10, the dielectric constants of both polymers expectedly decrease slightly with an increase in frequency. The dielectric constants were observed to vary from 3.19 to 2.84 for poly(*o*TFA-ddm) and from 2.42 to 2.19 for cFPBO within the frequency range of 1 Hz−1 MHz. Typically, the dielectric constant of polybenzoxazines is approximately 3.0−3.5 at 1 MHz, slightly higher than the dielectric constant of typical low dielectric constant materials (k < 3.0).[15] The introduction of fluorinated structures into benzoxazine resins can significantly reduce the dielectric constants of the corresponding polybenzoxazines. Fluorinated substitution lowers the dielectric constant by decreasing the polarizability and the moisture absorption and by increasing free volume.[33] Particularly, the bulky $-CF_3$ group is able to reduce efficient molecular packing and increase the free volume.

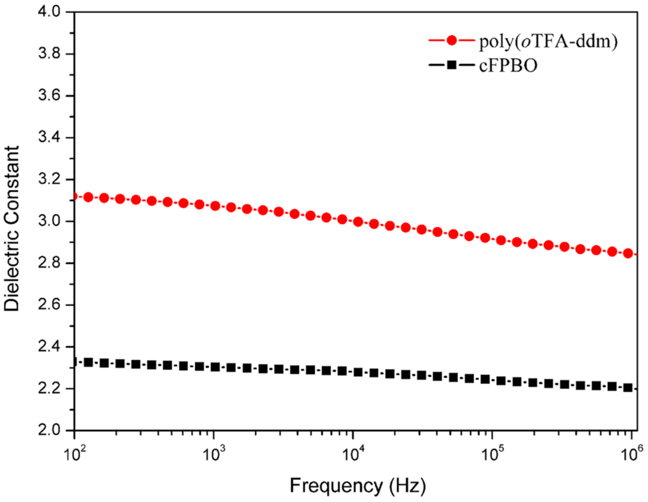


Figure 10. Dielectric constant versus frequency of poly(*o*TFA-ddm) and cFPBO at room temperature.

As a result, the dielectric constants of both poly(*o*TFA-ddm) and cFPBO containing $-CF_3$ group are lower than those of normal non-fluorinated polybenzoxazines. In addition, the benzoxazole formation between the neighboring hydroxyl and trifluoroacetamide converts the polarizable hydroxyl into less polarizable benzoxazole group, resulting in a lower dielectric constants of cFPBO.

Figure 11 shows the dependence curves of the dielectric loss of poly(*o*TFA-ddm) and cFPBO within the frequency range of 1 Hz−1 MHz. Normally, a low value of dielectric loss is always required for the application as interlayer dielectric materials.[34,35] The dielectric loss were observed to vary from 0.012 to 0.008 for cFPBO. This values are lower than 0.019−0.032 obtained for poly(*o*TFA-ddm) because the benzoxazole groups are significantly less polarizable than the *o*-hydroxylacetamide species. Moreover, the dielectric loss is 0.022 at 1 MHz for poly(*o*TFA-ddm), whereas that of cFPBO is as low as 0.010. Therefore, the values of both dielectric constant and dielectric loss show that the newly developed cFPBO is suitable for applications as low-k materials, in particular at a wide

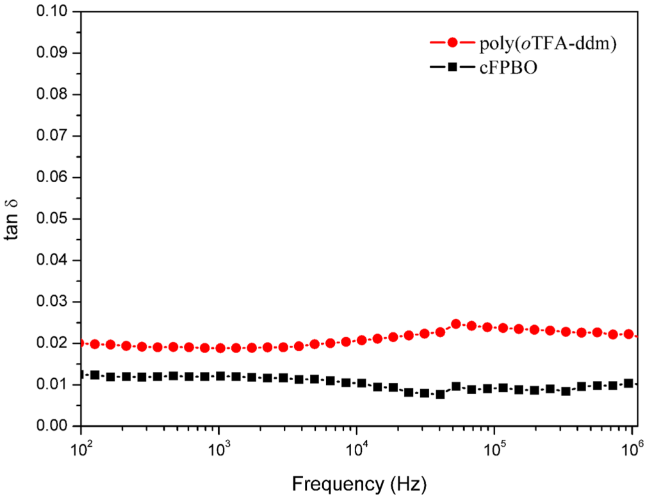


Figure 11. Dielectric loss versus frequency of poly(*o*TFA-ddm) and cFPBO at room temperature.

application temperature range as shown in the subsequent section.

