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Phenolic Naphthoxazines as Curing Promoters for Benzoxazines

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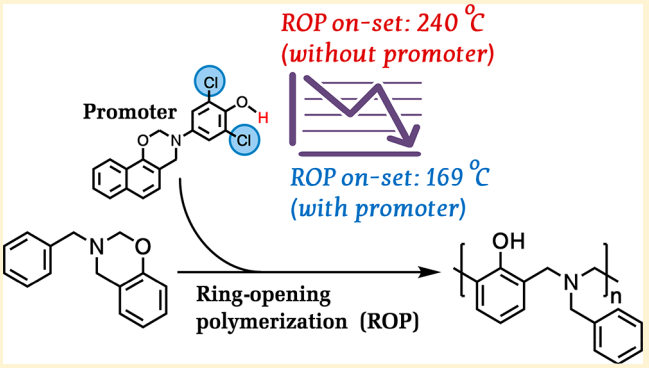
Supporting Information

ABSTRACT: The effect of phenolic hydroxyl bearing naphthoxazines as catalysts for the ring-opening polymerization (ROP) of simple 1,3-benzoxazines was investigated. The latent catalytic role of napthoxazines in the curing process of the mixtures was demonstrated by DSC and FT-IR investigations. It was found that phenolic naphthoxazines cause clear reduction in ROP temperature, particularly when electron-withdrawing groups are attached and an onset ROP temperature as low as 169 °C is attained. Thermal properties of the final polymers were also analyzed, and no significant effect of naphthoxazines on the thermal stability of the cured polybenzoxazines was observed.



INTRODUCTION

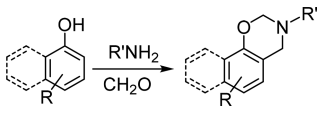
Polybenzoxazines (PBZs) and polynaphthoxazines (PNZs) emerged as contender alternative phenolics in the past decade because these materials exhibit superior properties compared to many other resins. PBZs and PNZs have high glass transition temperatures (T_g) generally more than 160 °C up to 400 °C, high char yields, and flame retardancy with low smoke and toxicity.[1−5] Moreover, these materials display remarkable tensile strength and modulus, limited water uptake unlike other traditional phenolics, dimensional stability during curing, and chemical resistance.[6−9] Hence, PBZs and PNZs are preferred for applications where harsh conditions present such as those using aerospace materials and high performance circuit boards, etc.[10]

PBZs and PNZs can be synthesized only from their corresponding monomers, namely 1,3-benzoxazines or naphthoxazines. The other isomers, however, do not yield analogous polymers. Although benzoxazines were first reported in the 1940s and their initial applications were for medicinal purposes, the potency of these compounds in material science was recognized much later.[11−17] One of the important aspects of these compounds is their simple synthesis. A primary amine, a suitable phenolic compound, and formaldehyde are the components of the synthesis (Scheme 1). Most of the amines and phenols are already commercially available, and therefore these monomers can be produced in a large scale with cost efficiency. Moreover, using various types of phenols and amines with different functional groups attached provides a high design flexibility for the corresponding polymers with tailored properties.[18,19] For example, cross-linking density of the PBZs can be increased by using allyl,[20,21] propargyl,[22] coumarine,[23] or heteronucleobase[24] functionalities. Alternatively, PBZs can be altered by selecting long-chain alkylamines[25,26] and amino alcohols[27,28] in monomer synthesis, etc. Moreover, polymeric benzoxazines were also synthesized using several chemistries to produce main-, side-, and end-chain polybenzoxazine precursors.[29−39] Consequently, many different specific benzoxazines for various purposes are readily accessible.

The polymerization of these monomers is a kind of thermally driven cationic ring-opening process (ROP) that proceeds over an oxazine ring.[40−42] The required polymerization temperatures generally lie between 220 and 260 °C, and for some monomers even higher temperatures are needed. As stated, ROP is based on cationic species that can easily be stabilized by N and O atoms on an oxazine ring.[43−45] Generally, initiation is triggered by the residual phenolic −OH groups present in monomers. These residues provide protons that are acting as cationic initiator and protonate either N or O atom of the heterocycle. Depending on the protonated site, the bond cleavage of O−CH_2−N differs, producing either aryl ether or aryl aminomethyl repeat units. Eventually, due to the thermal effect, aryl ether units rearrange and PBZ forms (Scheme 2). Interestingly, polymerization of benzoxazines through photochemically generated acids yield mostly soluble oligomers with complex structures.[46]

Benzoxazine monomers can readily be polymerized without any added catalyst, but generally high temperatures are required which is considered to be a major drawback in terms of energy consumption and necessity of thermal resistant equipment.

