

# Photoinitiated Polymerization of Bisphenol A Epoxy Diacrylates with *bis*[4(2-hydroxy-3-acryloyloxypropoxy)phenyl]sulfide

Malgorzata Gil, Barbara Gawdzik, Beata Podkościelna

Faculty of Chemistry, MCS University, pl. Marii Curie-Skłodowskiej 3, 20-031 Lublin, Poland

Received 30 May 2011; accepted 31 October 2011

DOI 10.1002/app.36423

Published online 31 January 2012 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** Photopolymerization of commercially available bisphenol A epoxy diacrylates with *bis*[4(2-hydroxy-3-acryloyloxypropoxy)phenyl]sulfide (BES-DA)—a monomer synthesized by our group in previous study was carried out. As this compound is solid at room temperature in its polymerization reactive diluent *N*-vinyl-2-pyrrolidone, which is also comonomer, has been applied. As a photoinitiator, 2-hydroxy-2-methyl-1-phenylpropan-1-one (Darocur 1173) was used. Thermal and mechanical properties of the obtained compositions were studied. The results show

that thermal properties of both epoxy diacrylates improve with the increasing concentration of BES-DA. The addition of *N*-vinyl-2-pyrrolidone causes decrease of their storage moduli and glass transition temperatures. Simultaneously, it allows to increase the conversion of double bonds. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2839–2845, 2012

**Key words:** copolymers; photopolymerization; epoxy acrylates; *bis*[4(2-hydroxy-3-acryloyloxypropoxy)phenyl]sulfide; thermal and mechanical properties

## INTRODUCTION

One method of producing highly crosslinked networks is through the photoinitiated polymerization of multifunctional monomers containing acrylate or methacrylate moieties. The kinetics of these systems has been studied extensively in recent years.<sup>1–3</sup> According to Lee et al.,<sup>4</sup> several parameters have influence on the final monomer-to-polymer conversions such as light intensity, monomer functionality, and reactivity, type, and concentration of photoinitiator, cure depth, and temperature.

On the basis of the mechanism of photoinitiation, photopolymerization reactions can be broadly divided into free radical and cationic systems. In the most popular free radical systems, light-sensitive photoinitiator molecules present within a monomeric liquid react with photons of light to generate highly reactive free radicals.<sup>5</sup> These radicals initiate the polymerization process, attacking reactive double bond groups in monomer molecules and converting them into a polymer. Multifunctional monomers or oligomers that contain multiple reactive groups are commonly used to create solid networks of polymers in rapid crosslinking reactions. A wide variety of commercially available monomers and oligomers can be used in this process. The most popular are

epoxy-acrylates, acrylourethanes, polyesters containing acrylic polymerisable groups at the chain ends, and unsaturated polyester resins obtained by diluting unsaturated polyester in acrylated monomers (reactive diluents).<sup>6,7</sup> Monomeric acrylates and methacrylates are less frequently used because they are relatively volatile, toxic, and have an unpleasant odor.<sup>8</sup> Solid monomers obviously have lower toxicity.

Studies of Khudyakov et al.<sup>9</sup> show that structure and functionality are the main factors influencing polymerization kinetics. In a given monomer composition, the photoinitiator plays the key role, being responsible for the curing speed, double bond conversion, and final mechanical properties.<sup>10</sup>

