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## Polyesters with trioximidazolidine rings

### RAPID COMMUNICATION

**Summary** — Polyesters containing trioximidazolidine rings in the chains were synthesized using *N,N'*-bis(2-hydroxyethyl) parabanate (BHEP) or *N,N'*-bis(2-hydroxypropyl) parabanate (BHPP) as diol components. The product obtained from BHPP as well as classical polyester, prepared with use of propylene glycol, were crosslinked with either styrene or propylene glycol dimethacrylates. Both resins containing trioximidazolidine rings showed shorter gelation time and shorter time of thermal stability at temp. 70 °C in comparison with classical polyester resins. Crosslinked resins were cured with Interlox BP-50-P1 in presence of *N,N'*-dimethylaniline. It was found, using derivatographic method, that the resins prepared this way, containing the rings in the chain, degrade at lower temperature than typical polyester resins. However, DSC measurements show that the former ones exhibit higher glass transition temperature ( $T_g$  in Table 3).

**Key words:** polyester resins, polycondensation, trioximidazolidine ring, *N,N'*-bis(2-hydroxyalkyl) parabanates, thermal stability, gelation time.

Polymers containing trioximidazolidine rings were usually obtained by closing the ring during the polymerization reaction or by chemical modification of certain polymers, such as polyureas, with oxalyl chloride [1–3]. Depending on the final structure and molecular weight, the polymers were suggested to be the components of films, fibres or foams or proposed as wear resistant construction polymers of high thermal stability [4]. Introduction of trioximidazolidine rings into the polymer structure may be achieved also in a different way, namely by carrying out polyreaction using monomers already containing parabanic acid (PbAc) rings [5]. This alternative route of the synthesis of PbAc ring containing polymers was expected to provide new polymers showing good thermal properties.

The aim of this work was to use hydroxyalkyl derivatives of PbAc [6, 7] for the synthesis of new polymers containing trioximidazolidine rings and to find whether introduction of such rings into the structure of typical polyester resin would change its thermal properties.

### EXPERIMENTAL

#### Materials

The following materials were used in this work:

- hydroxyalkyl derivatives of PbAc were prepared as described in [6],
- phthalic anhydride and maleic anhydride (pure, Chemical Works Kędzierzyn-Koźle, Poland),
- diethylene glycol (DEG) and propylene glycol (PG) (both pure, Orlen, Płock Poland),
- styrene (p.a. Fluka, Switzerland),
- propylene glycol dimethacrylate (PGDMA) was synthesized as described in [8],
- Interlox BP-50-P1 (50 % solution of benzoyl peroxide in dibutyl phthalate, Peroxid Chemie GmbH, Germany),
- *N,N'*-dimethylaniline (pure, Sigma-Aldrich, USA).

#### Synthesis of unsaturated polyester resins

22.2 g (0.15 mole) of phthalic anhydride, 14.7 g (0.15 mole) of maleic anhydride, 13.7 g (0.13 mole) of diethylene glycol (DEG), and 14 g (0.17 mole) of propylene

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glycol (PG), or 34.5 g of *N,N'*-bis(2-hydroxyethyl) parabanate (BHEP) or 39.3 g *N,N'*-bis(2-hydroxypropyl) parabanate (BHPP) were placed into 250 cm<sup>3</sup> three-necked round-bottomed flask equipped with mechanical stirrer, Liebig condenser and thermometer. The flask content was stirred under nitrogen for 15 min at room temperature. Then 0.005 wt. % of hydroquinone was added as 10 % solution in acetone and the temperature raised to 170–190 °C. The extent of reaction was controlled by measuring of the amount of water distilled off and the acid number (AN) in the reaction mixture. When BHEP or BHPP were used, AN was corrected allowing for the contribution of decomposition of trioximidazolidine ring [7]. After completing the reaction, the mixture was cooled down to temperature 40–50 °C and diluted in styrene or PGDMA to obtain a homogeneous mixture.

### Curing

The test samples were prepared by curing the resins with Interlox BP-50-P1 (50 % solution of benzoyl peroxide in dibutyl phthalate) in the presence of *N,N*-dimethylaniline accelerator (10 % solution in styrene).

### Analytical Methods

The acid number (AN) was determined by titration with 0.1 M NaOH.

Refractive index of unsaturated polyester resins was determined with Abbe refractometer.

<sup>1</sup>H NMR spectra of polyesters were recorded using TESLA spectrometer BS586, 80 MHz, Czechoslovakia (in d<sub>6</sub> — DMSO) with HMDS internal standard.

