

# Carboxylated Polyurethanes Containing Hyperbranched Polyester Soft Segments

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In this contribution we focus on the synthesis and characterization of polyurethanes containing hyperbranched polyester soft segments (HB PU) with functional carboxylic groups in order to enable the preparation of stable HB PU dispersions. Carboxylated hyperbranched polyurethanes were synthesized using a hyperbranched polyester based on 2,2-bis(methylol)propionic acid of the fourth pseudo-generation (Boltorn® H40) and hexamethylene (HDI) or isophorone diisocyanate (IPDI). The reactivity of hyperbranched polyester with HDI was lower than expected, possibly due to the presence of less reactive hydroxyl groups in the linear repeat units. A gel was formed at mole ratios  $r_{\text{NCO/OH}} = 1:2$  or  $1:4$ . The synthesis of HB PU was performed with partly esterified hyperbranched polyester with lowered hydroxyl functionality. The carboxyl groups were incorporated in the HB PU backbone by reaction of residual hydroxyl groups with *cis*-1,2-cyclohexanedicarboxylic anhydride. HB PU aqueous dispersions were stable at least for two months, although their films were brittle. The tensile strength and Young's modulus of blends of linear and HB PU decreased with increasing content of HB PU whereas elongation at break remained nearly constant, which was explained in terms of looser chain packing due to more open tree-like hyperbranched structures.

Key words: Polyurethanes, polyurethane anionomers, hyperbranched polymers, aqueous dispersions

## Introduction

Polymers with nonlinear architecture are set to become one of the top classes of polymers at the beginning of the third millennium<sup>1</sup> by offering many new and interesting properties and being ideal candidates for a wide range of applications in various branches of industry. Indeed, dendritic polymers with a highly branched molecular architecture, i.e. dendrimers and hyperbranched polymers, have attracted a great deal of scientific attention in recent years due to the significant differences in their macroscopic properties, such as solubility, viscosity, thermal, and rheological properties, compared to linear analogues. Dendrimers are well defined, perfectly branched monodisperse polymers with dendritic and terminal repeat units, and are produced by a time-consuming stepwise synthetic route. On the other hand, hyperbranched (HB) polymers are made by one-pot or pseudo-one-pot reactions, which is of greater interest from a large volume application viewpoint. However, HB polymers consist of not only fully reacted dendritic and terminal functional repeat units, but also partially reacted linear repeat units regarded as defects in their branched structures, which leads to a lower degree of branching and a larger polydispersity. Nevertheless, HB polymers as low-cost materials find uses as multifunctional crosslinkers, additives and modifiers, soluble functional supports, and as materials with optical, electronic and magnetic properties, etc. They are used as materials in, for example: sensors, low VOC coatings, high solid, UV-curable and powder coatings, delivery devices, additives (toughening agents, blend components for improvement of mechanical properties or

processing characteristics) or catalysts, and are potentially useful in the fields of nanoscience and nanotechnology, supramolecular polymer chemistry, biology and others.<sup>2–6</sup>

One of the most widely investigated families of HB polymers are hydroxy-functional aliphatic hyperbranched polyesters, synthesized from 2,2-bis(methylol)propionic acid (bis-MPA) as  $AB_2$  monomer and various core molecules, e.g. tris-(methylol)propane or ethoxylated pentaerythritol as the  $B_f$  monomer. Bis-MPA is added in incremental monomer addition mode to control polymer molar mass and distribution.<sup>7–9</sup> Polymers based on bis-MPA with ethoxylated pentaerythritol as the core molecule are the commercially available Boltorn® *Hx* polyesters, where *x* denotes the pseudo-generation number (Perstorp Specialty Chemicals AB, Sweden). HB polyesters are, by comparison with their linear analogues, less liable to hydrolysis and show better chemical resistance.<sup>10</sup> Their properties can also be adjusted for specific applications by partial or complete modification of the functional hydroxyl end-groups by incorporation of e.g. nonpolar alkyl, cycloalkyl or aromatic groups, crystallizable poly( $\epsilon$ -caprolactone) groups, polar (carboxyl, sulfonic or tertiary amine) functional groups or UV-curable methacrylate groups, which makes them potentially useful as binders in coatings.<sup>4,10,11</sup>

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Polyurethane (PU) segmented block copolymers (PU thermoplastic elastomers) are a well-known family of technically important polymers with a wide range of applications due to their excellent mechanical properties.<sup>12</sup> Because of their good film-forming properties they are extensively used in coatings applications by employing linear polyether or polyester polyols as the soft segments and diisocyanates and low molar mass diols as the hard segments.<sup>12–15</sup> The use of hydroxy-functional HB polyesters or modified HB polyesters containing various functional groups (see above) instead of linear polyols results in HB-PU with different material properties such as good flow, excellent chemical resistance or good mechanical properties.<sup>10,11,16</sup>

In our research group we have been investigating the synthesis of linear carboxylated polyurethanes (PU) as precursors for polyurethane aqueous dispersions,<sup>17–22</sup> blends and semi-interpenetrated networks with polymethacrylates<sup>23</sup>, as well as the properties of Boltorn® Hx polyesters<sup>24–26</sup> and hyperbranched polyurethanes (HB PU) based on Boltorn® H40.<sup>27</sup> The incorporation of carboxylic functional groups in the PU backbone improves solubility and dispersibility without having to use an emulgator in otherwise water-insoluble polymers.<sup>12–15</sup> Carboxylated PU can be dispersed in water after the formation of ionic groups by neutralization of the carboxylic groups with a base, e.g. triethylamine. Carboxyl-modified polymers have also shown some improved properties such as adhesion, dyeability, ionic conductivity, etc. In this contribution we present the results on the synthesis and characterization of polyurethanes containing hyperbranched polyester soft segments (HB PU) with functional carboxylic groups in order to enable the preparation of stable HB PU dispersions. For this purpose we also studied model hyperbranched polyurethanes made of hexamethylene diisocyanate and Boltorn® H40. Since the films of HB PU were brittle and could not be used to test their mechanical properties, we also prepared and tested blends of carboxylated linear and HB PU.

