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Article

Benzoxazine monomers and polymers based on 3,3′-dichloro-4,4′-diaminodiphenylmethane: synthesis and characterization

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Abstract: As a result of this work, a previously unreported benzoxazine monomer based on 3,3'-dichloro-4,4'-diaminodiphenylmethane was obtained, characterized by ^{1}H and ^{13}C NMR spectroscopy, and its thermal and rheological properties were studied. A comparison between the properties of benzoxazines based on diamines (3,3'-dichloro-4,4'-diaminodiphenylmethane and 4,4′-diaminodimethylmethane). The effect of the reaction medium on the structure of the oligomeric fraction and the overall yield of the main product was studied. The synthesized monomers can be used as thermo- and fire-resistant binders for polymer composite materials, as well as hardeners for epoxy resins.

Keywords: benzoxazines, polybenzoxazines, diaminodiphenylmethane, 3,3′-dichloro-4,4′-diaminodiphenylmethane, heterocycles, thermosetting binders

1. Introduction

Polybenzoxazines are a relatively new class of thermosetting polymers with a number of advantages, including high mechanical properties and heat resistance, near-zero curing shrinkage, and low moisture absorption. The combination of these properties is responsible for the growing interest in benzoxazines as universal binders for composite materials and coatings, including in electronics and the aerospace industry [1],[2].

Bifunctional monomers based on various architectures built up from diamines and monofunctional phenols seem to be more perspective compared to the those based on diphenols and monoamines, since they are characterized by enhanced mechanical properties and higher heat, thermal and fire resistance [3–6].

However, until recently, the synthesis of benzoxazine monomers based on diamines and monophenols was practically impossible. At the first stage of the condensation reaction hyperbranched crosslinked structures based on diamine and paraformaldehyde are formed, which can precipitate from the reaction mixture, thereby reducing the main product yield [7]. This circumstance excludes the possibility of carrying out a one-stage synthesis. In a number of works [8–13], it was shown that upon certain conditions, namely, carrying out the reaction in a solvent mixture of toluene / ethanol (2:1), it is possible to obtain the target product in one stage.

At temperatures above 180 °C, these monomers undergo thermal polymerization with the opening of the oxazine ring without the release of low-molecular by-products with the formation of crosslinked polymers and can be used as binders for composite materials, both as a separate component of a thermosetting system, and as a co-monomer in systems with epoxy resins [14], bismaleimides, polyurethanes, cyan ethers, phthalonitriles, etc. to form highly crosslinked copolymers [15].

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Benzoxazine monomers can be processed by resin transfer molding (RTM) and vacuum infusion due to the wide processing window [16–19].

Within this work, the thermal and rheological characteristics of diamine-based benzoxazines were investigated. It is believed that the addition of chlorine atoms to the diamine structure will improve the fire and heat resistance properties of materials.

2. Materials and Methods

2.1. Starting Materials

4,4'-diaminodiphenylmethane (d) 97% (Alfa Aesar, Kandel, Germany), 4,4'-diamino-3,3'-dichlorodiphenylmethane (quamin or q) 97% (Chimex Limited, Saint Petersburg, Russia), phenol purified by distillation, paraformaldehyde 91% (ERCROS, Barselona, Spain) used without cleaning; toluene, isopropanol (Komponent-Reaktiv, Moscow, Russia) were dried using molecular sieves and distilled before use.

2.2 Synthesis of benzoxazine monomers based on diamines of various structures

The calculated amount of diamine, phenol and solvent was loaded (Table 1) into a 500 ml round-bottom flask equipped with a magnetic stirrer and a reflux condenser. The dissolution of solid reagents was carried out at 60 °C, then the calculated amount of paraformaldehyde was loaded. The temperature was raised to 80-90 ° C and the synthesis was carried out for 8 hours. Then the solvents were removed and the product was dried at 90 °C in a vacuum oven for 6 hours. The benzoxazine monomers were obtained as yellow glassy substances with a softening point temperature range of 80–100 ° C in a 90–95% yield. Resulting monomers were used for further polybenzoxazines synthesis without additional purification.

Table 1. The amount of starting reagents for the synthesis of benzoxazine monomers based on diamines of various structures in various solvents.

Reagent		**Benzoxazine monomer**		
		P-q		**P-d**
		toluene	**toluene/isopropanol = 2:1**	**toluene/isopropanol = 2:1**
Diamine	g	26,715	20	20
	mol	0,100	0,075	0,100
Phenol	g	18,822	14,091	18,99
	mol	0,200	0,150	0,200
Paraformaldehyde, 91% (10% excess)	g	14,52	10,87	14,65
	mol	0,440	0,330	0,440
Solvent	ml	150	150	150

2.3 Curing of benzoxazines

Benzoxazine monomers were cured according to the following regime: 2 hours at 180 °C, 4 hours at 200 °C, 2 hours at 220 °C; all samples were degassed at 130 °C for 1 h before curing. The completeness of the curing process was controlled by the absence of an exothermic effect on the DSC thermogram.

2.4 Measurements

^{1}H, ^{13}C NMR spectra were measured in a $CDCl_3$ solution using a Bruker AV-600 spectrometer (Bruker Corporation, Bremen, Germany) operating at frequencies of 600 and 162 MHz, respectively. Chemical shifts are reported in parts per million and referenced to the signals of deuterated solvents. ^{1}H NMR chemical shifts are reported relative to the signals of tetramethylsilane. The spectra were

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processed using the MestReNova Lab package (version 12.0.4, MESTRELAB RESEARCH, S.L, Santiago de Compostela, Spain).

Differential scanning calorimetry (DSC) was measured on a Netzsch DSC 204 F1 Phoenix instrument (Netzsch, Selb, Germany) in a nitrogen atmosphere (20 ml/min) at a heating rate of 10 deg/min.