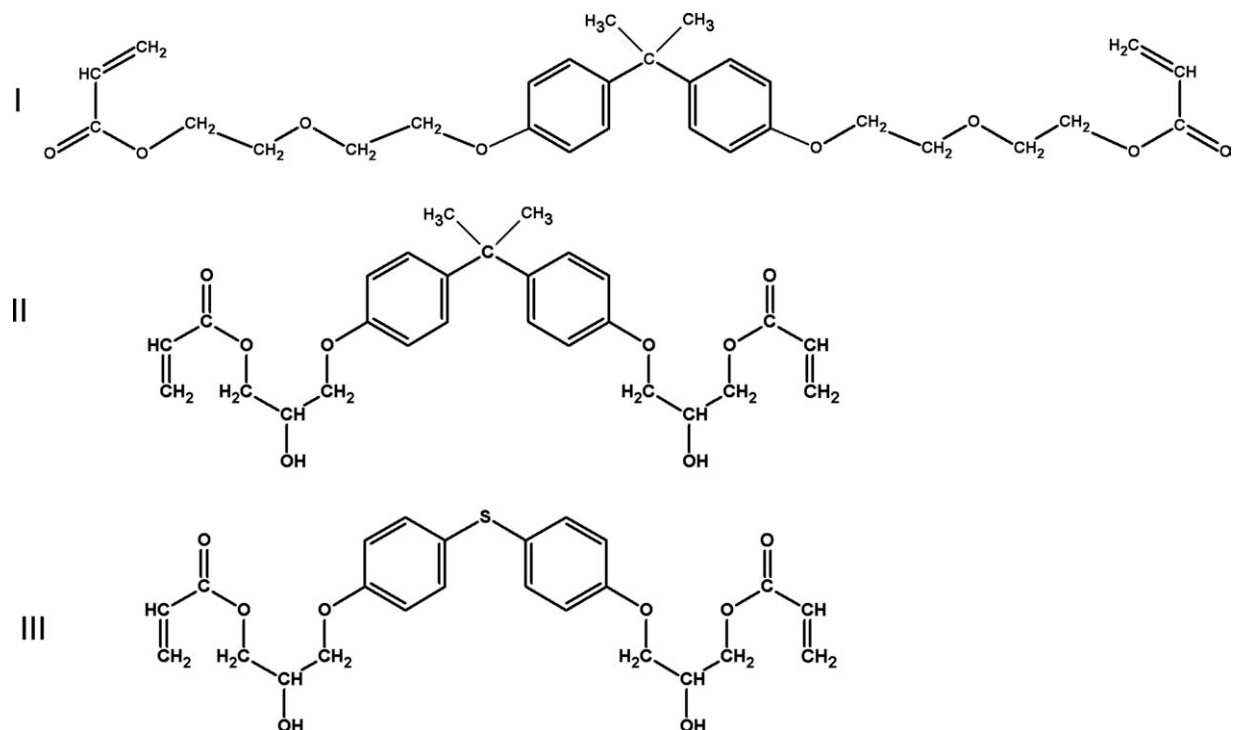
In this work, photopolymerization of commercially available bisphenol A epoxy diacrylates with *bis*[4(2-hydroxy-3-acryloyloxypropoxy)phenyl]sulfide (BES-DA)—a monomer synthesized by our group is presented. As this compound is solid at room temperature in its polymerization reactive diluent *N*-vinyl-2-pyrrolidone (NVP), which is also comonomer, has been applied. As a photoinitiator 2-hydroxy-2-methyl-1-phenylpropan-1-one (Darocur 1173) was used. Thermal and mechanical properties of the obtained compositions were studied.

## EXPERIMENTAL

### Materials

Two derivatives of bisphenol A epoxy diacrylate EB150 and EB600 were bought from CYTEC

Correspondence to: B. Gawdzik (barbara.gawdzik@poczta.umcs.lublin.pl).



**Figure 1** Chemical structures of the compounds used in photopolymerization. (I) EB150, (II) EB600, and (III) BES-DA.

(Viesbaden, Germany), *N*-vinyl-2-pyrrolidone from Fluka AG (Buchs, Switzerland) whereas Darocur 1173 (2-hydroxy-2-methyl-1-phenylpropan-1-one) were bought in Ciba (Basel, Switzerland). BES-DA was synthesized by esterification of diepoxide derivative of 4,4'-tiodiphenol according to the procedure published earlier.<sup>11,12</sup>

Chemical structures of the bisphenol A epoxy diacrylate monomers are presented in Figure 1.

