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# Photo- and thermally initiated polymerization of methacrylate monomer derivative of bis(4-hydroxyphenyl)sulfide with *N*-vinyl-2-pyrrolidone

**Beata Podkościelna**

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**Abstract** The results of the studies concerning photo- and thermally initiated copolymerization of bis[4(2-hydroxy-3-methacryloyloxypropoxy)phenyl]sulfide (BES-DM) with *N*-vinyl-2-pyrrolidone (NVP) and thermo-mechanical properties of resulting compositions are presented. BES-DM was obtained in the two-step reaction. In the first step, the epoxy resin was synthesized. It was obtained in the reaction of bis(4-hydroxyphenyl)sulfide with 2-(chloromethyl)oxirane. In the second step, esterification of the obtained diglycidyl ether was carried out with the use of methacrylic acid. New copolymers with different degrees of crosslinking were obtained. The study describes the effect of crosslinking degree and the method of polymerization initiation on the properties of the new compositions. Density, viscosity, glass temperature, Young's modulus, hardness, tensile strength were determined before and after curing for the compositions of BES-DM and NVP. Moreover, the dynamic-mechanical and thermal properties for the chosen samples of copolymers were studied.

**Keywords** Photo-polymerization · Thermal properties · Calorimetry · Methacrylate derivatives · Bis(4-hydroxyphenyl)sulfide

## Introduction

Polymerization of (meth)acrylate monomers and oligomers has merited special attention as an easy method of preparing products for various applications. Their polymerization runs rapidly in the presence of peroxide or azonitrile initiators. In this way, polymerization of multifunctional monomers is carried out and leads to the formation of highly cross-linked products [1–5]. When the reaction is initiated by UV light or by electron beam, its course is not so rapid and the properties of the final product can be easily controlled [6]. In recent years, photo-initiated polymerization developed significantly with a high rate of growth in many important areas such as dental filler composites, coatings, inks, optical elements, photo-resists, printing plate, etc. [7–14]. However, monomeric acrylates and methacrylates are relatively volatile, toxic and have an unpleasant odor [15]. Oligomeric acrylates are considerably less volatile but they exhibit high viscosities. Obviously, solid monomers have lower toxicity. Oligomers containing highly reactive (meth)acrylate groups at both molecule ends are often used in industry. They are successfully applied not only as casts but also as thermally and photochemically cured paints and lacquers, resistant to corrosion and protective coating in electrotechnique and optical communication branch.

The earlier studies focused mainly on the synthesis of new monomers (derivatives of aromatic methacrylates) and their copolymerization in the form of polymeric microspheres for chromatography [16–20]. Owing to the fact that methacrylate derivatives are widely used as monomers for photo-polymerization, it was tried to use the new compounds for the synthesis of photo-initiated composition.

This study presents photo- and thermally polymerizations of bis[4(2-hydroxy-3-methacryloyloxypropoxy)phenyl]sulfide (BES-DM). This compound is solid at a room temperature so in its polymerization, the reactive diluent *N*-vinyl-2-pyrrolidone (NVP) (which is also a comonomer) has been applied. 2,2-Dimethoxy-2-phenyl-acetophenone

B. Podkościelna (✉)
Faculty of Chemistry, MCS University,
pl. M. Curie-Skłodowskiej 5, 20-031 Lublin, Poland
e-mail: beatapod@poczta.umcs.lublin.pl

(Irgacure 651, photo-initiator) and α,α′-azoisobisbutyronitrile (AIBN) were used as the initiators. In addition, the study aims to compare the thermal and mechanical properties of the obtained compositions.

## Experimental

### Materials

*N*-vinyl-2-pyrrolidone, 2,2-dimethoxy-2-phenyl-acetophenone (Irgacure 651) α,α′-azoisobisbutyronitrile (AIBN) were purchased at Fluka AG (Buchs Switzerland).

Bis[4(2-hydroxy-3-methacryloyloxypropoxy)phenyl]sulfide was synthesized by esterification of diepoxide derivative of bis(4-hydroxyphenyl)sulfide. The esterification was conducted with methacrylic acid in the presence of triethylbenzylammonium chloride (TEBAC) as a catalyst at an elevated temperature. The diepoxide derivative was obtained in the reaction of bis(4-hydroxyphenyl)sulfide and 2-(chloromethyl)oxirane in the two-phase systems consisting of water and an organic phase. The detailed information about synthesis conditions of the studied methacrylate derivative and its epoxide precursor was presented in the previous work [17].

