

ORGANOSOLUBLE XANTHONE-BASED POLYIMIDES: SYNTHESIS, CHARACTERIZATION, ANTIOXIDANT ACTIVITY AND HEAVY-METAL SORPTION

ORGANSKO TOPNI POLIAMIDI NA OSNOVI KSANTONA: SINTEZA, KARAKTERIZACIJA, ANTIOKSIDATIVNA AKTIVNOST IN SORPCIJA TEŽKIH KOVIN

Moslem Mansour Lakouraj¹, Ghasem Rahpaima², Razieh Azimi¹

¹University of Mazandaran, Faculty of Chemistry, Department of Polymer Chemistry, Babolsar, Iran

²Islamic Azad University, Department of Chemistry, Lamerd Branch, Lamerd, Iran
lakouraj@umz.ac.ir

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To improve the solubility, thermal properties and processability of polyxanthenes, a new class of polyxanthenes, poly(xanthone-imide)s (PXIs), with a high yield was prepared using a two-step chemical imidation of 2,7-diaminoxanthone with pyromellitic dianhydride (PMDA), 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and 2,2'-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6-FDA)). These PXIs were characterized with FT-IR and ¹H NMR spectroscopies. They presented a good solubility in aprotic polar solvents such as N,N-dimethyl acetamide (DMAc), N,N-dimethyl formamide (DMF), N-methyl pyrrolidone (NMP) and dimethyl sulfoxide (DMSO), and showed inherent viscosities in a range of 0.34–0.58 dL/g. These PXIs exhibited lower glass-transition temperatures than the original polyxanthenes and a high thermal stability. The obtained results of the UV-vis absorption and photoluminescence indicated that the maximum absorption and fluorescence emission of PXIs were in the range of 300–304 nm and 432–510 nm, respectively. The antioxidant activity of PXIs was evaluated with a DPPH assay. The antioxidant values for PXIs were greater than for the parent xanthone (X). The polyimides were investigated for the extraction of environmentally noxious metal ions such as Cr (VI), Co (II), Ni (II), Cu (II), Pb (II) and Cd (II) from aqueous solutions.

Keywords: poly(xanthone-imide)s, antioxidant activity, fluorescence, organosolubility, heavy metals

Za izboljšanje topnosti, toplotnih lastnosti in predelovalnost poliksantonov je bila pripravljena nova vrsta poliksantonov, poli(ksanton-imidov) (PXIs) z visokim izkoristkom, z uporabo dvostopenjske kemijske sinteze 2,7-diaminoksantona z piro-melitim dianhidridom (PMDA), 3,3',4,4'-benzofenon tetrakarboksilnega dianhidrida (BTDA) in 2,2'-Bis-(3,4-Dikarbofenil) heksafluoropropan dianhidrida (6-FDA)). Ti PXI-ji so bili karakterizirani s FT-IR in ¹H NMR-spektroskopijo. Predstavljajo dobro topnost v aprotičnih polarnih topilih, kot je N,N-dimetil acetamid (DMAc), N,N-dimetil formamid (DMF), N-metil piroolidon (NMP) in dimetil sulfoksid (DMSO) in kažejo nespremenljivo viskoznost v območju 0,34–0,58 dL/g. Ti PXI-ji kažejo nižjo temperaturo prehoda v steklasto stanje kot originalni poliksantoni ter veliko termično stabilnost. Dobljeni rezultati UV-absorpcije in fotoluminescence kažejo, da je maksimalna absorpcija in emisija fluorescence PXI-jev v območju 300–304 nm, oziroma 432–510 nm. Antioksidativna aktivnost PXI-jev je bila ocenjena z DPPH preizkusom. Vrednost protioksidativnosti za PXI-je je bila večja kot pri matičnem ksantonu. Poliamidi so bili preiskovani za ekstrakcijo okoljsko škodljivih kovinskih ionov, kot so Cr (VI), Co (II), Ni (II), Cu (II), Pb (II) in Cd (II) iz vodnih raztopin.

Ključne besede: poli(ksanton-imidi), antioksidacijska aktivnost, fluorescenca, organska topnost, težke kovine

1 INTRODUCTION

Xanthenes have a conjugated planar ring system consisting of two benzene rings bridged through a carbonyl group and an oxygen atom. This unique structure shows an admirable thermo-oxidative and hydrolytic stability with numerous potential beneficial properties such as antioxidant,^{1,2} antihistamine,^{3,4} anti-inflammatory,^{5,6} antibacterial,^{7,8} antifungal,⁹ antiviral^{10,11} and anticancer^{12,13} effects. Consequently, it seems to have a great potential as a structural pattern in high-performance polymers. Although several different synthetic and natural xanthenes were introduced^{14–18} few of such biologically active compounds were investigated in a polymer synthesis.¹⁹

Polyxanthenes can be used for high-temperature applications and as electrical insulating materials due to their excellent solvent and chemical resistance, good physical and electrical properties even at high temperatures. However, a poor processability of the polymers is the main drawback as they have high glass or melting temperatures and are often insoluble in common organic solvents.^{20,21}

On the other hand, due to oxidative-degradation reactions that may occur during various stages of the polymer lifecycle including the manufacturing, processing and end-use stages, it is essential to place antioxidant building block in polymer matrices. These polymers, whose antioxidant moieties are covalently attached to the backbone of a polymer, have unique advantages: they are

non-volatile and they do not penetrate into the skin and tissue.

