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## Thermal properties of polyurethanes and polyacrylates with trioxoimidazolidine rings

### RAPID COMMUNICATION

**Summary** — New polyurethanes and polyacrylates containing imidazolidine rings were obtained from *N,N'*-bis(2-hydroxyalkyl)parabanates and Izocyn T-80 or acrylic and methacrylic acid, respectively. The polymers show usually higher thermal stability or heat resistance in comparison with their analogues obtained from aliphatic diols or classic polyacrylates.

**Key words:** *N,N'*-bis(hydroxyalkyl)parabanates, addition polymerization, radical polymerization, thermal stability.

#### WŁAŚCIWOŚCI TERMICZNE POLIURETANÓW I POLIAKRYLANÓW Z PIERŚCIENIAMI TRIOKSOIMIDAZOLIDYNOWYMI

**Streszczenie** — Zaproponowano syntezy poliuretanów i poliakrylanów z monomerów zawierających gotowy pierścień imidazolidynowy. Jako monomerów użyto parabanianów *N,N'*-bis(2-hydroksyalkilowych) otrzymanych w wyniku hydroksyalkilowania kwasu parabanowego tlenkami etylenu i propylenu. Wprowadzenie pierścieni imidazolidynowych do struktury poliuretanów w reakcjach parabanianów i butano-1,4-diolu z Izocynem T-80 (tabela 1) powoduje zwiększenie ich temperatury zeszklenia (tabela 2, rys. 1 i 2). Dwumetakrylany i dwuakrylany z pierścieniami trioksoimidazolidynowymi otrzymane z PBHA i kwasów akrylowego i metakrylowego poddano polimeryzacji rodnikowej stosując jako inicjator nadtlenuk benzoilu. Analiza termiczna wykazała zwiększoną odporność termiczną poliakrylanów i polimetakrylanów z pierścieniami trioksoimidazolidynowymi w porównaniu do klasycznych, alifatycznych poliakrylanów i polimetakrylanów oraz poli(diakrylanów) i poli(di-metakrylanów) (tabela 2, rys. 2 i 3).

**Słowa kluczowe:** parabaniany *N,N'*-bis(hydroksyalkilowe), poliaddycja, polimeryzacja rodnikowa, stabilność termiczna.

Polymers with parabanic acid (PbAc) rings (2,4,5-trioxoimidazolidine rings) incorporated into polymer chain show high thermal stability [1–4], good mechanical properties like flexibility [5] and abrasion resistance [1], and good adhesion to glass and metals [6]. The films and fibers may be formed from their composites with glass fibers or other fibrous fillers, while foams of high thermal stability are fabricated from their mixtures with porophors [7, 8]. Initially polymers with trioxoimidazolidine rings were obtained from monomers, which did not contain the ring. Its formation took place during polymerization or polycondensation step, when cyanofornamidyl isocyanate [9] or diisocyanates and bisoxamidoesters [7] were used, respectively as monomers. Later trioxoimidazolidine rings were introduced into already formed polyureas [10, 11] or polycarboimides [12] by reaction with oxalyl chloride. Recently the monomers with parabanic rings were applied [for in-

stance 4,4'-(hexamethylene-1,6-diyl)bis(2,4,5-trioxoimidazolidine-1,3-diyl) dibenzoyl dichloride] in condensation with various bisphenols [13].

Here we offer the new possibility of synthetic path to polyurethanes and polyacrylates based on monomers with imidazolidine rings, namely *N,N'*-bis(2-hydroxyalkyl)parabanates (BHAP) obtained by hydroxyalkylation of PbAc with ethylene and propylene oxides [14, 15]. The influence of trioxoimidazolidine rings on thermal stability and heat resistance of synthesized polymers was also elucidated.

### EXPERIMENTAL

#### Materials

*N,N'*-bis(2-hydroxyethyl)parabanate (BHEP) and *N,N'*-bis(2-hydroxypropyl)parabanate (BHPP) were obtained according to the published procedure [14].