IR spectra of polyester in KBr pellets were recorded using Specord 71 IR, Carl Zeiss and PARAGON 1000 FTIR Perkin Elmer spectrometers.

The thermal properties of uncured polyesters and cured polyester resins were determined using Paulik-Paulik system MOM derivatograph (Hungary), using 0.3 g samples in temperature range 20–1000 °C and recording time of 100 min. The amplifications of 1/15 for differential thermal analysis (DTA) and 1/10 for differential thermal gravimetry (DTG) were applied.

DSC thermograms were recorded using Mettler-Toledo type 822<sup>e</sup> instrument in the temperature range

20–300 °C at heating rate 10 deg/min under nitrogen atmosphere (PN-EN ISO 11357-1:1997).

The unsaturated polyester resins were characterized by measuring of:

- content of non-volatiles (PN-86/C-89082/08),
- gelation time at 80 °C (PN-EN ISO 2535:2002 87/C),
- maximum temperature and time of temperature rise in curing at 80 °C (PN-EN ISO 584:2002)
- time of stability at elevated temperature (PN-86/C-89082/09).

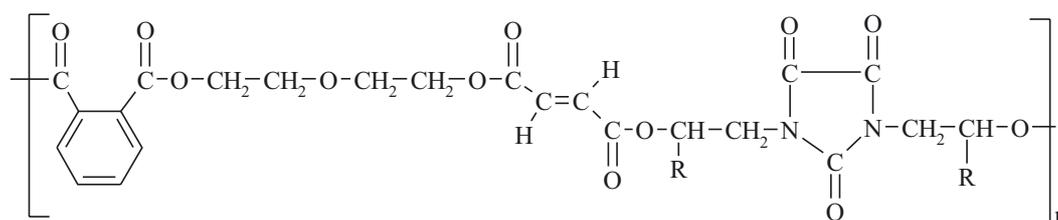
### RESULTS AND DISCUSSION

An improvement in the temperature of thermal deformation of polyester resins can be achieved by increasing the crosslinking density or by polyester chain stiffening. The stiffening is obtained by using unsaturated diacids or diols containing rings that enter the main chain of the polyester [9]. In this work, *N,N'*-bis(hy-

**Table 1.** Composition, polycondensation conditions and acid number for classical unsaturated polyester resins and the resins prepared from BHEP and BHPP

No. of resin	Diols	Condensation conditions		Acid number mg KOH/g	cross-linking monomer
		temperature °C	time h		
1	DEG, PG	170–190	5.5	36.5	styrene
2	DEG, PG	170–190	5.5	38.8	PGDMA
3	DEG, BHEP	170	3	143	styrene
4	DEG, BHEP	170	3	145	PGDMA
5	DEG, BHPP	170	3.5	139	styrene
6	DEG, BHPP	170	4	137	PGDMA

droxyalkyl) parabanates (BHEP and BHPP) were used as diols. These compounds contain trioximidazolidine rings, which are known to improve substantially thermal stability of polymers [4, 10]. The effect of the presence of these rings on the polycondensation conditions of unsaturated polyester resins were compared with those of the classical resins prepared from maleic and phthalic anhydrides and diethylene and propylene glycols (Table 1). The resulting polyesters had the following structure:



where: R= H-, CH<sub>3</sub>-

### Properties of uncured polyester resins

Polyesters are usually obtained in the reactions between glycols and dicarboxylic acids carried out at 170–190 °C (Table 1). However, when *N,N'*-bis(hydroxyalkyl) parabanate was used, the reaction mixture gelled at 190 °C. To avoid gelation, the condensation temperature was reduced to *ca.* 170 °C. The extent of reaction was controlled by measuring of the amount of reaction water released from the reacting system. Moreover, the acid number (AN) of the mixture was measured. In the synthesis of polyester resins the final AN is usually 25–45 mg KOH/g. In the case of diols with trioxoimidazolidine rings, one should correct the measured AN since the rings open in the presence of KOH [7]. The calculated AN related to the presence of BHEP or BHPP in the polyester was 113 or 106 mg KOH/g, respectively. Hence, the corrected final AN at the end of polycondensation was 138–158 and 131–151 mg KOH/g for BHEP and BHPP, respectively. In this moment one should point out that trioxoimidazolidine ring did not undergo decomposition in the condensation process. This was confirmed by the following reasoning:

— The value of AN of *ca.* 140 mg KOH/g was obtained at the end of reaction. It did not decrease upon further heating. Should the ring decomposed, AN would have dropped down to *ca.* 25–45 mg KOH/g, the value typical for the classical polyester.

