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J. Lustoň^a; J. Kronek^a; I. Janigová^b

^a Centre of Excellence GLYCOMED, Polymer Institute of the Slovak Academy of Sciences, Bratislava, Slovakia ^b Polymer Institute of the Slovak Academy of Sciences, Bratislava, Slovakia

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Synthesis and Polymerization Reactions of Cyclic Imino Ethers. 4. Aromatic Poly(ester amide)s of the AA+BB Type on the Basis of 2-Oxazolines

J. LUSTOŇ^{1,*}, J. KRONEK^{1,**} and I. JANIGOVÁ^{2,***}

¹Polymer Institute of the Slovak Academy of Sciences, Centre of Excellence GLYCOMED, Bratislava, Slovakia

²Polymer Institute of the Slovak Academy of Sciences, Bratislava, Slovakia

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Poly(ester amide)s were prepared by thermally initiated polymerization from two aromatic bis(2-oxazoline)s and four aromatic dicarboxylic acids. Polymerizations were performed in bulk and in solution. The structure of the polymers formed was confirmed by spectral analysis. The synthesis is limited by the thermal stability of the starting compounds. Limitation of the solution polymerization is the solubility of the starting compounds and the products in the solvent used. The prepared polymers have very good thermal properties.

Keywords: Addition polymerization, high temperature materials, ring opening polymerization, thermal initiation, poly(ester amide)

1 Introduction

2-Oxazolines react in a thermally initiated addition reactions with a wide variety of reagents, for example with carboxylic acids, phenols, thiols and amines (1). These reactions can be used either for the preparation of tailor-made polymers by polyaddition reactions of bis-(2-oxazoline)s with difunctional reagents, or by the construction of AB_x monomers containing a 2-oxazoline unit and another functional group which reacts with 2-oxazoline (2, 3). The reaction between 2-oxazolines and acids results in the opening of an oxazoline ring and the formation of ester-amide structure. When the bis(2-oxazoline)s and dicarboxylic acids are used for the reaction, the poly(ester-amide)s are formed. This mode represents a typical polyaddition reaction of the AA + BB type.

Although this reaction has been known for years (4-6), surprisingly, only a little is known about the preparation and the properties of the poly(ester amide)s prepared from

bis(2-oxazolines) and dicarboxylic acids. Jäger (5) first described the preparation of poly(ester amide) from 1,4-bis(2-oxazolin-2-yl)benzene and adipic acid. Later on, Kagiya et al. (4) produced the crystalline polymers from 1,4-bis(2-oxazolin-2-yl)benzene and 1,2-bis(2-oxazolin-2-yl)ethane by a reaction with adipic acid. On the other hand, the model reactions have been studied by several authors (7–9). Kinetic study of carboxylic acid – bis(2-oxazoline) addition reactions has shown that the reaction is of a second order without any noticeable side-reactions (7). The hypothesis of equal reactivity in bisoxazolines was also verified experimentally. The authors measured the rate constants of the coupling reaction and the activation enthalpy obtained for 1,3-bis(2-oxazolin-2-yl)benzene. Good correlation was found between the Arrhenius activation energy given by Chalamet (10) and the coupling reaction of polymers (7). On the other hand, Sano (8) in his kinetic study of the carboxylic acid–2-oxazoline reaction has found that a side reaction between the formed amide group and 2-oxazoline proceeds readily in excess of 2-oxazoline. However, the rate constant of this reaction is 2 orders of magnitude lower than that of the reaction with carboxylic acids.

Recently, we published a study (9) of the thermally initiated polymerization of aromatic bis(2-oxazolines) with aliphatic dicarboxylic acids of the general formula HOOC(CH₂)_nCOOH (n = 2–10). In an extension of these studies, we oriented on the systems, where both reaction

*Address correspondence to: Jozef Lustoň, Polymer Institute of the Slovak Academy of Sciences, Center of Excellence GLYCOMED, Dúbravská cesta 9, 84236 Bratislava, Slovakia. Tel: 00421 2 54772461; E-mails: upollust@savba.sk; Jozef.Luston@savba.sk.

**E-mail: upolkron@savba.sk.

***E-mail: upoljani@savba.sk

comonomers are aromatic compounds. It is obvious that we cannot obtain fully aromatic poly(ester amide). This is due to the presence of the ethylene linker between ester and amide groups however, the thermal properties of the prepared polymers were very good. In this paper, we are describing a process in which the aromatic 1,3-bis(2-oxazolin-2-yl)benzene (IBOX) and 1,4-bis(2-oxazolin-2-yl)benzene (TBOX) and four different aromatic dicarboxylic acids are used for the preparation of new materials with specific properties.

2 Experimental

^1H and ^{13}C -NMR spectra were measured on a AMX-300 spectrometer (Bruker) operating at 300.13 MHz for ^1H and 75.47 MHz for ^{13}C and a DRX-500 NMR spectrometer (Bruker) operating at 500.13 MHz for ^1H and 125.77 MHz for ^{13}C . The samples were measured in DMSO- d_6 at a room temperature. The solvent was used as a lock and internal standard (δ (^1H) = 2.50 ppm, δ (^{13}C) = 39.6 ppm). Melting points were measured on a Koffler melting point apparatus (VEB Analytik, Germany) and are uncorrected. Number average molar masses were measured by vapor pressure osmometry (Knauer, DMSO, 90°C). Thermal analysis was done with a Mettler Toledo DSC instrument at a heating rate of 10 K/min. Thermogravimetry was performed using a Mettler-Toledo TGA/SDTA 851^e instrument in nitrogen atmosphere with a heating rate of 10°C/min. Indium and aluminum were used for temperature calibration.