### Curing procedure

We prepared copolymers of bisphenol A epoxy diacrylate derivatives and BES-DA. High viscosities of both substrates caused that only the composition containing 5% of BES-DA was possible to obtain. For this reason in further studies *N*-vinyl-2-pyrrolidone (NVP) as the active solvent was added.

Compositions were obtained by dissolving bisphenol A epoxy diacrylate derivative in NVP in a three-necked flask equipped with a stirrer, a water condenser, and a thermometer. At 80°C, BES-DA was added in small portions while stirring. In this way, the compositions containing 5, 10, and 15% of BES-DA were prepared. Detailed recipes used in the syntheses are given in Table I.

All compositions were polymerized with UV light in the presence of 1 wt % of Darocur 1173 for 30 min. Photopolymerization was made in an irradiation chamber equipped with two commercially available low-pressure mercury lamps 310–360 nm (Phi-

lips, TL20W/05 SLV) at room temperature. The irradiated samples were distanced 15 cm from each lamp. Foils of copolymers were obtained by their photopolymerization between two quartz glass panes. The width of all obtained foils was 2 mm.

### Characterization

#### Dynamic mechanical analysis

To study mechanical properties of the obtained foils, special stripes were prepared. Their diameters were as follows: 60 × 10 × 2 mm<sup>3</sup>.

Dynamic mechanical measurements were performed using dynamic mechanical analyzer DMA Q 800 (TA Instruments, USA) based on the flexural modulus. The analyzer was provided with a dual cantilever device and movable element vibrating with the amplitude 10 Hz. Measurements were performed at a constant heating rate of 4°C/min in the temperature range 10–170°C in air atmosphere. Dynamic mechanical properties of the cured compositions were estimated from the changes of storage modulus ( $E'$ ) and from the changes of  $\tan \delta$  at constant frequency depending on temperature.  $\tan \delta$  is defined as tangent of angle of phase shift between loss modulus ( $E''$ ) and  $E'$ ,  $\tan \delta = E''/E'$ . Glass transition temperatures were taken as the maximum of the  $\tan \delta$  versus temperature curves. From the  $\tan \delta$  curves also crosslinking densities were determined. The crosslinking density ( $\nu_c$ ) for the obtained networks was calculated by applying the equation

TABLE I  
Viscosities of the Studied Compositions

Composition	Bisphenol A epoxy diacrylate (% w/w)		BES-DA (% w/w)	NVP (% w/w)	Viscosity at 25°C (mPas)
	EB150	EB600			
100EB150	100	–	–	–	1085
75EB150/25NVP	75	–	–	25	220
67EB150/33NVP	67	–	–	33	80
50EB150/50NVP	50	–	–	50	53
100EB150/5S	100	–	5	–	
75EB150/25NVP/5S	75	–	5	25	
67EB150/33NVP/5S	67	–	5	33	
50EB150/50NVP/5S	50	–	5	50	
100EB150/10S	100	–	10	–	
75EB150/25NVP/10S	75	–	10	25	
67EB150/33NVP/10S	67	–	10	33	
50EB150/50NVP/10S	50	–	10	50	
100EB150/15S	100	–	15	–	3640 <sup>a</sup>
75EB150/25NVP/15S	75	–	15	25	2305
67EB150/33NVP/15S	67	–	15	33	205
50EB150/50NVP/15S	50	–	15	50	90
100EB600	–	100	–	–	
75EB600/25NVP	–	75	–	25	
67EB600/33NVP	–	67	–	33	
50EB600/50NVP	–	50	–	50	
100EB600/5S	–	100	5	–	
75EB600/25NVP/5	–	75	5	25	
67EB600/33NVP/5S	–	67	5	33	
50EB600/50NVP/5S	–	50	5	50	
100EB600/10S	–	100	10	–	
75EB600/25NVP/10S	–	75	10	25	
67EB600/33NVP/10S	–	67	10	33	
50EB600/50NVP/10S	–	50	10	50	
100EB600/15S	–	100	15	–	
75EB600/25NVP/15S	–	75	15	25	
67EB600/33NVP/15S	–	67	15	33	
50EB600/50NVP/15S	–	50	15	50	