### Characterization

IR spectra were determined on a Perkin-Elmer 1700 FTIR spectrometer using KBr pallets. Differential scanning calorimetry (DSC) thermograms were obtained with the use of a DSC Netzsch 204 calorimeter (Netzsch, Günzbung, Germany). All DSC measurements were carried out in aluminum pans with a pierced lid with the sample weight ~5–10 mg under nitrogen atmosphere (30 mL/min). Dynamic scans were performed at a heating rate of 10 K/min in the temperature range 20–450 °C. Curing characteristics, such as temperature of the peak maximum and final cure temperature were also determined.

Thermogravimetric analysis (TGA) was performed on a MOM 3427 derivatograph (Paulik, Paulik and Erdey, Budapest, Hungary) at a heating rate of 10 °C/min in the air, in the temperature range 20–1000 °C with the sample weight of 100 mg. The loss weight temperature ($T_{10\%}$,), the decomposition temperatures ($T_1$, $T_2$, $T_{\max}$) and final decomposition temperature ($T_f$) were determined.

Dynamic mechanical measurements were performed using the dynamic mechanical analyzer DMA Q 800 (TA Instruments, USA), provided with a dual cantilever device with a span length of 35 mm. Runs at 10 Hz were carried out at a constant heating rate of 4 °C/min over the temperature range 20–220 °C. The size of the samples was 35 × 12 × 4 mm. Viscoelastic properties of the crosslinked material were estimated on the basis of the changes of storage modulus, mechanical loss as well as based on the changes of tan$\delta$ at constant frequency depending on temperature.

Mechanical properties were determined extensively detail using a Zwick Roell testing machine (model Z010, Germany). The specimen dimensions were 120 × 10 × 4 (±0.2) mm. Measurements were conducted at a room temperature with a crosshead speed of 2 mm/min. Three specimens were tested for each copolymer and a mean value was taken.

Viscosities of the monomers were measured at different temperatures by means of a rotating spindle rheometer (Brookfield, model DV-III) using appropriate spindles and standard solutions (Table 1).

Hardness was determined by a Shore apparatus.

### Preparation of compositions

The compositions consisting of BES-DM, NVP and an initiator (Irgacure 651 or α,α′-azoisobisbutyronitrile) were prepared. The compositions of the following weight ratio of BES-DM to NVP were prepared: 0.5:1; 1:1; 1.5:1; 2:1; 3:1. The constant concentration of initiator was applied in their preparation.

Each composition was placed into a form to fill it. The form consisted of two glass plates, each of them of 3 mm in diameter and a distance underlay of 4 mm. The glass plates were covered with a thin layer of anti-adhesive grease. After the composition was placed, the form was screwed up and left to get deaerated in the desiccator chamber. After cooling down to room temperature, the compositions containing Irgacure 651 were placed inside the irradiation chamber where they were exposed to UV light with two mercury lamps of 500 W each. It was found that the most suitable time of radiation was 30 min and such a time was observed during the polymerization of each kind of composition. Forms with the compositions containing α,α′-azoisobisbutyronitrile were placed into a heating chamber for 5 h at the temperature gradient: 50–100 °C.

To study the mechanical properties of the cured compositions, the special stripes were prepared. Their dimensions were as follows: 120 × 10 × 4 mm$^3$.

**Table 1** Properties of the liquid compositions

| Ratio of monomers BES-DM:NVP | Viscosity at 25 °C/mPas | Refraction index $N_D^{20}$ | Density/ g/cm$^3$ |
|---|---|---|---|
| 0.5:1 | 11.5 | 1.5339 | 1.0995 |
| 1:1 | 24 | 1.5380 | 1.1298 |
| 1.5:1 | 114 | 1.5487 | 1.1405 |
| 2:1 | 262 | 1.5525 | 1.1516 |
| 3:1 | 1163 | 1.5571 | 1.1527 |