Scheme 1. Synthesis of Benzoxazine and Naphthoxazine



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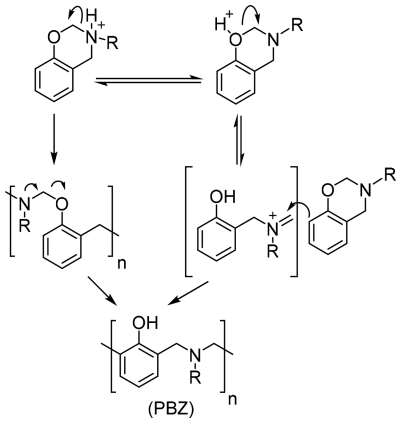
Scheme 2. Acid-Catalyzed ROP of a 1,3-Benzoxazine



Obviously, lower curing temperatures would be practical for many applications. Therefore, several catalysts to promote ROP of benzoxazines and naphthoxazines were reported tried by various research groups. For example, Lewis acids were found to reduce the curing temperatures down to 120−160 °C.[41] Typically, PCl_5, $POCl_3$, $TiCl_4$, $AlCl_3$, $FeCl_3$, etc., acted as efficient catalysts particularly when with solvents and ring-opening of oxazine took place even at room temperature. Moreover, acetylacetonato complexes of fourth period transition metals with nucleophiles promoted the polymerization efficiently and 120 °C as onset of ROP temperatures were obtained.[47] On the other hand, due to highly active catalytic nature of Lewis acid catalysts, they often initiate ROP during storage and lead to viscosity increase in formulations. Thus, latent catalytic systems which are dormant at room temperature or certain temperature intervals are highly desirable. Structurally different molecules other than benzoxazines or special benzoxazines such as diamines,[48,49] thiols,[50−54] toluene sulfonates,[55] and colloidal sulfur[56,57] can act as ROP latent catalysts. It should be noted that thiols are generally highly active at low temperatures but prone to storage problems. However, in some specific cases, disulfides play a better latent catalytic role than thiols.[58] As stated, designed benzoxazines with certain groups in the structure can also catalyze the ROP process. This approach provides additional for some applications since the system would only contain benzoxazines based structures and final product would not be contaminated by residual catalysts. Functional groups having acidic character on benzoxazines can obviously reduce the ROP temperatures. Thus, several benzoxazines were synthesized bearing −COOH and −OH functionalities.[59−61] In this connection, it should be pointed out that decarboxylation observed with COOH groups during the polymerization process generate voids in the final polymer.[62] Thus, −OH groups appear to be more beneficial as catalyst preventing problems associated with gas formations. For example, hydroxyethyl terminated ether chain-functional benzoxazines were found to reduce ROP temperature compared to the nonfunctional benzoxazines.[27] The mechanistic role of hydroxylethyl group in the polymerization was studied, and it was found that hydroxyethyl groups accelerate polymerization via interaction between −OH group and cationic intermediates formed during ROP. Similar effects were also observed for methylol containing monomers via hydrogen bonding between heteroatoms of oxazine and methylol group.[28] Moreover, phenolic monomers were also synthesized as built-in catalysts and effectively reduced ROP temperatures.[59] Despite these considerable efforts, further improvements in the reduction of polymerization temperature, particularly with cheap catalysts, still remains highly desirable and major concern for benzoxazine-based high performance thermosets. Herein, we describe a latent catalyst based on naphthoxazines to reduce the ROP of benzoxazines to practical temperatures, and the system would contain only benzoxazines and naphthoxazines. Technical aspects regarding applications of naphthoxazines as curing promoters of benzoxazine-based systems are reported elsewhere.[63]

EXPERIMENTAL SECTION

Materials. 1-Naphtol (Fluka AG, ≥99%), 4-amino-2,6-dichlorophenol (Alfa Aesar, 97%), paraformaldehyde (Aldrich, 95.0−100.5%), 4-aminophenol (Merck, ≥99%), *p*-anisidine (Aldrich, ≥99%), phenol (Aldrich, ≥99%), benzylamine (Aldrich, 99%), sodium hydroxide (Merck, ≥99%), potassium hydroxide (reagent grade, Aldrich, 90%), magnesium sulfate (Acros, 97%), methanol (MeOH, Merck, ≥99.9%), acetonitrile (ACN, Merck, 99.9%), ethyl acetate (EtOAc, Merck, ≥99.5%), tetrahydrofuran (THF, Sigma-Aldrich, ≥99.9%), dimethyl sulfoxide (DMSO, Sigma-Aldrich, ≥99%), *N,N*-dimethylformamide (DMF, Sigma-Aldrich, ≥99.8%), and ethanol (EtOH, Carlo Erba, ≥99.9%) were used as received. B-a monomer (bisphenol A and aniline based) was synthesized according to the literature.[2]

Characterization. All ^{1}H NMR spectra were recorded on an Agilent NMR System VNMRS 500 spectrometer at room temperature in $CDCl_3$ or DMSO-d_6 with $Si(CH_3)_4$ as an internal standard. FTIR spectra were recorded on a PerkinElmer FTIR Spectrum One spectrometer. Differential scanning calorimetry (DSC) was performed on PerkinElmer Diamond DSC from 30 to 320 °C with a heating rate of 10 °C min^{-1} under nitrogen flow. A typical DSC sample was 2−5 mg in a 30 μL aluminum pan. Thermal gravimetric analysis (TGA) was performed on PerkinElmer Diamond TA/TGA with a heating rate of 10 °C min^{-1} under nitrogen flow.