<sup>a</sup> At 60°C.

derived from the theory of rubber elasticity:  $E' = 3\nu_e RT$ , where  $E'$  is the storage modulus in the rubbery plateau region,  $R$  is a gas constant, and  $T$  is the absolute temperature ( $T = T_g + 50^\circ\text{C}$ ).<sup>13,14</sup>

The calorimetric measurements were carried out in the Netzsch DSC 204 calorimeter (Germany) operating in a dynamic mode. The dynamic scans were performed at a heating rate of  $10\text{ K min}^{-1}$  in the temperature range  $-10^\circ\text{C}$  to a maximum of  $550^\circ\text{C}$  under nitrogen atmosphere ( $30\text{ mL min}^{-1}$ ). The mass of the sample was  $\sim 10\text{ mg}$ . As a reference, an empty aluminum crucible was used. Heat of decomposition ( $\Delta H$ ) was determined.

Thermogravimetric analysis (TG) was performed on a MOM 3427 derivatograph Paulik and Erdey (Hungary) at a heating rate of  $10^\circ\text{C min}^{-1}$  in air, in the temperature range of  $20\text{--}1000^\circ\text{C}$  with the sample mass of  $100\text{ mg}$ . As a reference,  $\alpha\text{-Al}_2\text{O}_3$  was used. Initial decomposition temperature (IDT), temperature at the maximum rate of weight loss ( $T_{\text{max}}$ ), and final decomposition temperature (FDT) were determined.

In order to determine the degree of double bonds conversion, attenuated total reflection infrared spectroscopy was made on a Thermo Scientific, Nicolet research spectrometer 8700 ATR-IR. In this technique, the infrared beam enters the ATR crystal from one of the side faces. If the refractive index of the crystal is higher than that of polymeric material and the incident angle of the beam is higher than the critical angle, then the infrared beam is totally reflected at the crystal/polymer interface and the beam travels inside the crystal and exits from the other side face.<sup>15</sup>

## RESULTS AND DISCUSSION

### Mechanical properties

The studied compositions and their viscosities are presented in Table I. From these data, one can see that viscosity of EB150 is lower than that of EB600. Consequently, their compositions containing NVP

**TABLE II**  
DMA Data for the Studied Compositions

Composition	Storage modulus, $E'$ (MPa)	Glass transition temperature, $T_g$ (°C)	Cross-linking density, $\nu_e$ (mmol/cm <sup>3</sup> )
100EB150	2534	65.2	9.5
75EB150/25NVP	2444	70.5	13.4
67EB150/33NVP	2567	85.7	17.4
50EB150/50NVP	2240	52.6/66.0	11.3
100EB150/5S	2852	76.0	4.3
75EB150/25NVP/5S	3078	87.4	7.8
67EB150/33NVP/5S	3092	88.5	8.6
50EB150/50NVP/5S	2690	91.4	5.9
100EB150/10S	2788	71.6	1.8
75EB150/25NVP/10S	3032	84.4	2.6
67EB150/33NVP/10S	2934	92.9	6.0
50EB150/50NVP/10S	2938	96.5	7.8
100EB150/15S	2554	75.1	–
75EB150/25NVP/15S	3067	85.3	–
67EB150/33NVP/15S	3262	86.8	6.1
50EB150/50NVP/15S	2715	82.0	7.6
100EB600	3757	97.4	3.5
75EB600/25NVP	3501	114.1	4.5
67EB600/33NVP	3207	128.6	5.6
50EB600/50NVP	2900	95.4/137.5	–
100EB600/5S	3854	84.7	–
75EB600/25NVP/5S	3429	105.7	5.8
67EB600/33NVP/5S	3369	123.9	7.0
50EB600/50NVP/5S	2976	116.7	8.3
100EB600/10S	3813	78.3	–
75EB600/25NVP/10S	3334	114.2	3.4
67EB600/33NVP/10S	3687	131.0	5.2
50EB600/50NVP/10S	2958	126.7	5.3
100EB600/15S	4376	77.0	5.6
75EB600/25NVP/15S	3762	111.7	7.2
67EB600/33NVP/15S	3612	125.1	–
50EB600/50NVP/15S	3104	123.0	7.5