Aromatic polyimides are well-known high-performance polymers that have a high thermal stability, excellent mechanical and chemical properties. Due to these advantageous properties, polyimides are widely used as adhesives, films, composite matrices, coatings, membranes, and in the electronic-packaging industry.²²⁻²⁵

Therefore, in continuation of our ongoing work on polyxanthenes²⁶ and also in order to improve the physical properties of polyxanthenes, in the present study, we attempted to insert a xanthone unit into the backbone of a polyimide to develop new organosoluble polyxanthenes. For this purpose, at first, 2,7-diaminoxanthone was prepared and then used for a polymerization with pyromellitic dianhydride (PMDA), 3,3', 4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and 2,2'-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6-FDA). The structures of the resulting poly(xanthone-imide)s were characterized with NMR and FT-IR spectroscopies. The physical properties of these PXIs, including their viscosity, solubility, thermal stability, morphology, and their spectroscopic properties such as ultraviolet-visible absorption and fluorescence emission were studied. In addition, PXIs were also evaluated for their antioxidant activities with a 2,2-diphenyl-1-picrylhydrazyl (DPPH) assay. Furthermore, their ability to eliminate environmentally toxic heavy-metal ions such as Pb (II), Cd (II), Co (II), Ni (II), Cu (II) and Cr (VI) were studied in aqueous media.

2 EXPERIMENTAL WORK

2.1 Materials

N-methyl-2-pyrrolidone (NMP), N,N-dimethylacetamide (DMAc), acetic anhydride and pyridine were purchased from Merck and purified with distillation under a reduced pressure over calcium hydride and stored above a 4° A molecular sieve. Pyromellitic dianhydride (PMDA), 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and 2,2'-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6-FDA) were dried in a vacuum oven at 110 °C for 5 h. All the other materials and solvents, such as DMF, pyridine and DMSO were purchased from TCI Chemical Co., Fluka Chemical Co. (Buchs, Switzerland) and Merck Chemical Co. and used as received.

2.2 Measurements

A Bruker Tensor 27 spectrometer (Bruker, Karlsruhe, Germany) and a 400-MHz Bruker Avance DRX spectrometer in DMSO-d₆ were used for recording FT-IR, ¹H and ¹³C NMR spectra, respectively. Inherent viscosities (*h_{inh}*) of the polymers were determined in NMP at 0.5 g per 100 mL concentration, with an Ubbelohde viscometer (Schott-Gerate, Hofheim, Germany) at 25 °C. A thermogravimetric analysis (TGA) was conducted

with a TA Instruments TGA-50 (Shimadzu, Kyoto, Japan) in a temperature range of 50–650 °C at a heating rate of 10 °C/min under nitrogen atmosphere.

Glass-transition temperatures (*T_g*) of the polymers were determined with a Perkin-Elmer Pyris 6 differential scanning calorimeter at a heating rate of 10 °C/min under nitrogen atmosphere. The UV-visible absorption and fluorescence emission spectra were recorded on Cecil 5000 and Perkin-Elmer LS-3B spectrophotometers in an NMP solution, respectively. X-ray powder diffraction patterns were performed at room temperature (about 25 °C) with an X-ray diffractometer (GBC MMA instrument) with Be-filtered Cu-K_α (0.15418 nm) operating at 35.4 kV and 28 mA. The 2θ scanning range was set between 4° and 50° at a scan rate of 0.05° per s. The concentration of metal cations in the liquid phase was determined with an atomic-absorption instrument (BRAIC WFX-130 AA).

2.3 Monomer synthesis

As illustrated in **Figure 1**, the 2,7-dinitroxanthone (DNX) and 2,7-diaminoxanthone (DAX) were prepared according to our published article.²²

2.4 Polymer synthesis

The general synthetic route used to produce the PXIs was as follows. A 100-mL two-necked, round-bottomed flask equipped with a magnetic stirrer bar, nitrogen-gas inlet tube and calcium chloride drying tube was charged with 0.226 g (1.0 mmol) of diamine (DAX) and 10 mL of dry NMP. The mixture was stirred at room temperature for 0.5 h. Then 1.0 mmol of a dianhydride was added and the mixture was again stirred at room temperature for 24 h, forming a viscous solution of a poly(amic acid) (PAA) precursor in NMP. The PAA was converted into polyimide with the chemical-imidization process.²⁷ The chemical imidization was carried out by adding 3 mL of a mixture of acetic anhydride/pyridine (6:4, v/v) into the PAA solution, while stirring it at room temperature for 1 h. Then the mixture was stirred at 130 °C for 12 h to yield a homogeneous solution. The polymer solution was slowly poured into methanol to form a precipitate. The precipitate was then filtered, washed thoroughly with hot methanol and dried overnight under vacuum at 80 °C.