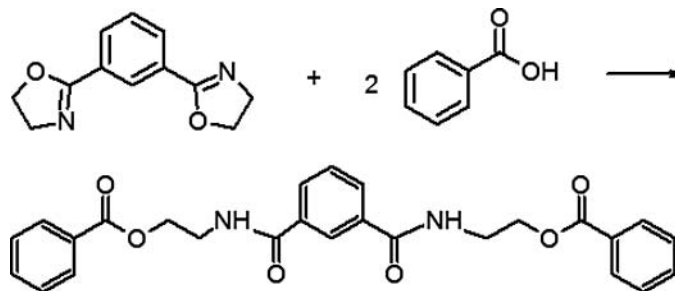
2.1 Materials

Starting materials, 1,4-bis(2-oxazolin-2-yl)benzene (TBOX) and 1,3-bis(2-oxazolin-2-yl)benzene (IBOX) were prepared according to the known methods (9). Terephthalic acid (TPA), isophthalic acid (IPA), pyridine-2,6-dicarboxylic acid (PyDA), and 4,4'-biphenyldicarboxylic acid (BiDA) were used as received from Aldrich.

Other reagents were commercially available (Aldrich) and were used as obtained. The solvents used for polymerizations and measurements were distilled and dried over molecular sieves.

2.2 Polymerization in Melt

The calculated amounts of bis(2-oxazoline) (2 mmol) and aromatic diacid (2 mmol) were weighed into a test tube which was evacuated several times, filled with argon, and sealed. The ampoule was immersed in a metal bath preheated to the polymerization temperature and heated for the desired time. After cooling, the polymer was dissolved in DMF (5 ml), and precipitated in a non-solvent (methanol or water). The polymer was separated, washed with a non-solvent, and dried in a vacuum oven.



Sch. 1. Model reaction.

2.3 Polymerization in Solution

The calculated amounts of bis(2-oxazoline) (2 mmol) and aromatic diacid (2 mmol) were weighed into a test tube and DMF (1 ml) was added. The reaction mixture was bubbled with argon for 5 min, and sealed. The ampoule was immersed in an oil bath, preheated to the polymerization temperature and heated for desired time. Hot viscous polymer solution was precipitated in a non-solvent (methanol or water). Polymer was separated, washed with a non-solvent, and dried in a vacuum oven.

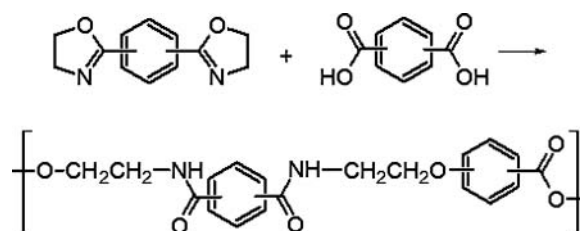
3 Results and Discussion

3.1 Polymerizations

The model reaction of aromatic bis(2-oxazoline)s TBOX and IBOX with aromatic benzoic acid has shown (9) (Sch. 1) that the thermally initiated reaction proceeds smoothly and in high yields also in the case when the reaction temperature was lower than the melting point of one of the comonomers.

Therefore, we investigated the reaction of TBOX and IBOX as AA monomers with aromatic diacids as BB monomers. TPA, (m.p. >300°C), IPA (m.p. = 341–343°C), PyDA (m.p. = 248–250°C), and BiDA (m.p. >300°C) were used as the second BB monomer. The reaction scheme for the reaction of TBOX with IPA is shown in Scheme 2.

The basic requirement for polymerizations is the homogeneity of the polymerization mixture. Therefore, we performed polymerizations at the temperature higher than the melting point of at least one monomer, used in polymerization. Polyadditions were performed at 200°C for IBOX



Sch. 2. Polyaddition reactions.

Table 1. Bulk polymerization of aromatic bis(2-oxazolines) with aromatic diacids at 200 and 250°C

<i>Bis(2-oxazoline)</i>	<i>Diacid</i>	<i>Temperature</i> [°C]	<i>Melting point</i> [°C]	<i>Mol. Weight</i> [Da]	<i>Remark</i>
TBOX	PyDA	250	—	—	Decomp.
TBOX	IPA	250	—	—	Black
TBOX	IPA	250 ^a	157–164	3300	Brownish
TBOX	TPA	250	—	—	Decomp.
TBOX	BiDA	270	—	—	Not solub.
IBOX	PyDA	200	—	—	Decomp.
IBOX	IPA	200	Soft~ 120	5300	Hard polym.
IBOX	TPA	200	~170	4600	
IBOX	BiDA	200	—	—	Not solub.

^aReaction time was 10 min.

(m.p. = 138–140°C) and at 250°C for TBOX (m.p. = 238–241°C). This means that bis-(2-oxazoline)s behave like “solvents” for dissolution of acids. The results of the polymerization of TBOX and IBOX are in Table 1.