are less viscous. With the increase of NVP concentration, viscosities of the obtained compositions become lower.

In Table II mechanical properties of the studied compositions after photopolymerization are presented. The viscoelastic properties of the obtained copolymers were measured in a wide temperature range 10–170°C at a heating rate of 4°C/min. From these data, one can see that the storage modulus for EB600 is much higher than that of EB150. The addition of NVP causes significant decrease of storage moduli for the EB600 compositions. For the sample containing 0% of NVP, it is equal to 3757 MPa, for the copolymer containing 25% NVP decreases to 3501 MPa whereas for 50% only 2900 MPa. In the case of EB150 compositions, the addition of the reactive solvent does not significantly affect the storage modulus. Its values drop from 2534 for pure EB150 to 2240 MPa for the copolymer containing 50% NVP.

Analyzing their glass transition temperatures, similar tendencies can be observed. Pure EB600 has a significantly higher glass transition temperature than

pure EB150. The addition of 25 and 33% of NVP causes the increase of glass transition temperatures of both composition types. For the compositions containing 50% of NVP, two glass transition temperatures are found. Probably in these cases, the separation phase takes place and the regions of homopolymer can appear in the whole composition structure. Such nanoheterogeneities are typical for radiation-induced epoxy acrylate networks.<sup>16</sup> In the structure of composition containing EB600 poly (EB600) of  $T_g$  about 95–97°C is disclosed.

In the case of the composition containing EB150 and 50% of NVP, a significant decrease of  $T_g$  takes place. It corresponds to  $T_g$  poly(NVP). According to Brandrup et al.<sup>17</sup> for free radical-generated poly(NVP), it is equal to 54°C. In our study,  $T_g$  for poly(NVP) determined in this way is even lower. The second  $T_g$  corresponds to poly(EB150). Its value obtained from DSC measurements is equal to 65.2°C.

The addition of tetrafunctional BES-DA changes  $T_g$  of both composition types. In the case of the composition containing EB150, the increase of  $T_g$  is observed.  $T_g$  of the samples containing EB150 and BES-DA are higher than that of pure EB150, but their values do not depend on the concentration of BES-DA. For the compositions with NVP, an increase of  $T_g$  takes place when the addition of BES-DA is 5 and 10%. The addition of 15% BES-DA causes only insignificant increase of their  $T_g$ . When tetrafunctional BES-DA was added to EB600, decrease of  $T_g$  is observed. For the compositions with NVP, the addition of BES-DA causes an increase of their  $T_g$ ; but its concentration has rather ambiguous impact.

Values of crosslinking densities show further differences between the studied compositions. Compositions containing EB150 and NVP have the largest crosslinking densities. The addition of solid BES-DA leads to their decrease. With the increase of NVP concentration, an increase of crosslinking densities is observed. For compositions containing EB600 values of crosslinking densities are similar independently of NVP concentrations. Addition of tetrafunctional BES-DA maintains crosslinking densities on similar level.

