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Conference paper

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Synthesis and characterization of vinyl derivatives of naphthalene-2,7-diol as a photoluminescent dopant useful in optical materials

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Abstract: In this study synthesis and characterization of the new methacrylic derivatives of naphthalene-2,7-diol are presented. This reaction was performed in the three stages. In first stage 2,7-NAF was reacted with dimethyl sulfate in the NaOH solutions at 0 °C. Next, the obtained 2,7-NAF.Me was modified by epichlorohydrine leading to epoxide compound (2,7-NAF.Me.EP). Finally, the reaction of opening oxirane rings by methacrylic acid was carried out. The chemical structures of all derivatives were confirmed by ^{1}H and ^{13}C NMR. Next, copolymerization reaction with methyl methacrylate (MMA), styrene (St) or divinylbenzene (DVB) was carried out. New monomer (2,7-NAF.MePM) possesses only one double bond and it can be used as a dopant in optical materials technology. The studies of their thermal properties were investigated by means TG/DTG/QMS coupled method. The influence of photoluminescence dopant on thermal stability of the obtained copolymers was also discussed.

Keywords: copolymerization; naphthalene-2,7-diol; NMR; photoluminescence; POC-16; thermogravimetric analysis.

Introduction

Recently, dye-doped polymers got attention because of their low cost, light weight, flexibility and processsability into thin films and optical fibers for nonlinear and linear optical applications such as photonic devices (sensors, laser diodes, data recording, wavelength conversion, light amplification, optical computing four wave mixing and optical telecommunication) [1–7].

The most important advantage of dye-doped polymers is that their properties can be optimized for high mechanical, thermal and temporal stabilities. According to Lua et al. one of the aromatic group contained in organic dye benzyl dimethyl ketal (BDK) increases the photosensitivity to decrease the long term exposure during written gratings [8].

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Photoluminescent optical materials are used in different optical applications. According to Lee et al. photoluminescent dye-doped (Rhodamine B and Coumarin 6) nanofibers can be used for polymer-based nanodevices [9]. For optical telecommunication purposes difunctional dopants are especially useful as they can participate in polymerization typical for thermoplastics.

This paper presents synthesis of the new monomer and use it as photoluminescent dopant to produce polymers with good optical properties. Our previously research concerned synthesis and copolymerization of dimethacrylic derivatives of naphthalene-2,7-diol [10–13]. These monomers are characterized by good photoluminescent and thermal properties but they are tetrafunctional (possess two double bonds) and the obtained polymers are crosslinked. This phenomenon is undesirable in optical materials technology. For this reason, our current study are focused on the synthesis of the monomer having a good optical properties and is able to form linear polymers. Such compound is proposed now, it is mono methacrylic derivative of naphthalene-2,7-diol (2,7-NAF.MePM). The structure of the new monomer was confirmed by spectroscopic methods (^{1}H and ^{13}C-NMR). Next, the new monomer was added as photoluminescent dopant during the free radical polymerization of commercially available monomers (methyl methacrylate MMA, styrene St or divinylbenzene DVB). Copolymers were produced with different weight ratio (1 : 10 and 1 : 20) of St, MMA or DVB. In order to determine the effect of photoluminescent dopant, three homopolymers of St, MMA and DVB have been also received. Their thermal behaviors were investigated by TG/DTG/QMS coupled analysis method.

For the studies coupled thermal (TG, DSC) and spectroscopic (MS) methods were chosen. By using the methods it was possible to obtain complete simultaneously characterization of phenomena occurring during the temperature increase. Based on thermal analysis (TG) we get information about the temperature at which mass change occurs and about the quantity of this change. It is also possible to conclude about thermal stability of the analysed samples. The knowledge what we get from differential scanning calorimetry (DSC) concerns exo- and endothermic phenomenon arising during the analysis. Identification of gas evolved during the temperature increase by quadrupole mass spectrometer (QMS) allows to predict probable mechanism of polymers degradation and depolymerisation. These are the basics that allow to determine the usefulness of tested material in optical materials technology. The influence of dopant on thermal stability of the obtained copolymers was discussed. Additionally their absorption/emission spectra were measured.

Experimental

Studied materials and curing procedure

Chemicals

Naphthalene-2,7-diol, epichlorohydrin, methacrylic acid, styrene, methyl methacrylate, $(CH_3CO_2)_2Cr_3(OH)_2$, hydroquinone were from Fluka AG (Buchs Switzerland). Benzoyl peroxide (BPO) was purchased in Merck (Darmstadt, Germany) and used as an initiator. Propane-2-ol, sodium hydroxide and HCl were from POCH (Gliwice) Poland. All chemicals were used as received.