Capillary-coupled thermogravimetric analysis (TGA) with quadrupole mass spectrometer (QMS) were carried out on a Netzsch TG 209 F1 Iris and QMS 403 D Aeolos respectively. TGA was carried out at a heating rate of 20 deg/min and an inert atmosphere flow rate of 50 ml/min. The temperature of transport capillary was 230 °C. The curves were processed using the Netzsch Proteus Thermal Analysis version 6.1.0. QMS was carried out in analog scan mode on the detector CH-TRON and in mass mode SCAN-F. The detector voltage was 1200 V. The holding time for the measurement was 0.5, 1 and 2 s. The curves were processed using the Inficon AG QUADSTAR v7.02.

Flammability tests were carried out in accordance with UL-94, the dimensions of the samples were 127 x 12.7 x 2 mm.

Studies of rheological properties were carried out on a Brookfield CAP 2000+ rotational viscometer and an AR 2000 EX rheometer from TA Instruments at a constant shear rate of 200 rpm.

IR spectra were recorded on a Nicolet 380 Fourier spectrophotometer with an ATR accessory.

The morphology of polymer samples based on P-q and char yield were investigated by scanning electron microscopy on a JSM-6510 device (JEOL, Japan) at an accelerating voltage of 15 kV.

The char samples after ignition during vertical test according to UL-94 standard were used for obtaining of the SEM images and IR spectrum.

3. Results and Discussion

3.1. Synthesis of benzoxazine monomers based on diamines

The preparation of benzoxazines based on di- and polyamines is complicated by the peculiarity of the first stage of the reaction. The formation of hyperbranched triazine chains (Figure 1), which can lead to the reaction mass gelation [7], either leading to a decrease in the yield of the main product, or complete impossibility of one-step synthesis of benzoxazines based on diamines.

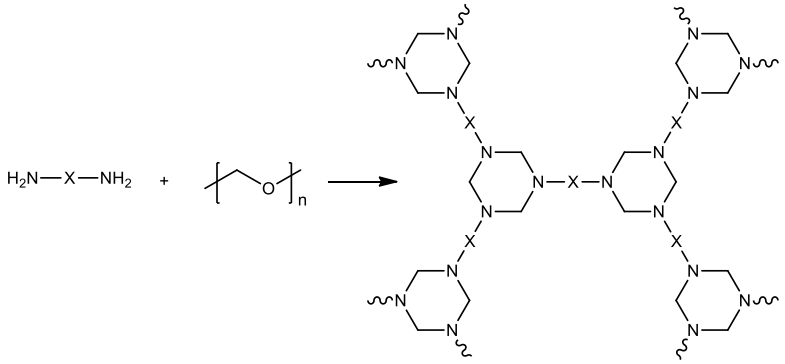

Figure 1. Side reaction for the production of benzoxazine monomers based on diamines.

Despite the aforementioned fact, benzoxazines based on 4,4'-diaminodiphenylmethane/quamine, phenol and paraformaldehyde were obtained successfully (Figure 2) by two methods.

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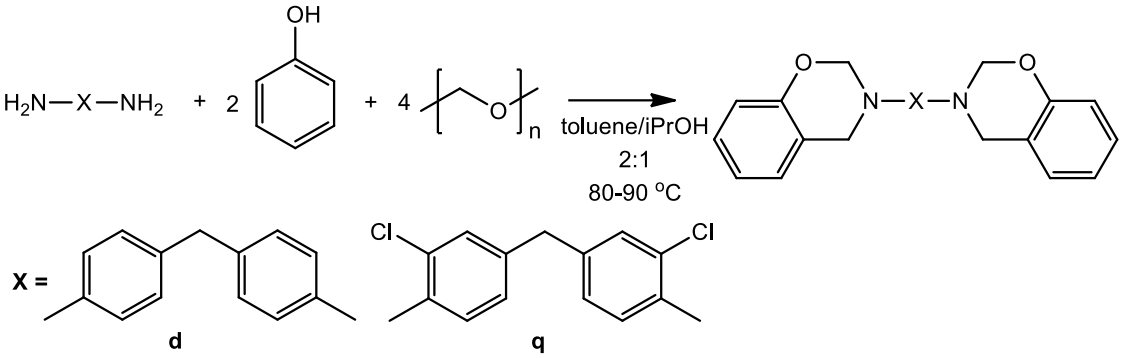

Figure 2. Synthesis of benzoxazine monomers based on diamines.

A low-intensity signal with a chemical shift at δ_H = 5.1 ppm in the ^{1}H NMR spectra of the products obtained via this method (Figure 3, Table 2) indicates a small number of triazine structures.

In the second method, a toluene / isopropanol mixture with 2: 1 volume ratio was used. Due to the hydroxyl groups affinity to isopropanol and increased general solvation, triazine structures are not formed (Figure 3, 4, Table 2) [20].

The yields of benzoxazines in the two preparation methods were up to 90-95%. The problem of insoluble products formation in a toluene medium was not relevant since paraformaldehyde was loaded gradually after the complete dissolution of quamine and phenol, thereby making branched triazine structures unlikely to form. An excess of paraformaldehyde of 10% and optimal temperature for the condensation reaction of 80-90 °C were applicated in order to exclude the formation of compounds with the Mannich bridge.

Benzoxazine monomer based on 4,4'-diaminodiphenylmethane (P-d) was obtained by analogous method in toluene/isopropanol solvents mixture.

On the basis of the obtained ^{1}H NMR spectroscopic data, it can be concluded that a large number of branched triazine structures that can precipitate are not formed in the toluene medium. This is achieved by gradually loading reagents. Thus, although carrying out the reaction in a solvent mixture of toluene/isopropanol yields a much purer product, the toluene medium may also be used because in this case the amount of triazine impurities is relatively small. This is consistent with the low activity of quamine due to the presence of chlorine atoms in its aromatic rings.