PXI-a. A yield of 97 %, FTIR (KBr, cm⁻¹): 3020 (aromatic C-H stretching), 1775 (C=O asymmetric stretching), 1714 (C=O symmetric stretching), 1658 (C=O stretching of the carbonyl group), 1466 (C=C stretching), 1375 (C-N stretching), 1145 (C-O stretching). ¹H NMR (400 MHz, DMSO-d₆): δ 7.52–8.84 (8 H, aromatic protons).

PXI-b. A yield of 96 %, FTIR (KBr, cm⁻¹): 3050 (aromatic C-H stretching), 1780 (C=O asymmetric stretching), 1705 (C=O symmetric stretching), 1660 (C=O stretching of the carbonyl group), 1470 (C=C stretching),

1370 (C-N stretching), 1155 (C-O stretching). $^1\text{H NMR}$ (400 MHz, DMSO-d_6): δ 7.61–8.52 (12 H, aromatic protons).

PXI-c. A yield of 93 %, FTIR (KBr, cm^{-1}): 3010 (aromatic C-H stretching), 1785 (C=O asymmetric stretching), 1755 (C=O symmetric stretching), 1658 (C=O stretching of the carbonyl group), 1475 (C=C stretching), 1385 (C-N stretching), 1140 (C-O stretching). $^1\text{H NMR}$ (DMSO-d_6): δ 7.29–7.79 (12H Aromatic).

2.5 Antioxidant activities

The antioxidant activity of the compounds (PXI-a, b and c) was determined spectrophotometrically, using a stable 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical according to the already reported method, with a slight modification.²⁸ A stock solution of the PXIs (0.5 mg/mL) was prepared in DMSO, and 50 μL of the prepared PXI solution was added to 5 mL of a 0.004 % ethanol solution of the DPPH radical. After 30 min of incubation in dark at room temperature, the absorbance was observed against a blank at 517 nm. The assay was carried out in triplicate and the percentage of inhibition was calculated using the following formula:

$$\% \text{ inhibition} = (\text{AB} - \text{AA}) / \text{AB} \times 100$$

where AB = absorption of the blank and AA = absorption of the test.

2.6 Water absorption

Two examination methods were investigated for the water-absorption capacity of poly(xanthone-imide)s. Method I: the polymer (0.2 g) was poured in 30 mL water at 25 °C for 24 h, followed instantly by weighing. Method II: a polymer powder was boiled in water at 100 °C for 30 min, and its weight difference was determined with the measurements before and after the insertion.

2.7 Adsorption capability

Solid-liquid extractions of Cd (II), Cu (II), Co (II) and Ni (II) as their chloride salts, Pb (II) as nitrate salt and Cr (VI) as $\text{Cr}_2\text{O}_7^{2-}$ ($\text{K}_2\text{Cr}_2\text{O}_7$) were carried out either

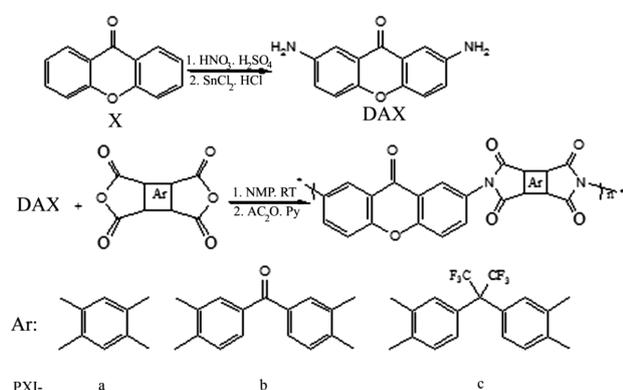


Figure 1: Synthesis and designations of poly(xanthone-imide)s (PXIs)
Slika 1: Sinteza in oznaka poli(ksanton-imidov) (PXI-jev)

individually or in the mixture. Approximately 10 mg of the appropriate polymer powder was shaken with 10 mL of an aqueous solution of the metal salt for 3 d at 25 °C. The initial concentration of the salts was 10 mg L^{-1} . After filtration, the concentration of each metal cation in the liquid phase was determined with the atomic-absorption technique, and direct information regarding the extraction percentage of metal ions by the polymer was obtained using a calibration curve, made for each metal ion from the standard solutions of (5, 10, and 20) $\mu\text{g/g}$.