Synthesis of 2,7-NAF.Me

In a 500 cm^3 round bottomed four-necked flask equipped with a mechanical stirrer, a thermometer, a water condenser and dropping funnel, aqueous solution of NaOH (30 g NaOH + 300 mL H_2O) was placed together with 48 g of naphthanene-2,7-diol. Next, after cooling (0 °C) 28.5 mL of dimethyl sulfate was dropwise within 1 h. Stirring was continued for 2 h at room temperature. After the reaction, the resulting precipitate was filtered off and washed with distilled water. While, the filtrate was acidified by HCl solution ($1_{HCl} : 1_{H2O}$) and in this way about 40 g of a solid was obtained.

Finally, the obtained solid was dissolve in aqueous solution of NaOH (80 g NaOH + 400 g H_2O), and the filtrate was acidified by HCl solution (1 : 1). The resulting precipitate (24 g) was filtered off and dried. The obtained 2,7-NAF.Me was purified on chromatographic column (chloroform). The chemical structure of 2,7-NAF.Me was confirmed by NMR spectroscopy (Figs. 1 and 2).

Synthesis of 2,7-NAF.Me.EP

In a 100 cm^3 round bottomed three-necked flask equipped with a mechanical stirrer, a thermometer and dropping funnel 6.45 g of 2,7-NAF.Me, 36 mL of epichlorohydrine (EP) and 28 mL of propan-2-ol were added and the mixture was heated at 72 °C. Next, aqueous solution of NaOH (2.23 g NaOH + 15 mL H_2O) was added dropwise for 15 min (dropping funnel). The reaction continued for 10 min at 72 °C. After the reaction, the content of the flask was transferred to a separator funnel where the aqueous layer was separated. Next, the organic layer was distilled off by rotary evaporation under reduced pressure. At the end, the content of the flask was dissolve in 30 mL of toluene and by azeotropic distillation excess of water was removed. After distilling off toluene the 9.5 g of 2,7-NAF.Me.EP was obtained (Epoxide number = 0.39; Theoretical epoxide number = 0.43). The chemical structure of 2,7-NAF.Me.EP was confirmed by NMR spectroscopy (Figs. 1 and 2).

Synthesis of 2,7-NAF.Me.PM

In a 100 cm^3 round bottomed flask 9 g of 2,7-NAF.Me.EP, 3.02 mL of methacrylic acid, 0.14 of $(CH_3CO_2)_7Cr_3(OH)_2$ (a catalyst) and 0.0015 g of hydroquinone (polymerization inhibitor) were added. The reaction was carried out by rotary evaporation at 75 °C for 2 h and next at 80 °C for 4.5 h. At the end, the content of the flask was dissolve at 25 mL of acetone, filtered off and next the product was distilled off by rotary evaporation under reduced pressure (11.8 g).

The chemical structures of all newly obtained compound were confirmed by NMR spectroscopy (Figs. 1 and 2).

Copolymerization

The compositions consisting of 2,7-NAF.MePM and one of the vinyl monomers: styrene (St), methyl methacrylate (MMA) or divinylbenzene (DVB) as well as an initiator (dibenzoyl peroxide, BPO) were obtained. In their preparation, constant concentration of the initiator (1 %) and two different mass ratios of 2,7-NAF.MePM to vinyl monomers (1 : 10 and 1 : 20) were applied (Table 1) [10]. The mixture containing: 2,7-NAF.MePM, one of the vinyl monomer and initiator was placed together in to a glass form and heated in water bath for 12 h (at 60 °C), next copolymer was transferred to a heater chamber and heated at 80 °C for 4 h.

Methods

The ^1H NMR spectra were recorded on a Brucker 300 MSL instrument (Brucker, Germany) operating at the 1H resonance frequency of 300 MHz. Chemical shifts were referred to deuterated chloroform ($CDCl_3$) serving as an internal standard. The ^{13}C NMR spectrum of the newly obtained compound in $CDCl_3$ or DMSO was made using the same apparatus.

Thermal analysis was carried out on a STA 449 Jupiter F1, Netzsch (Selb, Germany) under the following operational conditions: heating rate 10 °C min^{-1}, a dynamic atmosphere of helium (50 mL min^{-1}) in the temperature range of 25–600 °C, sample mass of about 5 mg, sensor thermocouple type S TG-DSC. As a reference, empty Al crucible was used. The identification of gas composition coming out during depolymerization and decomposition process were detected and analyzed by QMS 403C Aëolos (Germany) coupling on-line to STA instrument. The mass spectrometer was connected on-line to STA instrument by quartz capillary heated to