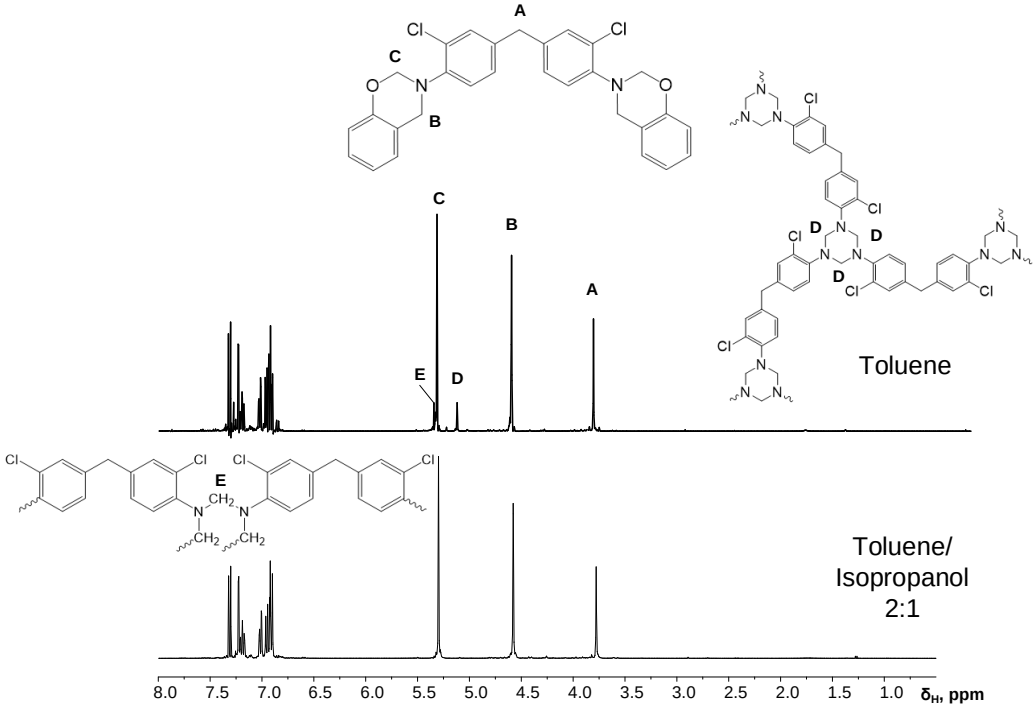

Figure 3. ^{1}H NMR spectrum of benzoxazine based on quamine in various solvents.

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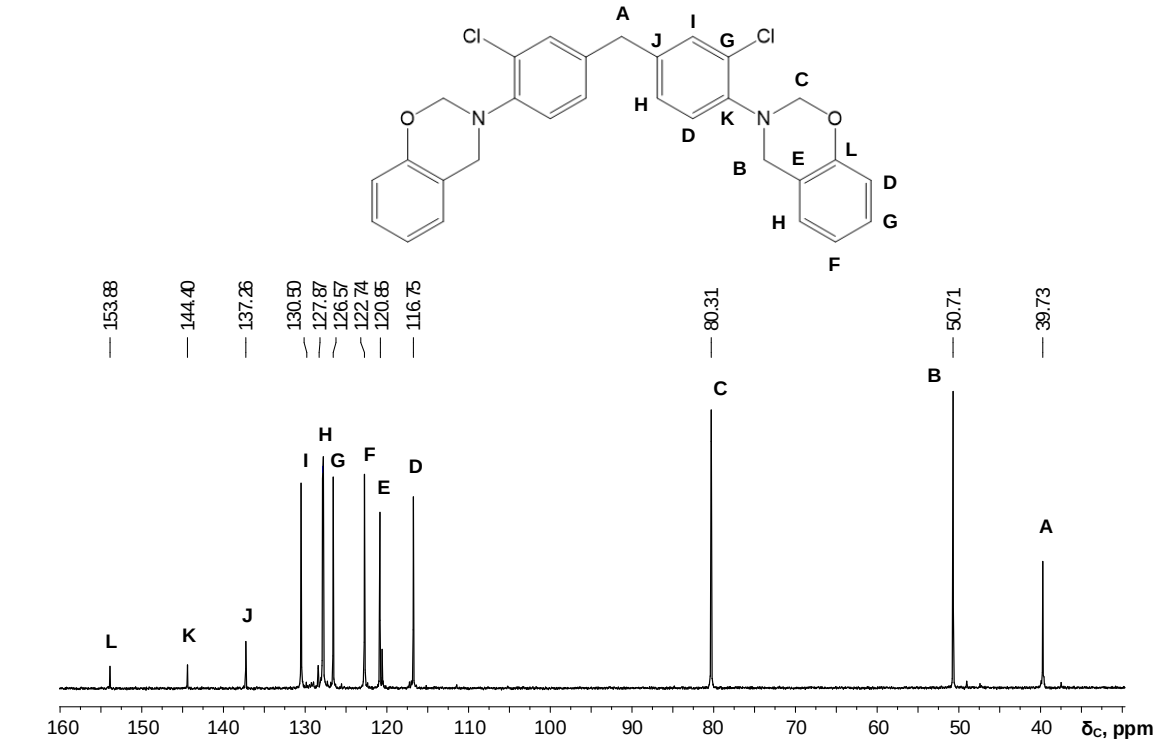

Figure 4. ^{13}C NMR spectrum of benzoxazine based on quamine in toluene/isopropanol 2:1.

Table 2. The results of ^{1}H and ^{13}C NMR spectroscopy of benzoxazine monomers.