3 RESULTS AND DISCUSSION

3.1 Polyimide synthesis and characterization

Three polyimides containing a xanthone group were prepared in high yields (90–97 %) with a polycondensation of equal molar amounts of the diamine with commercially available aromatic dianhydrides, such as PMDA, BTDA and 6-FDA, as shown in **Figure 1**. The polycondensation was carried out in NMP at room temperature for 24 h to form poly(amic acid)s, followed by chemical imidization with acetic anhydride and pyridine. The inherent viscosity of the polymers, as a suitable criterion for evaluating the molecular weight, was measured at a concentration of 0.5 g/dL in NMP at 25 °C. The inherent viscosities of the polyimides were in a range of 0.34–0.58 dL/g, indicating moderate molecular weights. All the polymers were characterized using the FT-IR and $^1\text{H NMR}$ techniques. In **Figure 2**, the FT-IR spectrum of the PXI-b is shown as a representative polyimide. The FT-IR spectra of the PXI-b exhibited characteristic absorption bands of the five-membered imide ring at 1780 and 1705 cm^{-1} (typical of the imide carbonyl asymmetric and symmetric stretching), 1660 cm^{-1} (C=O stretching of the xanthone carbonyl group), 1470 cm^{-1} (C=C stretching), 1370 cm^{-1} (C-N stretching), together with a strong absorption band at 1155 cm^{-1} (C-O stretching). $^1\text{H NMR}$ spectra for the poly(xanthone-imide), PXI-b, is shown in **Figure 3**. The spectrum showed characteristic resonance signals of aromatic protons in the region of 7.61–8.52 $\mu\text{g/g}$.

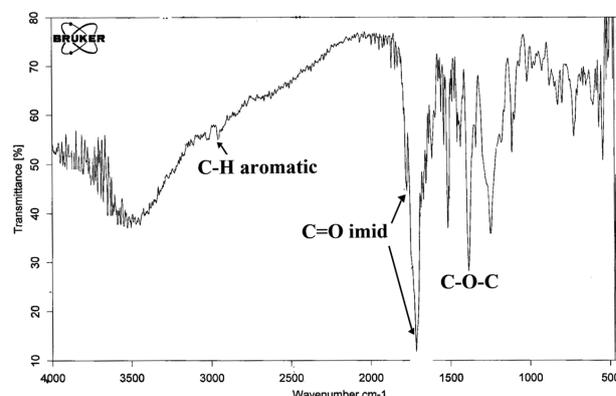


Figure 2: FT-IR spectrum of PXI-b
Slika 2: FT-IR spekter PXI-b

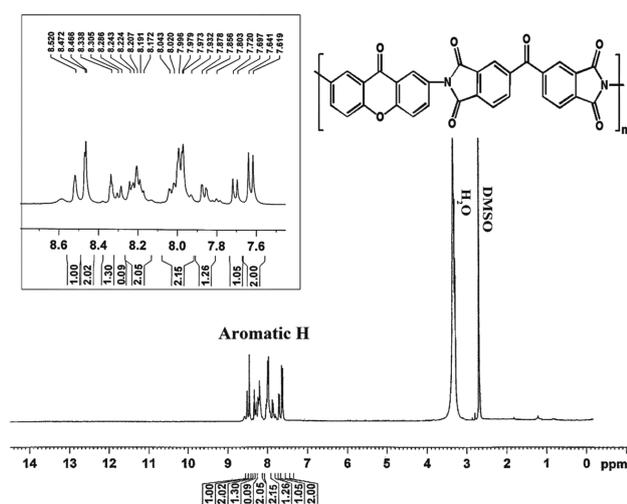


Figure 3: ^1H NMR spectrum of PXI-b
Slika 3: ^1H NMR spekter PXI-b

3.2 Solubility and viscosity

The solubility behavior of the poly(xanthone-imide)s depended on their chain-packing ability and intermolecular interactions, which were affected by the rigidity, symmetry and regularity of the molecular backbone. The solubility behavior of the PXIs was experienced in several organic solvents using a 5 % (w/v) concentration at room temperature, and the results are tabulated in **Table 1**. These poly(xanthone-imide)s had a higher solubility than the earlier reported polyxanthenes.²¹ The solubility of these polyimides varies depending on the dianhydride used. A comparison of the solubility values for PXIs shows that the presence of carbonyl and hexafluoroisopropylidene groups in the PXI-b and PXI-c enhances their solubility at room temperature. However, the solubility of these poly(xanthone-imide)s could be improved by attaching bulky trifluoromethyl ($-\text{CF}_3$) groups onto the polymer chain.