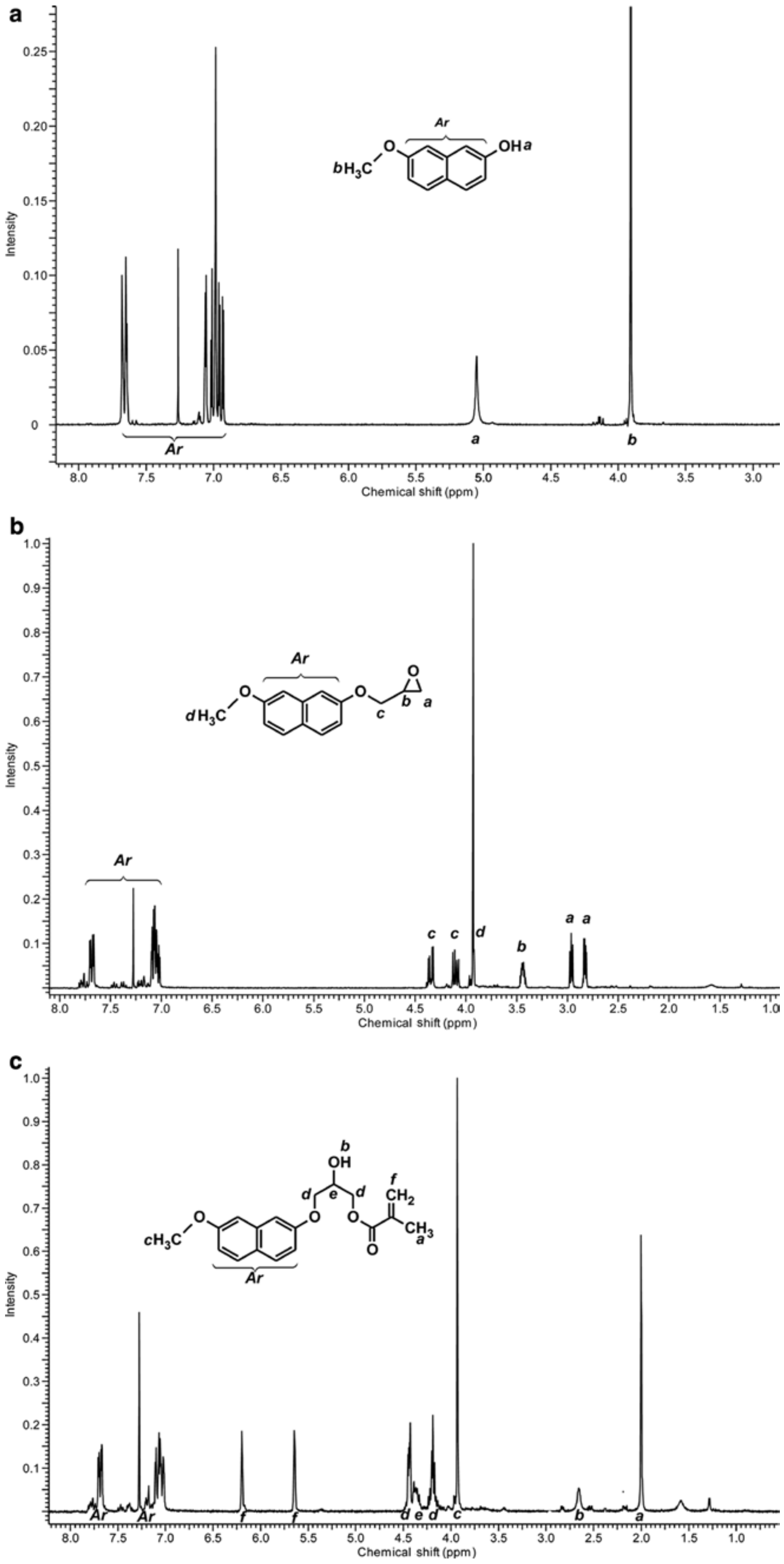

Fig. 1: ^{1}H NMR for 2,7-NAF.Me (a), 2,7-NAF.MeEP (b), 2,7-NAF.MePM (c).