## Experimental

### Materials

Hydroxy-functional hyperbranched polyester Boltorn® H40 ( $M_n = 2,580 \text{ g mol}^{-1}$ ,  $M_w/M_n = 2.6$ , hydroxyl number =  $486 \text{ mg g}^{-1}$  KOH corresponds to  $8.66 \text{ mmol OH groups per g}$  and  $22.34 \text{ OH groups per mol}$ )<sup>24</sup> is a commercially available fourth pseudo-generation hydroxy-functional HB polymer synthesized from 2,2-bis(methylol)propionic acid (bis-MPA) as the  $AB_2$  monomer and ethoxylated pentaerythritol (PP50) as the  $B_4$  core molecule (Chart 1); it was kindly provided by Perstorp Specialty Chemicals AB. The following chemicals were used as received: hexamethylene diisocyanate (HDI, Fluka), polytetramethylene oxide (PTMO 2000, BASF), butyryl chloride (BuCl) and *cis*-1,2-cyclohexanedicarboxylic (CH) anhydride (Acros Organics), dibutyl tin dilaurate (DBTDL, Acima); bis-MPA, 1,4-butanediol (BD), isophorone diisocyanate (IPDI), pyridine, triethylamine (TEA), *N,N*-dimethylformamide (DMF) and

*N,N*-dimethylacetamide (DMAc) were obtained from Aldrich, while tetrahydrofuran (THF) and ethyl methyl ketone (butan-2-one) were obtained from Merck.

### Synthesis

**Model hyperbranched polyurethanes:** DBTDL (0.0012 g, 0.0004 % with respect to the HB polyester polyol) was added as catalyst to Boltorn® H40 (4.553 g, 1.765 mmol, 39.44 mmol OH), and dissolved in 30 mL DMF. HDI was added to this solution in various amounts to obtain the following mole ratios of  $r_{\text{NCO/OH}}$  groups: 1:2 (1.782 g, 10.60 mmol, 21.2 mmol NCO), 1:4 (0.891 g, 5.298 mmol), 1:8 (0.446 g, 2.649 mmol), and 1:16 (0.223 g, 1.325 mmol). The solution was stirred and kept at 60 °C under an argon atmosphere. The course of the reaction was followed by IR spectroscopy and stopped after the formation of a gel ( $r_{\text{NCO/OH}} = 1:2, 1:4$ ) or when the isocyanate stretching band at  $2276 \text{ cm}^{-1}$  had disappeared ( $r_{\text{NCO/OH}} = 1:8, 1:16$ ).

**Carboxylated hyperbranched polyurethanes (HB PU, Scheme 1):** TEA (100 mL) was added to Boltorn® H40 (50.72 g, 0.44 mol OH) solution in dry THF (280 mL) under argon atmosphere. BuCl (29.26 g, 0.27 mol) was added gradually while stirring at 25 °C and the mixture was allowed to react for 22 h. The product (58.38 g, 0.14 mol OH, yield 83 %) was precipitated in water and dried in vacuum at 55 °C. After dissolution in dry DMF, DBTDL (0.0021 g, 0.004 % with the respect to Boltorn® H40) was first added as a catalyst followed by HDI (3.855 g, 22.9 mmol) or IPDI (5.095 g, 22.9 mmol). The reaction proceeded at 60 °C for 46 h (until NCO band at  $2276 \text{ cm}^{-1}$  disappeared), and after the addition of CH anhydride (14.119 g, 91.68 mmol) in DMF (75 mL) and pyridine (30 mL) it went on at 80 °C for 7 h. The obtained carboxyl-terminated hyperbranched PU was precipitated in water and dried under vacuum at 55 °C (yield 76 %).