Synthesis of Naphthoxazines with Phenolic −OH Groups. A typical procedure is as follows: In a 100 mL round-bottomed flask, 1-naphthol (3 g, 0.021 mol) and 4-amino-2,6-dichlorophenol (3.7 g, 0.0208 mol) were dissolved in acetonitrile (30 mL), and the solution was mixed at ambient temperature. Formaldehyde solution was as follows; paraformaldeyhde (1.25 g, 0.042 mol), ethanol (5 mL), and ≈50 mg of NaOH were mixed and heated until the solution became clear. This solution was added to acetonitrile solution immediately. The whole mixture was magnetically stirred at ambient temperature for 24 h. The reaction solution was concentrated using a rotary evaporator and then precipitated in warm water. The resulting solid was filtered and washed with warm water. After that, the solid dissolved in hot ethanol and reprecipitated in water, filtered, and washed with copious amounts of water. The product was dried in a vacuum oven at 50 °C for 24 h, and an orange solid was obtained (yield: ≈69%) Note: 4-aminophenol were used instead of 4-amino-2,6-dichlorophenol for aminophenol-based monomer. These naphthoxazines were abbreviated as Npz-PhOHCl$_2$ for 4-amino-2,6-dichlorophenol and Npz-PhOH for 4-aminophenol derivatives.

Synthesis of Anisidine-Based Naphthoxazine. Acetonitrile (30 mL) was added in a 100 mL round-bottom flask containing 1-naphthol (3 g, 0.021 mol) and *p*-anisidine (2.56 g, 0.021 mol). Formaldehyde solution (1.25 g, 0.042 mol) was added portionwise to this solution. The whole mixture was magnetically stirred at ambient temperature for 24 h. The solvent was evaporated using a rotary evaporator. The resulting product was dissolved in ethyl acetate (100−120 mL) and extracted with 0.4 N sodium hydroxide for various times. Then, ethyl acetate solution was washed with distilled water (100 mL) for two times to neutralize the solution. The solution was dried with anhydrous $MgSO_4$ and filtered. Ethyl acetate was evaporated with a rotary evaporator, and the product was dried in a vacuum oven at 50

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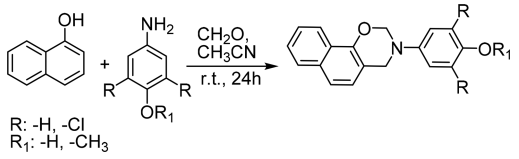
°C for 24 h. Finally, a brown solid was obtained (yield: ≈63%). The monomer is abbreviated as Npz-PhOCH$_3$.

Synthesis of Benzylbenzoxazine. Benzylamine (10.7 g, 0.1 mol), phenol (9.4 g, 0.1 mol), and paraformaldehyde (6 g, 0.2 mol) were mixed in 200 mL of 1,4-dioxane. The solution was heated to 105 °C for 16 h. After cooling the solution, 1,4-dioxane was removed using a rotary evaporator. Oily crude product was dissolved in diethyl ether, washed with 0.5 M NaOH solution 3−4 times, and finally washed with deionized water 2 times. The ether solution was dried with anhydrous Na_2SO_4 and then filtered to remove the salt. Then, diethyl ether was completely removed with a rotary evaporator, and viscous raw product remained. The raw product was recrystallized from an ethanol−water mixture and dried under vacuum at room temperature (rt). The product was obtained as white crystals (yield: 59%). The monomer is abbreviated as P-Bn (see Supporting Information for ^{1}H NMR spectrum, Figure S1).

RESULTS AND DISCUSSION

Generally, naphthols exhibit higher reactivity in several reactions than many phenols due to their extra electron-rich aromatic rings.[64] Based on Mannich reactions with these compounds conducted at low temperatures, aminophenols can produce −OH bearing oxazine monomers in one step.[59] In the case of ordinary phenols, similar monomers could only be synthesized by a three-step synthetic procedure containing imine formation, reduction of imine to amine, and finally ring-closing with formaldehyde.[65] By taking the advantage of reactivity of naphthols, free −OH-containing naphthoxazines were synthesized in one step at rt (Scheme 3). Two different

Scheme 3. Synthesis of Naphthoxazines Npz-PhOH (R: −H, R_1: −H), Npz-PhOHCl$_2$ (R: −Cl, R_1: −H), and Npz-PhOCH$_3$ (R: −H, R_1: −CH$_3$)



aminophenols, namely 4-amino-2,6-dichlorophenol and 4-aminophenol, were used in the synthesis to produce phenolic naphthoxazines (Npz-PhOHCl$_2$ and Npz-PhOH, respectively). Anisidine-based naphthoxazine was also synthesized as an −OH-capped sample with a methyl group (Npz-PhOCH$_3$). It should be noted that Npz-PhOH and Npz-PhOCH$_3$ were synthesized previously for organic or medicinal chemistry purposes by other or similar chemical methods.[66,67] Also, although Npz-PhOH was previously reported,[68] Npz-PhOHCl$_2$ is synthesized for the first time as a novel promoter, and the other two naphthoxazines were used only for comparison.