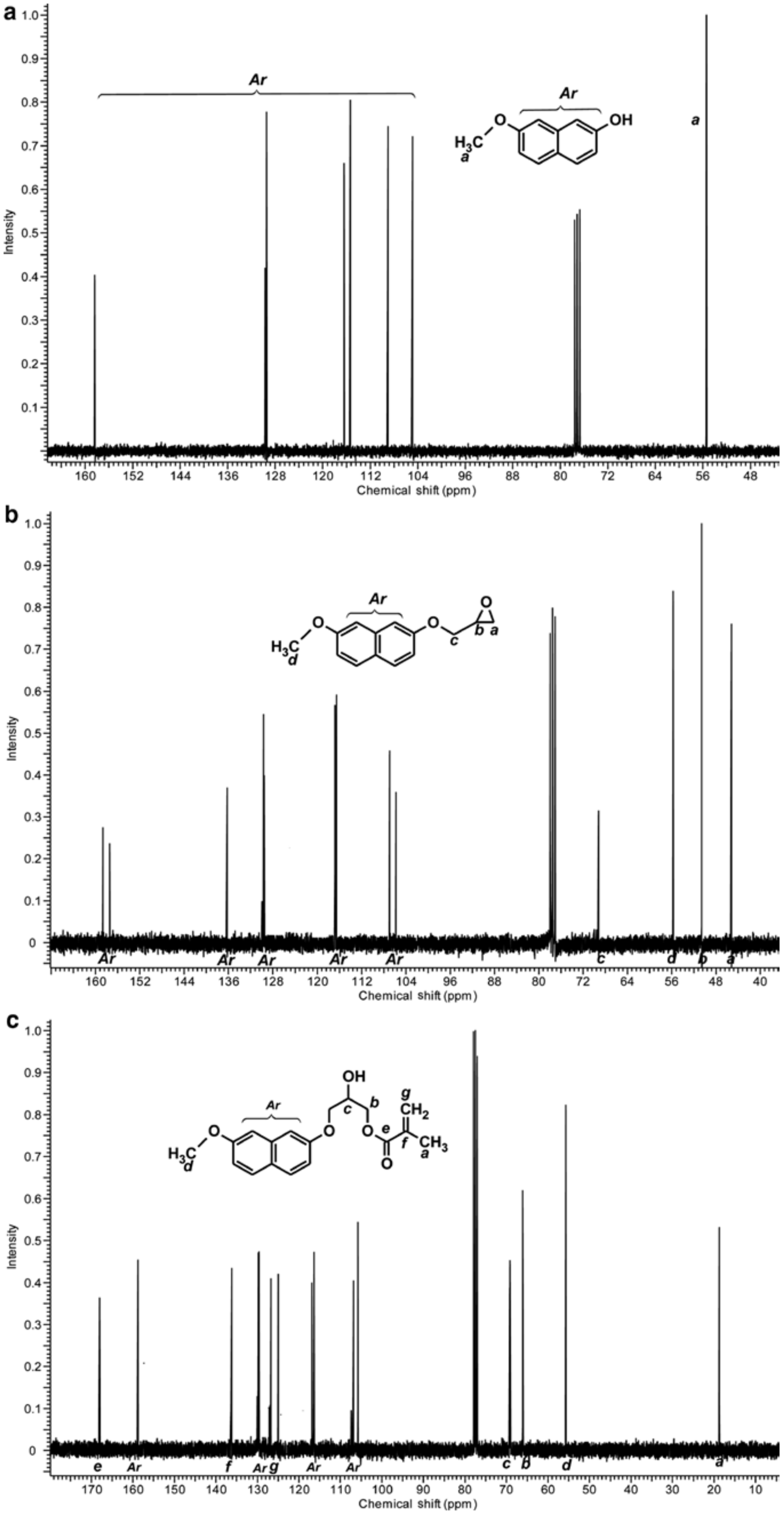

Fig. 2: ^{13}C NMR for 2,7-NAF.Me (a), 2,7-NAF.MeEP (b), 2,7-NAF.MePM (c).

Table 1: Chemical compositions of all tested samples.

Sample number	Copolymer					(g)
		2,7-NAF.Me.DM	St	MMA	DVB	BPO
1	St-HOMO	–	2	–	–	0.020
2	2,7-NAF.Me.PM-St(1 : 10)	0.2	2	–	–	0.022
3	2,7-NAF.Me. PM-St(1 : 20)	0.1	2	–	–	0.021
4	MMA-HOMO	–	–	2	–	0.020
5	2,7-NAF.Me.PM-MMA(1 : 10)	0.2	–	2	–	0.022
6	2,7-NAF.Me.PM-MMA(1 : 20)	0.1	–	2	–	0.021
7	DVB-HOMO	–	–	–	2	0.020
8	2,7-NAF.Me.PM-DVB(1 : 10)	0.2	–	–	2	0.022
9	2,7-NAF.Me.PM-DVB(1 : 20)	0.1	–	–	2	0.021

300 °C. The QMS was operated with an electron impact ionizer with energy 70 eV. The measurements performed in scan mode for m/z, where m is the mass of molecule and z is a charge of the molecule in electron charge units in the range from 10 to 100 amu allowed to identify all possible volatile particles produced during the decomposition.

Spectral characteristics were carried out on a Metash V-5600 spectrophotometer in the 320–390 nm spectral range, wavelength accuracy – 1 nm. The luminescence measurement ware made using the spectrophotometer fiber OFS2000 Company Ocean Optics.

Results and discussion

NMR spectroscopy

^{1}H NMR

Figure 1a–c presents the ^{1}H-NMR spectra of the 2,7-NAF.Me, 2,7-NAF.Me.EP and 2,7-NAF.Me.PM. In the ^{1}H-NMR spectrum of the 2,7-NAF.Me protons in the methyl group ($-CH_3$) connected with oxygen give shape band at $\delta = 3.95$, whereas protons from the hydroxyl groups (–OH) at $\delta = 5.05$ ppm. The bands at $\delta = 6.93$–6.98, 7.26, 7.64–7.68 ppm correspond to the naphthalene ring.

