

# Synthesis, characterization and thermal polymerization of new 3,4-dihydro-2H-1,3-naphthoxazine monomers

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DOI: [dx.doi.org/10.14314/polimery.2017.086](https://doi.org/10.14314/polimery.2017.086)

**Abstract:** Two new 1,3-naphthoxazine monomers (M-A and M-B) were synthesized *via* a modified step-wise procedure in which methylene bromide was used for the ring-closure reaction. Condensation of 2-hydroxy-1-naphthaldehyde with 1,6-hexamethylenediamine or 1,4-phenylenediamine gives imine compounds, which were converted to 2-hydroxynaphthylamines by reduction with NaBH<sub>4</sub> in methanol. Ring-closure reaction between the 2-hydroxynaphthylamines and methylene bromide results in the formation of 1,3-naphthoxazine monomers M-A or M-B with good yields. The structures of the synthesized monomers were confirmed using different spectroscopic techniques (including FT-IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR), mass spectrometry, and elemental analysis. Thermal polymerization of the monomers was investigated by FT-IR and differential scanning calorimetry (DSC). Both the 1,3-naphthoxazine monomers undergo ring-opening polymerization, leading to the formation of the corresponding polynaphthoxazines [P(M-A) and P(M-B)]. The thermal stability of the polynaphthoxazines was thereafter studied by thermogravimetric analysis (TGA).

**Keywords:** 1,3-naphthoxazine, polynaphthoxazine, thermal polymerization, thermal properties.

## Synteza, charakterystyka i polimeryzacja termiczna nowych monomerów 3,4-dihydro-2H-1,3-naftoksazynowych

**Streszczenie:** Za pomocą zmodyfikowanej trój etapowej syntezy, w której do reakcji zamknięcia pierścienia zastosowano bromek metylenu, otrzymano dwa nowe monomery 1,3-naftoksazyny (M-A i M-B). Kondensacja 2-hydroksy-1-naftaldehydu z 1,6-heksametylenodiaminą lub 1,4-fenylenodiaminą pozwala na wytworzenie związków iminowych, które następnie przez redukcję NaBH<sub>4</sub> w metanolu są przekształcane w 2-hydroksynaftylaminy. Reakcja zamknięcia pierścienia pomiędzy 2-hydroksynaftylaminą i bromkiem metylenu prowadzi do utworzenia z dobrymi wydajnościami monomerów 1,3-naftoksazyny M-A i M-B. Struktury zsyntetyzowanych monomerów potwierdzono stosując różne techniki spektroskopowe, spektroskopię masową oraz analizę elementarną. Polimeryzację termiczną monomerów badano za pomocą spektroskopii w podczerwieni z transformacją Fouriera (FT-IR) i różnicowej kalorymetrii skaningowej (DSC). Oba monomery 1,3-naftoksazyny uległy polimeryzacji z otwarciem pierścienia dając odpowiednie polinaftoksazyny [P(M-A) i P(M-B)]. Za pomocą analizy termogravimetrycznej (TGA) zbadano stabilność termiczną otrzymanych polinaftoksazyn.

**Słowa kluczowe:** 1,3-naftoksazyna, polinaftoksazyna, polimeryzacja termiczna, właściwości termiczne.

Although benzoxazine compounds were first synthesized by Cope and Holly in 1940s [1], the potentials of these compounds were only realized recently [2]. Among all benzoxazine compounds, 1,3-benzoxazine compounds have attracted much attention of the research community as they are used in the production of polymeric materials through thermally activated ring-opening polymer-

ization [3]. Benzoxazines are a new class of oxygen and nitrogen heterocyclic compounds synthesized as alternatives to high-performance traditional phenolic resins for high temperature applications [4–6]. These compounds are generally synthesized through Mannich-like condensation of phenol, amine, and formaldehyde [7–9].

These compounds were the base for the production of a new class of phenolic materials namely polybenzoxazines, possessing high performance [10]. Polybenzoxazines can thus be regarded as a new class of heterocyclic high-performance polymers with high thermal stability and high mechanical strength. They are a type of addition-cure phenolic resins with unique features that over-

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come the shortcomings associated with traditional phenolic resins [11]. The major advantages of polybenzoxazines over traditional resins include high char yield, no catalyst or acid needed for cure, higher glass transition temperatures, very low water absorption, and no volumetric change upon cure [12–15]. Perhaps, the most important advantage of this type of polymers is the rich molecular design flexibility which allows the tailoring of molecular structures to suit desired properties [16]. Furthermore, a survey of existing literature has revealed that compounds containing 3,4-dihydro-1,3-oxazine ring systems exhibit a wide range of pharmacological and antibacterial activities [17–19]. These heterocyclic compounds are also studied extensively for the synthesis of biologically active compounds ranging from herbicides and fungicides to therapeutically usable drugs [20]. Biological activities exhibited by these compounds include among others antimicrobial, antitumor, anthelmintic, antimycobacterial, antituberculosis, and insect growth regulatory (IGR) activities [21–23].