The spectral characterization of monomers was performed via ^{1}H NMR and FTIR spectroscopies. ^{1}H NMR spectra of naphthoxazines are shown in Figure 1. The characteristic oxazine N−CH$_2$−O peaks emerge at 5.47, 5.52, and 5.61 ppm; also, Ar−CH$_2$−O peaks are observable as wide bands at 4.57, 4.52, and 4.55 ppm for Npz-PhOCH$_3$, Npz-PhOH, and Npz-PhOHCl$_2$, respectively. Moreover, the NMR spectrum of Npz-PhOCH$_3$ exhibits a −OCH$_3$ proton signal at 3.76 ppm. The phenolic nature of Npz-PhOH and Npz-PhOHCl$_2$ can be proved by −OH peaks at 8.88 and 9.01 ppm, respectively. ^{13}C NMR spectroscopy was used to further verify the chemical structure of Npz-PhOHCl$_2$ since this technique is useful to identify the characteristic signal of oxazine and the carbon

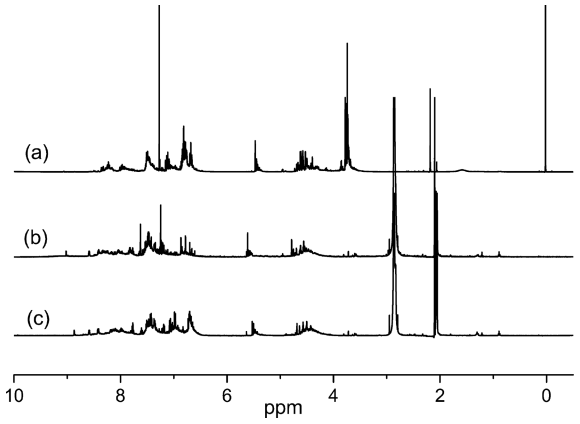


Figure 1. ^{1}H NMR spectra of Npz-PhOCH$_3$ (a), Npz-PhOHCl$_2$ (b), and Npz-PhOH (c).

attached to −OH groups. In Figure S2, the oxazine carbons are visible at 80.0 ppm (O−CH$_2$−N) and 51.4 ppm (Ar−CH$_2$−N). Moreover, the aromatic carbon attached to oxazine ring from the oxygen side is detectable at 149.5 ppm, and the aromatic carbon that has linkage with −OH appears at 159.9 ppm. FTIR spectra of the Npz-PhOH and Npz-PhOHCl$_2$ give additional evidence for the formation of oxazine ring in both structures (Figure 2). A vibration band of the substituted

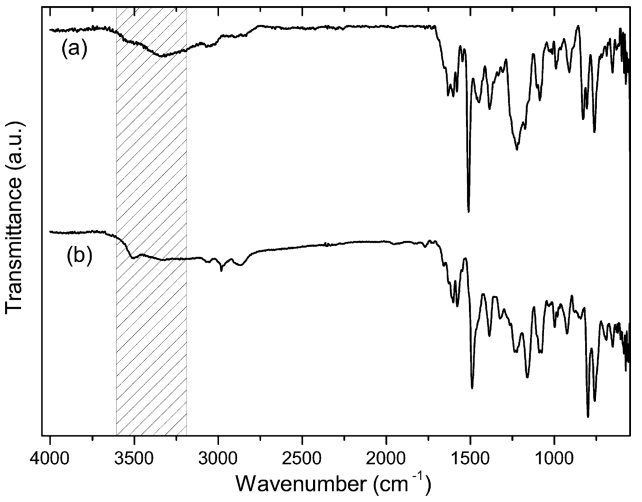


Figure 2. FTIR spectra of Npz-PhOH (a) and Npz-PhOHCl$_2$ (b).

aromatic ring of naphthoxazines also appears at 1490 and 1510 cm^{-1}, respectively. The C−O vibration band of monomers further verifies the presence of oxazine structure. The phenolic −OH groups are clearly visible as wide bands in the range of 3620−3176 cm^{-1}. Moreover, the stretching vibrations of aromatic C−H (3006−3096 cm^{-1}) and aromatic C═C (1453−1660 cm^{-1}) and the out-of-plane bending vibrations of aromatic C−H at 928 and 914 cm^{-1} are detected for both structures.

Figure 3 shows the DSC profile of the three compounds, and onset, end-set, and maximum curing temperatures are tabulated in Table 1.