The enhancement in solubility is clearly attributed to the additional effect arising from the bulky $-\text{CF}_3$ unit, which increased the disorder in the chains, causing a less close chain packing, thus facilitating the distribution of solvent molecules among the macromolecule chains. These PXIs showed a good solubility in polar aprotic solvents such as DMF, DMAc, DMSO and NMP at room temperature, while the corresponding polyxanthone homopolymers have no solubility in such solvents at

Table 1: Solubility behavior and inherent viscosities of poly(xanthone-imide)s

Tabela 1: Topnost in nespremenljiva viskoznost poli(xantonimidov)

PXIs code	NMP	DMF	DMSO	DMAc	THF	Acetone	ETOH	Inherent viscosity (dL/g)
PXI-a	+	+	+	+	-	-	-	0.58
PXI-b	++	++	++	++	-	-	-	0.43
PXI-c	++	++	++	++	-	-	-	0.34

(DMAc: N,N-dimethyl acetamide; DMF: N,N-dimethyl formamide; NMP: N-methyl pyrrolidone; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran; ETOH: ethanol); ++: soluble at room temperature; +: soluble during heating at 60 °C; -: insoluble)

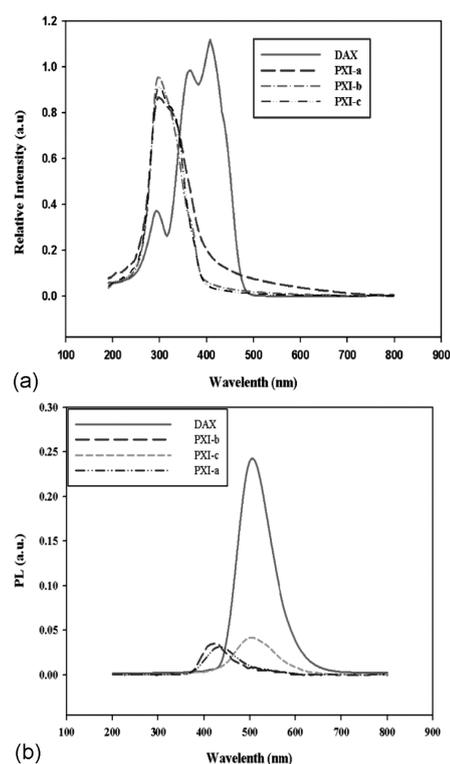


Figure 4: a) UV-vis absorption spectra and b) fluorescence emission spectra of the DAX and PXIs in NMP solution

Slika 4: a) UV absorpcijski spekter in b) emisijski spekter fluorescence DAX in PXI-jev v NMP raztopini

ambient temperature. This suggests that these polymers have potential applications in the areas such as film formation or casting process where the temperature is a determining factor.

3.3 Optical properties

Several classes of xanthone compounds were successfully used for protecting light-sensitive materials, controlling the harmful influence of light, especially of UV irradiation. The photophysical properties of the monomer and PXIs were examined with UV-visible and fluorescence spectroscopies in an NMP solution. The UV-vis absorption of the monomer and poly(xanthone-imide)s (**Figure 4a**) showed a strong absorption at 355 and 300–304 nm, respectively, in the NMP solutions due to the $\pi-\pi^*$ transition of the aromatic chromophores of a xanthone ring. In comparison with the parent xanthone,

the UV spectra of the corresponding poly(xanthone-imide)s were slightly blue shifted and broadened. The fluorescence emission spectra of the PXIs exhibited peak positions with the maxima at 413–510 nm (Figure 4b).

3.4 Thermal properties

The thermal behavior of the poly(xanthone-imide)s was evaluated with a thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) at a heating rate of 10 °C min⁻¹ and the results obtained from these thermograms are summarized in Table 2. DSC thermograms of the polyimides are shown in Figure 5. As indicated in Figure 5, the T_g values of these PXIs are in a range of 213–285 °C, while the reported values of T_g for the bare polyxanthenes were found to be higher than 370 °C.²¹ The results showed that the T_g values of these PXIs depend on the structure of the dianhydride component and they decrease with the increasing flexibility of the dianhydride structure.

Table 2: Characteristic thermal data of poly(xanthone-imide)s
Tabela 2: Podatki o toplotni značilnosti poli(ksanton-imidov)

Compound	T_g (°C)	T_5 (°C)	T_{10} (°C)	Char. yield (%)
PXI-a	285	415	460	60
PXI-b	218	380	400	61
PXI-c	213	370	394	46

T_g : glass-transition temperature; T_5 : temperature for a 5% weight loss; T_{10} : temperature for a 10% weight loss; Char. yield: weight of the polymer, kept at 700 °C

The polyimide derived from PMDA exhibits the highest T_g because of a rigid backbone, while the PXI-c obtained from 6-FDA showed the lowest T_g owing to the bulky CF₃ groups between the phthalimide units, which might be a result of reduced chain-to-chain charge-transfer interactions and poor chain packing of the bulky pendant -CF₃ groups. Indeed, the difference in T_g of the