Sample	Proton chemical shifts δ_H (ppm)				Carbon chemical shifts δ_C (ppm)			
	Oxazine ring		Diamine		Oxazine ring		Diamine	
	CH_2N	CH_2O	CH_2	CH (Ar)	CH_2N	CH_2O	CH_2	CH (Ar)
P-d	4,70	5,44	3,96	6,96-7,49	50,15	79,39	40,01	116,69-154,17
P-q	4,58	5,30	3,78	6,81-7,35	50,71	80,31	39,73	116,75-153,88

The structures of the obtained monomers and polymers were confirmed using IR spectroscopy. In the IR spectra of monomers (Figure 5), the absorption bands correspond to various vibrations in the oxazine ring: at 944 and 1205-1215 cm^{-1} – to the stretching vibrations of the C–N–C and C–O–C bonds, respectively; in the region of 1486-1489 cm^{-1} – to the stretching vibrations of the C-H bonds in the $–CH_2–$ groups; at 745-751 cm^{-1} – to the bending vibrations of $–CH_2–$ groups. In the IR spectra of polybenzoxazines, intensities of these bands decrease significantly, and a broadened band appears at 3380–3600 cm^{-1}, corresponding to the stretching vibrations of phenolic hydroxyl groups linked by hydrogen bonds. The absorption bands in the IR spectra of benzoxazine and polybenzoxazines based on them correspond to the literature data [21–24].

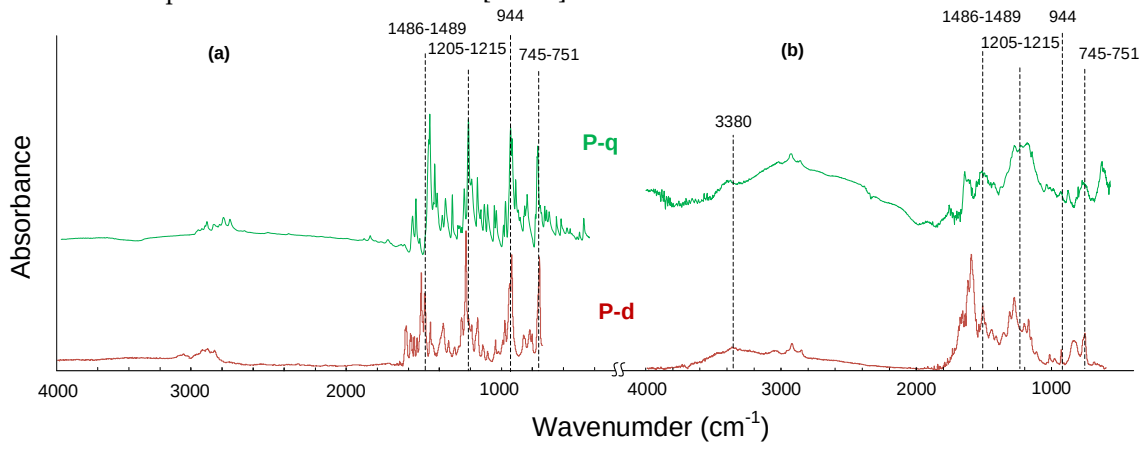

Figure 5. IR spectra of benzoxazine monomers (a) and polymers (b).

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3.2. Properties of diamine-based benzoxazine monomers

The kinetics of curing of various diamine-based benzoxazine monomers was investigated by using differential scanning calorimetry (DSC) (Figure 6, Table 3). The curves show that P-d polymerization proceeds under milder conditions than P-q. This may be due to the fact that the aromatic rings of the diamine in P-q are deactivated by chlorine atoms; therefore, the addition to the ortho position relative to the nitrogen atom will be somewhat difficult both sterically and energetically.

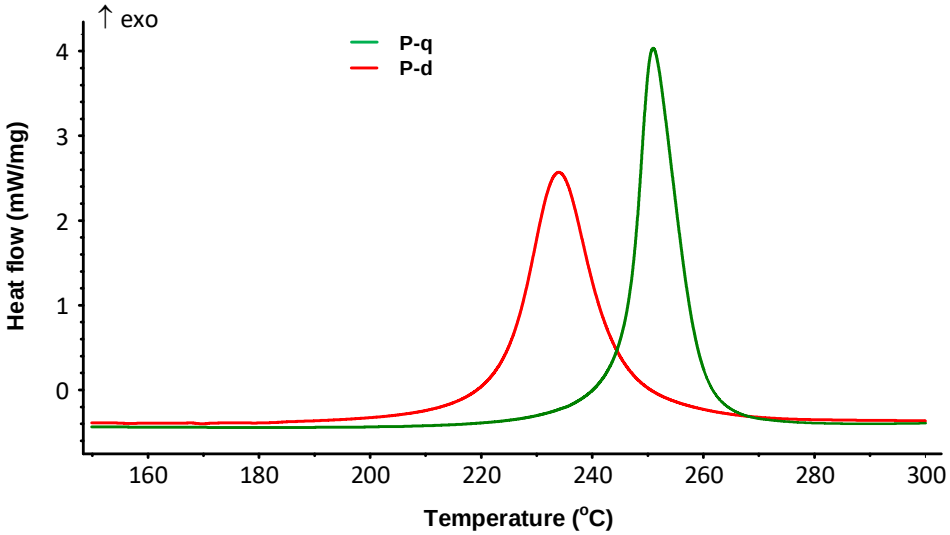

Figure 6. DSC curves of curing of benzoxazines based on diamines (heating rate 10 deg / min).

Table 3. The results of differential scanning calorimetry.