— In <sup>1</sup>H NMR spectrum of the polyester modified with BHPP, no signal at 8.4–9.2 ppm appeared, which, as was stated in [7], is characteristic for amide groups that should have formed in trioxoimidazolidine ring decomposition.

— Neither first nor second amide group band were observed in IR spectra of the polyesters.

**Table 2.** Properties of synthesized unsaturated polyester resins; numbers of resin correspond to those in Table 1

No. of resin	$n_D^{20}$	Content of non-volatiles wt. %	Gelation time at 80 °C min	Curing at 80 °C		Stability at temperature of 70 °C h
				Maximum curing temperature °C	Time of temperature rise at 80 °C s	
1	1.5401	65.4	8.25	132.6	10.25	576
2	1.5064	91.2	7.25	85.4	14.75	516
5	1.5396	77.9	11	90	14.5	306
6	1.5047	87.6	4	84	8	63

When AN reached the predetermined value, the polyester was dissolved in crosslinking monomer either styrene (typical) or PGDMA. The last one is much less toxic and less volatile therefore is recommended by European Union [11]. Unfortunately, the polyester ob-

tained from BHEP showed limited miscibility with both styrene or PGDMA, hence the typical *ca.* 70 wt. % solutions of the polyester could not be obtained [10]. It was not the case, however, when BHPP was used as the glycol component.

The content of non-volatile components was determined for polyesters modified with BHPP (Table 2). The classical styrene resin contains *ca.* 65.4 wt. % of non-volatiles. The presence of BHPP raised this figure up by *ca.* 12 wt. %. This would allow the modified resin processing at somewhat higher temperature than the classical ones.

Gelation time determined at 80 °C with the curing system typical for unsaturated polyester resins, *i.e.*, with 50 % solution (paste) of benzoyl peroxide in dibutyl phthalate, was shorter for resins crosslinked with PGDMA by 1 min as compared with that of the classical styrene resin. It was longer though by *ca.* 3 min for the resin obtained with using BHPP and styrene (5 in Table 2). The system containing both trioxoimidazolidine rings and PGDMA as the crosslinking monomer showed the highest reactivity. The gelation was as short as 4 min (by 75 % shorter than the classical polyester with PGDMA crosslinking agent). For the series of unsaturated polyester resins, the maximum temperature and time of temperature rise in curing at 80 °C was measured. For the classical resin (1 in Table 2) the time was *ca.* 10 min and the peak reached 133 °C. Replacement of styrene by PGDMA increased this time to *ca.* 15 min and reduced the peak height to 85.4 °C. The presence of trioxoimidazolidine rings in the resin structure reduced the gelation time (5 and 6 in Table 2) and time of thermal stability at elevated temperature (Table 2).

### Properties of cured unsaturated polyester resins

The highest thermal decomposition of the classical samples started at 360 °C. The resins prepared with BHPP (Table 3) showed somewhat lower decomposition temperature. However, the glass transition temperature of the latter resins, measured by DSC, was by 16 °C higher than that of the former one. We were unable to determine the glass transition temperature ( $T_g$ )

**Table 3.** Thermal properties of synthesized unsaturated polyester resins after curing and of classical resins, measured by derivatograph or DSC;  $T_x$  % is the temperature at which x wt. % of the sample evaporated

No. of resin	$T_5$ % °C	$T_{10}$ % °C	$T_{20}$ % °C	$T_{50}$ % °C	Temperature of highest decomposition rate, °C	$T_g$ °C
1	210	250	300	350	360	92
2	210	250	310	360	350	>300
5	215	240	265	320	310	108
6	200	220	250	300	310	>300

for the resins crosslinked with PGDMA (2 and 5 in Table 3). No signal due to glass transition was observed on DSC thermograms up to 300 °C. Hence our assumptions regarding the possibility of improving the temperature of thermal deformation of unsaturated polyester resins by introducing parabanic acid derivatives seem to be correct.

#### CONCLUSIONS

— Polyesters with trioximidazolidine rings can be obtained in reaction of phthalic and maleic anhydrides with diethylene glycol and *N,N'*-bis(2-hydroxypropyl) parabanate.

— The presence of trioximidazolidine rings in the resin structure reduced both gelation time and time of thermal stability at elevated temperature.

— Cured polyester resins showed lower decomposition temperatures but improved temperature of thermal deformation in comparison with classical unsaturated polyesters.

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