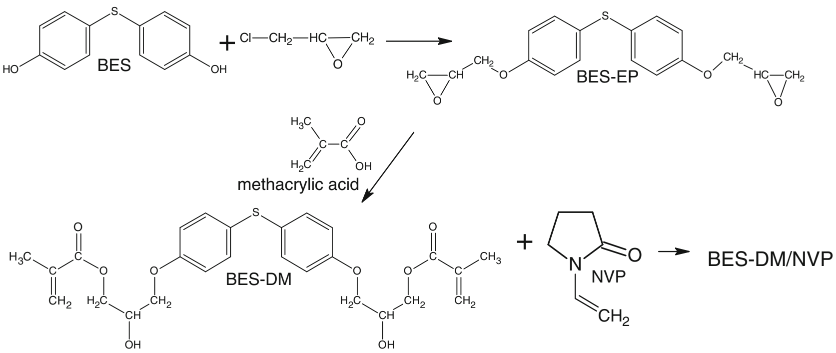

**Fig. 1** Scheme of copolymerization

## Results and discussion

Figure 1 presents the scheme of the synthesis of bis[4(2-hydroxy-3-methacryloyloxypropoxy)phenyl]sulfide (BES-DM) and its copolymerization with *N*-vinyl-2-pyrrolidone. BES-DM is a new aromatic tetrafunctional methacrylate monomer which in copolymerization with two functional NVP should give highly cross-linked copolymers. The compositions BES-DM/NVP reacted with the two polymerization initiators Irgacure 651 and α,α′-azoizobutyronitryl (AIBN). Only in the case when the initiator Irgacure 651 was applied, the polymerization product (in any ratio of monomers) was obtained. Cracking of the copolymers was observed while using the initiator AIBN (in case of which radicals are generated under the influence of temperature). Good products were obtained when heating was very slow, starting at 50 °C. The next increase by 10 °C should occur after 1 h. The final polymerization temperature was 100 °C.

Mechanical properties were obtained significantly better using the initiator Irgacure 651. In addition, the time of polymerization was considerably shorter and the quality of the obtained products better.

### Properties of the liquid compositions

Properties of the compositions before curing such as: viscosity, refraction index, and density are presented in Table 1. From these data one can see that BES-DM concentration has an influence on the properties of compositions. With its increase, significant increase of compositions viscosities is observed. Their densities and refractive indices have also tendency to increase.

### FTIR spectroscopy

The FTIR spectra of the new copolymer (1:1; BES-DM:NVP) are shown in Fig. 2. In the spectrum the aromatic skeletal absorption is observed at 1591, 1489, and 825 $\mathrm{cm}^{-1}$. The signal of –OH group occurs at 3352 $\mathrm{cm}^{-1}$. The signal of C=O group is found at 1700 $\mathrm{cm}^{-1}$ and that of methyl groups at 2945 $\mathrm{cm}^{-1}$.

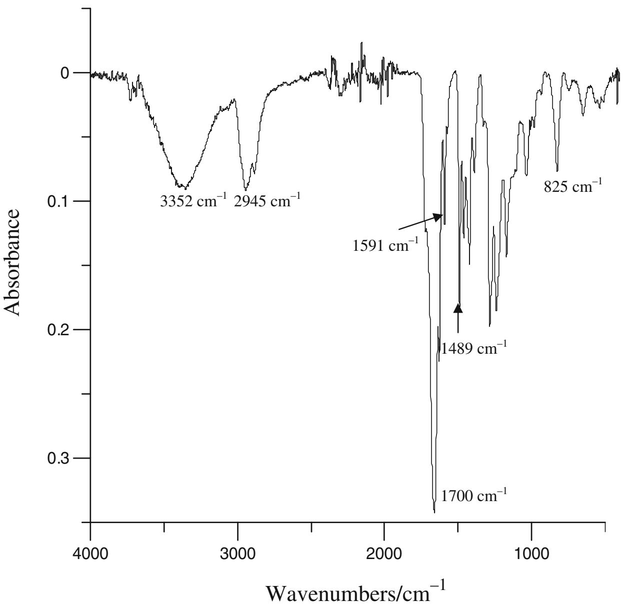

**Fig. 2** FTIR spectra of the BES-DM/NVP copolymers

### Properties of the cured compositions

From the data in Table 2 one can conclude that there are some differences between photo- and thermally initiated compositions. The compositions obtained in the presence of the photo-initiator are characterized by larger breaking stress values than those obtained in the presence of AIBN. Their Young moduli are also larger than those of thermally initiated ones. Relative elongations at break for the samples polymerized in the presence of Irgacure 651 and AIBN are also different. Only hardness of the studied compositions is characterized by comparable values. The larger share of a difunctional monomer (NVP) in the resulting copolymer is a decrease of breaking stress and Young's moduli with the simultaneous increase in relative elongations. This is due to smaller crosslinking of the obtained copolymers.

