Thermal Study on the Copolymers of Phthalonitrile and Phenylnitrile-Functional Benzoxazines

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ABSTRACT: *Ortho-, meta-,* and *para*-phenylnitrile–functional benzoxazines are polymerized at different compositions with phthalonitrile-functional monomers providing copolybenzoxazines of high thermal stability and easy processability. The most positive effect on these properties is obtained on copolymerizing phthalonitrile- and *ortho*-phenylnitrile–functional benzoxazines. Thermal decomposition of these polybenzoxazines is studied by thermogravimetry (TGA). It is demonstrated that only 30 mol % of phthalonitrile-functional benzoxazine added to the *ortho*-phenylnitrile–substituted monomer improves char yield significantly from 59 to 77 wt %, which is the value of neat phthalonitrile-based polybenzoxazine. Glass transition temperature (T_g) also dramatically increases from 180°C for neat *ortho*-phenylnitrile polymer to 294°C for the copolymer with 30 mol % of phthalonitrile-functional monomer. Additionally, the high melt viscosity of phthalonitrile-functional benzoxazines is dramatically decreased upon blending with phenylnitrile-functional monomer. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2937–2949, 1999
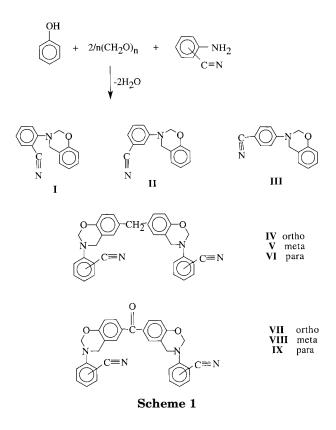
Key words: polybenzoxazine; phthalonitrile resin; phenylnitrile-based polymer; evolved gases analysis; thermal stability

INTRODUCTION

Nitrile-substituted aromatic compounds were used in the past as a precursor to obtain high molecular weight polymers. In these polymers, cyclotrimerization and formation of linear polymer chains containing —C≡N— group were reported as predominant products.[1] In all instances, the presence of catalysts was required for polymerization to occur. Metal halides such as $TiCl_4$ formed triazine rings from benzonitriles at temperatures < 300°C.[2] At temperatures > 300°C, only about 3% of high molecular weight polymer was obtained. A careful study of the reaction mechanism of benzonitrile polymerization

in the presence of catalyst showed that triphenyltriazine is an active intermediate and possible by-product of the polymerization, which then resulted in a linear polymer containing —C≡N— species.[3] Polymers with linear structures, polymethimines, were also prepared from benzonitrile in the presence of $ZnCl_2$ and HPO_3 as coreactants. First, triphenyltriazine–zinc chloride complex was formed at the temperature range of 200–300°C. Then, the proton produced from the $ZnCl_2$–HPO_3 complex attacked the triazine ring and led to the formation of the linear structure.[4] Analogous product was observed from the reaction of $ZnCl_2$ with melamine in the presence of the HPO_3 activator in the temperature range of 500–525°C. Linear polybenzonitrile, polyacrylonitrile, and other substituted linear polynitriles were prepared from the precursors by heating at higher temperatures over 400°C in the presence of $ZnCl_2$.[5] The reaction of nitrile groups

Scheme 1

als with high thermal stability and easy processability by copolymerizing them.
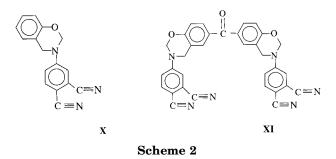
EXPERIMENTAL

All chemicals were used as received. Phenol (99.9%), paraformaldehyde (99%), 2-aminobenzonitrile (99%), 3-aminobenzonitrile (99.9%), and 4-aminobenzonitrile (98%) were purchased from Aldrich. 4-Aminophthalonitrile (97%) was purchased from Aestar Chemicals. 4,4′-Dihydroxybenzophenone and 4,4′-dihydroxyphenylmethane (bisphenol F) were obtained from Kennedy & Klim, Inc.

Synthesis of 3,4-Dihydro-2H-3-benzonitrile-1,3-benzoxazine Monomers

The monomers were synthesized by the solventless method (Scheme 1).[10] The stoichiometric amounts of phenol (0.01 mol), paraformaldehyde (0.02 mol), and 2-(3,4)-aminobenzonitrile (0.01 mol) were mixed together and heated at 120°C. The condensation reaction occurs in the melt state in complete absence of solvent. The synthesized monomers were purified by washing with 1N solution of NaOH and dried over sodium sulfate overnight. Synthesis of phthalonitrile-functional benzoxazine **X** and **XI** and their polymerization (Scheme 2) is described elsewhere.[7]

Preparation of Copolymers

The phenylnitrile and phthalonitrile-functional benzoxazine monomers were mixed and stirred at various mole percents of monomers in acetone at room temperature. Acetone was then evaporated in a vacuum oven at 40°C. The mixtures were copolymerized at 220 or 250°C in an air-circulating oven for 6 h. There was no evidence of phase separation on polymerization.