Three polymers were isolated under the given reaction conditions, namely, polymers from the combinations TBOX-IPA, IBOX-IPA and IBOX-TPA. A decomposition reaction prevented formation of polymer with PyDA. For the system TBOX-PyDA, the polymerization time had to be

shortened to 10 min; otherwise some degradation reactions took place. The melted TBOX was not the proper solvent in the reaction with BiDA, neither at 250 nor at 270°C. The problems with thermal stability appeared also in the polymerization of IBOX. The decomposition of PyDA was observed at 200°C. Low solubility, which prevented formation of regular polymer, was observed during the reaction of IBOX with BiDA. We succeeded in preparation of polymers from IBOX and both phthalic acids, IPA and TPA. In

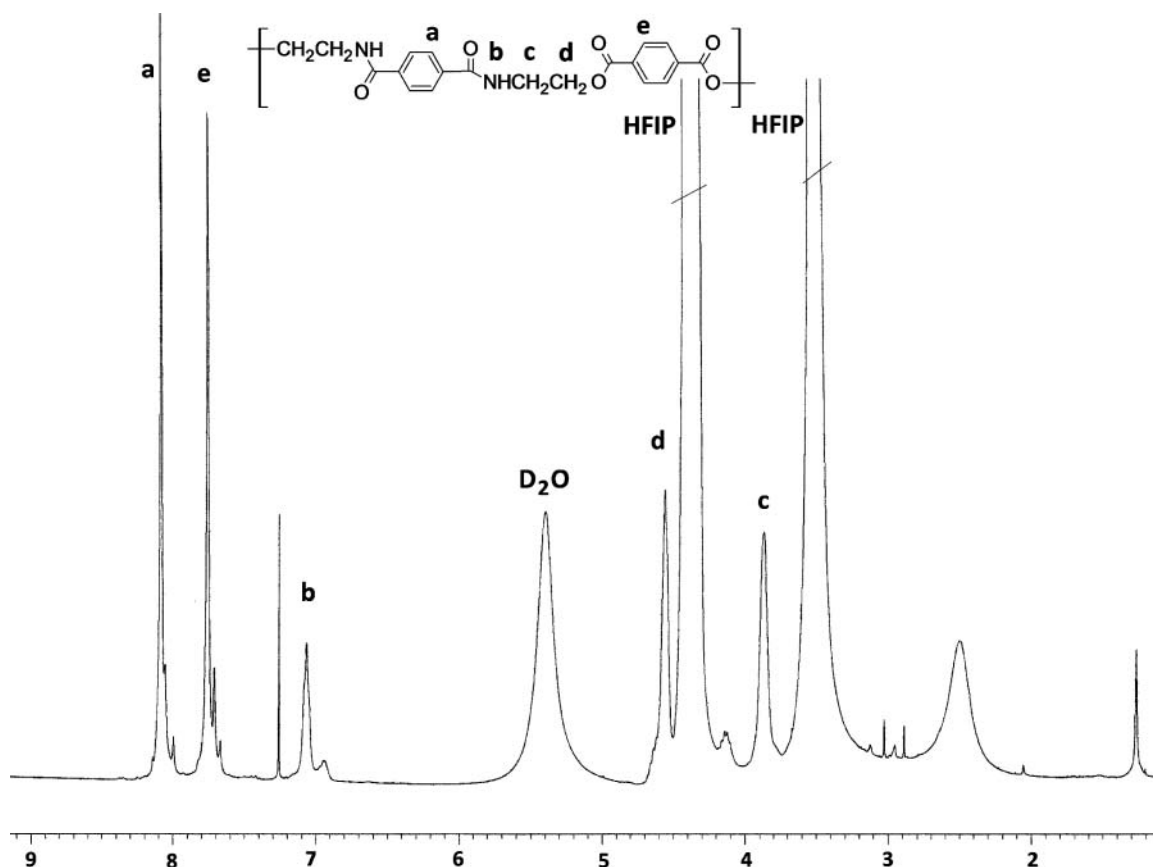
**Fig. 1.** The ¹H-NMR spectrum of polymer from TBOX and TPA.

Table 2. Polymerization of aromatic bis(2-oxazolines) with aromatic diacids in the presence of DMF

Bis(2-oxazoline)	Diacid	Temperature [°C]	Melting point [°C]	Mol. Weight [Da]	Remark
TBOX	PyDA	170	229–233	3800 ^a	Time 6 hr
TBOX	IPA	170	100–105	2700	
TBOX	TPA	170	—	—	White powd.
TBOX	BiDA	170	—	—	
IBOX	PyDA	170	140–144	2600	
IBOX	IPA	170	292–297	—	
IBOX	TPA	170	~180	2200	
IBOX	BiDA	170	—	—	

^aM_n calculated from ¹H-NMR spectrum was 4380 Da.

these cases, the polymers with number average molar mass around 5000 g/mol were obtained.

Small amount of DMF and the temperature of 170°C were used to improve homogeneity of the polymerization system. The results are given in Table 2.

Polymerization of TBOX with PyDA proceeded smoothly but polymerization time had to be shortened to 6 h since some decomposition was observed at longer re-

action times. The polymer was precipitated in methanol in the form of yellowish grains, the course of polymerization of TBOX with IPA was similar. The formed polymer precipitated during polymerization. After the completion of the polymerization, the reaction mixture was dissolved in DMF, and precipitated in methanol. During the polymerization of TBOX with TPA and TBOX with BiDA in the presence of DMF, one of the reaction components, diacids,