Parameter		P-d	P-q
Temperature characteristics of curing exotherm (°C)	Onset	224	242
	Peak	234	247
	End	246	253
Polymerization heat (J/g)		310	295

This statement is in good agreement with early studies by Ishida and colleagues [25,26]. He showed that benzoxazine monomers based on bisphenol A and aromatic amines polymerize not only according to the standard scheme with the formation of phenolic polymers with a Mannich bridge, but also with the participation of the p-position of the aromatic amine residue. The structure of the aromatic amine is important here. Amines with an activated aromatic ring (that is, with electron-donor substituents that increase the electron density in the o- and p-positions relative to the amino group) significantly increase the network density, while deactivated amines with a methyl group in the o- and p- positions, on the contrary, significantly reduce it (Figure 7) [27]. In other words, if the benzoxazine monomer has an electron-donor substituent in the m-position relative to the nitrogen atom or has no substituents in the aromatic ring of the diamine, then polymerization proceeds under milder conditions (lower temperature of the onset of polymerization and lower enthalpy of the curing reaction) and higher cross-link density and glass transition temperature in resulting polymer (Figure 6).

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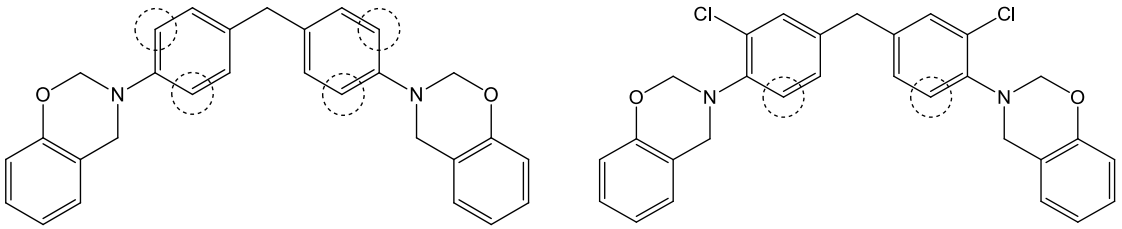

4 potential reactive sites
P-d

2 deactivated potential reactive sites
P-q

Figure 7. Possible reactive sites in the aromatic ring of a diamine on the activation of positions and influence of substituents.

In this case P-q monomer has an electron-withdrawing chlorine in o-position and as a result polyP-q has reduced T_g of 182 °C compared to polyP-d's 190 °C. Studies [28,29] report that the presence of electro-acceptor groups in amine or phenol aromatic ring can significantly affect the conditions for obtaining the benzoxazine monomer, and also can increase the polymerization temperature, which is observed during the curing of P-q too.

To determine the optimal curing mode of the obtained P-q, as well as the possibility of using it in the production of polymer composite materials and the processing method, we estimated the value of the viscosity in the dynamic mode (Figure 8). It can be seen that the obtained benzoxazine monomer has a rather wide technological window (115-225 °C) at a low viscosity (< 1 Pa·s), which makes it possible to process this monomer by the vacuum infusion method.

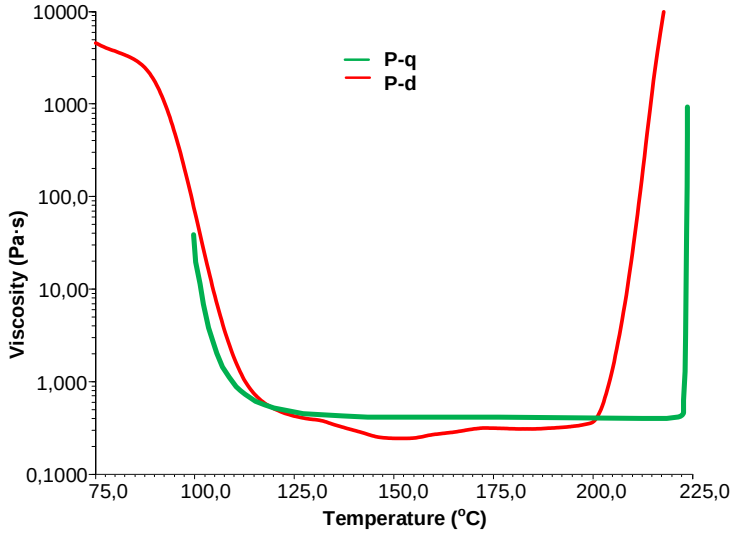

Figure 8. Change in the viscosity of benzoxazine monomers in the dynamic mode.

To evaluate the melting stability of P-q, viscosity curves were obtained at 130 °C for 2 hours. Figure 9 shows that the P-q viscosity remains constant at a given temperature for 2 hours. This aspect also speaks in favor of the possibility to produce polymer composite materials based on P-q benzoxazine monomer by vacuum infusion.

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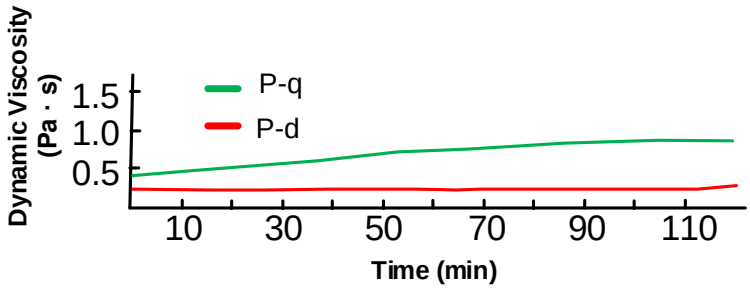

Figure 9. Change in the viscosity of benzoxazine monomers at 130 °C.

3.3. Thermal properties and fire resistance of diamine-based polybenzoxazines

Benzoxazine monomers were cured according to the following regime: 2 hours at 180 °C, 4 hours at 200 °C, 2 hours at 220 °C; all samples were degassed at 130 °C for 1 h before curing. The properties of the obtained polybenzoxazines were investigated using DSC, thermogravimetric analysis with a mass detector (TGA-MS), scanning electron microscopy (SEM), and flammability resistance was studied using the UL-94 standard.