occurs during pyrolysis of polyacrylonitrile. It has been reported that this thermal polymerization can be initiated by nucleophilic species that attack nitrile groups and form active species $-C^+{=}N^-$. The active species continue the reaction with the neighboring nitrile group and a ladderlike polymer is formed with tetrahydronaphthiridine ring structure.[6]

Phthalonitrile-functional polybenzoxazines are highly thermal stable resins as described later. Processibility of these polybenzoxazines was found to be significantly better than for other phthalonitrile resins.[7] Nonetheless, when compared with standard polybenzoxazines without nitrile substituents, their curing temperature and melt viscosities were somewhat higher, which make their processing more difficult.[8] It was reported that the *ortho*-nitrile group in the *ortho*-phenylnitrile–functional benzoxazine is the most reactive during polymerization when compared with *meta*- and *para*-nitrile analogues.[9] In general, phenylnitrile-functional benzoxazines exhibit easy processability, as represented by low melt viscosity, but their thermal stability needed further improvement. Therefore, it was intended to combine the properties of both classes of nitrile functional polybenzoxazines and develop materi-

Scheme 2

Characterization

The benzoxazine monomers, corresponding polybenzoxazines, and their copolymers were characterized by Fourier transform infrared spectroscopy (FTIR) on a Bomem Michelson 110 MB. One hundred coadded scans were taken at a resolution of 4 cm^{-1} using a liquid-nitrogen-cooled mercury–cadmium–telluride (MCT) detector after a 20 min purge with nitrogen. A thin film of the sample was cast from an acetone solution on a KBr plate. To follow polymerization of the benzoxazines, the cast film on the KBr plate was isothermally cured in an oven under circulating nitrogen.

^{1}H-NMR spectra were taken on a Varian Gemini-200 with a proton frequency of 200 MHz by coadding 64 transients. Deuterated chloroform was used as a solvent and tetramethylsilane (TMS) was used as an internal standard. Deuterated acetone was used as a solvent for partially polymerized samples.

The thermal stability of polybenzoxazines was investigated by thermogravimetric analysis (TGA) performed on a TA Instruments thermogravimetric analyzer, high resolution TGA 2950, which has a sensitivity of 1 μg and is equipped with an evolved gases analysis (EGA) furnace. The evolved gases were collected in the gas cell of the TGA/IR interface and analyzed on the FTS-60A Bio-Rad infrared spectrometer with a resolution of 8 cm^{-1}. The temperature of the transfer line and the gas cell was kept constant at 300°C for all experiments. Nitrogen was used as a purge gas for all testing. The char yield of the polybenzoxazines was determined as the solid residue which remained at 800°C under nitrogen purge. $T_{5\%}$ and $T_{10\%}$ are defined as the temperatures at 5 and 10% weight loss. A heating rate of 20°C/min was used for all tests. All TGA curves were taken from the samples without further postcuring treatment. Differential scanning calorimetry (DSC) was performed on TA Instruments Modulated DSC 2920 with a heating rate of 10°C/min using nitrogen purge and an empty aluminum pan as a reference. A hermetically sealed pan was used for all DSC tests.

The samples for dynamic mechanical analysis (DMA) were prepared by thermal polymerization of degassed monomers in the specifically designed mold. The mold consisted of a U-shaped silicon rubber spacer placed between two glass plates. The mold was placed vertically in the vacuum oven and 4 g of monomer was degassed for several hours at 160°C. Next, the mold was placed into the air-circulating oven and the monomers were polymerized by heating to 220 or 240°C for 6 h. The void-free specimens with dimensions of approximately 48 × 12 × 3 mm were then polished by sanding to obtain a smooth surface. Dynamic mechanical spectra were obtained with a Rheometrics Dynamic Mechanical Spectrometer (RMS-800) equipped with a 2000–200 g cm dual-range force rebalance transducer. Specimens were tested in a rectangular torsion fixture. A maximum strain of 0.1% was applied sinusoidally during each temperature sweep at a frequency of 1 Hz after determining that this strain falls within linear viscoelastic range by strain sweep experiment. The experiment was performed at a heating rate of 2°C/min from room temperature to 300–350°C. Samples were submitted to thermal soak time of 30 s for each temperature change.

Void-free disks for steady shear viscosity experiment were prepared by degassing about 1 g of benzoxazine monomers in room temperature vulcanized (RTV) silicon rubber mold for 60 min at 80°C under vacuum. Steady shear viscosity experiment was performed in the shear rate range of 0.01–100 s^{-1} with Rheometrics Dynamic Mechanical Spectrometer (RMS-800) equipped with a 2000–200 g cm dual range force rebalance transducer. A forced air-convection oven surrounded the test fixture, allowing elevated temperature control to better than 0.5°C. Samples were subjected to steady shear isothermally in a 25-mm parallel plate geometry with 1-mm gap.