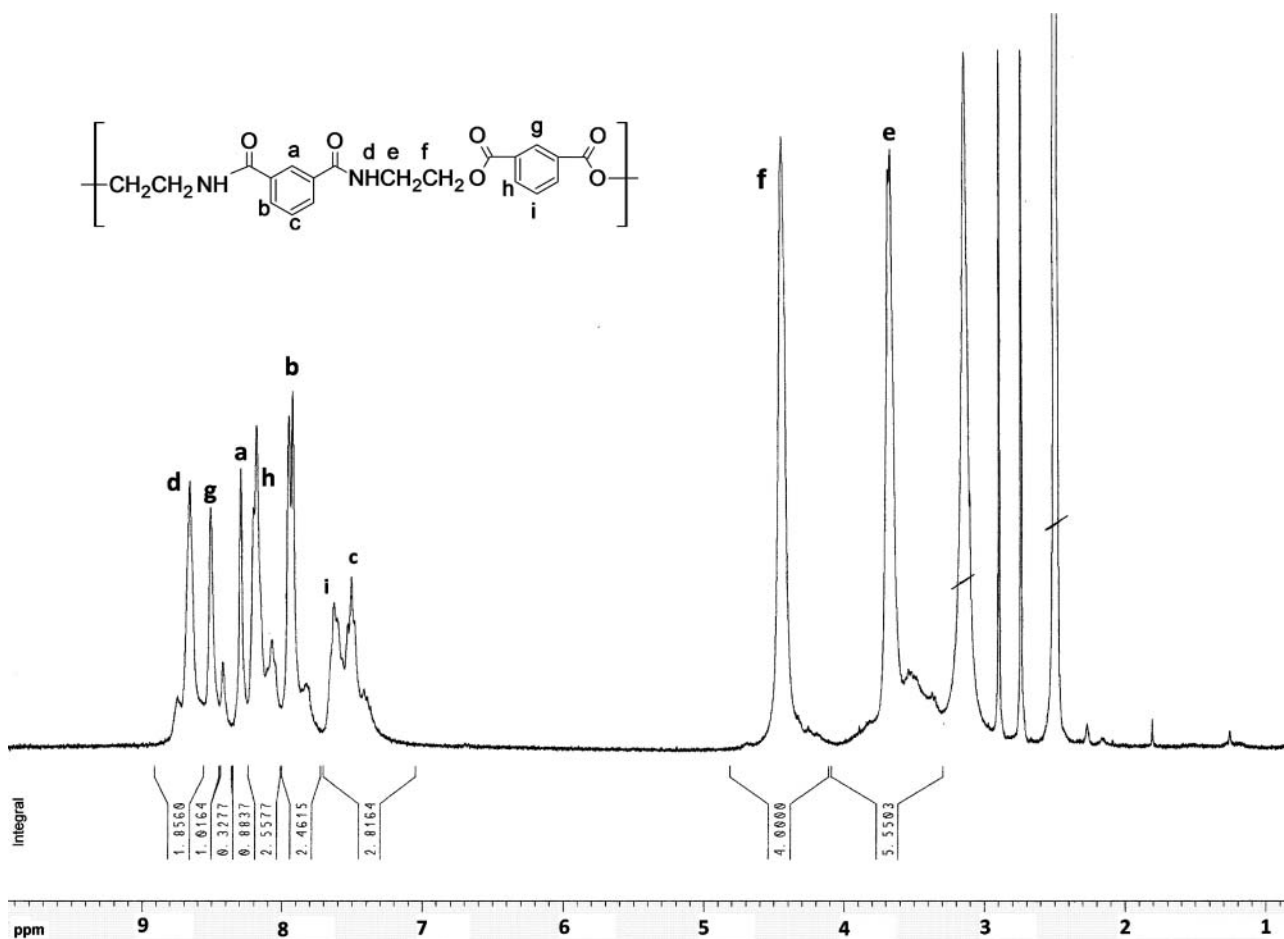


Fig. 2. The ¹H-NMR spectrum of polymer from IBOX and IPA.

