

## 研究简报

# Synthesis and properties of segmented polyurethane elastomers with molecularly uniform hard segments based on 1,5-naphthalene diisocyanate and 1,4-butanediol

Gunter Festel

Festel Capital-Innovations in Chemicals, Schuermattstrasse 1, CH-6331 Huenenberg

**Summary**: Segmented polyurethane (PUR) elastomers with different soft segments (polyether, polyester, polysiloxane) and molecularly uniform hard segments, based on 1,5-naphthalene diisocyanate (NDI) and 1,4-butanediol (BDO), were synthesized. They served as model elastomers for detailed investigations of the structure-properties relations of the hard segment phase of technologically relevant NDI based elastomers. The amount of microphase separation and with that the melting points and heats of fusion rose with increasing hard segment length and decreasing strength of the hydrogen bonds between the urethane NH groups and the soft segment O atoms in the order polyester, polyether and polysiloxane. Multipeak behaviour at the melting of the hard segments indicated the formation of semi-crystalline NDI/BDO hard domain regions, which transformed into better ordered crystalline domains on annealing. At temperatures above 180°C, decomposition reactions of the NDI/BDO hard segments were initiated by breaking the hydrogen bonds. This process began in the badly ordered areas of the semi-crystalline hard segment domains. Rapid decomposition occurred at temperatures above 250°C. The dynamic mechanical behaviour of the NDI based polyether elastomers showed a higher hard domain stability than elastomers based on other diisocyanates. They showed also in the service temperature range the highest storage modulus value  $G'$  over the broadest temperature range. This indicated a higher and less temperature dependent stiffness as well as a stronger effect as an active filler of the NDI/BDO hard segments.

**Key words**: Polyurethane elastomers; Naphthalene diisocyanate; Segmented polyurethanes; Monodisperse hard segments; Structure property relationships

## Introduction

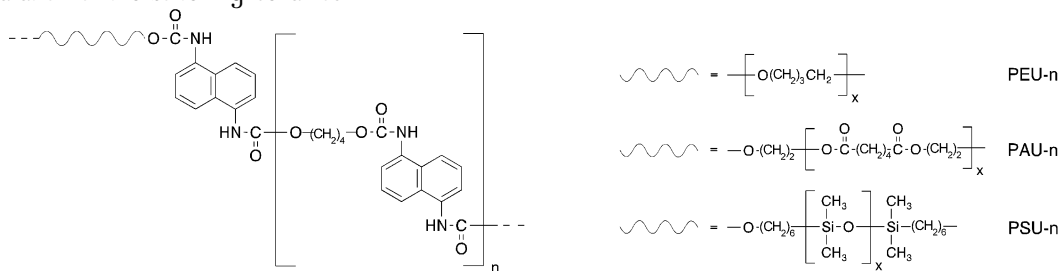
With the discovery and the development of the polyurethane (PUR) chemistry by Otto Bayer about 50 years ago<sup>[1]</sup>, the segmented PUR elastomers, as a new class of elastomeric materials, was accessible. These types of elastomers are multiblock copolymers  $(H-S)_n$  consisting of alternating sequences of urethane hard segments H and polyester or polyether soft segments S. Due to the segmental incompatibility of the 2 components, the hard segments are segregated into amorphous, crystalline and/or semi-crystalline domains, respectively, which act as multifunctional and thermoreversible crosslinks in the more or less liquid soft segment matrix, so that such materials show distinct elastic properties. The morphology, especially the extent of microphase separation between hard and soft segments as well as size, shape and ordering of the hard segment domains, has an immense influence on the physical and mechanical properties of these polymeric materials<sup>[2~5]</sup>.

Linear segmented PUR elastomers belong to the group of thermoplastic elastomers, because the single polymer chains are not covalently crosslinked and show exclusively physical interactions. The polymers exhibit a characteristic temperature dependent morphology, i.e. in contrast to vulcanized rubbers, they behave like

the melt of thermoplastic polymers at a temperature rise above the softening point of the hard segment domains, i.e. they are easily deformable. After cooling, the hard segments crystallize again and form new physical crosslinking sites. The thermoplastic properties are of great technological interest, because they combine a large variety of elastomeric applications with an easy processibility. Therefore, segmented PUR elastomers are considered to be premium grade elastomers. While polyester based elastomers have an excellent tensile strength, load-bearing capacity and resistance to abrasion, ozone, oxygen, fuel, oil and solvents, polyether based elastomers, on the other hand, provide excellent low temperature properties and resistance to hydrolytic attack.

Segmented PUR elastomers with 1,5-naphthalene diisocyanate (NDI) as hard segment compound and polyadipate diols as soft segment building units are known for their high performance and long service life in particularly demanding dynamic applications<sup>[6~8]</sup>. Systems with 1,4-butanediol (BDO) as chain extender give solid NDI elastomers, and chain extension with water results in microcellular materials. Technologically relevant PUR elastomers are mostly synthesized in a 2-step process, whereby the reaction of a polyester or polyether polyol with an excess of diisocyanate gives an isocyanate terminated prepolymer, which is chain extended with a short-chain diol. The polymers prepared with this method, show a broad hard segment length distribution and are often partially chemically crosslinked due to an excess of diisocyanate employed in the elastomer synthesis. Therefore, they are not suited for a detailed structure-properties analysis. In contrast, the synthesis of polymers with well-defined, molecularly uniform hard segments as model compounds facilitates the investigation of such materials. The interpretation of the obtained results can be done without consideration of polydispersity effects in the hard segment length distribution and may lead to a better understanding of the relations between morphology and properties.