RESULTS AND DISCUSSION

^{1}H-NMR Characterization

Figure 1(a) displays ^{1}H-NMR spectrum of the mixture of the benzoxazine monomers **I** and **X** in deuterated acetone. The resonances at 4.65 and 5.4 ppm correspond to the protons of the methylene bridges of the *ortho*-nitrile–functional benzoxazine **I**. The peaks that are slightly shifted downfield at 4.75 and 5.5 ppm correspond to the methylene protons of the phthalonitrile-functional benzoxazine **X**. The resonances in the region of 6.5–7.5 ppm are assigned to the aromatic protons. Figure 1(b) represents the solution of the mixture of abovementioned monomers partially polymerized at 240°C for 30 min. These peaks that are assigned to the proton resonances of the methylene bridges of the oxazine ring in benzoxazine **I** and **X** are shifted downfield by about 0.15
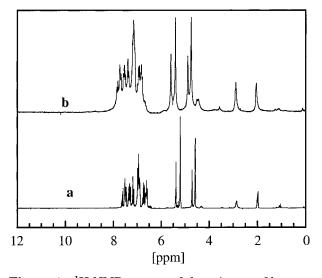
Figure 1 ^{1}H-NMR spectra of the mixture of benzoxazine monomers **I** and **X** (a), and cured at 240°C for 30 min (b).

Figure 2 DSC thermograms of benzoxazine **I** (a), benzoxazine **II** (b), benzoxazine **X** (c), 30 : 70 mixture of benzoxazine **I** and **X** (d), and mixture of benzoxazine **II** and **X** (e).

ppm in this spectrum of partially polymerized mixture. The resonances in the region of 4.4–4.5 ppm correspond to the protons of the open oxazine ring structures, such as dimers and low molecular weight oligomers.[11] The resonance at 2.9 ppm can be assigned to the protons of hydroxyl OH groups, which are produced on oxazine ring opening polymerization. The higher degree of polymerization could not be followed by this technique because of the solubility limitations. Therefore, polymerization and structure of the copolymers were investigated by DSC and FTIR.

DSC and FTIR Characterization of Polymerization

DSC thermogram [Fig. 2(d)] of the 30 : 70 mixture of phthalonitrile and *ortho*-nitrile–functional benzoxazine reveals two new major exotherms; the exotherm at 250°C is followed by a broad exotherm centered at 315°C (Fig. 2). The mixture of *meta*-nitrile and phthalonitrile-functional benzoxazines also show two exotherms centered at 225 and 292°C (e). For comparison, DSC thermograms of neat phthalonitrile (c), *ortho*-phenylnitrile (b), and *meta*-phenylnitrile–functional benzoxazines (a) are also displayed. It is obvious that the mixture exhibits different curing profiles when compared with the neat resins. These processes separate more when compared with the neat phthalonitrile-functional monomer **I** (thermogram b). To identify the processes, which occur during these exothermic reactions, structural changes during the polymerization of benzox-
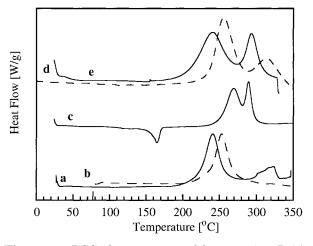
azine **I** and **X** were followed by FTIR (Fig. 3) at 240°C. This temperature was chosen based on the onset of the first exotherm in the DSC thermogram of this sample. The intensity of the bands at 975, 954, and 761 cm^{-1} (designated by asterisks) decreases with polymerization time (spectra b and c). At the same time, the intensity of the hydroxyl bands in the region of 3280–3390 cm^{-1} increased (not shown here). This confirms that oxazine rings from both comonomers were consumed in the curing process and oxazine ring
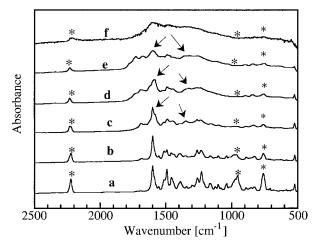

Figure 3 FTIR spectra of 30 : 70 copolymers from benzoxazine **I** and **X**, at room temperature (a), cured at 240°C for 30 min (b), at 240°C for 60 min (c), at 300°C for 60 min (d), at 400°C for 60 min (e), and 500°C for 30 min (f).

Figure 4 FTIR spectra of 30 : 70 copolymer from benzoxazine **II** and **X**, at room temperature (a), cured at 220°C for 30 min (b), at 220°C for 60 min (c), at 270°C for 60 min (d), at 400°C for 60 min (e), and 500°C for 60 min (f).
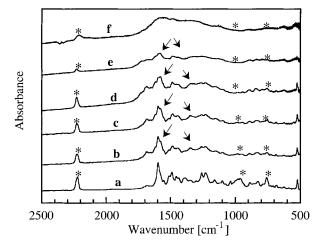
opening polymerization takes place at this temperature.