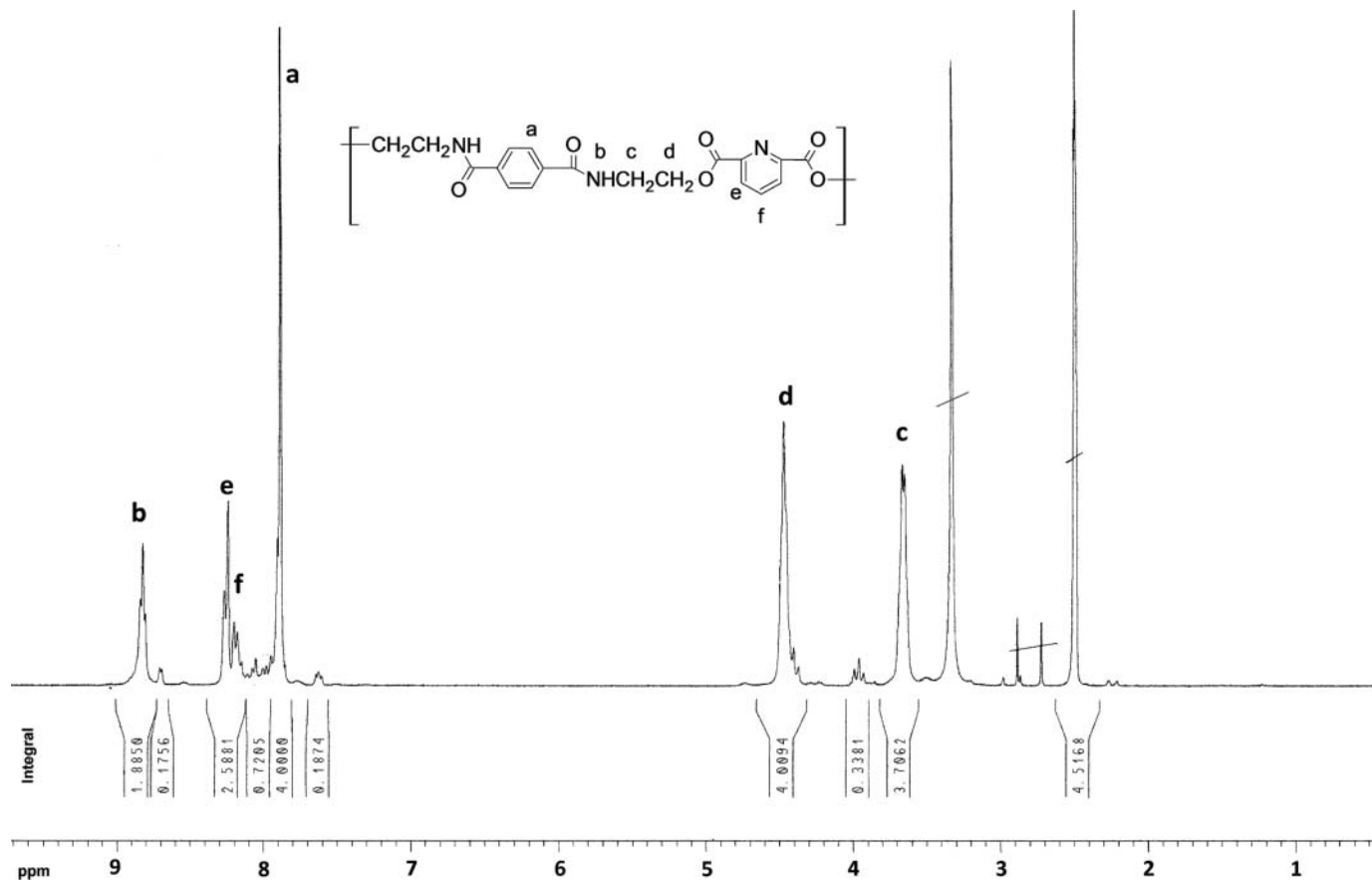


Fig. 3. The ¹H-NMR spectrum of polymer from TBOX and PyDA.

did not dissolve in the system. After ampoule was cooled, white powder which did not dissolve in DMF was obtained in both cases. The system IBOX-PyDA was also treated for only 6 h because of the decomposition of the product with the extension of the polymerization time. After processing and drying of the product, a very voluminous, yellow, transparent, easily powderable solid was obtained. A viscous, yellow solution was obtained during the polymerization of IBOX with IPA that after precipitation in water yielded white powder with melting temperature as high as 290°C. The monomers pair IBOX-TPA yielded during polymerization yellow, viscous solution which was precipitated in water as white powder. The reaction between IBOX and BiDA was stopped due to insolubility of the acid in the solvent.

3.2 Structure of Polymers

The ¹H-NMR spectrum of the copolymer prepared from TBOX and TPA is presented in Figure 1. This spectrum was measured in the mixture of hexafluoroisopropanol-chloroform (1:1), because of poor solubility of the polymer in DMSO.

We can see that two singlets with the chemical shift 8.09 and 7.76 ppm represent the ring protons of the two dif-

ferent phenylene rings. The first signal belongs to the ring carrying amide group while the second one was attributed to the ring with the ester group. In this case, amidic proton is located at the higher field and we found it at 7.06 ppm. The methylene protons are found at 4.56 and 3.87 ppm for CH₂O and CH₂NH, respectively. The spectrum correlates with the expected structure of poly(ester amide). The spectrum of the pair IBOX and IPA is in Figure 2. Amidic proton –NH– in DMSO can be found at the lower field than that of the aromatic protons, at 8.66 ppm.

Due to the two non-symmetric benzene rings, the aromatic protons are split into individual bands, and are located at 8.51, 8.33, 8.19, 7.93, 7.63, and 7.51 ppm. In this region of the spectrum we can also see the signals belonging to the products of the side reaction (e.g. 8.42 or 8.07 ppm), as described in the literature (11). Assignment of the protons is shown in the drawing. Aliphatic protons are found at 4.45 and 3.68 ppm. The spectrum corresponds to the suggested poly(ester amide) structure.

The pair of the comonomers TBOX and PyDA is shown in Figure 3, after thermal treatment.

The amide proton has the highest chemical shift 8.83 ppm followed by the protons of the pyridine ring at 8.26 and 8.19 ppm and the singlet of the terephthalic ring at 7.89 ppm. The bands of CH₂O and CH₂NH groups