### Double bond conversion

The results from DMA analysis are compared with those obtained by the ATR-IR method. In Table III, conversions of double bonds of the studied compositions determined in this way are presented. From these data, one can see that compositions without the active solvent are characterized by the smallest degree of double bond conversions. The increase of NVP concentration causes the increase of double bond conversions. This effect is associated with

**TABLE III**  
**Conversion of Double Bonds (ATR-IR) and Heats of Decomposition (DSC)**

Composition	Double bonds conversion (%)	Decomposition heat (J/g)
100EB150	56.0	149.3
75EB150/25NVP	72.4	173.7
67EB150/33NVP	79.3	225.7
50EB150/50NVP	75.8	309.0
100EB150/5S	50.3	144.9
75EB150/25NVP/5S	60.1	180.9
67EB150/33NVP/5S	72.1	206.2
50EB150/50NVP/5S	78.0	263.9
100EB150/10S	51.0	123.6
75EB150/25NVP/10S	56.2	131.9
67EB150/33NVP/10S	71.2	161.6
50EB150/50NVP/10S	74.1	237.4
100EB150/15S	45.5	105.7
75EB150/25NVP/15S	49.7	109.5
67EB150/33NVP/15S	65.9	123.4
50EB150/50NVP/15S	55.8	195.9
100EB600	54.2	52.1
75EB600/25NVP	69.1	89.0
67EB600/33NVP	75.6	135.9
50EB600/50NVP	80.5	142.2
100EB600/5S	37.7	89.1
75EB600/25NVP/5S	59.9	117.4
67EB600/33NVP/5S	72.5	160.6
50EB600/50NVP/5S	80.4	192.9
100EB600/10S	33.2	63.3
75EB600/25NVP/10S	56.8	109.5
67EB600/33NVP/10S	80.2	146.3
50EB600/50NVP/10S	79.9	197.7
100EB600/15S	31.6	76.3
75EB600/25NVP/15S	49.5	114.0
67EB600/33NVP/15S	60.9	128.4
50EB600/50NVP/15S	76.1	177.4

reducing the viscosities of the starting compositions leading to the increase of chains mobility and finally to the reactions with other chains or monomers. The addition of solid BES-DA monomer slightly reduces the degree of double bonds conversion. Larger the concentration of BES-DA, smaller the conversion of double bonds. The compositions containing 33 and 50% of NVP with 5 and 10% of BES-DA are characterized by the largest double bond conversions. Similar conclusions can be drawn from the data obtained by the DSC.

### Thermal properties

On the basis of the results obtained from the thermogravimetry studies, one can see that the initial decomposition temperatures of pure EB150 and EB600 after photopolymerization are similar (Table IV). The addition of active solvent causes insignificant increase of initial decomposition temperatures. Such a relationship is observed till the concentration of solvent reaches 50%. In these cases, the initial

decomposition temperatures begin to drop. This applies to both mixtures with and without the addition of BES-DA.

In Figure 2, one can observe the changes of initial decomposition temperatures of the studied compositions with the increasing concentration of tetrafunctional BES-DA. The addition of this compound increases the mentioned temperatures. Analyzing these data, one can see that this increase is more or less proportional to the BES-DA concentration.

From the data related to a maximum decomposition temperature, it can be seen that the addition of the solvent shifts the maximum toward lower temperatures. Probably, the addition of the active solvent weakens the binding forces in the net of crosslinked copolymer. The addition of tetrafunctional compound increases the maximum decomposition temperatures. Concentration of the BES-DA has rather insignificant influence on the mentioned temperatures.