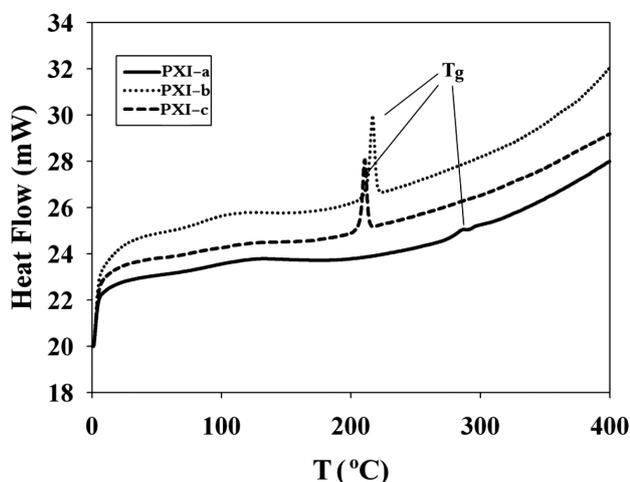


Figure 5: DSC thermograms of PXIs
Slika 5: DSC-krivulja za PXI-je

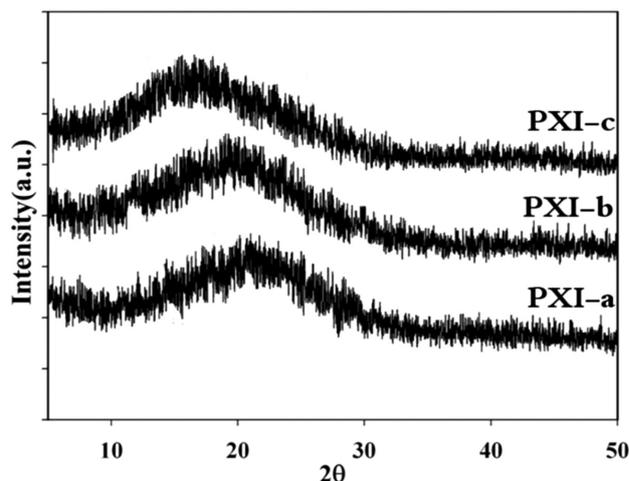


Figure 6: X-ray diffraction patterns of PXIs
Slika 6: Rentgenska difrakcija PXI-jev

PXIs can be attributed to the rigidity and close packing of the polymer chains. No melting endotherm or sign of a crystalline formation was observed in the DSC traces of the poly(xanthone-imide)s as confirmed by their WAXD patterns (Figure 6).

These observations disclose an amorphous nature of the polymers. The thermal stabilities of these poly(xanthone-imide)s were evaluated with TGA (Figure 7). The TGA data indicated a good thermal stability of the PXIs up to 460 °C with a weight loss of 10%. Also, the char yields of the poly(xanthone-imide)s at 600 °C were in a range of 46–67% implying that these polymers possess a good thermal stability. Summing up, it can be deduced that the PMDA-derived polyimide (PXI-a) has the highest thermal stability among those investigated, which can be related to the incorporation of rigid PMDA units. The introduction of hexafluoroisopropylidene units appears to reduce the packing density of molecular chains, which is strongly affected by the intermolecular interactions.

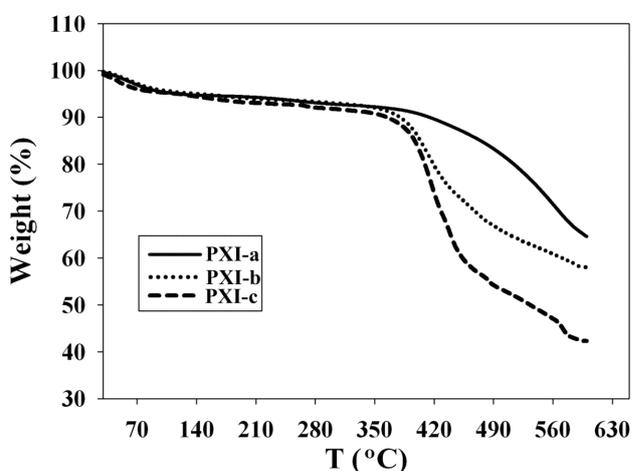


Figure 7: TGA thermograms of PXIs
Slika 7: TGA-krivulja PXI-jev

3.5 Antioxidant activity

Antioxidant polymers, both externally doped and chemically bounded, are extensively utilized in the field of polymeric materials showing antioxidant properties. In recent years, this research area has grown rapidly because antioxidant polymers have many industrial applications including materials science, biomedicine, pharmaceuticals, cosmetics and food packaging. Generally, chemically bounded polymeric antioxidants have unique advantages: they are non-volatile and do not penetrate into the skin and tissue. Consequently, the use of polymeric antioxidants, in which the antioxidant species are covalently bonded to the backbone of the polymer, especially in biocompatible materials, can be a key step toward a healthy life. The antioxidant activities of the parent xanthone (X) and PXIs were evaluated with a DPPH assay and the results are given in **Table 3**. The inhibition percentages determined with the DPPH assay for the monomeric diaminoxanthone was 27.07 %, whereas those of the PXIs were in a range of 47.80–61.30 %. It is evident that the polyxanthones exhibit a higher antioxidant activity than the xanthone itself. As illustrated in **Figure 8**, this behavior can be related to a more extended π -conjugation of the xanthone ring with imide nitrogen of poly(xanthone-imide).