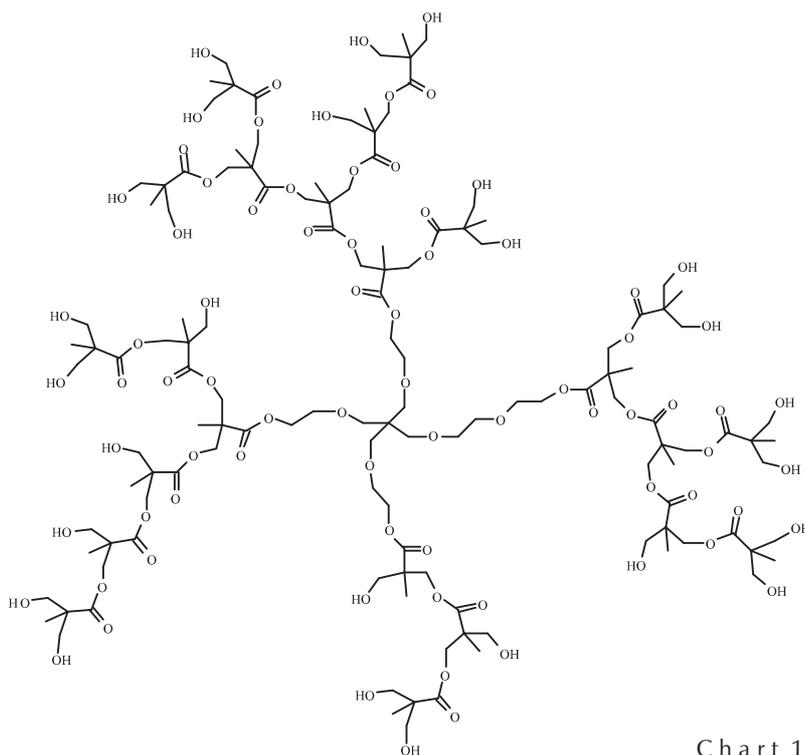
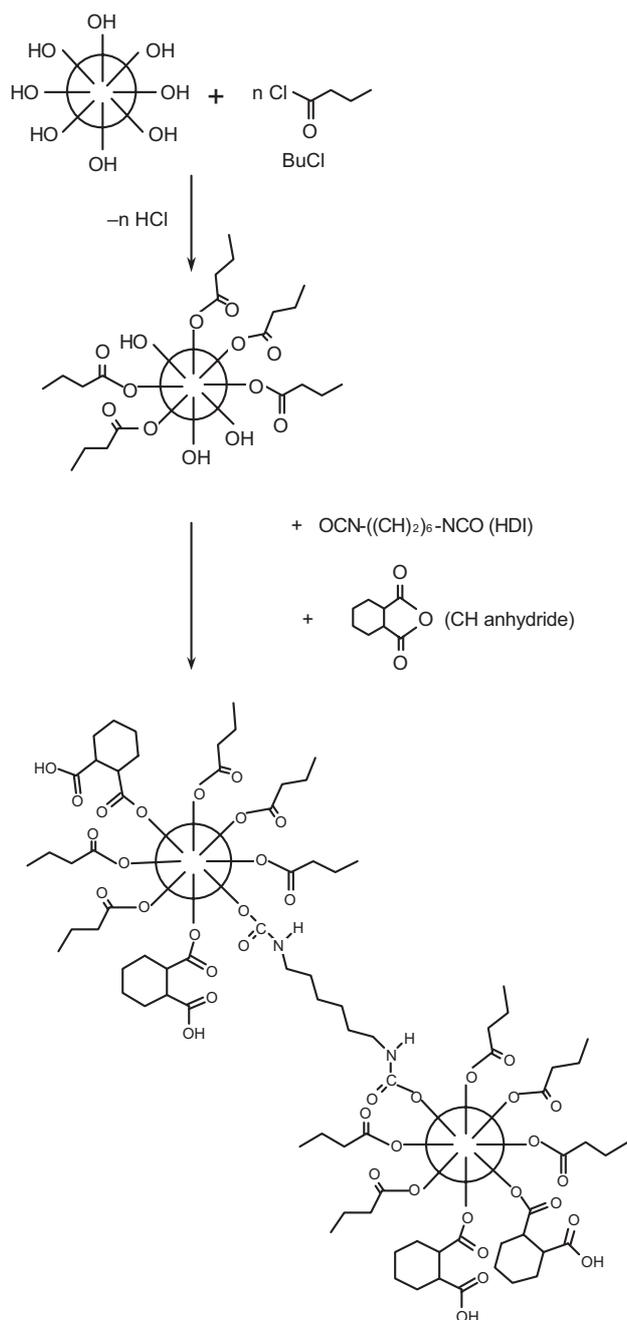


Chart 1.



Scheme 1 – Schematic representation of the synthetic route to carboxyl-terminated hyperbranched polyurethane

Shema 1 – Shematski prikaz sintetskog puta za karboksilirani visokorazgranati poliuretani

**Linear PU (LPU, Scheme 2):**<sup>19</sup> Macrodiol PTMO 2000 (100.0 g, 50.0 mmol,  $M_n = 2000 \text{ g mol}^{-1}$ ) was first vacuum dried at  $60^\circ\text{C}$  and then reacted with IPDI (83.25 g, 374.5 mmol) in the presence of DBTDL (0.01 % with respect to the polyol) as a catalyst at  $70^\circ\text{C}$  for 2 h under argon atmosphere. Chain extenders BD (18.00 g, 243.2 mmol) and bis-MPA (16.75 g, 124.8 mmol), dissolved in THF, were then added and the reaction proceeded for 64 h until the NCO stretching band at  $2276 \text{ cm}^{-1}$  had disappeared. Theoretically, the carboxyl groups of DMPA used in the second stage of the reaction may react with the isocyanate groups

resulting in branching points. However, the extent of this reaction under the experimental conditions used was quite low, only up to 4 %, due to the very low reactivity of the  $-\text{COOH}$  groups attached to the quaternary carbon atoms of DMPA.

**Preparation of aqueous HB PU dispersions:** carboxylic groups of HB PU (50 g) were neutralized by TEA (60 % excess with respect to  $-\text{COOH}$  groups) in a DMF or THF solution (100 mL) during stirring at room temperature for 22 h. Neutralized HB PU solution was dispersed in water (200 mL) during rigorous stirring, and the solvent was subsequently distilled off with a rotary evaporator at room temperature. Blends of linear and HB PU were prepared by mixing their solutions in mass ratios of 1:3, 1:1, and 3:1.

The samples for the investigation of mechanical properties were prepared by casting the PU dispersions in glass models ( $210 \cdot 80 \cdot 5 \text{ mm}$ ). They were first air dried for 24 h and then dried in a vented oven at  $90^\circ\text{C}$  for 48 h.