In the ^{1}H-NMR spectrum of 2,7-NAF.Me.EP protons in the methylene group ($-CH_2$) connected with an oxygen give shape bands at $\delta = 4.11$–4.13 and $\delta = 4.32$–4.39 ppm, whereas protons from the terminal methylene group ($-CH_2$) at $\delta = 2.81$–2.84, $\delta = 2.95$–2.98. Protons in the methyl group ($-CH_3$) give shape band at $\delta = 3.92$. The bands at $\delta = 7.05$–7.09, 7.28, 7.67–7.70 correspond to the naphthalene ring.

In the ^{1}H-NMR spectrum of 2,7-NAF.Me.PM protons of methylene group ($-CH_2$) give signals at $\delta = 4.17$–4.20 and $\delta = 4.43$–4.45, proton in hydroxyl group (–OH) at $\delta = 2.65$ and protons near the double bond ($-CH{=}CH_2$) give signals at $\delta = 5.64$ and $\delta = 6.20$ ppm. Protons in the methyl group connected with oxygen ($-O-CH_3$) give shape band at $\delta = 3.93$, terminal methyl group give signals at 2.00 ppm. The bands at $\delta = 7.02$–7.10, 7.18, 7.28, 7.67–7.71 correspond to the naphthalene ring.

^{13}C NMR

Figure 2a–c presents the ^{13}C NMR spectra of the 2,7-NAF.Me, 2,7-NAF.Me.EP and 2,7-NAF.Me.PM. All spectra show a set of three peaks at 76.7, 77.1, and 77.6 ppm come from the solvent, chloroform, and which can be neglected in spectrum interpretation. In the spectrum of 2,7-NAF.Me, the methyl group carbon ($-O-CH_3$) gives signal at 55.41 ppm. The signals at 104.86, 108.97, 115.33, 116.40, 129.42 and 158.37 ppm come from carbon atoms of the naphthalene ring.

In the spectrum of 2,7-NAF.Me.EP the terminal methylene group carbon (–CH_2) gives signal at 45.22 ppm, in methylene group (–O–CH_2–) connected with oxygen at 69.19 ppm, the carbon of epoxide group (–CH–) at 50.59 ppm and the methyl group carbon (–CH_3) gives signal at 55.69 ppm. The signals at 105.77, 106.90, 116.52, 129.71, 136.23, 157.50 and 158.70 ppm come from carbon atoms of the naphthalene ring.

In the spectrum of 2,7-NAF.Me.PM the terminal carbon atom of the double bond absorbs at 126.74 ppm and the more highly substituted one at 136.22 ppm. Carbon of the terminal methyl group absorbs at 18.76 ppm and connected with oxygen (–O–CH_3) at 55.69 ppm. The signal for the carbonyl group of ester appears at 167.97 ppm. The carbon of the methylene group absorbs at 66.11 ppm. The most highly substituted carbon atom (69.11 ppm) is bonded to the oxygen atom in hydroxyl group (–OH). The signals at 105.76, 106.88, 116.85, 129.59, and 158.70 ppm come from carbon atoms of the naphthalene ring.

Thermal and spectroscopy analysis

One of the most important information is the mass loss at the temperature at which optical fibers are drawn. Typical materials used to manufacture optical fibers are PMMA and PS. In the Laboratory of Optical Fibers Technology UMCS, the temperature at which from these materials polymer optical fibers are drawn is approximately 220 °C. In the future we are planning to use studied materials in POF and in mPOF (microstructured polymer optical fiber) technology and make a UV sensor therefore in the article the phenomena occurring till this temperature will be discussed. The observed mass loss to mentioned temperature will cause deterioration of the properties of optical fibers and may result in the inability to draw the fiber. Therefore, it is important that before proceeding to the studies, all materials have to be cleaned.

All tested materials were subjected to a thermoanalytical and spectroscopic analysis (Figs. 3–8). All the most important temperature parameters for optical materials technology are collected in the Table 2. Based

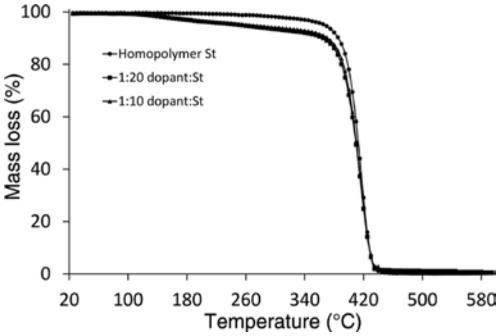

Fig. 3: TG curves of styrene samples.