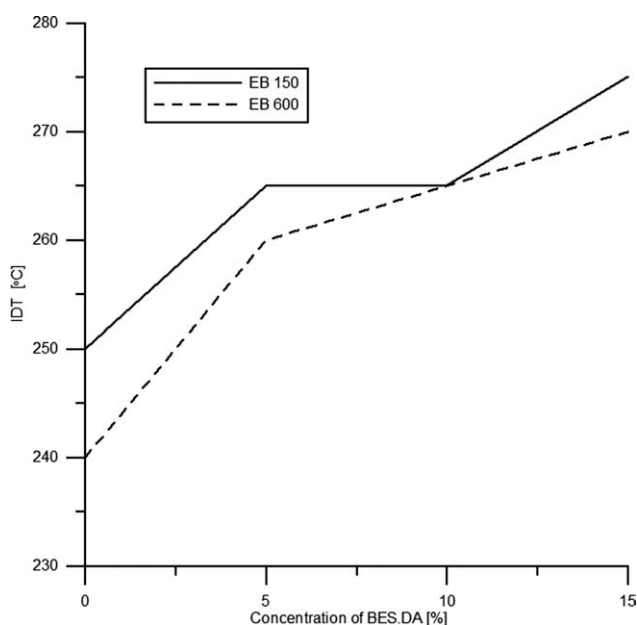
The results obtained from DSC studies confirmed the course of decomposition of the samples. The exemplary DSC thermograms is presented in Figure 3. On the basis of the effect of the energy created during the decomposition, one can determine the strength of bonds in the crosslinked polymer (Table III). Larger the effect, higher is the crosslinking degree. With the addition of the solvent, the amount of energy output increases. In the case of compositions containing EB150, the addition of BES-DA cause decrease of decomposition heats whereas for those containing EB600, its addition has rather insignificant influence on the amount of energy output. These results suggest that compositions containing EB600 are characterized by similar crosslinking degree independently of the BES-DA concentrations. Probably, for this effect, differences in the chemical structure of the used epoxy diacrylates are responsible.

### CONCLUSION

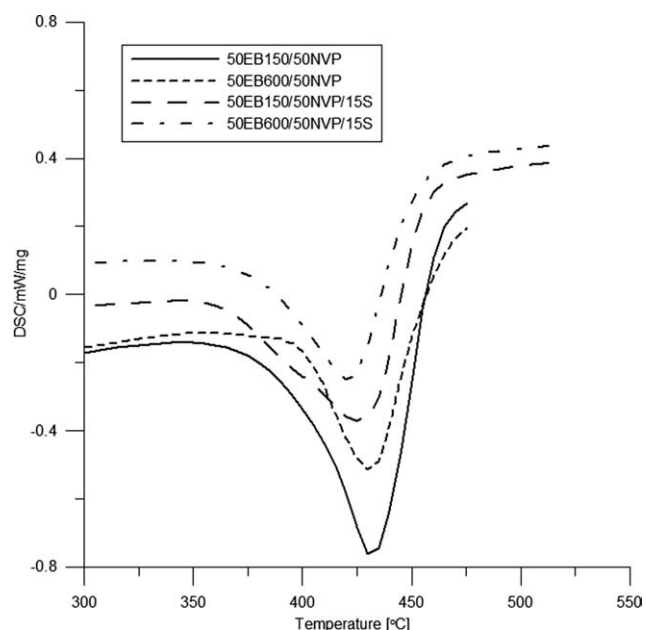
The results presented here show that the tetrafunctional BES-DA monomer can be used in photopolymerization of commercially available epoxy diacrylates. Because of solid state of substrates in preparation of their compositions NVP as an active solvent should be added. Its addition to pure EB150 or EB600 caused increase of their glass transition temperatures. Concentration of NVP should not exceed 50% because of phase separation. The largest double bond conversions were achieved for the compositions containing 33 and 50% of NVP with the addition of maximum 10% of BES-DA. An increase of BES-DA concentration influences thermal properties of the studied compositions. Compositions