The intensity decrease of the band at 2221 cm^{-1} is observed (designated by asterisks). New bands at 1686, 1657, 1580, and 1352 cm^{-1} (designated by arrows) suggest the formation of C≡N-containing species on nitrile reactions. The first two bands (1686 and 1657 cm^{-1}) are believed to appear as a result of oxazine polymerization and the intramolecular reaction of *ortho*-nitrile and oxazine ring, whereas the other listed bands are characteristic of triazine formation as it was reported elsewhere.[7]
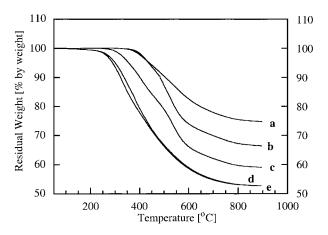

Figure 5 TGA curves of polybenzoxazine **IV** (c), polybenzoxazine **V** (d), polybenzoxazine **VI** (e), 10 : 90 copolymer from benzoxazine **X** and **IV** (b), and 50 : 50 copolymer of polybenzoxazine **X** and **IV** (a).
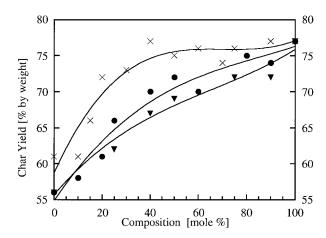

Figure 6 The dependence of char yield on the benzoxazine composition: (●) copolymer from **I** and **X**, (×) copolymer from **II** and **X**, (▼) copolymer from **III** and **X**.

The spectrum at 300°C (d) was taken to identify structural changes happening during the second exothermic process in the DSC thermogram of this *ortho*-phenylnitrile/phthalonitrile polybenzoxazine mixture. The only difference found in this spectrum is the appearance of a new band at 1722 cm^{-1}. This band can be assigned to the carbonyl groups, which are very likely formed on degradation of the methylene units in the Mannich bridge at this temperature. This is supported by the disappearance of the bands in the range of 2850–2900 cm^{-1}, which are assigned to these methylene bridges. This degradation is not accompanied by weight loss as was found in the TGA curves of this polybenzoxazine mixture. The nitrile band at 2221 cm^{-1} remains in the spectra even at higher temperatures up to 300–400°C (spectra d and e). However, the spectrum f of the charred sample at 500°C shows only a very low intensity broad band at 2200 cm^{-1}.

Figure 4 displays FTIR spectra of the mixture of phthalonitrile and *meta*-nitrile–functional benzoxazine. Spectrum a represents a thin film of the mixture of these two monomers at room temperature, where the nitrile single band appears at 2224 cm^{-1}. On curing at 220°C, the intensity of the bands at 980 and 760 cm^{-1} significantly decreases (designated by asterisks) and new bands at 1684, 1574, and 1354 cm^{-1} (designated by arrows) are observed in spectra b and c. These bands were previously assigned to the triazine cyclic species formed by cycloaddition reaction of phthalonitrile functionalities.[7] Therefore, it is believed that the first exotherm in the DSC thermogram of this mixture represents again the oxazine
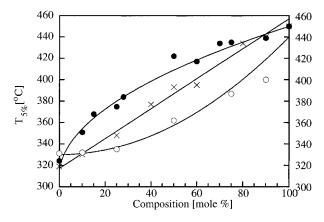
Figure 7 The dependence of $T_{5\%}$ on the benzoxazine composition: (●) copolymer from **I** and **X**, (×) copolymer from **II** and **X**, (○) copolymer from **III** and **X**.

ring opening polymerization accompanied by the phthalonitrile reaction. Spectrum d of samples cured at a higher temperature of 270°C for 1 h was taken to identify the second exotherm in the DSC thermogram of this mixture. The only difference found in this spectrum is also the appearance of the carbonyl band at 1720 cm^{-1} and increased intensity of the bands assigned to the C=N species of the cyclic triazine. The spectra taken at 300, 400, and 500°C show that the nitrile band at 2224 cm^{-1} does not disappear completely even when heating at 400°C for 1 h. Spectrum f represents a char from the *meta*-phenylnitrile/ phthalonitrile copolybenzoxazine heated at 500°C for 1 h in nitrogen. Similar to the *ortho*-nitrile
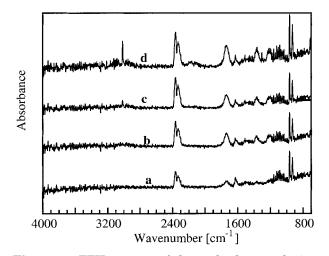
case, only a low intensity broad band at 2212 cm^{-1} also appears in the spectrum.

A part of the nitrile groups of the 30 : 70 mixture of phthalonitrile/*ortho*-phenylnitrile (*meta*-phenylnitrile) benzoxazine undergoes reaction at the polymerization temperature in addition to oxazine ring polymerization as was demonstrated by FTIR and DSC. Additionally, it was also shown that most of the remaining nitrile functionalities are consumed during the char formation process of these copolymers at higher temperatures above 400°C. The thermal stability of these copolymers is further investigated by TGA.