In this paper, new 1,3-naphthoxazine monomers were synthesized *via* a modified stepwise procedure in which formaldehyde was substituted with methylene bromide for ring-closure reaction in the last step of synthesis. As it known, formaldehyde has been classified as a suspected human carcinogen and a confirmed animal carcinogen by the International Agency for the Research on Cancer (IARC) [24]. For this reason, we therefore consider formaldehyde as hazardous and unsafe for use in the synthesis process. The synthesized monomers were polymerized through thermally activated ring-opening and the ther-

mal properties of the synthesized polymers were determined and the result reported herewith.

## EXPERIMENTAL PART

### Materials

2-Hydroxy-1-naphthaldehyde, hexamethylenediamine, *p*-phenylenediamine, and sodium borohydride were supplied from Sigma-Aldrich. Anhydrous  $\text{Na}_2\text{SO}_4$  and ethyl acetate were purchased from Fisher Scientific. Methylene bromide was delivered from Acros Organics. Methanol (purity 97 %) and absolute ethanol (purity 99.8 %) were also used. All chemicals were used as purchased without any further purification.

### Synthesis of 1,3-naphthoxazine monomers

Syntheses of 1,3-naphthoxazine monomers, denoted by M-A and M-B, are shown in Schemes A and B, respectively. Both syntheses consist of three steps.

The first step involves the reflux of the 2-hydroxy-1-naphthaldehyde separately with the diamines in 2:1 molar proportion in absolute alcohol for 5 h under nitrogen atmosphere.

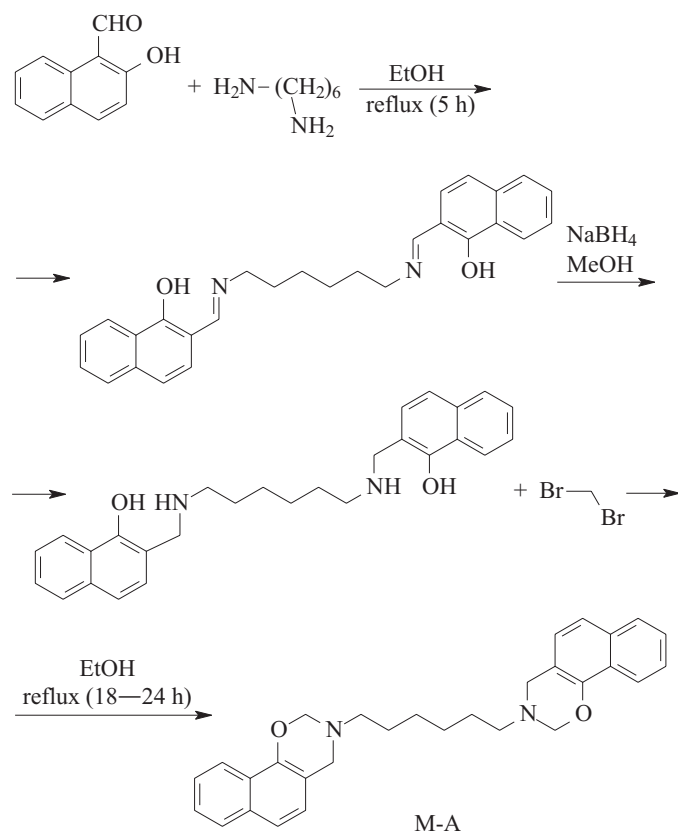
The next step was the synthesis of 2-hydroxynaphthylamines. For this purpose 150 mmol of the imine compounds were added into a conical flask containing 100 cm<sup>3</sup> of ethanol. To this solution there was added 100 mmol of  $\text{NaBH}_4$  in small portions at the ambient temperature, while stirring until the reaction was complete. 150 cm<sup>3</sup> of water was then added and the product was extracted with ethyl acetate, washed with water, dried overnight with anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated to dryness.