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Diacylates and dimethacrylates with PbAc rings were obtained according to [16].

Mixture of toluilene-2,4-diisocyanate (80 %) and toluilene-2,6-diisocyanate (20 %) (under technical name Izocyn T-80, Zachem Poland) was used as a source of isocyanate function used to synthesis of polyurethanes.

Benzoyl peroxide was used a radical initiator (pure, POCH, Poland).

### Synthesis of mixed linear polyurethanes

1.8 g (0.02 mole) of butan-1,4-diol (BD), 7 g (0.04 mole) of Izocyn T-80 and 25 mL of acetone were placed in a three-necked, 100 mL round bottom flask equipped with mechanical stirrer, reflux condenser and thermometer. Temperature of the mixture was maintained below 25 °C and progress of reaction was monitored by determination of isocyanate number (ICN). Then 0.02 mole of BHAP (4.04 g of BHEP or 4.64 g of BHPP) was added when ICN reached the 50 % of initial value and maintained under reflux at temperature 56 °C until ICN was zero. Then the solvent was evaporated and solid residue was dried to the constant mass ( $T = 60\text{ °C}$ ,  $p = 2 \cdot 10^{-3}\text{ MPa} = 15\text{ mm Hg}$ ).

### Reactions of diols with Izocyn T-80

0.02 mole of diol (4.04 g of BHEP, 4.64 g of BHPP or 1.8 g of BD) was placed in a three-necked, 100 mL flask equipped with mechanical stirrer, reflux condenser and thermometer and 40 mL of dioxane was added until substrate dissolved. Then 3.5 g (0.02 mole) of Izocyn T-80 was added and preparation of the product was continued as described in previous section.

### Syntheses of polyacrylates

In a sealed 20 mL glass ampoule 0.01 mole, *i.e.* 3.38 g of 2,2'-(1,3-trioxoimidazolidine)diethyl dimethacrylate (DEDM), 3.68 g of 2,2'-(1,3-trioxoimidazolidine)dipropyl dimethacrylate (DPDM), 3.10 g of 2,2'-(1,3-trioxoimidazolidine)diethyl diacrylate (DEDA) or 3.40 g of 2,2'-(1,3-trioxoimidazolidine)dipropyl diacrylate (DPDA) was placed and 0.5–1 g of benzoyl peroxide per 100 g of ester was added. Reaction mixture was stirred until became homogeneous and dried at 80 °C for 4 h before sealing of ampoule.

### Analyses

Number of isocyanate groups in reaction mixtures and products of reaction between BHAP and Izocyn T-80 was determined according to PN-EN ISO 11357-1:1997. Number-average molecular weight ( $\overline{M}_n$ ), weight-average molecular weight ( $\overline{M}_w$ ), z-average molecular weight ( $\overline{M}_z$ ) and molecular weight distribution were determined using Viscotec T60A gel chromatograph equipped with

three detectors' system: RI (refractive index detector), LS (light scattering detector) and DV (viscometer detector). Separation has been performed using two independent columns: PSS SDV (of 7.8 mm × 300 mm size with TSK bed — 100 and 1000 Å pore diameter gel, using the following recording parameters: temperature  $25 \pm 0.1\text{ °C}$ , volume flow of eluent 1 mL/min, the injection loop volume of 20 mL, concentration of polymer solution 4–5 mg/mL, analysis time 30 min. THF was used as eluent (distilled from over sodium prior to use). Calibration was based on common polystyrene references.

Thermal analyses (DTA, DTG and TG) of polyurethanes and polyacrylates were performed using Paulik—Paulik—Erdey derivatograph (MOM, Hungary) in ceramic crucible at 20–1000 °C temperature range, with 100 min registration time. The 200 mg sample was heating with rate 10 deg/min under air atmosphere.

Differential scanning calorimetry (DSC) studies were done using DSC822<sup>e</sup> Mettler Toledo calorimeter at 20–300 °C temperature range, heating rate 10 deg/min, samples 1–20 mg, under nitrogen atmosphere.