As seen both from Table 1 and Figure 3, the onset of curing and the maximum curing temperature are as low as 152 and 180 °C for Npz-PhOHCl$_2$. Moreover, the endothermic at 117 °C corresponding to the melting of the Npz-PhOHCl$_2$ crystal is

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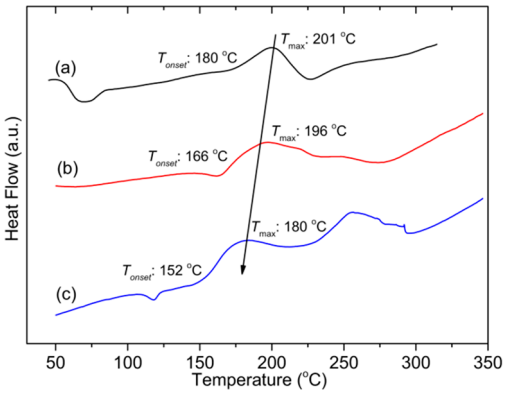


Figure 3. DSC thermograms of Npz-PhOCH$_3$ (a), Npz-PhOH (b), and Npz-PhOHCl$_2$ (c).

Table 1. DSC Characteristics of the Monomers[a]

monomer	onset temp of curing (°C)	max curing temp (°C)	end-set temp of curing (°C)	ΔH of curing (J/g)
Npz-PhOCH$_3$	180	201	226	−23
Npz-PhOH	166	196	219	−37
Npz-PhOHCl$_2$	152	180	206	−25

[a]DSC measurements were performed under nitrogen flow (20 mL min^{-1}) with a scan rate of 10 °C min^{-1}.

lower than that of many other naphthoxazines reported. Typically, the related temperatures for naphthoxazine functionalized with a cyanate ester group and aromatic amine-based naphthoxazine are 206 and 214 °C, respectively. In fact, these values are lower than the monomers Npz-PhOH and Npz-PhOCH$_3$ synthesized for comparison. As stated, acidic conditions would obviously decrease ROP temperature of the 1,3-oxazine ring. Therefore, a low ROP temperature for Npz-PhOHCl$_2$ is expected due to the contribution of phenolic −OH on the structure which has a more acidic character arising from the electron-withdrawing nature of the chlorine atoms. The effect of −OH group on ROP of benzoxazines was also demonstrated by using Npz-PhOCH$_3$ monomer as blank. Expectedly, the curing exotherm is higher than the other two monomers since this monomer contains no −OH groups. From these results, it can be deduced that the main effect on ROP temperature is the acidity of −OH group, and the strength of the acidity can be arranged by using additional electron-withdrawing groups on the aromatic ring of the amine in the synthesis. Moreover, Npz-PhOHCl$_2$ exposed to heat at different temperatures for 10 min to confirm the suitable temperature enough for the complete ring-opening (Figure S3). Accordingly, a complete ROP was observed after heating at 150 °C for 10 min.

In Figure 3, there is another broad exotherm after ROP of Npz-PhOHCl$_2$ between 237 and 279 °C. The end-set region of this exotherm is distorted and can be attributed to the degradation. However, onset and maximum temperature zones are uniform and correspond to an exothermic reaction. This reaction can possibly be an etherification reaction between −OH and −Cl groups. Although, such reactions are usually performed in the presence of a catalyst at mild conditions, etherification may still take place at such high temperatures with the effect of tertiary amine on polynaphthoxazines (Scheme 4). The basicity of tertiary amine can abstract proton from −OH generating a negatively charged nucleophilic oxygen. At such high temperature, this nucleophile can attack aromatic carbons where Cl atoms are attached. Subsequently, an amine salt can be formed through the reaction of amine with evolved HCl. Accordingly, the possibility of the formation of the aromatic C−O bond was tracked by FTIR spectroscopy. Therefore, two Npz-PhOHCl$_2$ samples were treated with different temperatures to distinguish the aromatic ether C−O bands from the C−O stretching vibrations of ring-opened oxazine. One of the samples was heated up to 170 °C to ring-open the oxazine and to prevent further possible etherification and the other sample exposed to heat up to 300 °C for the claimed etherification. The overlaid spectra of both samples are presented in Figure 4 which clearly exhibits different aromatic