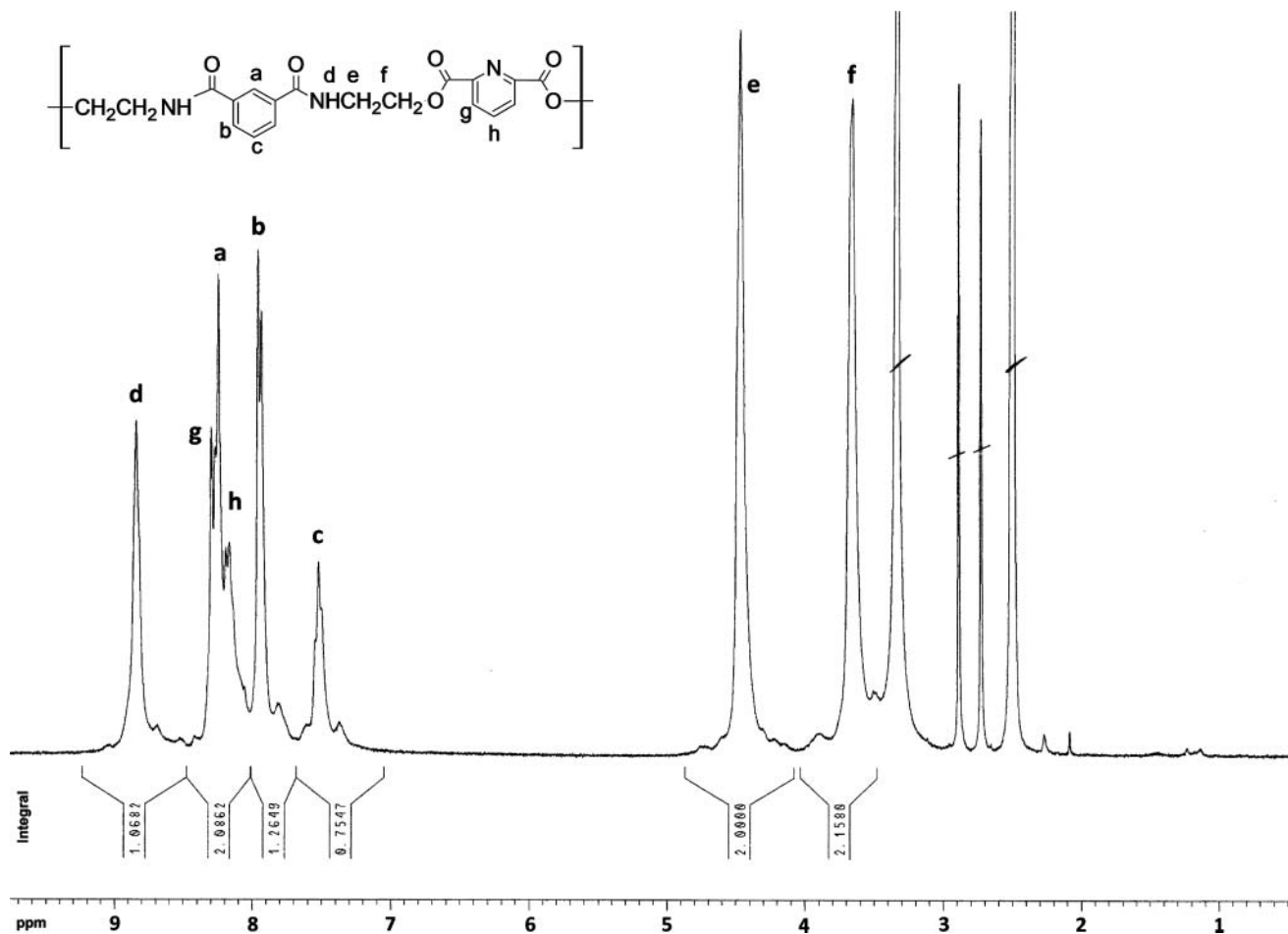


Fig. 4. The ¹H-NMR spectrum of polymer from IBOX and PyDA.

are found at 4.48 and 3.66 ppm, respectively. Small peaks beside the amide peak and in aromatic region indicate approximately 10% of the side reaction. The spectrum is in agreement with the proposed structure.

Figure 4 shows the NMR spectrum of the polyadduct of the IBOX and PyDA.

In this case the first amidic peak at 8.84 ppm is accompanied with the signals of aromatic protons that are split into more peaks at 8.26, 8.23, and 8.18 ppm, a doublet at 7.94 ppm and a triplet at 7.52 ppm. The aliphatic protons at 4.46 and 3.66 ppm belong to the CH₂O and CH₂NH groups.

The spectrum of the copolymer from IBOX and BiDA is presented in Figure 5.

The amide peak is found at 8.67 ppm. Isophthalic protons are found as a singlet at 8.33 ppm, a doublet at 7.97 ppm and a triplet of one proton at 7.54 ppm, while biphenyl is identified as two doublets at 8.06 and 7.84 ppm. Aliphatic hydrogens are found at 4.45 and 3.69 ppm for OCH₂ and NCH₂ groups. Small peaks at 8.46, 4.38 and 3.50 ppm belong evidently to the non reacting monomers.

The spectrum of the polymer prepared from IBOX and TPA is in Figure 6.

The proposed structure was again confirmed by the presence of the amide peak at 8.86 ppm, singlet of symmetrical terephthalic protons, and signals of isophthal fragment at 8.31, 7.95, and 7.53 ppm. Aliphatic hydrogens are located at 4.43 and 3.67 ppm for CH₂O and CH₂NH groups.

We can say that in all cases the expected structure of the prepared polymers was confirmed. In some cases the presence of side reactions (11) was observed with the degree of reaction below 10%. In general, we can see that the structure of the spectrum is as follows: a newly formed amide peak is usually found at nearly 9 ppm. Only in the case when the spectrum was taken in hexafluoroisopropanol-CHCl₃ mixture, amidic peak is located at about 7 ppm. Aromatic protons are found between 7 and 8.5 ppm. Aliphatic hydrogens are in the region 3.5 to 4.5 ppm.

3.3 Thermal Properties

The following polymers were prepared from the bis-oxazolines and diacids combinations, TBOX-BIDA, IBOX-BIDA, TBOX-IPA, IBOX-IPA, IBOX-TPA.

Thermal properties of the prepared new materials were measured by DSC in the temperature interval from 25 to