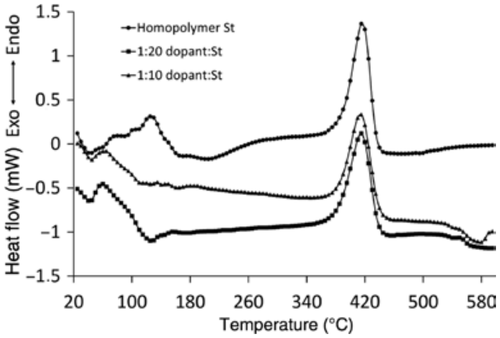

Fig. 4: DSC curves of styrene samples.

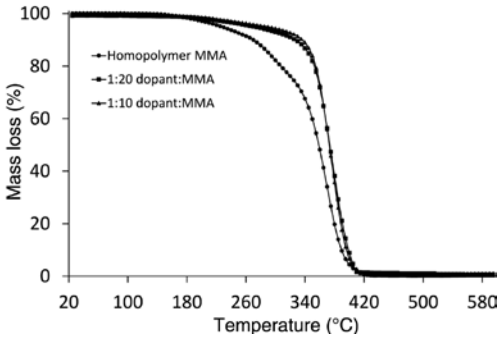

Fig. 5: TG curves of methyl methacrylate samples.

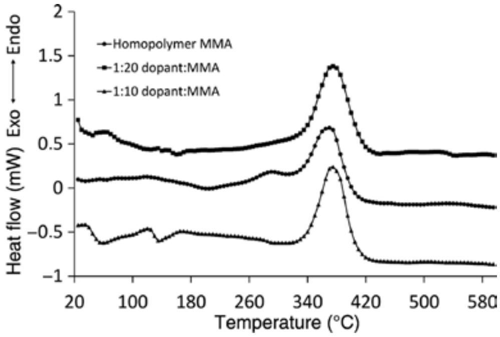

Fig. 6: DSC curves of methyl methacrylate samples.

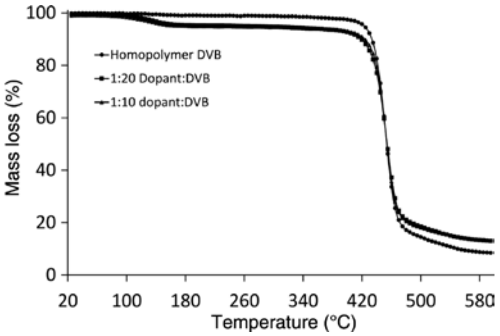

Fig. 7: TG curves of divinylbenzene samples.

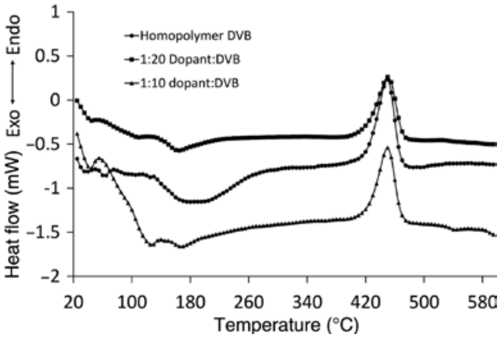

Fig. 8: DSC curves of divinylbenzene samples.

Table 2: Thermal stabilities of all samples.

	Sample no. 1	Sample no. 2	Sample no. 3	Sample no. 4	Sample no. 5	Sample no. 6	Sample no. 7	Sample no. 8	Sample no. 9
Mass loss at 220 °C/wt.%	0.8	4	4.2	4.3	2.1	2.6	1	5.2	4.8
DTG max/°C	417	415	416	369	376	377	453	454	453
Proper decomposition/°C	344	334	331	150	173	189	388	380	383
Mass loss at proper decomposition temperature/wt.%	3.2	6.2	7.5	0.4	0.9	1.6	2.2	6.5	6.5