Finally, 100 mmol of the 2-hydroxynaphthylamines and 200 mmol of methylene bromide were added to 100 cm<sup>3</sup> of absolute ethanol and the mixture refluxed for 18–24 h under the nitrogen atmosphere. The mixture was allowed to cool to the room temperature and the solvent was removed by rotary evaporation. 100 cm<sup>3</sup> of water was then added and the compound was extracted with ethyl acetate, washed with water, dried overnight with anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated to dryness. All the synthesized compounds were purified by recrystallization in water:ethanol mixture with 50:50 volume ratio.

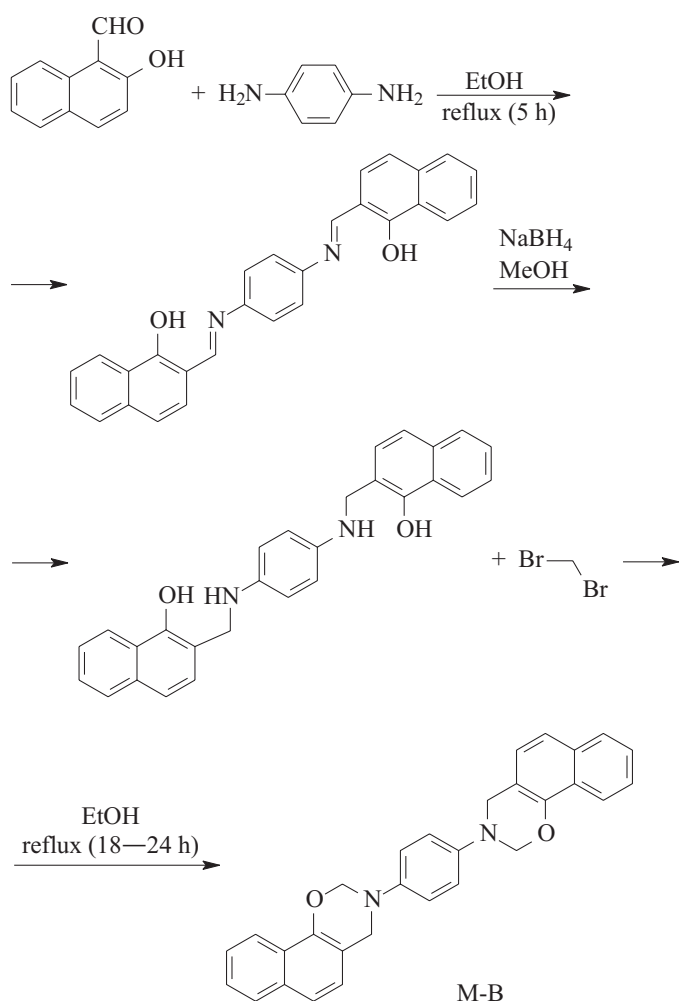
### Polymerization of the monomers

One of the monomers in amount of 4 g was placed on a clean glass plate and placed into a vacuum oven. The oven was then subjected to a stepwise curing procedure depending on the monomer used, using the following protocol:

- 180 °C (2 h), 200 °C (2 h), 220 °C (2 h) and 240 °C (2 h) for monomer M-A;
- 200 °C (2 h), 220 °C (2 h), 240 °C (2 h) and 250 °C (2 h) for monomer M-B.



Scheme A



Scheme B

After cure, the polybenzoxazines obtained [referred here-in as P(M-A) and P(M-B)] were allowed to cool to the room temperature and taken for thermal analysis evaluation.

### Methods of testing

Melting temperatures ( $T_m$ ) of the synthesized compounds were determined using a Barnstead electrothermal melting point instrument 9100 Model.

Fourier transform infrared spectroscopy (FT-IR) was used to the recorded spectra in the region 280–4000  $\text{cm}^{-1}$  on spectrophotometer Perkin Elmer FT-IR model 100 series (KBr Pellet).

$^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectral analysis was conducted on a JEOL 500 MHz NMR spectrometer using acetone- $d_6$  as the NMR solvent.

Gas chromatography-mass spectrometry (GC-MS) analysis was carried out using a Shimadzu model QP 5050A GC-MS analyzer.

Elemental analysis was performed with a Leco CHNS-932 Elemental Analyzer.

Differential scanning calorimetry (DSC) measurements were realized using a Mettler Toledo DSC 822° calorimeter.

TGA analysis was conducted using a Mettler Toledo TGA/DSC 1 STAR° System.