Thermogravimetric Analysis

The results of thermal analysis for all investigated resins are summarized in Table I. All phenylnitrile-functional resins and their copolymers with phthalonitrile-functional compounds exhibit high thermo-oxidative stability as was shown by TGA experiments performed in air. For most of the high performance resins, thermo-oxidation process starts at 500°C, and the char yield at 600°C is zero.[7] However, in the case of phenylnitrile and phthalonitrile copolybenzoxazines, the material still has significant char residue at 700°C, as shown in Table I. All copolymers of *ortho*-phenylnitrile and phthalonitrile-functional benzoxazines showed dramatically improved char yield and decomposition temperature $T_{5\%}$ over the *ortho*-phenylnitrile homopolymer.

Figure 5 shows TGA curves of polybenzoxazines derived from bifunctional monomers **IV**, **V**,

Figure 8 FTIR spectra of the evolved gases during degradation of 50 : 50 copolymer from *ortho*-phenylnitrile benzoxazine **I** and benzoxazine **X**: 360°C (a), 470°C (b), 490°C (c), and 530°C (d).
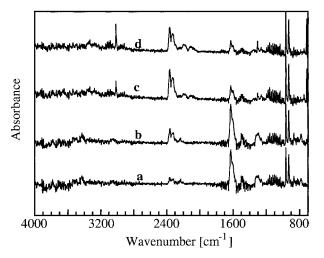

Figure 9 FTIR spectra of the evolved gases during degradation of 50 : 50 copolymer from *meta*-phenylnitrile benzoxazine **II** and benzoxazine **X**: 350°C (a), 400°C (b), 450°C (c), and 500°C (d).

Table I   Thermal Properties of Phthalonitrile and Phenylnitrile-Functional Polybenzoxazines and Their Copolymers

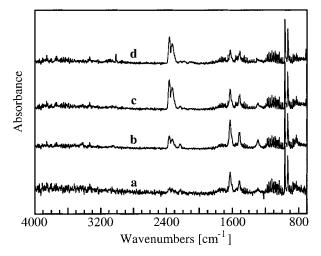| Monomer Unit	$T_{5\%}$ (°C)/N_2	$T_{10\%}$ (°C)/N_2	Char Yield (wt %)/N_2 at 800°C	$T_{5\%}$ (°C)/air	$T_{10\%}$ (°C)/air	Char Yield (wt %)/air at 700°C
I	332	371	60	365	407	41
II	317	355	56	357	398	18
III	331	369	55	343	374	30
50 : 50 Copolymer of **I** and **X**	430	515	77	—	—	—
IV	356	410	60	366	421	48
50 : 50 Copolymer of **IV** and **X**	438	508	76	—	—	—
VIII	410	537	74	448	528	46
IX	384	436	68	418	475	55
50 : 50 Copolymer of **VII** and **X**	410	510	76	445	526	21
30 : 70 Copolymer of **VII** and **XI**	496	520	80	—	—	—

Figure 10   FTIR spectra of the evolved gases during the degradation of 50 : 50 copolymer from *para*-phenylnitrile–functional benzoxazine **III** and benzoxazine **X**: 350°C (a), 400°C (b), 450°C (c), and 500°C (d).

Figure 12   FTIR spectra of the evolved gases during the degradation of polybenzoxazine **II**: 300°C (a), 350°C (b), 400°C (c), and 450°C (d).

and **VI**. The char yield of *ortho-*, *meta-*, and *para*-phenylnitrile–functional polybenzoxazines is in the range of 53–60 wt % and $T_{5\%}$ is in the range of 290–360°C. Char yield of an analogous polybenzoxazine based on aniline is 45 wt %. Copolymer prepared from 50 mol % of phthalonitrile benzoxazine **X** with *ortho*-phenylnitrile benzoxazine **IV** exhibited significantly improved char yield up to 76 wt % and temperature of decomposition ($T_{5\%}$) up to 438°C.

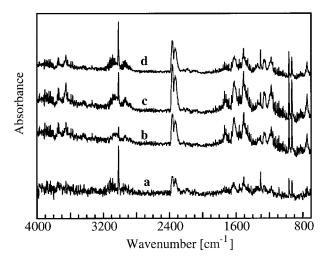Next, to verify this concept, the thermal stability of the copolybenzoxazines from monofunc-

tional phenylnitrile benzoxazine **I** and also monofunctional phthalonitrile benzoxazine **X** at different compositions was investigated. Figure 6 shows the dependence of char yield on the composition of copolymers. As expected, the copolymers of *ortho*-nitrile–functional benzoxazine with phthalonitrile analogue exhibit synergistic effect on char formation. On copolymerization of only 30 mol % of phthalonitrile compound with *ortho*-phenylnitrile resin, char yield increased to 77 wt %, which is the value of char yield for neat phthalonitrile resin. Positive effect on char formation was also observed on blending of *meta-* and *para-*