**Table 2** Properties of the compositions obtained after curing

| Ratio of monomers BES-DM:NVP | Breaking stress/MPa | Relative elongat. at break/% | Young's modulus/MPa | Shore's hardness *D* |
|---|---|---|---|---|
| 1:1 (AIBN) | 20.37 | 3.50 | 630 | 83.5 |
| 1.5:1 (AIBN) | 41.98 | 2.62 | 317 | 84 |
| 0.5:1 (IQ) | 52.00 | 2.51 | 2150 | 84.5 |
| 1:1 (IQ) | 52.37 | 2.20 | 2361 | 85 |
| 1.5:1 (IQ) | 53.01 | 2.08 | 2371 | 85.5 |
| 2:1 (IQ) | 53.04 | 1.92 | 2385 | 85.5 |
| 3:1 (IQ) | 55.05 | 1.91 | 2750 | 86 |

AIBN- $\alpha,\alpha'$-azoisobisbutyronitrile

IQ-2,2-dimethoxy-2-phenyl-acetophenone

**Table 3** DMA analysis of the compositions obtained

| Ratio of monomers BES-DM:NVP | Storage modulus (MPa) at temp. 30 °C | Temperature/°C | |
|---|---|---|---|
| | | $T_{max}$ for loss modulus | Tan $\delta_{max}$ |
| 1:1 (AIBN) | 939 | 58.3 | 83.1 |
| 1.5:1 (AIBN) | 662 | – | 86.8 |
| 0.5:1 (IQ) | 3364 | 126.3 | 143.4/181.1 |
| 1:1 (IQ) | 3092 | 104.1 | 115.8/176.2 |
| 1.5:1 (IQ) | 3130 | 99.9 | 164.9 |
| 2:1 (IQ) | 2966 | 98.7 | 121.0/173.9 |
| 3:1 (IQ) | 3246 | 87.2 | 117.6/171.2 |

## DMA

The DMA analyses in the glassy state and in the rubbery region were carried out to define how differently parameters influence the network of polymers [21]. The viscoelastic properties of the obtained copolymers were measured in a wide temperature range 30–220 °C at a heating rate of 4 °C/min. The obtained data are shown in Table 3 and Fig. 3. These data also confirm differences between the photo- and thermally initiated BES-DM/NVP compositions. Loss and storage moduli for the photo-initiated sample are significantly larger. Also tan $\delta_{max}$ values are larger. The curves of DMA analysis for the exemplary samples polymerized in the presence of Irgacure 651 and AIBN show quite different courses. For the photo-initiated BES-DM/NVP 1:1 sample, two maxima of tan $\delta$ at 115.8 and 176.2 °C are observed while for the thermally initiated sample only one at 83.1 °C.

## Thermal properties

Curing of BES-DM-NVP compositions was investigated by the DSC analysis [22]. The data obtained from the scans are summarized in Table 4. The exemplary DSC thermograms for the BES-DM/NVP 1:1 samples polymerized in the presence of Irgacure 651 and AIBN are presented in Fig. 4.