## RESULTS AND DISCUSSION

### Synthesis of the 1,3-naphthoxazine compounds

The use of two different diamines in the synthesis results in the formation of two different 1,3-naphthoxazine compounds. 3,3'-(1,6-Hexamethylene)bis(3,4-dihydro-2H-1,3-naphthoxazine) (M-A) was a beige brown solid with  $T_m = 108.20\text{--}119.42$  °C. M-A was obtained with yield 68 %. Characteristic of this product is given in Table 1. 3,3'-(1,4-Phenylene)bis(3,4-dihydro-2H-1,3-naphthoxazine) (M-B) was a dark red solid melting at  $T_m = 211\text{--}212$  °C. The yield of M-B synthesis was 72 % and characteristic of this product is given in Table 2.

Schemes A and B show the synthetic route for the 1,3-naphthoxazine monomers M-A and M-B. The first and second steps of the synthetic process are as reported in [7, 25] and involve condensation of the aromatic aldehydes and the primary amines to give imine compounds, followed by subsequent reduction with sodium borohydride in methanol to the corresponding 2-hydroxynaphthylamines. Condensation and reduction processes were ascertained using FT-IR spectroscopy. Appearance of bands

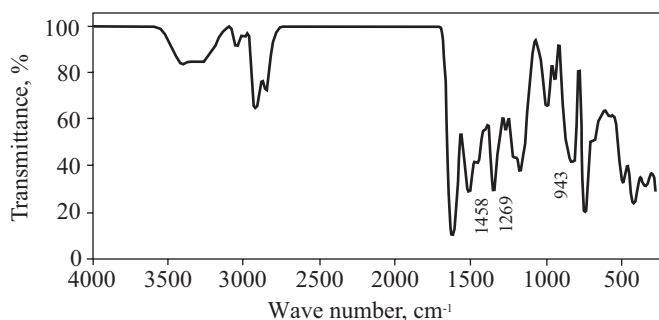
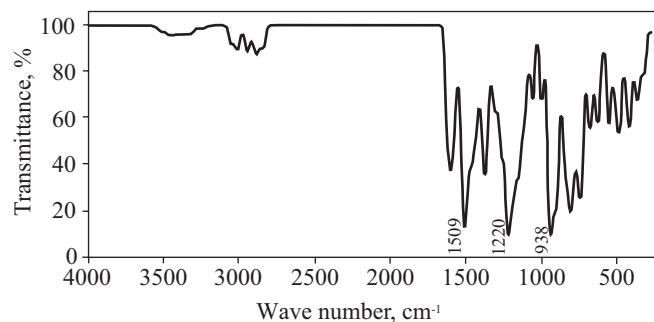
**Table 1.** Characteristic of 3,3'-(1,6-hexamethylene)bis(3,4-dihydro-2H-1,3-naphthoxazine) (M-A)

Method of testing	Results
FT-IR (KBr)	3399, 3050, 2925, 2856, 1621, 1513, 1458, 1351, 1260, 1175, 997, 943, 837, 744, 494, 421, 344 $\text{cm}^{-1}$
$^1\text{H}$ NMR (500 MHz, Acetone- $d_6$ , ppm)	9.12–6.82 (Ar-H), 4.92 (2H, O- $\text{CH}_2$ -N), 4.28 (2H, Ar- $\text{CH}_2$ -N), 1.42 ( $\text{CH}_2$ , aliphatic), 1.54 ( $\text{CH}_2$ , aliphatic), 1.78 ( $\text{CH}_2$ , aliphatic)
$^{13}\text{C}$ NMR (500 MHz, Acetone- $d_6$ , ppm)	158.22 (C, naphthalene), 152.24 (C, naphthalene), 137.64 (C, naphthalene), 132.72 (CH, naphthalene), 129.22 (CH, naphthalene), 129.24 (CH, naphthalene), 127.90 (CH, naphthalene), 124.20 (CH, naphthalene), 119.72 (CH, naphthalene), 113.62 (CH, naphthalene), 78.8 (2H, O- $\text{CH}_2$ -N), 52.2 (2H, Ar- $\text{CH}_2$ -N), 49.4 ( $\text{CH}_2$ , aliphatic), 30.6 ( $\text{CH}_2$ , aliphatic), 28.2 ( $\text{CH}_2$ , aliphatic)
GC-MS	$m/z = 452$ ( $\text{M}^+$ )
Elemental analysis: $\text{C}_{30}\text{H}_{32}\text{N}_2\text{O}_2$ (452.59)	Calculated (%): C, 79.54; H, 7.07; N, 6.19 Experimental (%): C, 79.44; H, 7.01; N, 6.10