Figure 11   FTIR spectra of the evolved gases during the degradation of polybenzoxazine **I**: 300°C (a), 350°C (b), 400°C (c), and 450°C (d).
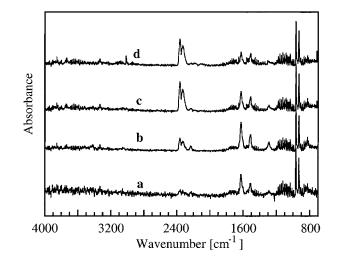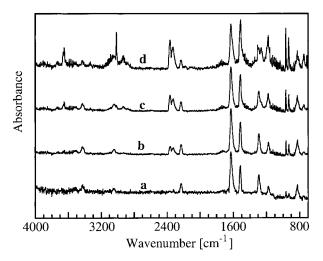

Figure 13   FTIR spectra of the evolved gases during the degradation of polybenzoxazine **III**: 300°C (a), 350°C (b), 400°C (c), and 450°C (d).

phenylnitrile–functional benzoxazines with phthalonitrile resin. Similar tendency was observed for $T_{5\%}$ as shown in Figure 7. The most positive effect on $T_{5\%}$ increase was observed for the copolymer of 50 : 50 composition of *ortho*-phenylnitrile and phthalonitrile-functional polybenzoxazines. This composition increased $T_{5\%}$ from 332 to 450°C, which is again the value of neat phthalonitrile-based polybenzoxazine. Copolymers based on *meta*-phenylnitrile and phthalonitrile resins showed a proportional increase in $T_{5\%}$. Although copolymerization of phthalonitrile and *para*-phenylnitrile compounds did not show a positive effect on $T_{5\%}$, copolymerization of phthalonitrile and phenylnitrile resins more significantly affected char formation than temperature of decomposition ($T_{5\%}$).

The concentration of nitrile groups corresponding to 30 : 70 phthalonitrile/*ortho*-phenylnitrile copolymer is sufficient to achieve maximum char yield. This is because *ortho*-phenylnitrile compounds undergo a special reaction providing a restricted Mannich bridge, not in the char formation process as it is for *meta*- and *para*-nitrile–based polybenzoxazines, but during polymerization of the resin.[9] Therefore, in addition to char yield, the decomposition temperature ($T_{5\%}$), which is influenced by the thermal stability of the polymer structure containing Mannich bridge, is also improved.[12]

To verify that the remaining nitrile functionalities are consumed in char formation process, the evolved gases during the degradation of these copolybenzoxazines were investigated. It was also intended to study the effect of the *ortho*-, *meta*-, and *para*-nitrile substituents on the char formation of their copolymers with phthalonitrile precursors.

TGA/FTIR Interface Analysis of Evolved Gases

Figure 8 shows FTIR spectra of the evolved gases during the thermal decomposition of 50 : 50 copolymers of *ortho*-phenylnitrile and phthalonitrile-functional benzoxazines taken during the TGA run. The derivatives of the TGA curve have two broad maxima centered at 400 and 600°C, which suggests the two major decomposition processes are occurring during the degradation of this copolymer. It was reported elsewhere[7] that only ammonia (two sharp bands at 930 and 960 cm^{-1}), carbon dioxide (bands at 2350 and 2370 cm^{-1}), and substituted benzenes (very low intensity bands at 1610, 1500, and 1050 cm^{-1}) evolved during the degradation of neat phthalonitrile-

functional polybenzoxazine. These species are also predominant decomposition products of the first degradation process of the copolymer with *ortho*-phenylnitrile–functional benzoxazine [Fig. 10(a)]. Additionally, the bands at 1720, 1200, and 1360 cm^{-1} appear in the spectra of this sample [Fig. 10(b, c, and d)]. The carbonyl band at 1720 cm^{-1} found in these spectra is unique to the *ortho*-phenylnitrile–containing copolybenzoxazine. The intensity of these bands increases as the degradation temperature increases. At the final stage of degradation (spectrum d), two broad bands with only low intensity at 2180 and 2210 cm^{-1} remain in this spectrum.

The TGA derivative curve of the 50 : 50 copolymer of the *meta*-phenylnitrile and phthalonitrile-functional resins show two maxima, a sharper peak centered at 400°C, and, at a later stage of degradation, a broader peak centered at 590°C. Expectedly, the evolved gases consist of different species as shown in Figure 9. Unlike the previous *ortho*-phenylnitrile case, a low-intensity nitrile band at 2227 cm^{-1} can be observed in the spectra at the early stage of degradation, indicating that remaining unreacted phenylnitriles evaporated during the degradation. This can explain the difference in the dependence of char yield versus composition of these two copolymers. Nitriles are more effectively consumed during the polymerization of *ortho*-phenylnitrile/phthalonitrile benzoxazine copolymer than is for the case of *meta*-phenynitrile/phthalonitrile copolybenzoxazine.

Para-nitriles in the copolymers were found to be the least effective for char formation as shown in Figure 6. Spectra of the evolved gases of the 50 : 50 copolymer from phthalonitrile and *para*-phenylnitrile–functional benzoxazines are shown in Figure 10. At the early stage of degradation, low-intensity bands at 2227 cm^{-1}, representing nitrile functional groups, and the bands at 1626, 1504, and 1299 cm^{-1} are found in this spectrum beside characteristic ammonia bands at 930 and 960 cm^{-1}. At the later stages of the degradation (spectra c and d), predominant products are carbon dioxide, ammonia, and the species represented by the bands at 2110–2180 cm^{-1}.