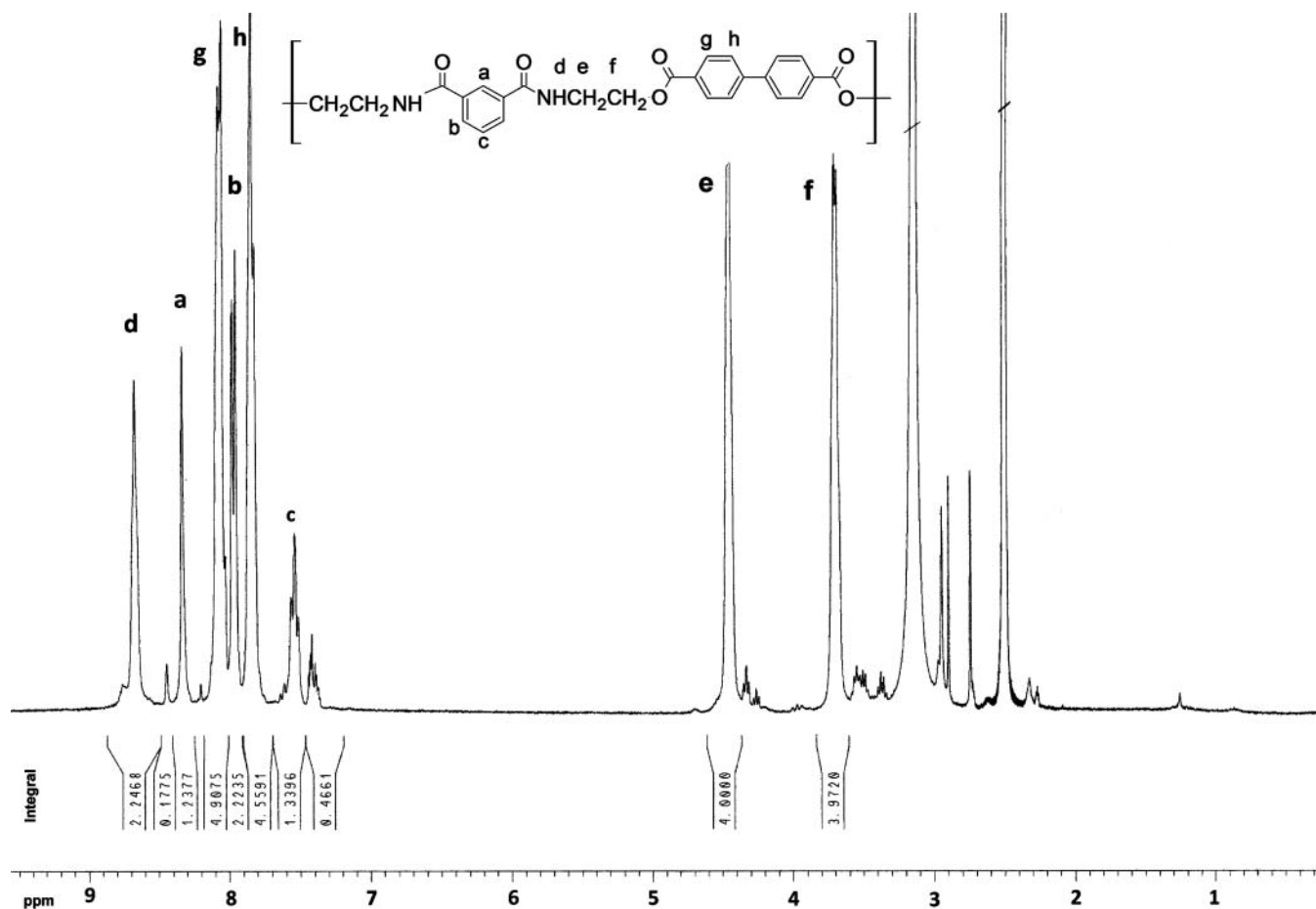


Fig. 5. The ¹H-NMR spectrum of polymer from IBOX and BiDA.

450°C and by thermogravimetry (TGA) in the temperature interval up to 590°C. The DSC records of the samples are shown in Figure 7.

It is evident that the composition of the polymerization mixture has a significant effect on the thermal properties of the prepared polymers. In the case of IBOX-BIDA we can see the melting endotherm at about 320°C, which is followed by the decomposition exotherm in the range 335–345°C. This value corresponds to DTG (Table 3) maximum of the decomposition peak (T_{\max}) at 356 °C.

Similar properties are exhibited at the sample TBOX-BIDA. Both samples were prepared in the solution poly-

merization at 170°C. The presence of the rigid structure of TBOX instead of IBOX causes the shift of the melting peak and the peak of the decomposition to higher temperatures-365°C and 370°C, respectively. The region of decomposition is again supported with DTG measurements. ($T_{\max} = 376^\circ\text{C}$). We suggest that the melting peak represents the reaction of the unreacted part of the BIDA acid. Another shape of the DSC curves we observed for the samples IBOX-IPA and TBOX-IPA. The significant endotherm is absent. The decomposition peaks of the samples are observed at 335°C for IBOX and 344°C for TBOX polymers. The values of DTG peaks again correlate with DSC measurements (Table 3). The last DSC curve corresponds to the polymerization mixture IBOX-TPA polymerized in the solution (170°C). The temperature of decomposition is 325°C. The value of T_{\max} is 346°C.

Table 3. The values of the temperature of the start of decomposition (T_{onset}), maximum of decomposition (T_{\max}) and the weight loss of the samples

Sample	$T_{\text{onset}} [^\circ\text{C}]$	$T_{\max\text{DTG}} [^\circ\text{C}]$	Weight loss [%]
IBOX/BiDA	300	356	82
TBOX/BiDA	324	376	87
IBOX/IPA	269	345	82
TBOX/IPA	282	352	87
IBOX/TPA	273	346	83

4 Conclusions

Thermally initiated polymerization of two aromatic bis(2-oxazolines) and four aromatic dicarboxylic acids was studied in a melt and in a solution. The reaction is a typical AA + BB polymerization. NMR measurements confirmed