According to the TGA data (Figures 10, 11,Table 4), the 5 and 10% mass-loss of polyP-q occurs at lower temperatures compared to polyP-d. However, probably due to the presence of chlorine atoms, polyP-q has a higher char yield.

Determination of the combustion resistance according to UL-94 standard showed that polyP-d has a category V-1, and polyP-q has an increased resistance to burning and so can be classified to V-0 category. In comparison with P-d, the quamine-based polymer is characterized by near-zero burning times, even with multiple ignitions. The obtained experimental data on flammability are in good agreement with the calculated data on the limiting oxygen index (LOI) according to the Van Crevelen-Hovtyzer rule [30] (1):

$$LOI = 17.5 + 0.4 \cdot CY \quad (1)$$

where CY is the coke yield according to the TGA data.

Table 4. Thermal properties of benzoxazines based on diamines.

Parameter		polyP-d	polyP-q
T_g (°C)[a]		190	182
UL-94	τ_1, s	28	5
	τ_2, s	49	0
	Flammability rating	V-1	V-0
LOI[b]		36	40
In Argon			
$T_{5\%}$ (°C)		391	380
$T_{10\%}$ (°C)		416	390
W_{800} (%)		46	57
W_{900} (%)		45	57
In air			
$T_{5\%}$ (°C)		-	375
$T_{10\%}$ (°C)		-	395
W_{800} (%)		-	5
W_{900} (%)		-	1

[a] Measured by DSC (supplementary).

[b] Calculated by Van Krevelen-Hovtyzer equation (char yield at 800 °C values were used for calculation) [30].

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One of the limiting factors of plastics high-temperature usage is their tendency not only to soften, but also to undergo the thermally-induced degradation. Thermal degradation is the upper limit of the polymer's operating temperature, above what polymers can degrade with the formation of low-molecular-weight products that can change its properties.

The study of polybenzoxazines decomposition allows us to understand the thermal stability of the material, as well as direct us to the creation of new and better structures with greater thermal resistance.

It was proposed that the thermal decomposition of polybenzoxazines occurs stepwise [31–33]. At the first stage of the destruction, aromatic compounds are formed (benzene, derivatives of phenol, aniline). On the second step - low-molecular compounds (hydrocarbons, carbon dioxide, aliphatic amines, etc.), followed by carbonization.

In present work, thermogravimetric analysis with a mass-detector was carried out. The structures formed during thermal destruction of polyP-q are described below (Table 5).

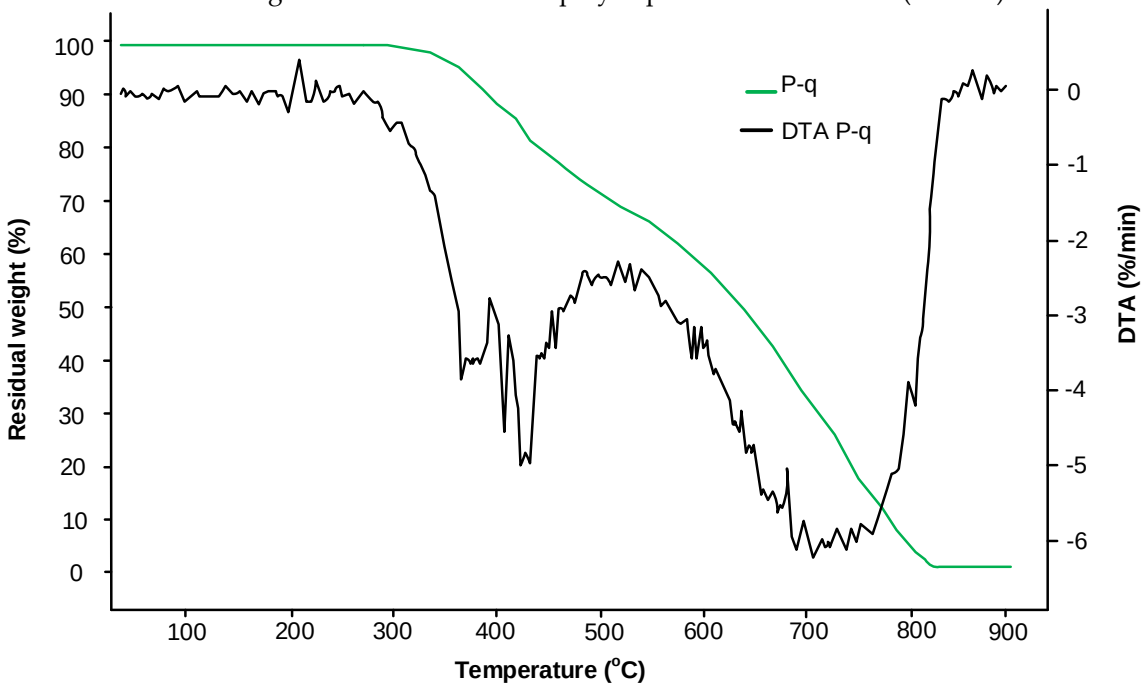

Figure 10. TGA and DTA curves of polyP-q in the air atmosphere.