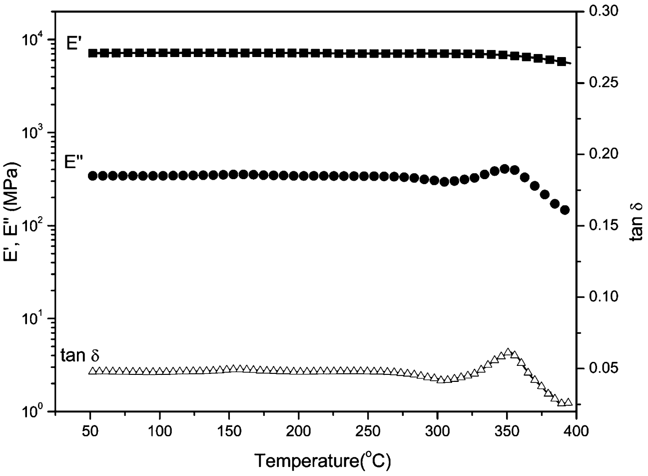


Figure 12. Dynamic mechanical spectra of cFPBO.

Thermal Properties of Cross-Linked CFPBO. The results of DMA of cFPBO are as shown in Figure 12 for the storage modulus (E'), loss modulus (E''), and tan δ. As shown in the figure, the T_g determined as the peak temperature of the tan δ curve is around 354 °C, whereas it is 350 °C with the E'' peak method. Of particular interest is that cFPBO shows a stable, constant storage modulus up to 300 °C due to the formation of polybenzoxazole, which is a stiffer molecular structure. Polymers with constant storage modulus in such a wide temperature range are rather rare. Furthermore, the T_g of cFPBO is as high as 354 °C, which is suitable for application as a matrix material of composites for a thermally demanding field. Of particular interest is that the precursor resin is readily processable. This is quite unusual for highly thermally stable polymers. Ordinarily, the T_g observed for thermoset polymers is near the polymerization temperature if the processing temperature is below the ultimate T_g of the material and is around ultimate T_g if it is polymerized above it. However, the current material, being processed near 200 °C yet showing T_g around 350 °C, is exceptional. This feature of bearing a $T_g \gg T_{\text{polymerization}}$ is a commonly observed processing advantage of benzoxazine resins, and the current resin herein studied also possess this advantage. Typically, polymers with high thermal stability are difficult to process, and their processing temperatures are high. Exceptionally easy processability of the current material, yet very high thermal properties, make this polymer attractive for various applications, such as in electronic, aerospace, automotive, and many other areas.

The thermal stability of cFPBO has also been studied by TGA, and the result is shown in Figure 13. The initial decomposition temperatures of 5% and 10% weight losses (T_{d5} and T_{d10}) for cFPBO under inert atmosphere are as high as 471 and 512 °C, respectively, as a consequence of the oxazole formation, and the char yield (Y_c) at 800 °C is 65%. The thermal property data of cFPBO are summarized in Table 1, which strongly demonstrate an exceptionally high thermal stability of cFPBO.

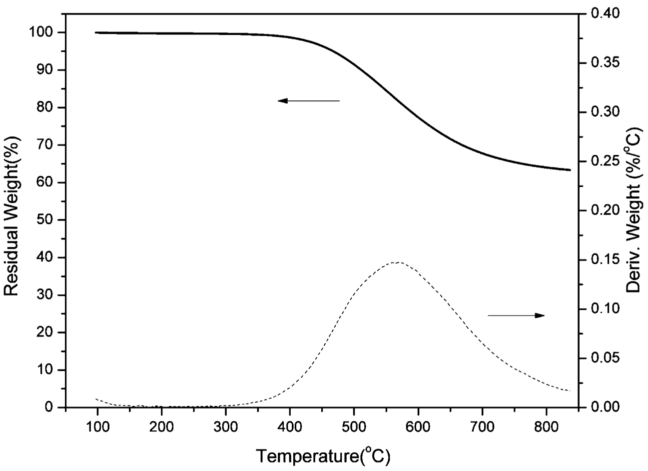


Figure 13. Thermogravimetric analysis of cFPBO.

Table 1. Thermal Properties of cFPBO

sample	T_g(DMA) (°C)	T_{d5} (°C)	T_{d10} (°C)	Y_c (wt %)
cFPBO	354	471	512	65

■ CONCLUSIONS

An o-trifluoroacetamide functional benzoxazine monomer has been successfully synthesized. The benzoxazine resin was shown to readily undergo a thermally mediated ring-opening polymerization below 200 °C without adding any initiators or catalysts and formed cross-linked polymeric networks. Moreover, the benzoxazole formation from the freshly generated o-amide polybenzoxazine was achieved at exceptionally low temperatures near 260 °C when the precursor polybenzoxazine was isothermally heat treated, which was significantly reduced compared with other o-amide functional benzoxazines. Furthermore, the fluorinated polybenzoxazole derived from difunctional benzoxazine monomer exhibited low dielectric constant (2.42−2.19 within the frequency range of 1 Hz−1 MHz) and high thermal stability with the glass transition temperature of 354 °C and a char yield of 65%.

Finally, the combination between the very long shelf life with the high reactivity under polymerization conditions in addition to the outstanding properties exhibited by each of the two possible families of polymers obtained from the same monomer makes oTFA-ddm a resin with extremely promising properties as raw material for high performance thermosets.

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Notes

The authors declare no competing financial interest.

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