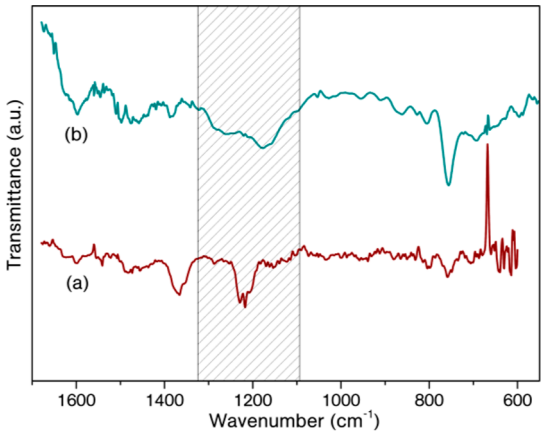
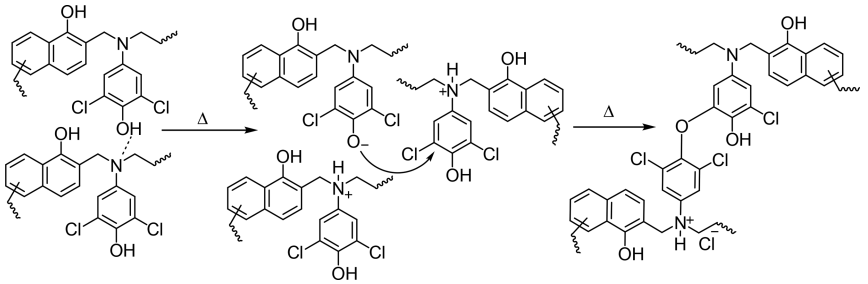


Figure 4. FTIR spectra of thermal treated Npz-PhOHCl$_2$ at 170 °C (a) and Npz-PhOHCl$_2$ at 300 °C (b).

C−O bonds for different temperatures. Accordingly, FTIR spectra comparison is giving clues about the possible

Scheme 4. Possible Etherification Reaction between PNZ Chains



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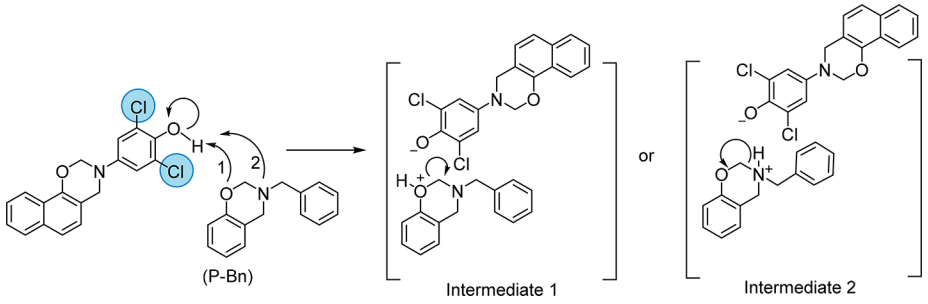
Scheme 5. Acid−Base Reaction between P-Bn and Npz-PhOHCl$_2$ Generating Two Different Types of Intermediates (Electron-Withdrawing Atoms on the Catalyst Are Highlighted)



etherification at high temperatures that is already observed as an exotherm in DSC analysis.

As previously stated, the initial stage of the polymerization of benzoxazines is the cleavage of methylene bridge on the oxazine by the residual protons (*vide ante*, Scheme 2). After bond cleavage, the formed cationic intermediates are stabilized by N and O atoms followed by the attack on aryl and rearrangement of labile bonds, finally producing PBZs. In a such polymerization, latent activation of catalyst during curing would be beneficial to solve the storage problems as reflected by the viscosity increment at the shelf. The DSC profile of Npz-PhOHCl$_2$ did not change after two months, indicating its stability for long time and latent catalytic nature.

Although Npz-PhOHCl$_2$ is curable at low temperatures, cured Npz-PhOHCl$_2$ is slightly soluble in common organic solvents such as DMSO, DMF, and THF, indicating that the polymerization of this monomer is limited and some oligomers remain in the final product. Therefore, postcuring was applied to have a complete network, but soluble parts still remained. As measured by GPC, the soluble part is mainly dimer having a molecular weight of $M_n \approx 700$ Da. These results revealed that Npz-PhOHCl$_2$ has limitation to be used in high performance applications where a stiff network is required. In light of these experiments, it seemed appropriate to use Npz-PhOHCl$_2$ in a different manner such as latent catalyst in certain formulations. For this purpose, Npz-PhOHCl$_2$ was used as catalyst by mixing with P-Bn monomer (Scheme 5) in two different mole ratios (3 and 5 mol %). As stated, the acidity of Npz-PhOHCl$_2$ is relatively high due to electron-withdrawing Cl atoms, and phenolic −OH group can protonate either O or N atom on the P-Bn monomer, resulting in two different types of intermediates (Scheme 5). Consequently, polymerization proceeds in two separate pathways. The resulting polymer would be a combination PBZ and PNZ; therefore, the final network would only be composed of phenolics, and any other component such as metal or noncurable organic catalysts residues are excluded from the system. These additives may act as potential void forming compounds or may alter the end properties of the PBZ network. Moreover, Npz-PhOHCl$_2$ is not corrosive compared to classical Lewis or organic acid catalyst, thus offering additional superiority.