As a tool for band assignments, evolved gases of the lower charring polybenzoxazines from **VI**, **VII**, and **VIII** were investigated. *Ortho*-phenylnitrile–functional polybenzoxazine shows almost complete consumption of phenylnitrile functionalities. There are only very low intensity bands at 2188 and 2109 cm^{-1} found in the spectra (Fig. 11), because nearly all nitrile groups are con-

Table II FTIR Analysis of the Evolved Gases of the Phenylnitrile-Functional Polybenzoxazines and Their Copolymers

T (°C)	FTIR Band (cm^{-1})	Assignments[a]	Degradation Products
Polybenzoxazine I			
350	2366 (m)	C=O stretch	Carbon dioxide
	2331 (m)	C=O stretch	
	963 (m)	NH stretch	Ammonia
	930 (m)	NH stretch	
	3656 (w)	Free OH stretching	Phenol or substituted phenols
	3050 (m)	C—H stretching of benzene ring	Phenol or substituted phenols
	1613 (w)	C=C quadrant stretching of benzene ring	Phenol or substituted phenols
	1504 (w)	C=C stretch of benzene ring	
	1295 (m)	C—O stretch interacting with OH deformation	
	1173 (w)	—CH$_2$— wag	
	737 (w)	C—H out-of-plane bending of benzene ring	
450 (only new bands)	1251 (w)	C—O stretch	Phenol or substituted phenols
	1241 (w)	C—O stretch	Phenol or substituted phenol
	1717 (m)	C=O stretch	
	2937 (w)	—CH$_2$— stretch	
	737 (m)	C—H out-of-plane bending of benzene ring	
	2188 (w)	NCN stretch	Carbodiimides
	2109 (w)		R—N=C=N—R
Polybenzoxazine II			
350	2227 (w)	CN stretch	Nitrile
	2366 (w)	C=O stretch	Carbon dioxide
	2331 (w)	C=O stretch	
	963 (m)	NH stretch	Ammonia
	930 (m)	NH stretch	
	3338 (w)	NH stretch	Aminobenzonitrile
	3423 (w)	NH stretch	
	3050 (w)	C—H stretching of benzene ring	Aminobenzonitrile Aminobenzonitrile
	1621 (s)	NH$_2$ deformation	
	1600 (s)	C=C quadrant stretching of *meta*-substituted benzene ring	
	1500 (m)	C=C stretching of benzene	Aminobenzonitrile
	700 (m)	NH$_2$ wag	Aminobenzonitrile
	1313 (m)	Ph—N stretch	Aminobenzonitrile
500 (only new bands)	2183 (w)	Out-of-phase stretch of NCN	Carbodiimides
	2080 (w)		R—N=C=N—R
	3656 (m)	Free OH stretch	Phenol or substituted phenol
	1251 (w)	—C—O stretch	Phenol or substituted phenol
	1248 (m)	—C—O stretch	
	1295 (w)	—C—O stretch	
	737 (m)	C—H out-of-plane bending of benzene ring	
	700 (m)		

Table II *Continued*

T (°C)	FTIR Band (cm^{-1})	Assignments[a]	Degradation Products
Polybenzoxazine III			
350	3421 (w)	NH stretch	Aminobenzonitrile
	3521 (w)	NH stretch	
	2227 (w)	CN stretch	Aminobenzonitrile
	1617 (s)	NH_2 deformation	Aminobenzonitrile
	1512 (s)	C=C stretching of benzene ring	Aminobenzonitrile
	1290 (m)	Ph—N stretch	Aminobenzonitrile
	1160 (w)	C—N—C stretch	
	968 (w)	NH stretch	Ammonia
	920 (w)	NH stretch	Ammonia
	815 (m)	C—H out-of-plane bending of benzene ring	
500 (only new bands)	3050m (w)	C—H stretching of benzene ring	
	2183 (w)	Out-of-phase stretch of NCN	Carbodiimides
	2079 (w)	bond	R—N=C=N
	3656 (w)	Free OH	Phenol or substituted phenols
	1254 (m)	C—O stretch	Phenols or substituted phenols
	740 (m)	C—H out-of-plane bending of benzene ring	

[a] FTIR band assignments are according to the refs. 12 and 13.

sumed during polymerization.[9] The presence of aminophenylnitrile species was found only in the spectra of early-stage decomposition products of *meta*-phenylnitrile–functional polybenzoxazine as shown in Figure 12. Figure 13 shows the FTIR spectra of the degradation products of *para*-phenylnitrile–functional polybenzoxazine. Substituted phenols were identified in the later stage of the degradation of *meta*- and *para*-phenylnitrile–functional polybenzoxazines. The *para*-phenylnitrile–based polybenzoxazine contains the highest concentration of the phenylnitrile species as represented by the intensity of the band at 2227 cm^{-1}. The highest concentration of aminophenylnitrile species was also found in the evolved gases of *para*-nitrile and phthalonitrile-functional copolybenzoxazines. No aminophenylnitrile species were found in the spectra of the *ortho*-phenylnitrile and phthalonitrile-based copolymers.