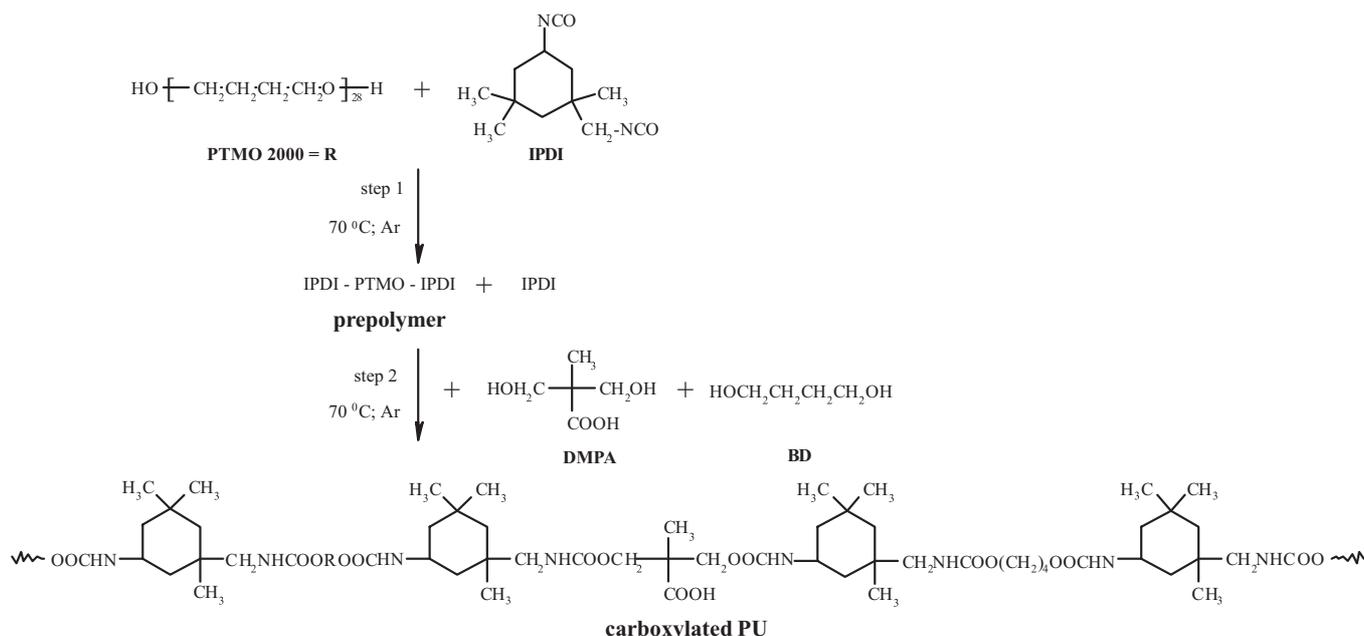
### Characterization

Infrared spectra were recorded on a Perkin-Elmer FTIR 1725X spectrophotometer as KBr pellets. The  $^1\text{H}$  (300 MHz) and  $^{13}\text{C}$  (75 MHz) NMR spectra were recorded at  $25^\circ\text{C}$  on a Varian VXR 300 or Unity Plus 300 spectrometer using TMS as the internal standard and  $\text{DMSO}-d_6$  as the solvent. Integrals in the  $^{13}\text{C}$  NMR spectra were obtained by using an inverse gated decoupling mode with a suppressed NOE effect and a relaxation delay of 15 s.

The relative molar mass averages of the synthesized HB PU were determined by size exclusion chromatography with poly(methyl methacrylate) calibration (SEC) using a Perkin Elmer liquid chromatograph with differential refractometer LC-30 as the detector, as well as a Plgel  $5 \mu\text{m}$  Mixed D column and precolumn (Polymer Laboratories Ltd.). The eluent used was  $0.1 \text{ mol L}^{-1}$  LiBr in DMAc with the flow rate of  $0.5 \text{ mL min}^{-1}$ . The absolute molar mass averages were determined by SEC in combination with light scattering (SEC-MALS) at  $25^\circ\text{C}$ . The SEC-MALS measurements were performed using a Hewlett Packard pump series 1100 coupled to a Dawn-DSP laser photometer equipped with an He-Ne laser ( $\lambda_0 = 633 \text{ nm}$ ) and to an Optilab-DSP interferometric refractometer (Wyatt Technology Corp.). Separations were carried out using a PLgel  $5 \mu\text{m}$  Mixed-C column (300 mm length and 7.5 mm ID, Polymer Laboratories, Ltd) with a precolumn in a 0.5 % solution of LiBr (Aldrich) in *N,N*-dimethylacetamide (DMAc, Aldrich) at a flow rate of  $0.9 \text{ mL min}^{-1}$ .

The glass transition temperature ( $T_g$ ) was measured by differential scanning calorimetry (DSC) on a Perkin Elmer DSC-7 and Pyris 1 instruments. Samples of approx. 20 mg were sealed in aluminum pans and measurements were performed with a rate heating:  $20^\circ\text{C min}^{-1}$  in the temperature range between  $-80$  or  $-65^\circ\text{C}$  and  $120^\circ\text{C}$  under a nitrogen atmosphere, rapidly cooled (quenched at a rate cooling  $200^\circ\text{C min}^{-1}$ ), kept at  $-80$  or  $-65^\circ\text{C}$  for 10 min and heated again to  $120^\circ\text{C}$  at  $t = 20^\circ\text{C min}^{-1}$ .  $T_g$  was determined during the second heating cycle; the accuracy of determination was about  $\pm 2^\circ\text{C}$ .