on obtained data it can be seen that the most stable HOMO-polymer (polymer obtained from only one type of monomer) is PS (St-HOMO) (0.8 wt.% at 220 °C), while for the MMA-HOMO at the same temperature 4.2 wt.% mass loss is observed. DVB-HOMO is a crosslinking polymer and because of that, it cannot be used as optical material (due to increase scattering). It was added in the context of comparison. As it is a crosslinking polymer its thermal properties can be much better than for the linear polymers (mass loss 1 wt.% at 220 °C). The addition of photoluminescence dopant can lead to disturbances in the polymerization process, what can be observed for St and DVB (sample no. 2, 3 and 8, 9), where 5-fold increase in mass loss at 220 °C is observed. In the case of MMA copolymers, an improvement in thermal properties can be seen (sample no. 5 and 6). Based on DTG data it can be concluded that the maximum decomposition temperature in the case of samples containing DVB is the highest (which is related to the nature of the polymer – crosslinked polymer), and is about 453 °C. For St samples, its value is about 416 °C, and for MMA 376 °C. The introduction of photoluminescence dopant does not cause major changes in this parameter. Temperature of proper decomposition is the moment in which continuous mass loss is recorded. In the case of samples based on DVB discussed temperature varies in the range of 380–388 °C (samples no. 7–9), whereas the mass loss of the DVB-HOMO is the smallest and is 2.2 wt.% and 6.5 wt.% for the copolymers. In the case of St samples (samples no. 1–3), the onset temperature of decomposition ranges between 331 and 344 °C and it can be seen that a 10 wt.% dopants addition causes a mass loss of 7.5 wt.%, and 5 wt.% of dopant causes a mass loss of 6.2 wt.%. Proper decomposition temperature for MMA samples (samples no. 4–6) is much lower and varies in the range of 150–189 °C, while the mass loss is 0.4–1.6 wt.%. Using the data obtained based on mass spectroscopy (Figs. 9–13), the analysis of volved gasses, and thus conclusions what is the reason for the mass loss till 220 °C for all studied materials have been made. The mass loss registered for samples based on St (Fig. 3) is associated with the appearance (from 75 °C) of ion m:28 (Fig. 9). Most likely, it is related to the release of vinyl groups. Looking at the results obtained from DSC (Fig. 4) in this temperature range numerous endothermic effects can be observed, which confirms the release of these groups. It should be taken into account that at the same temperatures the thermal cure of the samples may occur. A similar situation is observed for DVB samples. Looking at the TG data (Fig. 7) it can be observed that the DVB-HOMO is thermally stable up to a proper decomposition temperature. While for copolymers at a temperature of about 100 °C the mass loss was observed. Based on MS data (Fig. 13) the presence of ion m: 28, which correspond to the vinyl groups, can be seen. In addition, in this case,

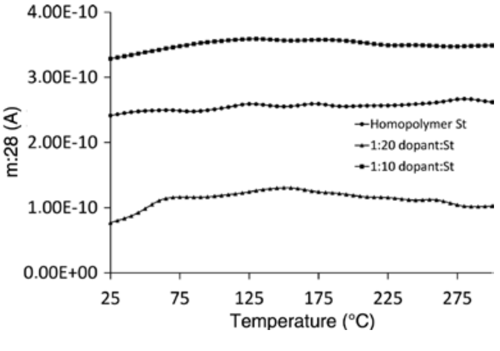

Fig. 9: Mass spectroscopy for Styrene m : 28/A.

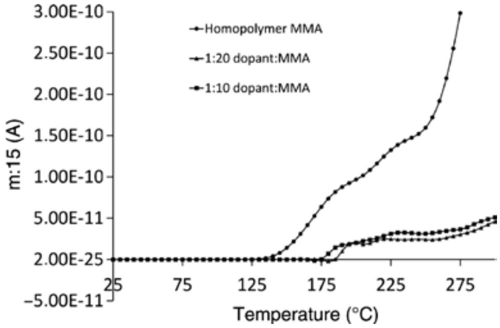

Fig. 10: Mass spectroscopy for MMA m : 15/A.

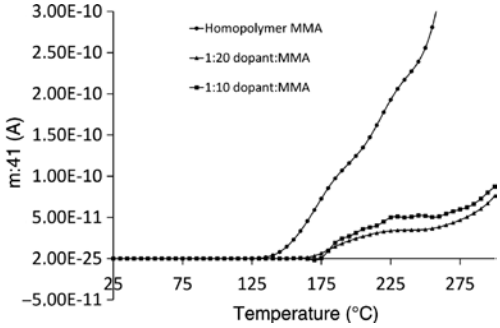

Fig. 11: Mass spectroscopy for MMA m : 41/A.

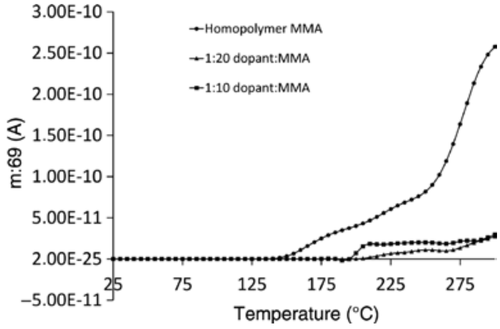

Fig. 12: Mass spectroscopy for MMA m : 69/A.

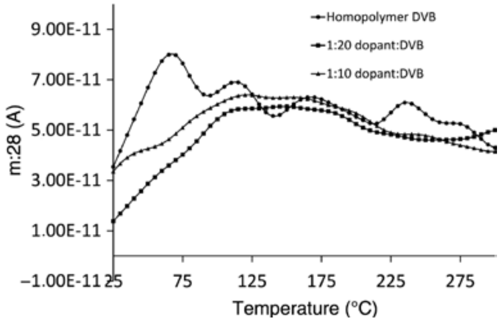

Fig. 13: Mass spectroscopy for DVB m : 28/A.

looking at the DSC graphs (Fig. 8), we can observe probably overlapping endothermic effects – evidence of bonds cracking and probable thermal hardening of the polymer – exothermic effects. Thermal data collected for MMA samples (Fig. 5) shows that at the temperature of about 125 °C mass loss is observed. Based on the MS analysis (Figs. 10–12) the presence of three ions: m : 15 most likely responsible for the presence of methyl groups, m : 41 is form by CH_2=$CHCH_2$ group which is typical for methacrylate derivatives and m : 69 which corresponds to $CH_2C(CH_3)O$ group also typical for methacrylate derivatives, was revealed.