The catalytic performance of Npz-PhOHCl$_2$ was studied by independent DSC investigations. In Figure 5 and Table 2, the comparative DSC profiles of P-Bn and the P-Bn/Npz-PhOHCl$_2$ system are presented. As expected, Npz-PhOHCl$_2$ acted as an effective catalyst for reducing the curing temperature of P-Bn. Increasing the Npz-PhOHCl$_2$ content in the mixture had more impact on the ROP temperature. Only 3 mol % of catalyst decreased the onset of curing of P-Bn from

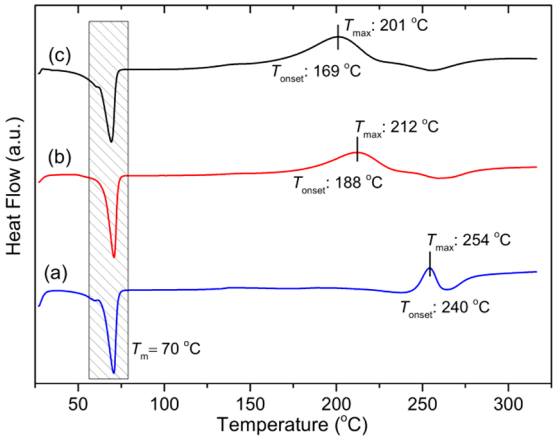


Figure 5. DSC Thermograms of P-Bn (a), P-Bn/Npz-PhOHCl$_2$ (3 mol %) (b), and P-Bn/Npz-PhOHCl$_2$ (5 mol %) (c).

Table 2. DSC Characteristics of P-Bn and Its Mixtures with Npz-PhOHCl$_2$[a]

monomer	onset temp of curing (°C)	max curing temp (°C)	end-set temp of curing (°C)	ΔH of curing (J/g)
P-Bn	240	254	263	−40.4
P-Bn/Npz-PhOHCl$_2$ (3 mol %)	188	212	232	−98.9
P-Bn/Npz-PhOHCl$_2$ (5 mol %)	169	201	221	−86.3

[a]DSC measurements were performed under nitrogen flow (20 mL min^{-1}) with a scan rate of 10 °C min^{-1}.

240 to 188 °C, and 5 mol % catalyst dropped this temperature as low as to 169 °C. It is clear that Npz-PhOHCl$_2$ showed an ability to reduce the onset of ROP of benzoxazine below 177 °C, which is considered as standard curing temperature for aerostructures. Moreover, a second exotherm observed in the DSC thermogram of Npz-PhOHCl$_2$ (see Figure 3) is not detectable because it is diluted in the system, and the possible etherification reaction is prevented. It should be emphasized that the Npz-PhOHCl$_2$ content can be increased more than 5 mol % since the catalyst is also curable and takes part of the network. Thus, increased amount of Npz-PhOHCl$_2$ would obviously reduce the ROP temperature even more, but in a such case a careful consideration is needed since some drawbacks may occur due to the composition of end-structure. Typically, high amounts of Npz-PhOHCl$_2$ may decrease the network stiffness (*vide ante*).

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Apart from DSC analysis, a simple FTIR study was performed for the latent catalyst property of Npz-PhOHCl$_2$ in P-Bn. For the purpose, a mixture of P-Bn/Npz-PhOHCl$_2$ (5 mol %) was prepared and subjected to FTIR analysis as prepared and 1 week later. Figure 6 shows the overlaid FTIR

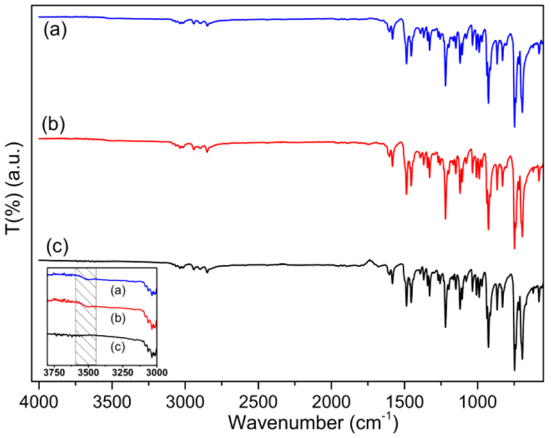

Figure 6. FTIR spectra of P-Bn/Npz-PhOHCl$_2$ after 1 week storage (a), fresh P-Bn/Npz-PhOHCl$_2$ mixture (b), and P-Bn (c).

spectra of P-Bn and P-Bn/Npz-PhOHCl$_2$ mixture. As can be seen, there is no detectable change in spectra; even the phenolic −OH band at 3508 cm^{-1} remained the same in both the bandwidth and peak. Accordingly, Npz-PhOHCl$_2$ is stable at rt for at least 1 week in P-Bn and thus can be used as a latent catalyst with classical benzoxazines without a storage problem.

Thermal stability of the PNZs derived from Npz-PhOCH$_3$, Npz-PhOH, Npz-PhOHCl$_2$, and PBZs from P-Bn and P-Bn/Npz-PhOHCl$_2$ (5 mol %) was measured by using thermogravimetric analysis (TGA). TGA traces and related thermal properties are presented in Figure 7 and Table 3, respectively.