The particle diameter of linear and HB PU, and their blends, was measured on a Microtract FRA9200 instrument



S c h e m e 2 – Schematic representation of the synthetic route to carboxylated linear polyurethane

S h e m a 2 – Shematski prikaz sintetskog puta za karboksilirani linearni poliuretani

in the range between 150 nm and 700  $\mu\text{m}$ , whereas the mechanical properties were recorded on a dynamometer Zwick Materialprüfung 1465, Standard DIN 53 504, shape S2, at a speed of 200  $\text{mm min}^{-1}$ .

## Results and discussion

### Reactivity of Boltorn® H40 with hexamethylene diisocyanate (HDI)

The reaction system of a multifunctional HB polyester with a large number of  $-\text{OH}$  functional groups and a diisocyanate with two  $-\text{NCO}$  groups should lead to gelation even at a low conversion. Therefore, we first followed the reaction between Boltorn® H40 and HDI with different mole ratios between the  $-\text{NCO}$  and  $-\text{OH}$  groups (from 1:2 up to 1:16) to determine the critical  $r_{\text{NCO/OH}}$  ratio below which gelation does not occur (Table 1). The polymerization was followed

by FTIR spectroscopy, and the structure of the products was confirmed by NMR spectroscopy.

The average functionality ( $f_{\text{avg}}$ ) was calculated according to Eq. 1:<sup>28</sup>

$$f_{\text{avg}} = \frac{2N_A f_A}{N_A + N_B} \quad (1)$$

where  $N_A$  is the number of molecules which are not in excess (HDI),  $f_A$  is the functionality of HDI (molecule A), and  $N_B$  is the number of molecules which are in excess (Boltorn® H40).

The extent of reaction at the gel formation ( $p_{\text{NCO,crit}}$ ) was calculated using Eq. 2:<sup>28</sup>

$$p_{\text{NCO,crit}} = \frac{1}{\sqrt{r(f-1)}} \quad (2)$$

T a b l e 1 – Experimental parameters, relative molar mass averages, polydispersity index (PDI), and the glass transition temperature ( $T_g$ ) of model HB PU

T a b l i c a 1 – Eksperimentalni parametri, relativni prosjeci molnih masa, indeks polidisperznosti (PDI) i temperatura staklastoga prijelaza ( $T_g$ ) modelnih HB PU

Sample Uzorak	Ratio Omjer $r_{\text{NCO/OH}}$	$\Lambda$ , L	$t_{\text{react}}$ at/pri 60 °C (h)	$p_{\text{NCO,crit}}^2$	$\frac{L \cdot 10^{-3} \cdot \bar{M}_w}{\text{g mol}^{-1}}$	$\frac{10^{-3} \cdot \bar{M}_n}{\text{g mol}^{-1}}$	PDI	$T_g$ °C
H40/2	1:2	3.43	1 (gel)	0.30	–	–	–	–
H40/4	1:4	3.00	1 (gel)	0.42	–	–	–	–
H40/8	1:8	2.40	46*	0.59	436	43	10.1	17.6
H40/16	1:16	1.72	45*	0.84	46	27	1.7	32.0

\* time when NCO band at 2276  $\text{cm}^{-1}$  disappeared/vrijeme, kad nestane NCO trak kod 2276  $\text{cm}^{-1}$

<sup>1</sup> calculated according to Eq. 1<sup>28</sup> / izračunato po jednadžbi 1<sup>28</sup>

<sup>2</sup> calculated according to Eq. 2<sup>28</sup> / izračunato po jednadžbi 2<sup>28</sup>

where  $r$  is the mole ratio of  $-NCO$  and  $-OH$  groups and is less than 1, and  $f$  is the functionality of the branch unit (22.4), i. e. the number of  $-OH$  groups per mol of Boltorn® H40.

As can be seen from Table 1, the gel formed before completion of the reaction at ratios 1:2 and 1:4. Therefore, further experiments were performed with the mole ratio  $r_{NCO/OH} = 1:8$ . Overall reaction time was approximately 45 h at 60 °C, which was longer than expected, and possibly due to the high amount of less reactive hydroxyl groups especially in linear repeat units.<sup>24</sup> The molar mass as well as polydispersity index (PDI,  $M_w/M_n$ ) were higher at  $r_{NCO/OH}$  ratio 1:8 with  $f_{avg} = 2.40$  than at mole ratio  $r_{NCO/OH} = 1:16$  with  $f_{avg} = 1.72$  leading to a lower degree of polymerization. The molar mass distribution at ratio  $r_{NCO/OH} = 1:8$  was multimodal with three peaks at relative molar masses 1.080,000, 116,000, and 42,000 g mol<sup>-1</sup>, whereas the glass transition temperature was lower than at  $r_{NCO/OH}$  1:16 ratio, presumably due to the higher amount of flexible oligomethylene chains of incorporated HDI (Table 1).

### Synthesis and characterization of carboxylated hyperbranched and linear polyurethanes

The synthesis of carboxylated HB PU using the poly(bis-MPA) macrodiol was performed with the mole ratio  $r_{NCO/OH} = 1:8$  and hexamethylene or isophorone diisocyanate. We tested various synthetic routes:<sup>29</sup> (i) reaction of the prepolymer of HDI and bis-MPA and Boltorn® H40; (ii) one-step synthesis (prepolymer of HDI and Boltorn® H40 reacted with *cis*-1,2-cyclohexanedicarboxylic anhydride to introduce  $-COOH$  groups into the PU backbone; the residual  $-OH$  groups were esterified by acetic anhydride) and (iii) two-step synthesis: we first synthesized a partly esterified poly(bis-MPA)<sup>30</sup>, which then reacted with HDI or IPDI; residual unreacted  $-OH$  groups were esterified by CH anhydride. The first route was not applied since the reaction time was too long due to a very low reaction rate between the carboxylated prepolymer and Boltorn® H40. The second route resulted in high molar mass products ( $M_n = 107,000$  g mol<sup>-1</sup>), however, there was a problem with reproducibility due to poor control of the reaction leading to gelation in some cases.