The tentative band assignments and identification of degradation products is summarized in Table II. The bands at 2188 and 2109 cm^{-1}, which were found in the solid phase of the degradation products of the investigated polybenzoxazines and their copolymers, are assigned to the carbodiimide species R—N=C=N—R.[13] It is presumed that their presence is the result of the evaporation of not fully carbonized dimers formed on nitrile cyclization, and/or they can represent species formed on decomposition of Mannich bridge of the polybenzoxazine-crosslinked structure.

The crosslinked network formation of this class of polybenzoxazines was further investigated by DMA.

Dynamic Mechanical Analysis and Steady Shear Viscosity

It was mentioned that the polymerization of *ortho*-phenylnitrile–functional benzoxazine derived from **I** follows a different pathway than its *meta*- and *para*-nitrile analogues.[9] Despite the fact that the polymer from **I** shows relatively high shear modulus of 2.2 GPa at room temperature, the dependence of loss modulus versus temperature is very broad and does not display any significant maximum. The loss modulus starts dropping at 175°C, which is likely the glass transition temperature (T_g) of this material. The dependence of tan δ versus temperature is also very broad with the maximum around 200°C.[9] When compared with standard polybenzoxazines based on unfunctional primary amines, this broad dependence of loss modulus and tan δ is atypical.[14]

DMA spectra of 30 : 70 copolymer of phthalonitrile-functional benzoxazine **X** and *ortho*-phenylnitrile benzoxazine **I** are shown in Figure 14. The loss modulus maximum shifted to 294°C, which is almost the same G'' maximum of the neat phthalonitrile resin and the maximum is much sharper.[7] The maximum of tan δ curve is centered at 340°C and storage modulus does not show a significant drop as a function of temperature. This suggests that a higher degree of crosslinking was obtained through the polymerization of phthalonitrile in addition to the polymerization of *ortho*-nitrile and oxazine ring.

One advantageous characteristic property of benzoxazine monomers is their low melt viscosity, which makes them easily processable when compared with other resins such as phenolics.[15] This is due to the lack of intermolecular hydrogen bonding in the closed oxazine ring structure. Figure 15 shows the dependence of steady shear viscosity versus temperature for phthalonitrile-functional benzoxazine (c), the 30 : 70 mixture of phthalonitrile benzoxazine/*ortho*-phenylnitrile benzoxazine (b), and neat *ortho*-nitrile–functional benzoxazine (a). The neat phthalonitrile benzoxazines exhibit high melting point (160°C) and high melt viscosity than standard benzoxazine resins without nitrile functionality. On the other hand, phenylnitrile monofunctional benzoxazines are viscous liquids at room temperature with viscosity of 6×10^5 Pa s, which further decreases to 1 Pa s at 80°C (Fig. 15). The blending of these two compounds provided easily processable material, as shown by lowering the melt viscosity to 0.9 Pa s at 120°C for the 30 : 70 mixture of phthalonitrile and *ortho*-phenylnitrile resin. Additionally, these materials provide high char yield, high thermal stability, and high T_g.
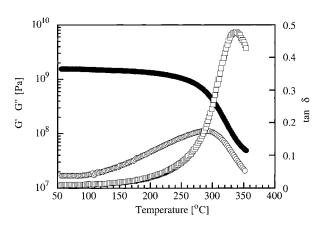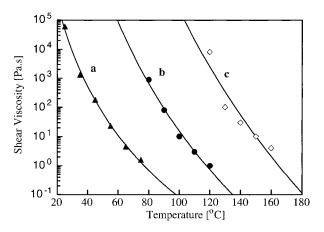

Figure 15   Steady shear viscosity versus temperature for benzoxazine monomer **I** (a), 30 : 70 mixture of benzoxazine **I** and **X** (b), and benzoxazine **X** (c).

CONCLUSIONS

Polybenzoxazines of high thermal stability were prepared from the phenylnitrile and phthalonitrile-functional benzoxazines and their copolymers. TGA/FTIR interface analysis of the evolved gases during degradation of these polybenzoxazines confirmed that high char yield is a result of the reaction of part of the nitrile functionalities during cure and additional conversion of the remaining nitriles during the char formation process. The most effective consumption of nitrile functionalities was found for *ortho*-phenylnitrile–based polybenzoxazines and its copolymers with phthalonitrile-based resin. As a result, these polybenzoxazines showed the best performance among phenylnitrile-functional polybenzoxazine and their copolymers as is indicated by high T_g, low melt viscosity, and high char yield.

Figure 14   DMA spectra of the 30 : 70 copolymer of polybenzoxazine **X** and **I**: (●) G', (○) G'', and (□) tan δ.

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