**Table 2.** Characteristic of 3,3'-(1,4-phenylene)bis(3,4-dihydro-2H-1,3-naphthoxazine) (M-B)

Method of testing	Results
FT-IR (KBr)	3457, 3012, 2946, 2886, 1601, 1509, 1466, 1377, 1220, 1059, 1000, 938, 809, 745, 680, 629, 556, 489, 422, 367 cm <sup>-1</sup>
<sup>1</sup> H NMR (500 MHz, Acetone-d <sub>6</sub> , ppm)	8.18–6.46 (Ar-H), 5.82 (2H, O-CH <sub>2</sub> -N), 4.90 (2H, Ar-CH <sub>2</sub> -N)
<sup>13</sup> C NMR (500 MHz, Acetone-d <sub>6</sub> , ppm)	154.2 (C, naphthalene), 134.1 (C, benzene), 132.4 (C, naphthalene), 25.5 (C, naphthalene), 112.7 (C, naphthalene), 127.7 (CH, naphthalene), 126.9 (CH, naphthalene), 125.2 (CH, naphthalene), 124.8 (CH, naphthalene), 121.4 (CH, naphthalene), 119.3 (CH, naphthalene), 83.2 (2H, O-CH <sub>2</sub> -N), 54.2 (2H, Ar-CH <sub>2</sub> -N)
GC-MS	<i>m/z</i> = 444 (M <sup>+</sup> )
Elemental analysis: C <sub>30</sub> H <sub>24</sub> N <sub>2</sub> O <sub>2</sub> (444.52)	Calculated (%): C, 80.98; H, 5.40; N, 6.30 Experimental (%): C, 80.90; H, 5.32; N, 6.21

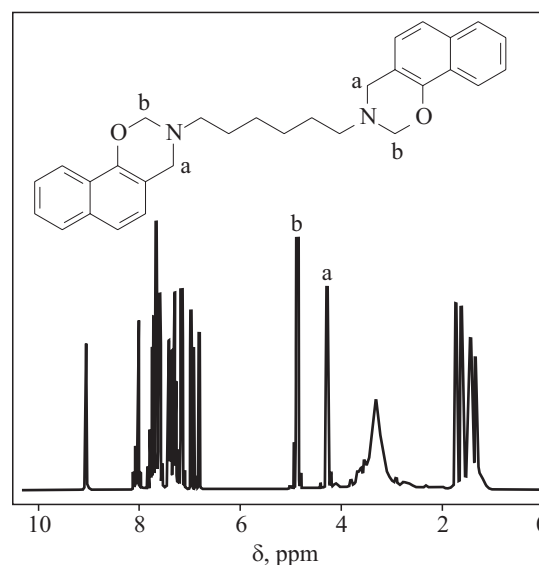
in the region 1620 and 1601 cm<sup>-1</sup> (corresponding to the C=N bond) in the FT-IR spectrum confirms the presence of condensation products. Appearance of another band in the region 3276 and 3281 cm<sup>-1</sup> (corresponding to NH bond) and absence of band corresponding to the C=N bond proves formation of the reduced compounds M-A and M-B. The third step involves the reflux of the 2-hydroxynaphthylamines obtained in excess of methylene bromide, which results in ring-closure reaction leading to the target 1,3-naphthoxazine monomers M-A and M-B in good yields. There are a number of infrared absorption bands that confirm the formation of benzoxazine compounds. FT-IR spectra of the monomers M-A and M-B are presented in Figs. 1 and 2, respectively. The bands used to confirm the formation of benzoxazine compounds are those due to asymmetric stretching modes of C-O-C which are seen at 1260 cm<sup>-1</sup> for monomer M-A and 1220 cm<sup>-1</sup> for M-B, bands due to

**Fig. 1.** FT-IR spectrum of M-A**Fig. 2.** FT-IR spectrum of M-B

asymmetric trisubstituted benzene which appear at 943 and 1458 cm<sup>-1</sup> for monomer M-A and 938 and 1466 cm<sup>-1</sup> for monomer M-B and bands due to asymmetric stretching vibration of Ar-H which appear at 3050 and 3012 cm<sup>-1</sup> for monomer M-A and M-B, respectively.

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of M-A monomer are provided as Figs. 3 and 4. The characteristic resonance attributed to 1,3-naphthoxazine structures were observed in the spectra of both the monomers. The resonance due to O-CH<sub>2</sub>-N and Ar-CH<sub>2</sub>-N are observed at 5.02 and 4.16 ppm for monomer M-A as well at 5.82 and 4.90 ppm for monomer M-B. <sup>13</sup>C NMR spectra of both monomers M-A and M-B equally confirm the presence of carbon chemical shifts corresponding to O-CH<sub>2</sub>-N and Ar-CH<sub>2</sub>-N which are located at 78.8 and 52.2 ppm for M-A while at 83.2 and 54.2 ppm for M-B.