Spectral analysis

The graphs in Figs. 14 and 15 show the absorption spectra measured in terms of 320–500 nm. The maximum absorption is observed for 340–345 nm spectral range therefore these materials may be used in UVA (is an electromagnetic radiation with a wavelength from 315–400 nm) optical sensors. Figures 16 and 17

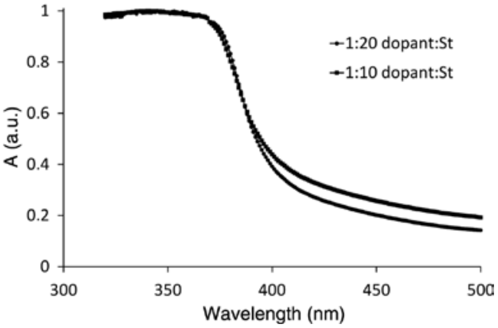

Fig. 14: Absorption spectra for PS compositions.

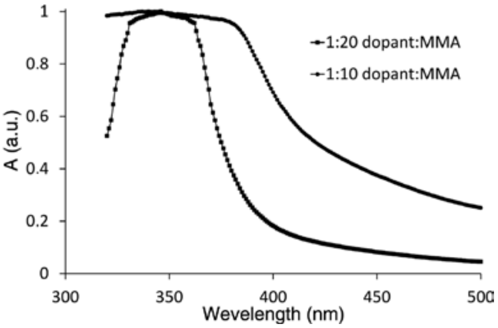

Fig. 15: Absorption spectra for MMA compositions.

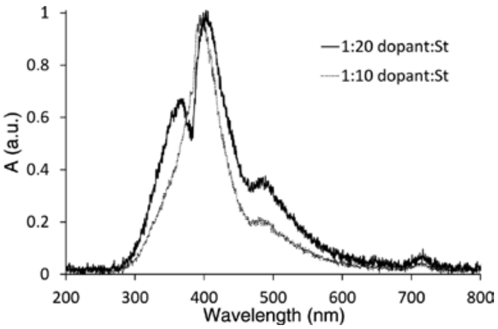

Fig. 16: Luminescent spectra for PS compositions.

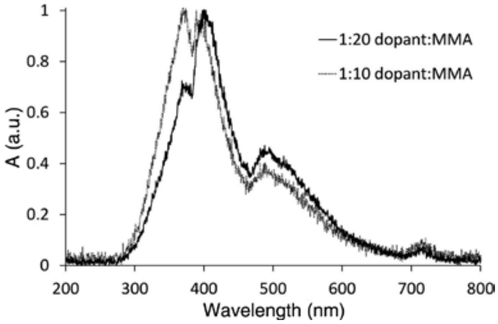

Fig. 17: Luminescent spectra for MMA compositions.

show luminescence spectrum measured in the UV-VIS 190 nm–880 nm. In measurements special prepared cylindrical samples (13 mm external diameter, 18 mm length) with optically polished both front faces were used. After excitation by UV radiation, the polymer emits blue-violet radiation (maximum at about 400 and 490 nm), which corresponds with the range of wavelength for blue light (450–500 nm) and violet (380–430 nm). Based on the previous received photoluminescence derivatives of naphthalene-2,7-diol [10] our new obtained materials shows some differences in the emission of radiation (where maximum was found at about 510 nm). This changes are probably results from chemical structure of 2,7-NAF.MePM (mono derivatives of naphthalene-2,7-diol).

Conclusions

Synthesis of the new photoluminescent dopant, derivative of naphthalene-2,7-diol was proposed. This monomer was obtained in three step reaction and the structure of the all obtained compounds were confirmed by spectroscopic methods. During the copolymerization reaction nine new copolymers were obtained. The addition of photoluminescent cause the polymerization disturbance what can be observe for St and DVB samples by comparing their thermal stability to HOMO-polymers. In case of MMA an improvement was observed. The maximum decomposition temperatures do not change by adding the dopant and this is observed for all measured samples. Based on MS spectra it was concluded that the mass loss for St and DVB samples is related to the appearance of ion m : 28 which corresponds to the mass of vinyl groups. The mass loss observed for MMA compositions is related to the evaporation of three ions: m : 15 most likely responsible for the presence of methyl groups, m : 41 is form by $CH_2{=}CHCH_2$ group and m : 69 which corresponds to $CH_2C(CH_3)O$ group which are typical for methacrylate derivatives. Based on spectral analysis it was found that St and MMA composition may be used in UVA optical sensors.

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