Table 3: Antioxidant inhibition percentages of X and PXIs

Tabela 3: Protioksidativni odstotek inhibicije X in PXI-jev

Compound	Inhibition percentage
X	27.0
PXI-a	49.4
PXI-b	61.3
PXI-c	47.8

The PXI-b, obtained from BTDA, exhibited the highest antioxidant activity because of the presence of the carbonyl group between two phenyl rings, which increases the stability of radicals due to further conjugation. On the contrary, the PXI-c, obtained from 6-FDA, exhibited the lowest antioxidant activity because of the saturated carbon in the $C(CF_3)_2$ groups between the phthalimide units, which can effectively interrupt the conjugation. Thus, placing a xanthone unit into the polymer backbone is a simple way of preparing macromolecular systems with a high antioxidant power that may have the potential for use as biomaterials in biological media.

3.6 Water absorption

The water uptake affects the final application of these high-performance materials, especially in the sorption of heavy metals in water. Though the absorbed water reduces the physical properties such as the mechanical, electrical and dielectrical properties and T_g , it also provides for a better presentation in the other high-tech fields such as the membrane technology. The polymers dealt with in this study have two imide groups and one

xanthone moiety per repeating unit; the polar groups interact with water, which leads to partly hydrophilic materials. Two methods described in the literature²⁹ were used for the water-absorption measurement of the PXIs: at 25 °C for 24 h and at 100 °C for 30 min. As can be seen in **Table 4**, the PXI-b derived from BTDA showed a higher percentage of water absorption (up to 5.4 %) in comparison with the water absorption of the PXI-a and PXI-c based on PMDA and 6FDA (up to 5.0 and 4.8 %, respectively). This is probably due to the existence of the carbonyl group in the backbones of BTDA-based polymers.

Table 4: Water absorption of PXIs

Tabela 4: Absorpcija vode PXI-jev

Compound	Method 1(%)	Method 2(%)
PXI-a	4.7	5.0
PXI-b	5.1	5.4
PXI-c	4.4	4.8

3.7 Adsorption capability

The PXI-b (10 mg) was dissolved in 10 mL of an aqueous solution of heavy metals such as Co (II), Pb (II), Cd (II), Ni (II), Cu (II) and Cr (VI). The mixtures were agitated magnetically at reasonable min^{-1} for 3 d and the solids were separated with filtration. The concentration of metal ions in the filtrate was analyzed via atomic absorption spectroscopy. The quantity of the adsorbed metal ions was calculated with the following equation:

$$Q_t = (C_0 - C_A) \times V/w$$

where Q_t is the amount of metal ions adsorbed into the unit of the composites (mg g^{-1}), C_0 and C_A are the concentrations of metal ions in the initial solution and in the aqueous phase after the adsorption, respectively (mg mL^{-1}). V is the volume of the aqueous phase (mL) and w is the weight of the polymer (mg). The effectiveness of the metal-ion adsorption from the solution (% R) was calculated using the following equation:

$$R = (C_i - C_e) / C_i \times 100$$

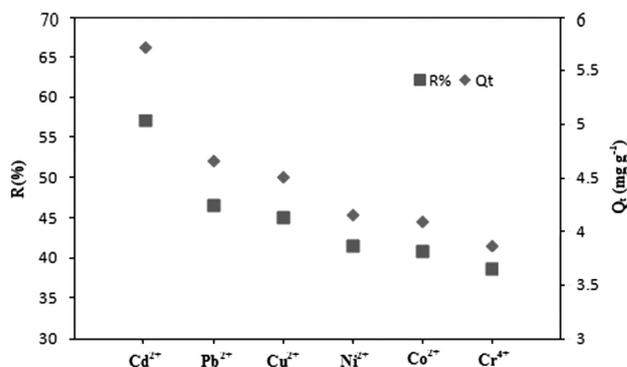


Figure 8: Sorption of transition-metal cations in water using PXIs

Slika 8: Sorpcija kationov prehodnih kovin v vodi z uporabo PXI-jev

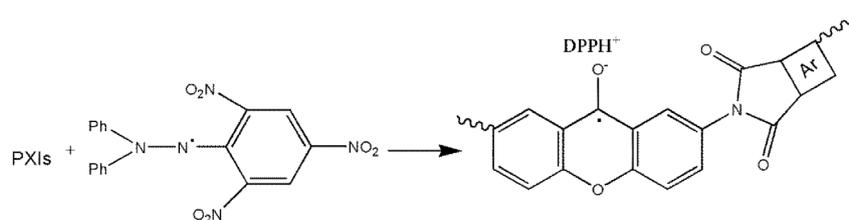
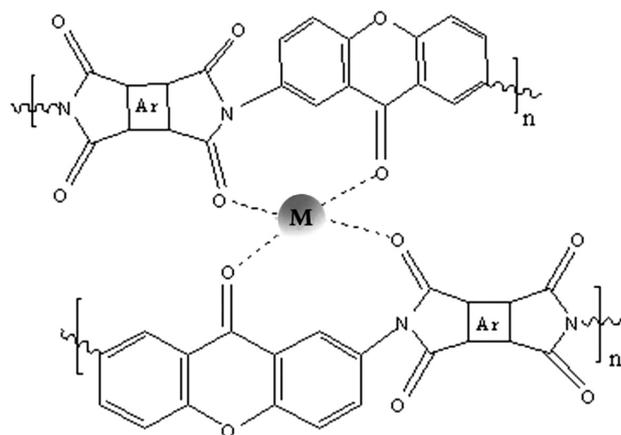


Figure 9: Proposed DPPH radical-scavenging mechanism

Slika 9: Predlagani radikalni splakovalni mehanizem DPPH

where C_i and C_e are the initial concentration and the concentration at the equilibrium of metal ions in the solution, respectively.

Figure 9 depicts the solid-liquid extraction results for the elimination of individual metal cations from the aqueous solution at 25 °C. As can be seen in **Figure 9**, both parameters, Q_i and $\%R$, increased in the order of Cd (II) > Pb (II) > Cu (II) > Ni (II) > Co (II) > Cr (VI), which is comparable with the order of their ionic radii. In **Figure 9**, the extraction for the smallest metal ion Cr (VI) is about 39 % and for the largest metal ion Pb (II), it increases up to 47 %, while the extraction for Cd (II) has the highest quantity; these results were compared with those of poly(azoxanthone-esters)³⁰ in **Table 5**. Therefore, it can be suggested that the carbonyl functional groups along the polymer chains provide a coordinating site to chelate with the metal ions (**Figure 10**).



M: Cr (VI), Co (II), Cu (II), Pb (II), Ni (II), Cd (II)

Figure 10: Chelation of PXIs with metal cations

Slika 10: Kelacija PXI-jev s kovinskimi kationi

Table 5: Heavy-metal sorption capability (%) of PXI-b in comparison with poly(azoxanthone-ester)

Tabela 5: Sposobnost sorpcije težkih kovin (%) PXI-jev v primerjavi s poli(azoksanton-estra)

Compound	Cd ²⁺	Pb ²⁺	Cu ²⁺	Ni ²⁺	Co ²⁺	Cr(VI)
PAXEO	59.7	48.8	45	44.2	43.6	40
PXI-b	57.3	47	45.2	42	41.1	39

4 CONCLUSION

A series of organosoluble poly(xanthone-imide)s with an antioxidant activity was prepared through a two-step chemical imidation of 2,7-diaminoxanthone with commercially available dianhydrides and they it was characterized using different spectroscopic techniques. These polyxanthones showed an amorphous nature with lower glass-transition temperatures (T_g) and a higher solubility than the previously reported polyxanthones. These polymers indicated inherent viscosities in a range of 0.34–0.58 dL/g, showing a moderate molecular weight and being soluble in polar aprotic solvents such as DMF, NMP, DMSO and DMAc at room temperature. The T_{10} values and high char yields for the poly(xanthone-imide)s indicate their good thermal stability. The introduction of a xanthone ring to the main chains of the polyimides imparts advantageous properties of the xanthone nucleus to the polyimides.

The UV-vis absorption spectra of the monomer and poly(xanthone-imide)s exhibited a strong absorption at

355 nm and 300–304 nm, respectively, and the fluorescence emission spectra of the PXIs exhibited peak positions with the maxima at 413–510 nm in the NMP solutions.

The antioxidant capacities of the PXIs were investigated. Good antioxidant activities were obtained for all the poly(xanthone-imide)s. Interestingly, the results showed that antioxidant activities were enhanced after an insertion of xanthone into the polymeric chain.

Also, the solid-liquid extractions were carried out in an aqueous solution and the results showed that the PXIs are effective for eliminating risky heavy metals such as Co (II), Pb (II), Cd (II), Ni (II), Cu (II) and Cr (VI) from wastewaters.

Summing up, an insertion of the xanthone structure into the polymer backbone provides for a high antioxidant activity of polyxanthone imides that may have a potential for application in pharmaceutical and food industries, and also in the solid-phase extraction of environmentally risky cations.

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