The GC-MS spectra of monomers showed molecular ion peaks centered at *m/z* equal to 452 and 444, which are equivalent to the molecular weight of monomers M-A and M-B, respectively. The result of elemental analysis also shows that the experimental data are in agreement with the calculated data.

**Fig. 3.** <sup>1</sup>H NMR spectrum of M-A

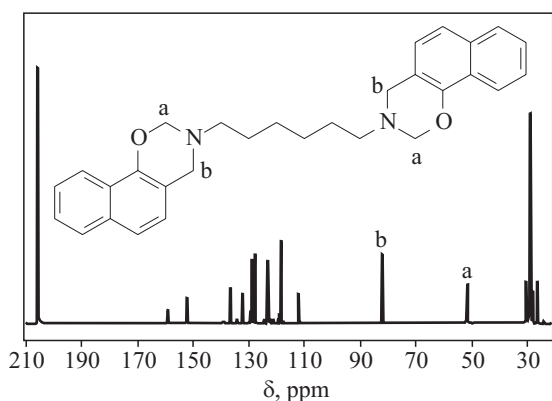


Fig. 4.  $^{13}\text{C}$  NMR spectrum of M-A

### Polymerization behavior of the 1,3-naphthoxazine monomers

To understand the thermal polymerization behavior of the monomers, the results of DSC and FT-IR measurements were studied in detail. As it is known, 1,3-naphthoxazines generally exhibit exothermic ring-opening re-

action around 200–250 °C, what can be ascertained by DSC. The thermograms of monomers M-A and M-B are shown in Figs. 5 and 6, respectively. It can be seen that the exothermic peak temperatures for the ring-opening polymerization of monomer M-A and M-B are centered at 226 and 248 °C, with the onset temperatures of 200 and 212 °C, respectively. Thus, monomer M-A shows lower temperature of ring-opening polymerization compared to the temperature observed for monomer M-B. The FT-IR spectra of M-A and M-B after curing at different temperatures are shown in Figs. 7 and 8, respectively. It was observed that there is a considerable decrease in the intensity of the characteristic peaks at 943 and 938  $\text{cm}^{-1}$  assigned to naphthoxazine and a corresponding increase in the intensity of the peak at 3400  $\text{cm}^{-1}$  assigned to -OH as the cure reaction proceeds until the complete disappearance of the two peaks are attained. This confirms that as a result of increase in temperature, the ring-opening polymerization reactions, shown in Schemes C and D, have taken place in both M-A and M-B monomers, respectively.