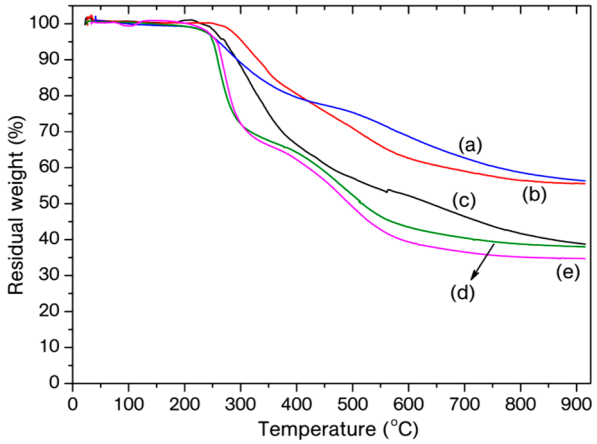

Figure 7. TGA thermograms of cured Npz-PhOHCl$_2$ (a), Npz-PhOH (b), Npz-PhOCH$_3$ (c), P-Bn/Npz-PhOHCl$_2$ (5 mol %) (d), and P-Bn (e).

According to $T_{5\%}$, $T_{10\%}$, and T_c values and TGA, all the three PNZs are more thermally stable than PBZs. The initial degradations of cured P-Bn and Npz-PhOHCl$_2$ are closer to each other, but the char yields differ up to 24%. The initial degradation temperature of Npz-PhOHCl$_2$ is lower than other naphthoxazines since curing of this monomer is complicated, and as stated before oligomers remain in the cured form; thus,

Table 3. Thermal Properties of the Cured Npz-PhOHCl$_2$, Npz-PhOH, Npz-PhOCH$_3$, P-Bn, and P-Bn/Npz-PhOHCl$_2$[a]

sample	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	T_c (%)
P-Bn	257	265	35
P-Bn/Npz-PhOHCl$_2$[b]	250	258	38
Npz-PhOCH$_3$	272	292	41
Npz-PhOH	301	327	56
Npz-PhOHCl$_2$	263	293	59

[a] $T_{5\%}$: the temperature for which the weight loss is 5%. $T_{10\%}$: the temperature for which the weight loss is 10%. T_c: the char yield at 800 °C. [b] The amount of Npz-PhOHCl$_2$ is 5 mol %.

evaporation of these small molecules can lead having lower $T_{5\%}$ and $T_{10\%}$ temperatures. On the contrary, possible self-etherification reactions under heat exposure may contribute to the thermal stability of cured Npz-PhOHCl$_2$ at high temperatures, resulting in a 59% of char yield. The char yields of these three naphthoxazines are higher compared to P-Bn due to ease of polyaromatization of naphthyl groups. The effect of Npz-PhOHCl$_2$ on char yield is also seen in TGA trace of P-Bn/Npz-PhOHCl$_2$ mixture since only 5 mol % Npz-PhOHCl$_2$ has a positive effect on char as 3% at 800 °C. On the other hand, the effect of the Npz-PhOHCl$_2$ on thermal properties of classical bisbenzoxazine (abbreviated as B-a, benzoxazine derived from bisphenol A and aniline) was also investigated by TGA (Figure S4), and the effect of catalyst on the thermal properties was observed as insignificant.

CONCLUSION

Npz-PhOHCl$_2$ undergoes thermally activated curing at temperatures much lower than that of conventional benzoxazines. The self-polymerization of Npz-PhOHCl$_2$ was found to be insufficient to produce a stiff polynaphthoxazine network; thus, this compound cannot be used solely as a material. However, the results revealed that Npz-PhOHCl$_2$ has high catalytic potential for the polymerization of benzoxazines. Accordingly, it was shown that the electron-withdrawing groups on naphthoxazines bearing phenolic −OHs are more acidic than their analogues and thus reduce the onset temperature of ROP of benzoxazines down to 169 °C. Furthermore, Npz-PhOHCl$_2$ was used with P-Bn and played a latent catalytic role since the mixture of P-Bn/NpzPhOHCl$_2$ had revealed no spectral change after 1 week and catalyst can be activated only by heating. Besides, Npz-PhOHCl$_2$ was also stable and did not undergo self-polymerization even after two months of storage. Apart from catalytic benefits, cured Npz-PhOHCl$_2$ exhibited high char yield as much as 59% at 800 °C. Similarly, cured P-Bn/Npz-PhOHCl$_2$ (5 mol %) mixture showed better char yield compared to pristine cured P-Bn. Consequently, naphthoxazines bearing phenolic −OH with neighboring electron-withdrawing functional groups have high acidity to catalyze ROP of benzoxazines acting as dormant species, and the system would only contain benzoxazines or naphthoxazines with improved char yields.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.8b00218.

Figures S1−S4 (PDF)

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Notes

The authors declare no competing financial interest.

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