<sup>1</sup>H NMR spectra of polyesters were recorded using spectrometer BS586A, 80 MHz, TESLA, former Czechoslovakia (in d<sub>6</sub>-DMSO) with HMDS internal standard.

IR spectra of polyesters in KBr pellets were recorded by Specord 71 IR, Carl Zeiss and PARAGON 1000 FT-IR Perkin Elmer spectrometers.

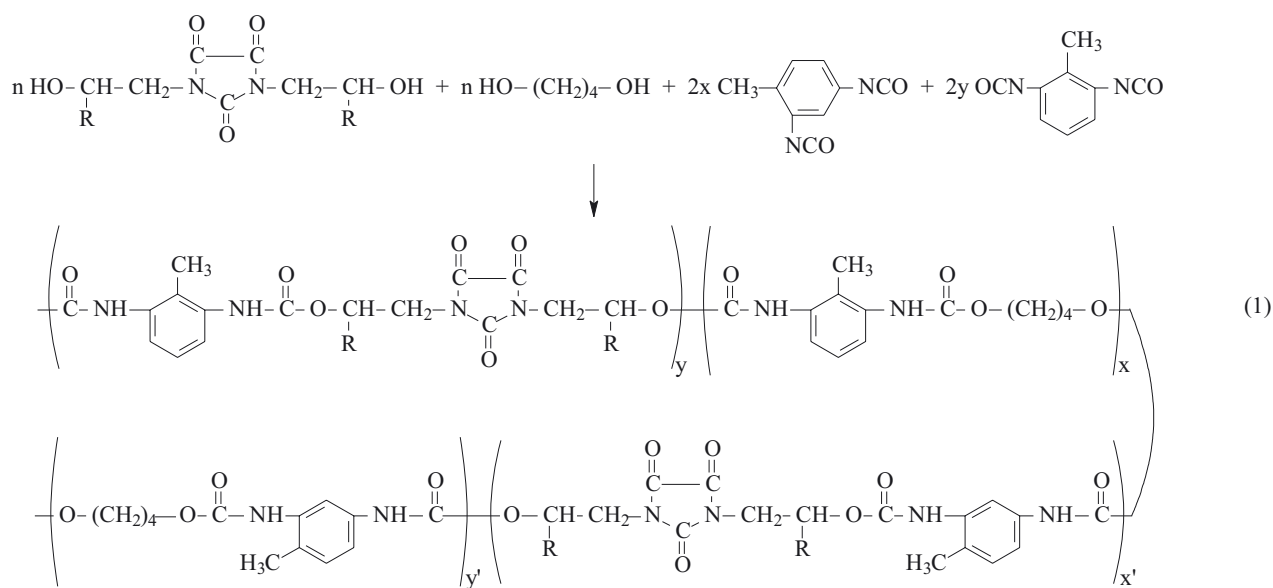
## RESULTS AND DISCUSSION

Preliminary results of the reaction of BHAP with phenyl isocyanate allowed us to establish the optimal reaction conditions for addition of diols with imidazolidine ring to isocyanates [16]. Here we have applied that procedure and used it for obtaining the linear polyurethanes with trioxoimidazolidine rings.

Equimolar reactions of BHAP (BHEP, BHPP) and/or BD with Izocyn T-80 (Table 1, syntheses 1–4) lead to polymers defined in equation below:

**Table 1.** Conditions of synthesis reactions of linear polyurethanes with trioxoimidazolidine rings

Number synthesis	Diols	Molar ratio diols:Izocyn T-80	Solvent	Temperature of reaction °C	Time of reaction min
1	BD	1:1	acetone	25 56	120
2	BD, BHEP	1:1:2	acetone	25 56	105
3	BD, BHPP	1:1:2	acetone	25 56	120
4	BHEP	1:1	dioxane	60–70	60
5	BHPP	1:1	dioxane	60–70	60



where: R = H-, CH<sub>3</sub>-, x + x' + y + y' = n

**Table 2.** Thermal stability and heat resistance of polyurethanes and polyacrylates with trioximidazolidine rings determined upon thermoanalytical measurement