**TABLE IV**  
**Thermal Properties of the Studied Compositions**

Composition	Initial decomposition temperature, IDT (°C)	Temperature at the maximum rate of weight loss, $T_{\max}$ (°C)	Final decomposition temperature, FDT (°C)
100EB150	250	385	680
75EB150/25NVP	265	348	685
67EB150/33NVP	265	365	700
50EB150/50NVP	262	358	730
100EB150/5S	265	393	680
75EB150/25NVP/5S	290	381	700
67EB150/33NVP/5S	275	365	710
50EB150/50NVP/5S	265	346	700
100EB150/10S	265	388	700
75EB150/25NVP/10S	285	361	690
67EB150/33NVP/10S	275	355	690
50EB150/50NVP/10S	270	362	700
100EB150/15S	275	360	685
75EB150/25NVP/15S	–	–	690
67EB150/33NVP/15S	288	365	690
50EB150/50NVP/15S	286	372	700
100EB600	240	370	790
75EB600/25NVP	270	368	745
67EB600/33NVP	265	354	715
50EB600/50NVP	265	365	715
100EB600/5S	260	380	780
75EB600/25NVP/5S	280	363	740
67EB600/33NVP/5S	285	370	750
50EB600/50NVP/5S	280	370	750
100EB600/10S	270	360	770
75EB600/25NVP/10S	–	–	755
67EB600/33NVP/10S	280	360	730
50EB600/50NVP/10S	–	–	730
100EB600/15S	270	380	765
75EB600/25NVP/15S	–	–	770
67EB600/33NVP/15S	285	360	730
50EB600/50NVP/15S	280	360	710



**Figure 2** Changes of initial decomposition temperatures of the studied compositions with increasing concentration of tetrafunctional BES-DA.



**Figure 3** DSC thermogram for the exemplary compositions.

containing 15% of BES-DA indicate the highest initial decomposition temperatures.

Generally, compositions modified by BES-DA have better thermal and mechanical properties than the epoxy diacrylates of bisphenol A. They can be applied as products with excellent thermal and mechanical resistance and good chemical properties for the production of covering materials for example in the aerospace industry.

## REFERENCES

1. Fouassier, J.-P.; Rabek, J. F. *Radiation Curing in Polymer Science and Technology*; Elsevier: New York, 1993.
2. Fouassier, J.-P. *Photoinitiation, Photopolymerization, and Photocuring*; Hanser: Munich, Vienna, New York, 1995.
3. Chuda, K.; Smolinski, W.; Defoort, B.; Rudz, W.; Gawdzik, B.; Rayss, J.; Coqueret, X. *Polimery* 2004, 49, 505.
4. Lee, J. H.; Prud'homme, R. K.; Aksay, I. A. *J Mater Res* 2001, 16, 3536.
5. Dendukuri, D.; Panda, P.; Haghgooe, R.; Kim, J. M.; Hatton, T. A.; Doyle, P. S. *Macromolecules* 2008, 41, 8547.
6. Yu, Q.; Nauman, S.; Santerre, J. P.; Zhu, S. *J Mater Sci* 2001, 36, 3599.
7. Scoconi, M.; Rossetti, S.; Leonardi, M. *RadTech Europe 2003 Conference Proceedings*, Berlin, Germany, November 3-5, 2003, vol. II, p. 635.
8. Autian, J. *Environ Health Perspect* 1975, 11, 141.
9. Khudyakov, I. V.; Legg, J. C.; Purvis, M. B. *Ind Eng Chem Res* 1999, 38, 3353.
10. Karasu, F.; Dworak, C.; Kopeinig, S.; Hummer, E.; Arsu, N.; Liska, R. *Macromolecules* 2008, 41, 7953.
11. Podkościelna, B.; Bartnicki, A.; Gawdzik, B. *J Appl Polym Sci* 2009, 111, 1257.
12. Podkościelna, B.; Maciejewska, M.; Bartnicki, A. *J Appl Polym Sci* 2012, 123, 59.
13. Ward, I. M. *Mechanical Properties of Solid Polymer*; Wiley: London, 1971.
14. Worzakowska, M. *J Therm Anal Calorim* 2010, 101, 685.
15. Choe, Y. *Macromol Res* 2003, 11, 311.
16. Krzeminski, M.; Molinari, M.; Troyon, M.; Coqueret, X. *Macromolecules* 2010, 43, 8121.
17. Brandrup, J.; Immergut, E. H.; Grulke, E. A., Eds. *Polymer Handbook*, 4th ed.; Wiley-Interscience, 1999; Vol. 1, p. VI/217.