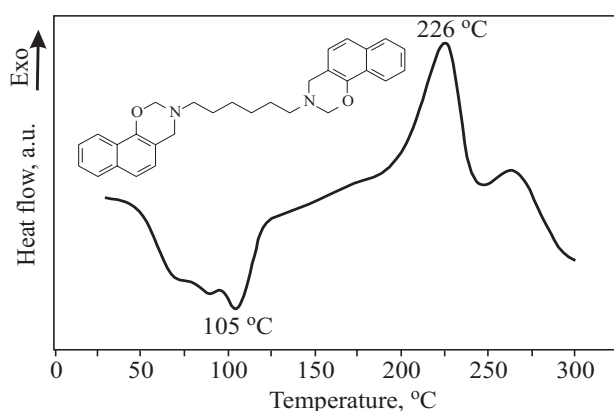


Fig. 5. DSC thermogram of M-A

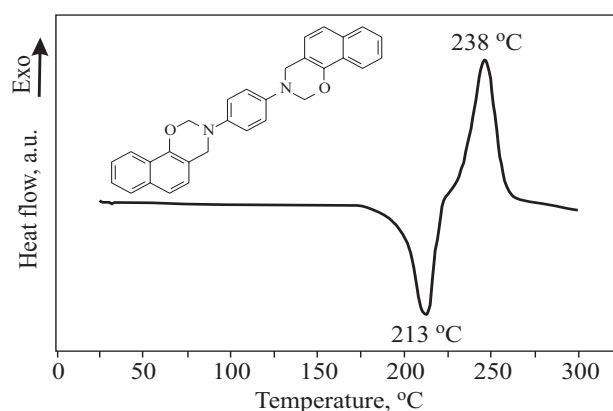


Fig. 6. DSC thermogram of M-B

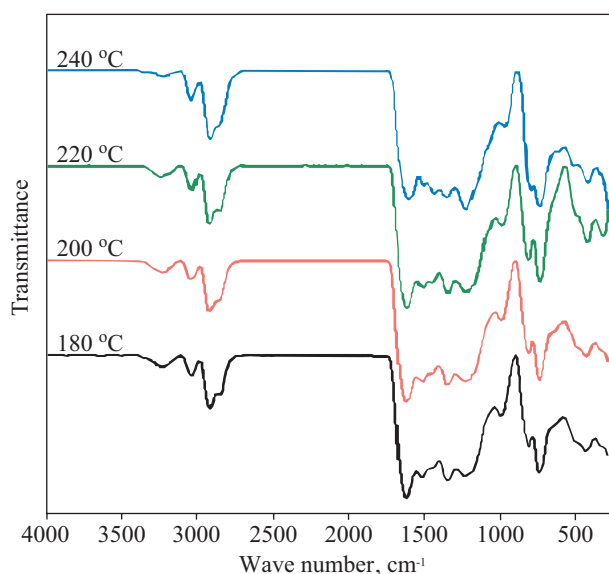


Fig. 7. FT-IR spectra of monomer M-A after different thermal treatment

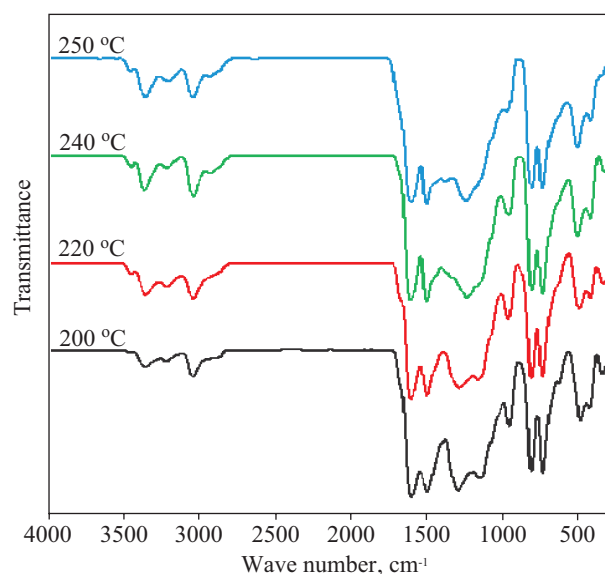


Fig. 8. FT-IR spectra of monomer M-B after different thermal treatment



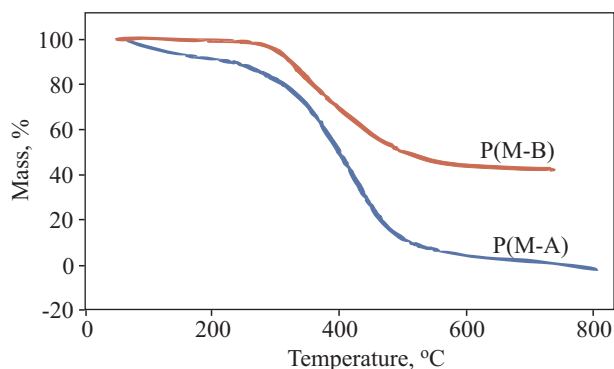
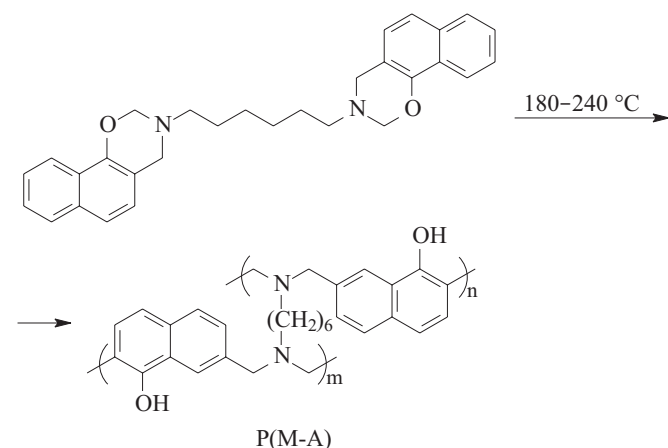