Number synthesis	Polymer	Temperature of maximal decomposition, °C	T <sub>5%</sub> , °C	T <sub>10%</sub> , °C	T <sub>20%</sub> , °C	T <sub>50%</sub> , °C	T <sub>g</sub> , °C
1	PU from BD	290	260	270	280	290	105
2	PU from BD and BHEP	270	240	260	270	330	130
3	PU from BD and BHPP	300	250	270	280	300	102
4	PU from BHEP	295	160	235	280	350	100
5	PU from BHPP	280	170	230	245	290	84
6	poly(DEDM)	355	150	210	315	355	—
7	poly(DPDM)	355	150	170	210	330	—
8	poly(DEDMA)	355	310	335	345	360	205
9	poly(DPDMA)	355	195	240	330	360	176
10	poly(methyl acrylate)	—	—	—	—	328 [17]	6 [18]
11	poly(methyl methacrylate)	210—260	—	—	—	283 [19]	105 [17]

Instrumental analysis results corroborate well the proposed structure of discussed polyurethanes. In the <sup>1</sup>H NMR spectra of obtained products the resonance at 9.5 ppm from the protons of carbamate NH- group and multiplet in the 6.9—7.5 ppm region characteristic for aromatic protons are observed. Moreover, in the <sup>1</sup>H NMR spectra of polymers obtained from BD and/or BHEP the resonance centered at 4.2 ppm from protons of methylene group attached to oxygen of carbamate are observed, while in the spectrum of the product obtained from BHPP the signal at 4.9 ppm is consistent with protons of methine group in the same chemical vicinity [15, 16]. In their IR spectra the broad band at 3600—3100 cm<sup>-1</sup> from valence vibrations of carbamate NH is found. The bands at 1618, 1602, 1535 and 1444 cm<sup>-1</sup> are attributed to aromatic ring. Also the C=O valence bands of trioximidazolidine ring and carbamate at 1776 and 1739 cm<sup>-1</sup> are present as well as deformation vibration of N-C, N-H at

1535 cm<sup>-1</sup>. The bands at 1216 and 1118 cm<sup>-1</sup> can also be found which are characteristic for C-O of carbamate group.

In order to compare the thermal stability of the polymers obtained with linear polyurethanes obtained from aliphatic diols, the synthesis of polyurethane from BD and Izocyn T-80 was performed (Table 1, synthesis 1). We have found that introduction of trioximidazolidine ring into the polymer chain did not change considerably the thermal stability of the product (Table 2, syntheses 1—3, Fig. 1). However, we found that polymers obtained from equimolar mixture of BD and BHEP showed enhanced heat resistance in comparison with typical linear polyurethanes (Table 2, syntheses 1 and 2, Fig. 2).

The polyurethanes obtained from equimolar mixtures of BHAP and Izocyn T-80 had no higher heat resistance than those obtained from BD and BHAP equimolar mixtures (Table 1 and 2, syntheses 4 and 5, Fig. 2). Thus,