The third route allows better control over the course of polymerization. Namely, the functionality, i.e. number of  $-OH$  groups, is lowered by reacting some of the  $-OH$  groups of Boltorn® H40 with BuCl. The number of remaining free  $-OH$  groups, needed for the second step of the synthesis, was calculated by <sup>1</sup>H NMR spectroscopy recorded under quantitative experimental conditions (Fig. 1, see Experimental). From the ratio of the integrals of  $-OH$  groups at 4.6 and 4.9 · 10<sup>-6</sup> and  $-CH_3$  groups at 1.0 – 1.2 · 10<sup>-6</sup><sup>24</sup> for Boltorn® H40 and partly esterified Boltorn® H40, the number of  $-OH$  groups in partly esterified Boltorn® H40 was 2.47 mmol g<sup>-1</sup>.

The characteristics of the two HB PU based on HDI and IPDI are listed in Table 2. The molar masses as well as the polydispersity index of HB PU-HDI are higher than of those of HB PU-IPDI. The broad molar mass distribution (Fig. 2) indicates non-uniform sequences of repeat units possibly

originating from a non-uniform esterification of Boltorn® H40. The flexible oligomethylene units of HDI lower the  $T_g$  of HB PU-HDI as compared to HB PU-IPDI with its more rigid cycloaliphatic IPDI unit.

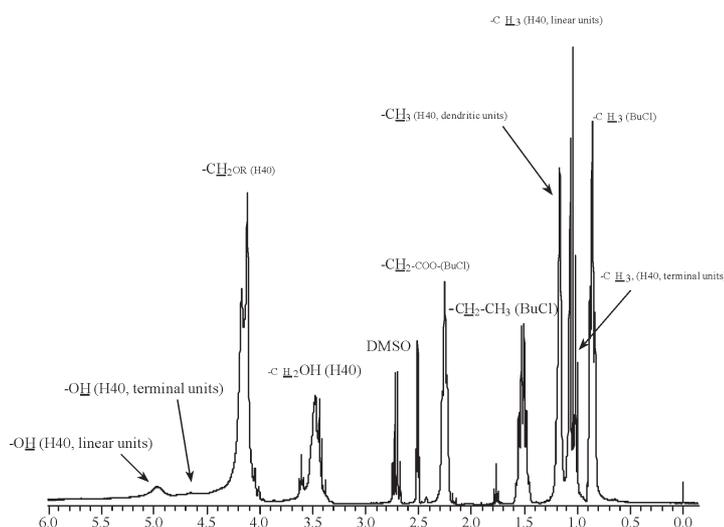


Fig. 1 – <sup>1</sup>H NMR spectrum of Boltorn® H40 partially esterified with butyryl chloride

Slika 1 – Spektar <sup>1</sup>H NMR uzorka Boltorn® H40, djelimično esterificiranoga butiril-kloridom

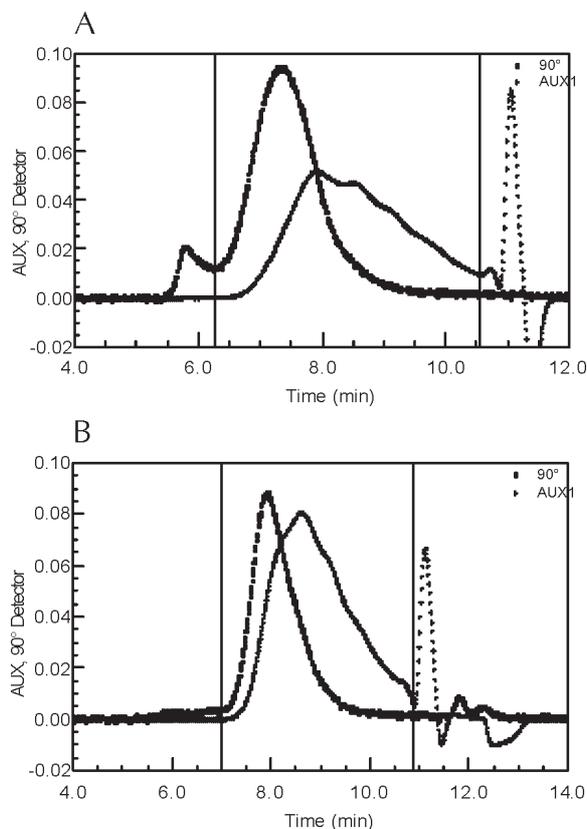


Fig. 2 – 90° LS and RI curves of a) HB PU-HDI with hexamethylene diisocyanate and b) HB PU-IPDI with isophorone diisocyanate

Slika 2 – 90° LS i RI krivulje a) HB PU-HDI s heksametilen-diizocijantom i b) HB PU-IPDI s izoforon-diizocijantom

Table 2 – Absolute molar mass averages, polydispersity index, and the glass transition temperature of carboxylated hyperbranched and linear polyurethanes

Tablica 2 – Apsolutni prosjeci molnih masa, indeks polidispersnosti i temperatura staklastoga prijelaza ( $T_g$ ) karboksiliranih visokorazgranatih i linearnih poliuretana

Sample Uzorak	$10^{-3} \cdot M_w$ g mol <sup>-1</sup>	$10^{-3} \cdot M_n$ g mol <sup>-1</sup>	PDI	$T_g$ °C
HB PU-HDI	109	26	4.2	-19.1
HB PU-IPDI	38	14.2	2.7	-14.8
Linear PU	17.2	8.6	2.0	29.8