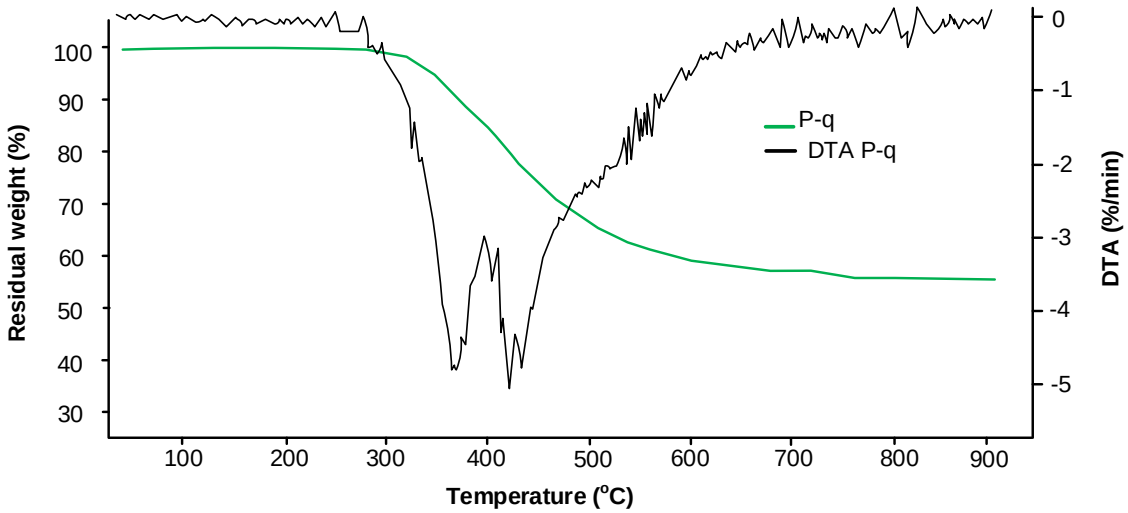

Figure 11. TGA and DTA curves of polyP-q in the argon atmosphere.

The result obtained is generally in satisfactory agreement with previously published studies. It can be noted that, both in air and in an inert atmosphere in the range of 300-500 °C, the destruction

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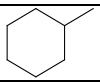
of benzoxazine cycles occurs predominantly and a small amount of potentially toxic chlorine-containing substances is released. As it can be seen from the Table 5, at low temperatures from 343 and 700 °C in air, compounds containing chlorine: HClO and CH_3Cl are formed with fraction 0,04 and 0,11% respectively. More compounds containing chlorine are formed in an argon atmosphere at different temperatures (373-445 °C). For example, CH_3Cl (26,86%), $^+CH_2CH_2Cl$ (3,93%), CH_3CH_2Cl (4,59%), CH_3OCl (5,5%), $^+CH_2CH_2NH_3Cl$ (4,59%). Above 500 °C, there is almost no loss of mass in the intert atmosphere. In air, thermo-oxidative destruction is most intense at 700 °C. The data obtained indicate a low lability of chlorine atoms in the composition of polybenzoxazine, which is a positive factor in terms of safety and environmental friendliness.

Table 5. Results of TG-MS analysis of volatile products of P-q in air and inert atmosphere.

№	Probable structure	*m/z* calculated	*m/z* observed	Intensity × 10^{12}	Fraction[a], %	T, °C
			Air			
1	$^+CH_2–N–CH_2^+$	43,04				
2	$^+CH_2N=CH_2$	42,03	42,3	24	10,52	
3	$CH_3N=CH_2$	43,04				343
4	CH_3Cl	49,99	50,4	0,25	0,11	
5	HClO	51,97	52,3	0,1	0,04	
6	CO_2	43,99	44,2	200	87,66	
7	$CH_3CH_2NH_2$	45,06	45,3	2,8	1,23	700
8	NO_2	45,99	46,2	1	0,44	
			Argon			
9	CO_2	43,99	44,2	5,8 8,6	18,87	373 445
10	CH_3Cl	49,99	50,2 51,3	3,0 3,2 3,9 3,0 3,4 4,0	26,86	373 438 445 373 438 445
11	$^+CH=CH_2CN$	52,02	52,3	2,9 3,3 3,1	12,19	373 438 445
12	$^+CH_2CH_2Cl$	63,0	63,3	3,0	3,93	373, 438, 445
13	CH_3CH_2Cl	64,01	65,3	3,5	4,59	438
14	CH_3OCl	65,99		4,2	5,50	445
15	$^+CH_2NH_3Cl$	66,02	66,8	3,5	4,59	445
16	$HOCH_2NHCH_2OH$	77,05	77,4	3,5	4,59	438, 445
17	$C_6H_5^+$	77,04				
18	C_6H_6	78,05	78,4	3,6	4,72	438
19	$CH_3CH_2N=NCH_2CH_3$	86,08	85,4	2,6	3,41	373
20	$C_6H_5NH_2$	93,06	93,3	2,8	3,67	438, 445
21	$C_6H_5CH_3$	92,06				
22	C_6H_5OH	94,04	95,5	2,5	3,28	373
23		98,11	98,1	2,9	3,80	445

[a]The fraction of the volatile product is equal to the ratio of the intensity of the given substance to the sum of all intensities at whole temperature range.