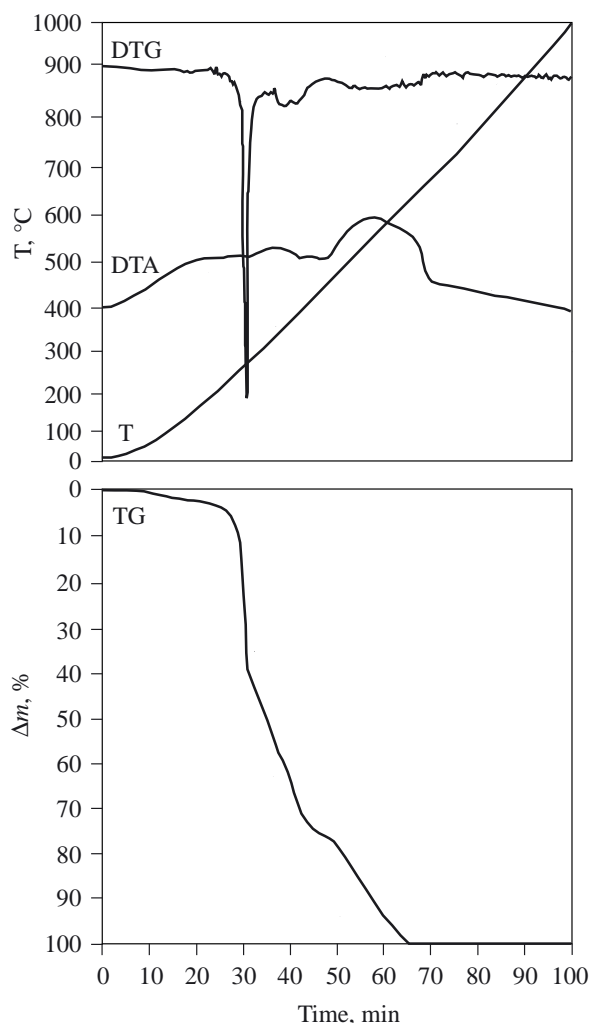


Fig. 1. Thermal analysis of PU from BHEP and BD (synthesis 2)

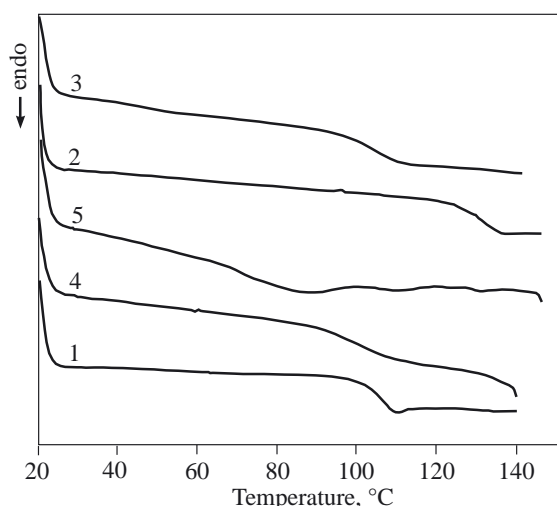


Fig. 2. DSC curves of obtained polyurethanes at second heating cycle; numbers of curves are the same as numbers of syntheses

further increase in trioxoimidazolidine rings probably causes a steric hindrance within the polymer structure and weakens interchain interactions.

In order to change the thermal resistance and heat resistance we have modified polyurethanes introducing the trioxoimidazolidine rings from BHAP. The obtained polyurethane with BD has much higher molecular weight and lower polydispersity than polyurethanes obtained from BHAP (Table 3). Polyurethanes from BHEP and BHPP have similar molecular weights and polydispersity, with slightly higher polyurethanes from BHPP (Table 3, syntheses 2 and 3). Polyurethanes obtained from equimolar amounts of BD and BHAP were not analyzed by gel chromatography due to their insolubility in organic solvents.

Table 3. Molecular weights and molecular weight distributions of polyurethanes obtained

Number of synthesis	Polymer	$\bar{M}_n$ g/mole	$\bar{M}_w$ g/mole	$\bar{M}_z$ g/mole	Molecular weight distribution $P = \bar{M}_w/\bar{M}_n$
1	PU from BD	27 860	48 160	76 710	1.729
2	PU from BHEP	1484	3703	6144	2.495
3	PU from PHPP	1699	4053	8344	2.386

Diacrylates and dimethacrylates obtained from BHAP [16] were polymerized here using benzoyl peroxide as a radical initiator. DSC analysis evidenced that polyacrylates obtained from BHEP showed glass temperature of 205 °C, while those obtained from BHPP showed glass temperature 176 °C (Table 2, syntheses 8 and 9, Fig. 3).