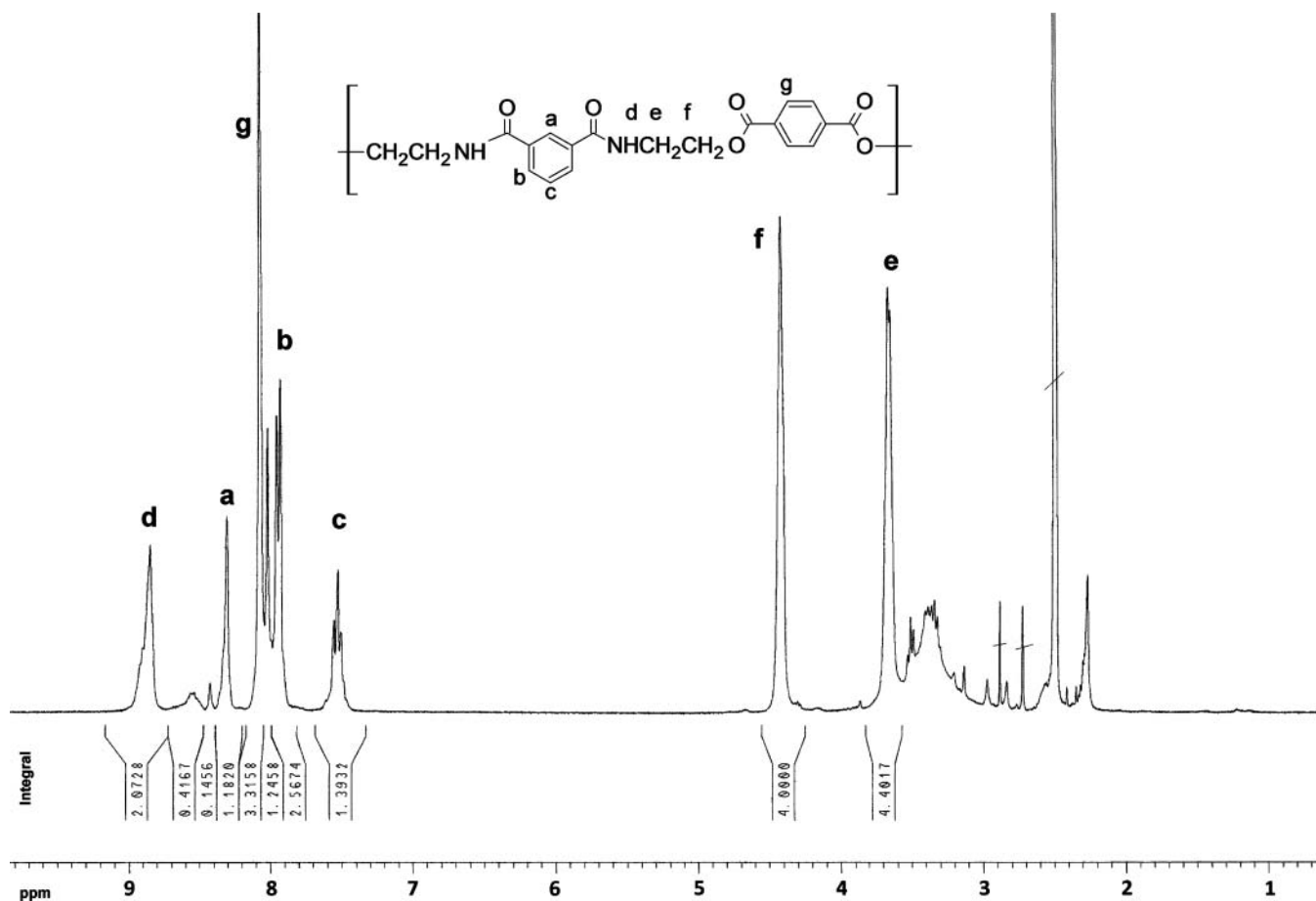


Fig. 6. The ¹H-NMR spectrum of polymer from IBOX and TPA.

the structure of polymers and the course of the reaction. The prepared polymers have lower molar masses than the polymers prepared from aliphatic diacids. In the case of aromatic components, the reaction is limited by the solu-

bility of monomers and products. On the other hand, the presence of carboxylic end-groups enables additional coupling reactions with chain extending agents. The prepared polymers have very good thermal properties.

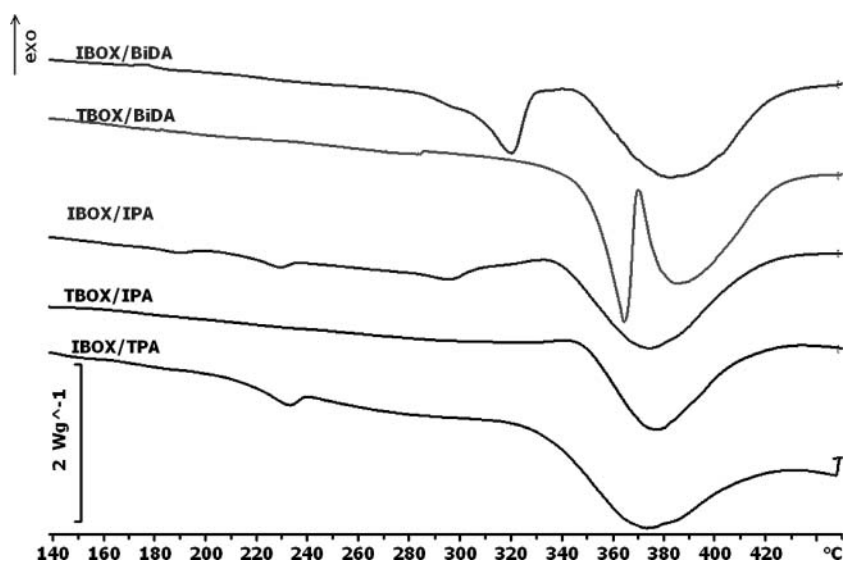


Fig. 7. The DSC records after second heating of the prepared polymers.

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