<sup>1</sup>H NMR spectra confirm that there are no residual –OH groups in both HB PU. The signals of terminal and linear –OH groups at 4.6 and 4.9 · 10<sup>-6</sup> are not present on the <sup>1</sup>H NMR spectrum of HB PU-HDI (Figure 3). There are new signals for H atoms belonging to the urethane –NHCOO– group (at 7.1 · 10<sup>-6</sup>), the ~C–CH<sub>2</sub>–O–R– group (esterified hydroxyl groups of HB polyester at 3.8 – 4.4 · 10<sup>-6</sup>), the –CH<sub>2</sub>–NHCOO– group (at 2.9 · 10<sup>-6</sup>), and to the –CH<sub>2</sub>– groups of HDI (at 1.4 · 10<sup>-6</sup>). The signals at 1.67, 1.83 and 2.7 · 10<sup>-6</sup> belong to the H atoms of *cis*-1,2-cyclohexanedi-carboxylic anhydride.

The molar mass averages and polydispersity index of linear PU are lower than those of HB PU, however the glass transition of linear PU is broader and its  $T_g$  much higher due to a high content of hard segments.

### Dispersions and films of synthesized carboxylated polyurethanes

Stable (for up to two months)  $w = 20 - 25$  % dispersions of two-step HB-PU, linear PU and mixtures of linear and HB PU-HDI were prepared using the conventional procedure of dispersing the polyurethanes in water after neutralization of –COOH groups by triethylamine. The particle diameter ( $d_{50}$ ) of linear PU was below 0.15 μm, whereas the  $d_{50}$  of the two-step HB-PU and their mixtures with linear PU was about 1 μm.

The films of linear PU and all the HB PU were transparent, whereas the films of the mixtures of linear and HB PU were

Table 3 – The glass transition temperature ( $T_g$ ) and mechanical properties of linear PU and of its blends with hyperbranched PU: tensile strength, Young's modulus, and elongation at break

Tablica 3 – Temperatura staklastoga prijelaza ( $T_g$ ) i mehanička svojstva linearnoga PU i njegovih smjesa s HB PU: natezna tvrdoća, Youngov modul i produljenje kod trganja

Composition of PU samples Sastav uzoraka PU	$T_g$ °C	Tensile strength Vučna tvrdoća	Elongation at break Produljenje do loma	Young's elasticity Youngov modul elastičnosti
		τMPa	ε%	(MPa)
Linear PU	29.8	30.5 ± 0.5	890 ± 9	320 ± 11
HB PU-HDI: linear PU = 1:3	21.2	13.6 ± 1.8	709 ± 29	145 ± 12
HB PU-HDI: linear PU = 1:1	-14.8 26.6	14.1 ± 1.0	902 ± 27	105 ± 18
HB PU-HDI: linear PU = 3:1	-6.5	*	*	*
HB PU-HDI	-19.1	*	*	*

\* not measured, films were brittle / zbog krhkosti filmova mjerenja nisu bila moguća

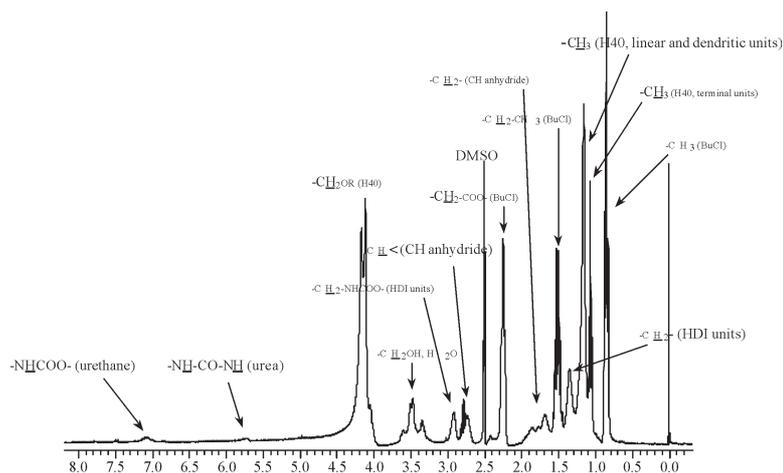


Fig. 3 – <sup>1</sup>H NMR spectrum of carboxylated polyurethane based on poly(bis-MPA) macrodiol and hexamethylene diisocyanate

Slika 3 – Spektar <sup>1</sup>H NMR karboksiliranoga poliuretana na osnovi poli(bis-MPA)-makrodiola i heksametilen-diizocijana

opaque. We observed only one  $T_g$  for blends with one component in excess, while there were two  $T_g$  in the 50:50 blend and these were shifted to lower and higher values in comparison to pure linear and HB PU-HDI, respectively (Table 3). The shifts in  $T_g$  confirm the existence of interactions between the two PU that are characteristic of partly miscible blends.<sup>31</sup>

Mechanical properties were only determined for films of linear PU and its blends with less than 50 % HB PU, because the films of HB PU and mixtures with 50 % or higher amount of HB PU were so brittle that specimens could not be prepared. The mechanical properties depend on the composition of the films: tensile strength and Young's modulus decrease with increasing amount of HB PU-HDI, while elongation practically does not change. Worsening of mechanical properties with increasing amount of HB PU-HDI is likely related to differences in morphology. Namely, hyperbranched species with tree-like structures prevent denser chain packing, resulting in increased free volume and mobility of chain segments and lowered  $T_g$  of the samples.