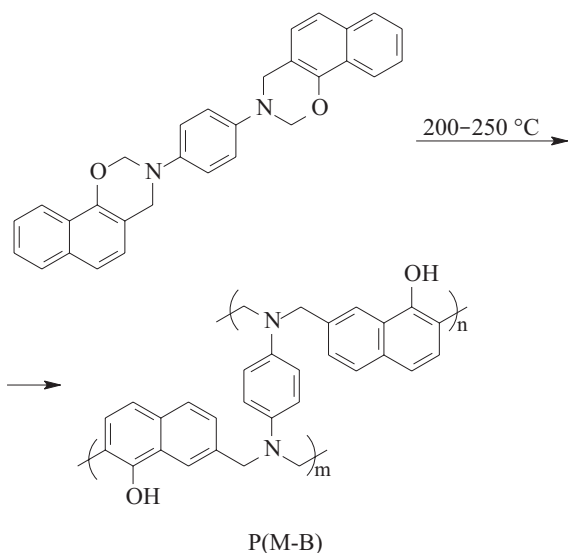
Fig. 9. TGA curves of polynaphthoxazines P(M-A) and P(M-B)

### Thermal properties of the synthesized polynaphthoxazines

The thermal stability of the polybenzoxazines was studied using TGA and results are listed in Table 3. The TGA curves of the polynaphthoxazines cured from M-A and M-B [referred herewith as P(M-A) and P(M-B), respectively] were recorded under the nitrogen atmosphere



Scheme C



Scheme D

at the heating rate of 10 deg/min up to 800 °C. From the TGA thermogram, it can be observed that both the two polynaphthoxazines decompose in two main stages at different temperature ranges. TGA curves of the polybenzoxazines P(M-A) and P(M-B) are shown in Fig. 9. The 5 and 10 % mass loss temperatures ( $T_{d\ 5\%}$  and  $T_{d\ 10\%}$ ) for P(M-A) are 119 and 222 °C, while for P(M-B) are 300 and 322 °C, respectively. The char yield observed for P(M-A) was 0 %, whereas for P(M-B) was 42 %. It can be seen that P(M-B) shows better thermal stability than P(M-A). The result is quite in agreement with what is obtainable in literature that aromatic based polybenzoxazines generally have better thermal stability than their aliphatic based counterparts.

Table 3. Thermal properties of the polymers P(M-A) and P(M-B)

Polymer	$T_{d\ 5\%}$ , °C	$T_{d\ 10\%}$ , °C	$T_d$ , °C	Char yield, %
P(M-A)	119	222	508	0
P(M-B)	300	322	524	42

### CONCLUSIONS

In search of new polymers with improved properties, two new 1,3-naphthoxazine monomers were synthesized *via* a modified stepwise procedure using aliphatic and aromatic diamine and next polymerized to obtain their corresponding polynaphthoxazines. The monomers were characterized in detail. The thermal properties of the obtained polynaphthoxazines were determined. The results of thermal stability are consistent with literature reports and showed that polynaphthoxazines synthesized using aromatic diamine generally possess higher thermal stability than their aliphatic based counterparts.

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Received 21 III 2016.

## W kolejnym zeszycie ukaza się m.in. następujące artykuły:

M. Żenkiewicz, K. Moraczewski, P. Rytlewski, M. Stepczyńska, B. Jagodziński – Metalizowanie bezprądowe tworzyw polimerowych

H. Karaer, İ. Kaya, H. Aydın – Synteza, charakterystyka, właściwości termiczne i elektrochemiczne polimerów iminowych zawierających jednostki pirydynowe i pirymidynowe (*j. ang.*)

R. Steller, G. Kędziora, G. Mitchener, K. Fiłon, R. Kołbuc, K. Lenart, J. Śliwiński – Poliolefiny napełniane odpadami sztywnej pianki poliuretanowej i kompatybilizowane metodą pulweryzacji ścinaniem w stanie stałym podczas wytłaczania

B. Chrayet, F. Ammari, F. Meganem – Wykorzystanie materiałów hybrydowych na bazie modyfikowanego poli(chlorku winylu) napełnionego naturalną gliną w ekstrakcji kationów metali (*j. ang.*)

M. Stepczyńska, K. Moraczewski, R. Malinowski, M. Żenkiewicz – Wpływ promieniowania UV na wybrane właściwości barwionej folii polilaktydowej (*j. ang.*)

K. Pepliński, P. Czyżewski, D. Górecki, D. Sykutera, M. Bieliński – Wybrane cechy geometryczne i wskaźniki wytrzymałościowe elementów wykonanych metodą modelowania uplastycznionym tworzywem

I. Kruszelnicka, D. Ginter-Kramarczyk, A. Rudawska, S. Zajchowski, J. Tomaszewska – Ocena kąta zwilżania kompozytów polimerowo-drzewnych poddanych działaniu osadu czynnego