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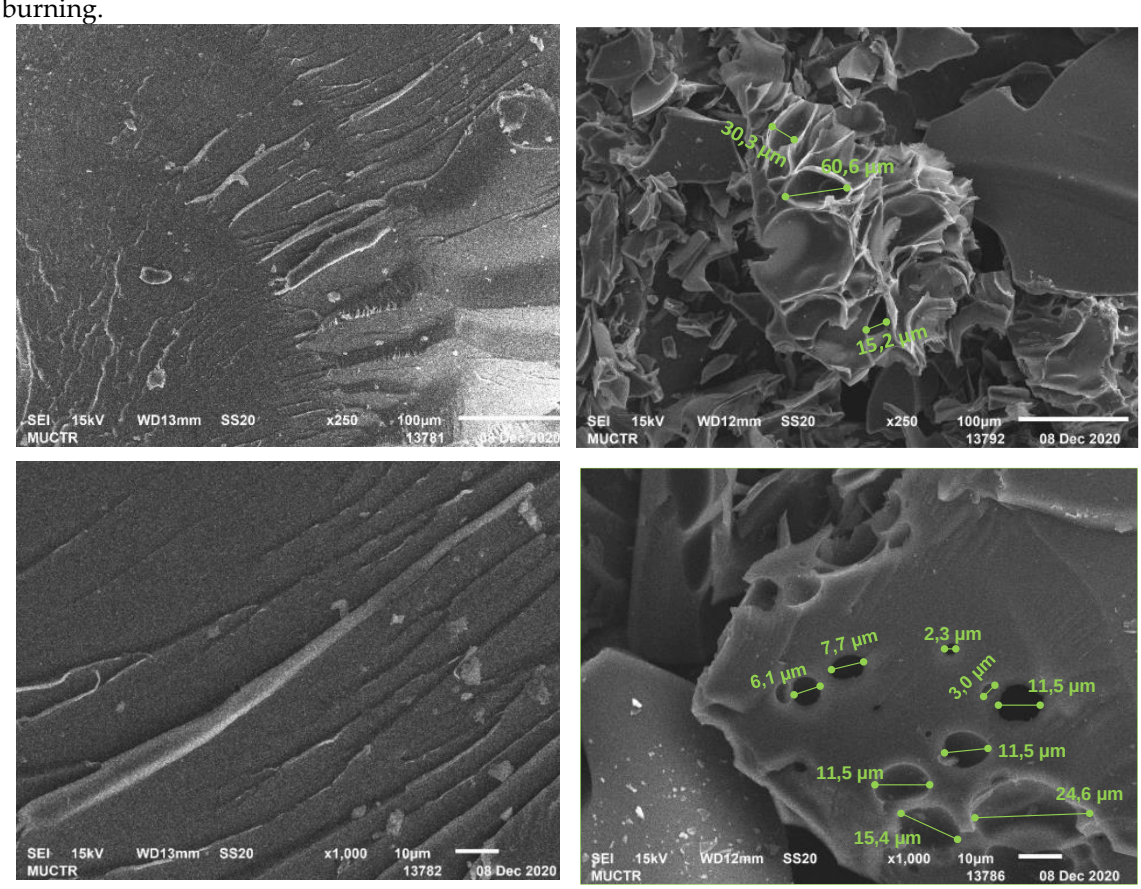
The surface of the fractured polymer sample and char yield were examined using SEM. The Figure 12a shows that the polymer has glassy bulky surface with no specific morphological features. Thus, we can conclude that this polymer is in a glassy state and is quite fragile. SEM image of char residue (Figure 12b) showed that during the burning of polybenzoxazine, a dense foamed protective layer with a pore diameter from 2.3 to 60,6 μm is formed, which prevents the polymer from further burning.



(**a**) (**b**)

Figure 13. SEM analysis of polybenzoxazine P-q (a) and char yield (b) surfaces.

The IR spectrum (Figure 13) of char residue of polybenzoxazine based on quamine was also investigated. It shows stretching vibrations of the C–Cl (700-800 cm^{-1}) bond after burning of the polymer sample. This observation is consistent with relatively low content of chlorine-containing ions during TGA and with the formation of a dense char residue in the UL-94 vertical test and presumably indicates the cessation of combustion on the sample surface without the flame penetrating deep into the sample.

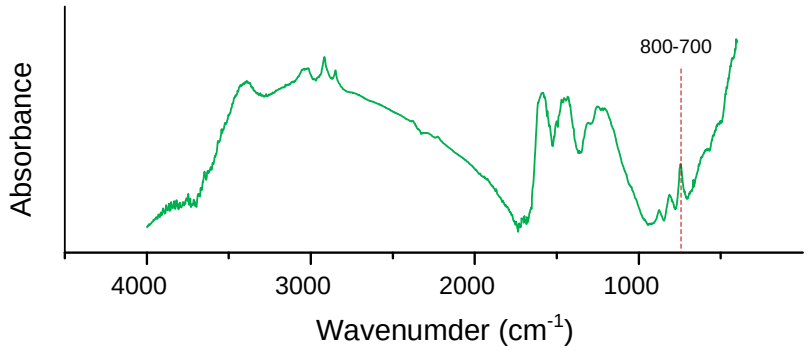


Figure 13. IR spectrum of the char residue of P-q based polybenzoxazine.

4. Conclusions

A new previously not reported in the literature benzoxazine monomer based on 3,3′-dichloro-4,4′-diaminodiphenylmethane (quamine) and phenol (P-q), has been obtained in high yield (90-95%). P-q has a fairly wide technological window with the viscosity of Pa·s at temperature range of 120-200 °C, so it can be used as a binder in the production of polymer composite materials by vacuum infusion or RTM. When compared to well-known commercial benzoxazine monomer P-d (obtained from phenol and 4,4′-diaminodiphenylmethane) the new polymer has higher char yield (57% for polyP-q and 46% for polyP-d at 800 °C) and UL-94 V-0 fire resistance rating. The obtained results indicate the possibility to applicate P-q as a (co)monomer in the production of fire-resistant binders for polymer composite materials, except for areas where the use of halogen-containing flame-retardants is not allowed.

Supplementary Materials: Figure S1: ^{1}H NMR spectrum of benzoxazine based on 4,4′-diaminodiphenylmethane in toluene/isopropanol 2:1. Figure S2: ^{13}C NMR spectrum of benzoxazine based on 4,4′-diaminodiphenylmethane in toluene/isopropanol 2:1. Figure S3: DSC curves of polybenzoxazines based on diamines (heating rate 10 deg / min). Figure S4: Mass spectrum of degradation of polybenzoxazine P-q in the air at 343 °C. Figure S5: Mass spectrum of degradation of polybenzoxazine P-q in the argon at 373 °C. Figure S6: Mass spectrum of degradation of polybenzoxazine P-q in the argon at 438 °C. Figure S7: Mass spectrum of degradation of polybenzoxazine P-q in the argon at 445 °C.

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