Thermal stability of polyacrylates and polymethacrylates with trioxoimidazolidine rings was higher if compared to classical alkyl polymers (Table 2, syntheses 6–11) [18, 19]. The vast thermal degradation was observed at 355–360 °C regardless of kind of BHAP and

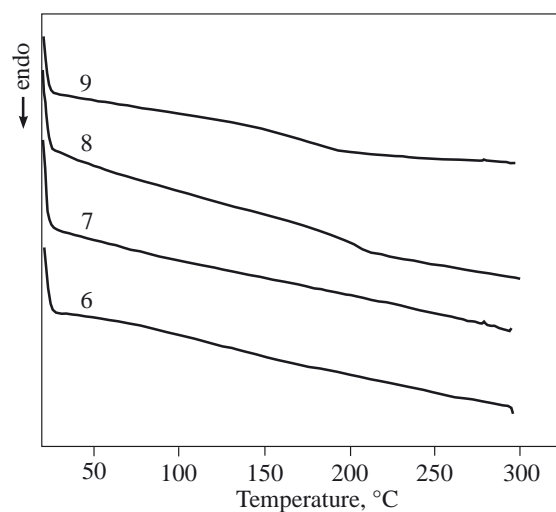


Fig. 3. DSC curves of polyacrylates and polymethacrylates with parabanic acid rings at second heating cycle; numbers of curves are the same as numbers of syntheses

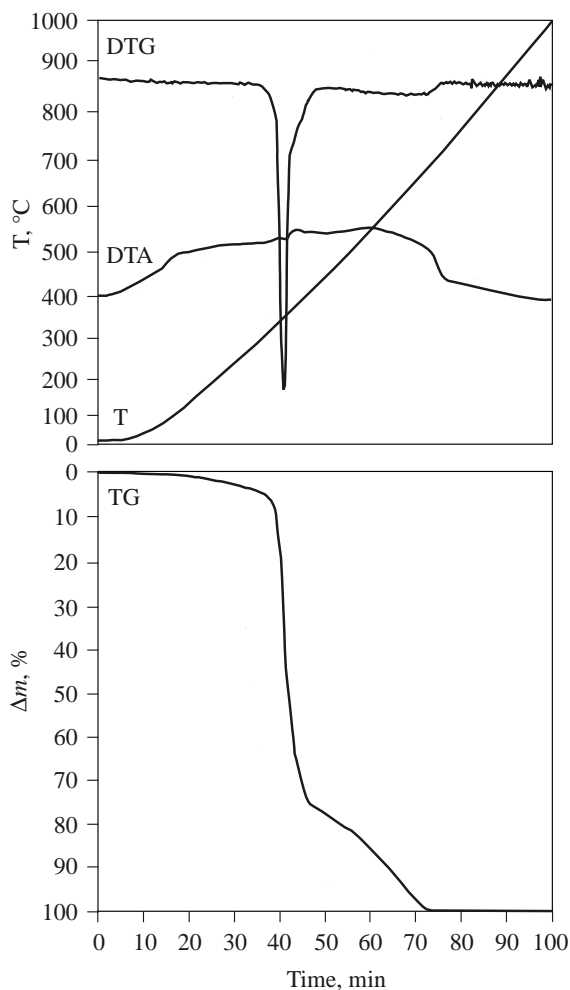


Fig. 4. Thermal analysis of poly(DED A)

unsaturated acid used (Fig. 4). Based on the results presented here one can conclude that obtained diesters can be applied as crosslinking agents and co-monomers causing the increase in thermal stability and heat resistance of polyacrylates and polymethacrylates.

#### CONCLUSIONS

New method of synthesis of polymers with trioxoimidazolidine rings was established, based on mono-

meric *N,N'*-bis(2-hydroxyalkyl)parabanates. The polymeric materials: polyurethanes, polyacrylates and polymethacrylates with trioxoimidazolidine rings promise usually considerable increase in thermal stability or heat resistance of those products.

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