## Conclusions

In the present work we investigated the reaction of the hyperbranched (HB) polyester based on 2,2-bis(methylol)propionic acid of the fourth pseudo-generation (Boltorn® H40) and hexamethylene diisocyanate in DMF solution. The reaction rate at 60 °C was quite low; however, a gel was formed when the molar ratio between the hydroxyl and isocyanate groups was equal to 2 or 4. With increasing molar ratio the average functionality of the reaction system decreased and consequently the molar mass averages and polydispersity index of polyurethanes also decreased.

Carboxylated hyperbranched polyurethanes (HB PU) were synthesized in a two-step procedure to make control of the course of the reaction easier: in the first step, the HB polyester was partly esterified with butyryl chloride, and in the second step, a partly esterified HB polyester with lowered hydroxyl functionality was reacted with hexamethylene or isophorone diisocyanate. Carboxylic groups were incorporated into the HB PU backbone by reaction of residual hydroxyl groups with *cis*-1,2-cyclohexanedicarboxylic anhydride. Stable aqueous dispersions were prepared from the synthesized HB PU giving transparent but brittle films. Therefore, HB PU were blended with linear carboxylated PU in various ratios and the resulting films were tested for their mechanical properties. The tensile strength and Young's modulus of blends decreased with increasing content of HB PU, whereas elongation at break was practically unchanged, which was ascribed to looser chain packing due to more open tree-like hyperbranched structures.

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## Abbreviations

### Kratice

bis-MPA	– 2,2-bis(methylol)propionic acid
BD	– 1,4-butanediol
BuCl	– butyryl chloride
CH anhydride	– <i>cis</i> -1,2-cyclohexanedicarboxylic anhydride
DBTDL	– dibutyl tin dilaurate
DMAc	– <i>N,N</i> -dimethylacetamide
DMF	– <i>N,N</i> -dimethylformamide
DMSO- <i>d</i> <sub>6</sub>	– deuterated <i>N,N</i> -dimethylsulfoxide
DSC	– differential scanning calorimetry
FTIR	– Fourier-transform infrared (spectroscopy)
HB	– hyperbranched
HDI	– hexamethylene diisocyanate
IPDI	– isophorone diisocyanate
LPU	– linear PU
NMR	– nuclear magnetic resonance
PDI	– polydispersity index
PTMO	– polytetramethylene oxide
PU	– polyurethane(s)
SEC	– size exclusion chromatography

SEC-MALS – size exclusion chromatography coupled to multiangle light scattering  
 TEA – triethylamine  
 THF – tetrahydrofuran

### List of symbols Popis simbola

$AB_2$  monomer – monomer with functionalities A and B  
 $B_f$  monomer – monomer with functionality B  
 $d_p$  – particle diameter, nm,  $\mu\text{m}$   
 $f_{\text{avg}}$  – average functionality  
 $f_A$  – number of functional groups of HDI (molecule A)

$f$  – functionality of the branch unit  
 $\overline{M}_w$  – mass average molar mass,  $\text{g mol}^{-1}$   
 $\overline{M}_n$  – number-average molar mass,  $\text{g mol}^{-1}$   
 $N_A$  – number of molecules which are not in excess  
 $N_B$  – number of molecules in excess  
 $n$  – amount of substance, mol  
 $p_{\text{NCO,crit}}$  – extent of reaction at the gel formation  
 $r$  – mole ratio  $n_{\text{NCO}}/n_{\text{OH}}$   
 $T_g$  – glass transition temperature,  $^{\circ}\text{C}$   
 $t$  – rate of temperature change,  $^{\circ}\text{C min}^{-1}$   
 $t_{\text{reac}}$  – reaction time, h  
 $\tau$  – tensile strength, MPa  
 $\varepsilon$  – elongation at break, %

### SAŽETAK

#### Karboksilirani poliuretani s visoko razgranatim poliesterskim mekanim segmentima

G. Prevec, E. Žagar i M. Žigon

Rad prikazuje sintezu i karakterizaciju poliuretana s mekanim segmentima od visoko razgranatoga poliestera (HB PU) s funkcionalnim karboksilnim skupinama s namjenom pripreme stabilnih disperzija HB PU. Za sintezu karboksiliranih HB PU upotrijebili smo visoko razgranati poliestri na osnovi 2,2-bis(metilol)propionske kiseline četvrte pseudo-generacije (Boltorn® H40) i heksametilen-diiizocijanata (HDI) ili izoforon-diiizocijanata (IPDI). Reaktivnost visoko razgranatog poliestra s HDI-om bila je niža od očekivane, vjerojatno zbog postojećih manje reaktivnih hidroksilnih skupina u linearnim jedinicama. Reakcijske smjese gelirale su kod množinskog omjera  $r_{\text{NCO/OH}} = 1:2$  i  $1:4$ . HB PU sintetizirali smo iz djelimično preostalog visoko razgranatoga poliestera s nižom –OH funkcionalnosti. Karboksilne skupine smo u lanac HB PU uveli s esterifikacijom neizreagiranih hidroksilnih skupina s anhidridom *cis*-1,2-cikloheksandikarboksilne kiseline. Vodene disperzije HB PU bile su stabilne najmanje dva mjeseca, filmovi su bili krhki. Ispitivanja na vučnu čvrstoću i na Youngov modul elastičnosti su pokazali da su se iznosi kod smjese linearnoga i HB PU s povećavajućim udjelom HB PU se smanjivali, dok je naprezanje na rastezanje do loma ostalo nepromijenjeno, što smo objasnili s manje gustim slaganjem lanaca zbog više otvorenih drvenastih visoko razgranatih struktura.

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