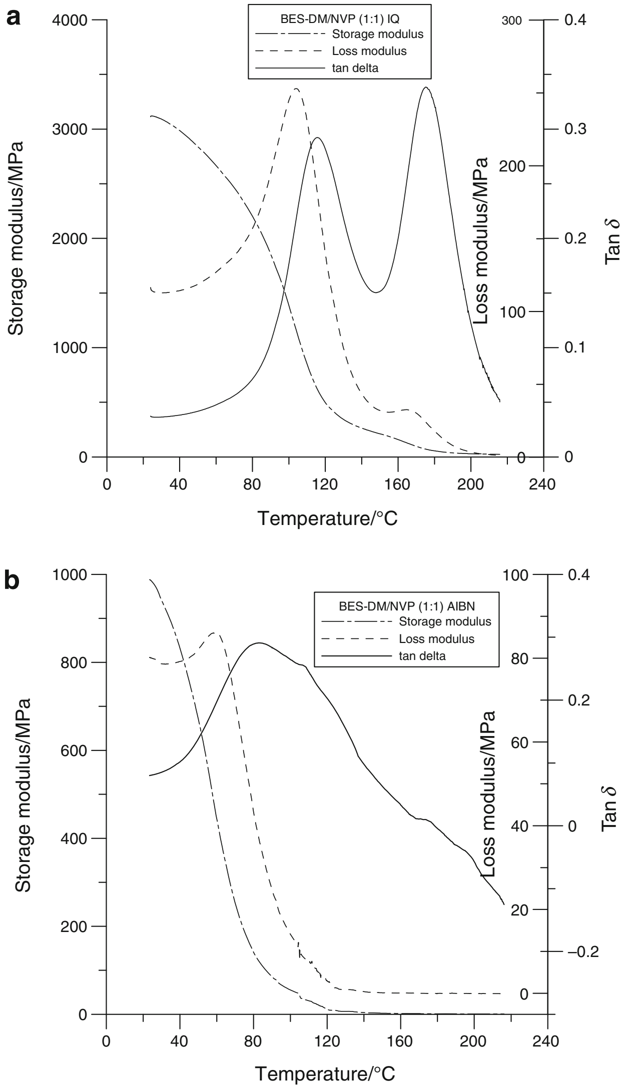

**Fig. 3** DMA analysis. **a** [BES-DM/NVP 1:1 (IQ)]; **b** [BES-DM/NVP 1:1 (AIBN)]

In Fig. 4 two endothermic peaks are shown. Therefore, it can be concluded that the obtained compositions are heterogeneous. The decomposition temperatures ($T_{R1}$ = 203.2

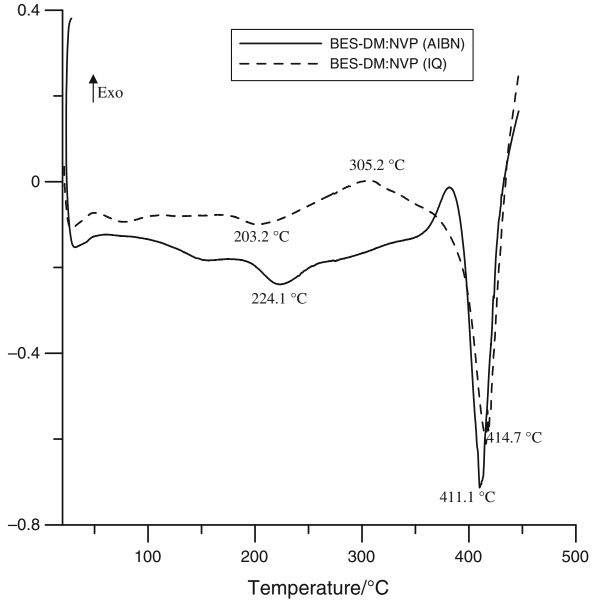

**Fig. 4** DSC analysis BES-DM/NVP 1:1 (IQ) and BES-DM/NVP 1:1 (AIBN)

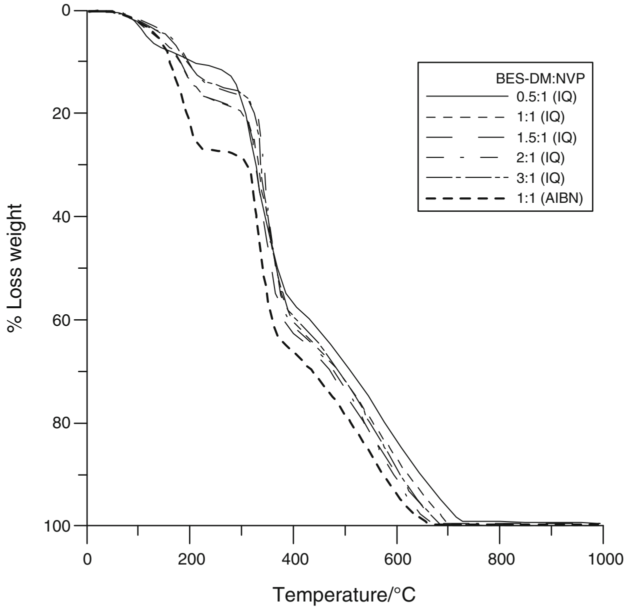

**Fig. 5** TG curves of the BES-DM/NVP copolymers

**Table 4** Thermal stabilities of the studied compositions

| Ratio of monomers BES-DM:NVP | °C | | | | |
|---|---|---|---|---|---|
| | $T_{10\%}$ | $T_1$ | $T_2$ | $T_{max}$ | $T_f$ |
| 1:1 (AIBN) | 140 | – | 185 | 350 | 680 |
| 1.5:1 (AIBN) | 145 | – | 190 | 360 | 695 |
| 0.5:1 (IQ) | 160 | 80 | 175 | 350 | 710 |
| 1:1 (IQ) | 155 | 80 | 180 | 360 | 705 |
| 1.5:1 (IQ) | 155 | 75 | 180 | 360 | 700 |
| 2:1 (IQ) | 165 | 75 | 180 | 360 | 695 |
| 3:1 (IQ) | 165 | 75 | 180 | 360 | 695 |

$T_{10\%}$ of the rate of weight loss

$T_1$, $T_2$ the first and the second decomposition temperature

$T_{max}$ the maximum decomposition temperature

$T_f$ the finally decomposition temperature

**Table 5** Data obtained from DSC thermograms

| Ratio of monomers BES-DM/NVP | $T_{R1}$/°C | $T_{R2}$/°C |
|---|---|---|
| 1:1 (AIBN) | 203.2 | 414.7 |
| 1:1 (IQ) | 224.0 | 411.1 |

$T_{R1}$, $T_{R2}$-decomposition temperature

and 224.0 °C) may correspond to degradation of polymerized NVP, whereas the decomposition temperatures ($T_{R2} = 414.7$ and 411.1 °C) probably indicate the final degradation of the copolymer BES-M/NVP. This is confirmed by the results of the DMA.

Thermal stabilities and degradation behaviors of BES-DM/NVP compositions were additionally investigated by means of thermogravimetric analysis. The parameters obtained from the TGA and DTG measurements in the air are presented in Table 4 and Fig. 5. These data confirm the results obtained from the DSC analysis. Independently of the initiator used, the final decomposition temperatures and maximum decomposition temperatures are also similar. The DTG curves contained three separated degradation steps. The first decomposition peak was observed in the range 70–110 °C with the maximum of weight loss ($T_1$) at 75–80 °C. The second decomposition stage took place between 120 and 240 °C with the maximum of weight loss ($T_2$) at 180–190 °C, and the third maximum decomposition peak was observed in the range 300–420 °C with the maximum of weight loss ($T_{max}$) at 350–360 °C.

The first decomposition peak ($T_1$) could be associated with the removal of water (high hygroscopicity of the polymer associated with the presence of basic nitrogen), the second ($T_2$) decomposition peak is associated with the removal of unpolymerized *N*-vinyl-2-pyrrolidone, and the third one ($T_{max}$) could be attributed to the maximum polymer decomposition volatile components. The final decomposition temperature ($T_f$) was in the range 680–710 °C. The obtained data show that the BES-DM-NVP compositions are thermally stable.

## Conclusions

The compositions BES-M/NVP were reacted with the two polymerization initiators: Irgacure 651 and

$\alpha,\alpha'$-azoizobutyronitryl (AIBN). Copolymerization with AIBN should be carried out very carefully in the temperature gradient. The copolymers obtained in the presence of the photo-initiator Irgacure 651 are characterized by larger breaking stress values than those obtained in the presence of the initiator AIBN. Loss and storage moduli for the photo-initiated samples are significantly larger. Thermal stabilities and degradation behaviors of the BES-DM/NVP compositions were additionally investigated by means of thermogravimetric analysis. The thermal and mechanical properties of the obtained copolymers are comparable.

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