The synthesis and properties of molecularly uniform oligourethane model compounds based on NDI and BDO with methyl urethane end groups DMU-*n* (*n*=number of NDI/BDO repeating units) and 4-methoxybutyl urethane end groups DMBU-*n* for technologically relevant NDI based elastomers has been given in a previous paper<sup>[9]</sup>. Based on that work, in this paper the synthesis and characterization of PUR elastomers with molecularly uniform NDI/BDO hard segments are described. Employing a 2000 mol. wt. polyoxytetramethylene (POTM) polyol, polyether based elastomers PEU-*n* were obtained; a 2000 mol. wt. polyethyleneadipate (PEA) gave polyester elastomers PAU-*n*, and a 2310 mol. wt. polydimethylsiloxane (PDMS) polysiloxane elastomers PSU-*n*. The primary objective is to illustrate the relations between the unusual properties of NDI based elastomers and the structural peculiarity due to the employment of NDI as diisocyanate compound. The different soft segments were chosen to obtain a wide range of properties of the synthesized PUR elastomers and to investigate the influence of the soft segment type on the material properties, i.e. the amount of microphase separation or the softening behaviour.



The results from the thermal, spectroscopical and mechanical measurements were discussed in comparison to corresponding polyether elastomers with molecularly uniform hard segments based on 4,4'-diphenylmethane diisocyanate (MDI) and trans, trans-4,4'-dicyclohexylmethane diisocyanate (tHMDI) with a comparable 2000 mol. wt. POTM polyol. Mainly the MDI based PUR elastomers have been the cause for a great deal of techno-

logical and scientific interest<sup>[10~13]</sup>.

## Experimental part

### Synthesis

Unless stated otherwise, all reagents were obtained from Fluka and used without any further purification. Phosgene (grade 2.0) was delivered by Messer-Griessheim. The synthesis and experimental data of the compounds **2**, **5**, **8** and **9** will be given in another paper<sup>[15]</sup>.

In the presentation of the experimental data POTM is used as an abbreviation for the oxypoly (oxytetramethylene) unit, PEA for the  $\alpha$ -oxy- $\omega$ -oxyethylenepoly (ethyleneadipate) unit and PDMS for the  $\alpha$ -oxyhexamethylene- $\omega$ -oxyhexamethylene (dimethyl)silicopoly (dimethylsiloxane) unit.

$\alpha$ -Chlorocarbonyl- $\omega$ -chlorocarbonyloxypoly (oxytetramethylene) (**1a**). 56 g (27.9 mmol) of a 2000 mol. wt. freeze-dried  $\alpha$ -hydro- $\omega$ -hydroxypoly (oxytetramethylene) (Desmophen 2000, Bayer) were dissolved in 200 mL of  $\text{CHCl}_3$  and reacted with a tenfold excess of phosgene. After removing the excess phosgene, the product was freeze-dried and used without further purification. 55.8 g (26.2 mmol) of **1a** were obtained. Yield: 94%. IR (film):  $1770\text{ cm}^{-1}$  ( $\text{C}=\text{O}$ ).  $^1\text{H-NMR}$  ( $\delta$ ,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ): 1.63 (m,  $-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-$ ), 1.83 (m,  $-\text{CH}_2-\text{CH}_2-\text{O}-\text{CO}-\text{Cl}$ , 4 H), 3.42 (m,  $-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-$ ), 4.35 (t,  $-\text{CH}_2-\text{O}-\text{CO}-\text{Cl}$ , 4 H).  $^{13}\text{C-NMR}$  ( $\delta$ ,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ): 25.5 ( $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-\text{CO}-\text{Cl}$ ), 25.6 ( $-\text{CH}_2-\text{CH}_2-\text{O}-\text{CO}-\text{Cl}$ ), 26.6 ( $-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-$ ), 69.9 ( $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-\text{CO}-\text{Cl}$ ), 71.0 ( $-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-$ ), 72.2 ( $-\text{CH}_2-\text{O}-\text{CO}-\text{Cl}$ ), 150.6 ( $-\text{O}-\text{CO}-\text{Cl}$ ).

$\alpha$ -(Chlorocarbonyloxy- $\omega$ -chlorocarbonyloxyethylenepoly (ethyleneadipate) (**1b**). 56 g (27.9 mmol) of a 2000 mol. wt. freeze-dried  $\alpha$ -hydroxy- $\omega$ -hydroxyethylenepoly (ethyleneadipate) (Polymeg 2000, BASF) were reacted as described for compound **1a**. 54.8 g (25.7 mmol) of **1b** were obtained. Yield: 92%. IR (film):  $1778\text{ cm}^{-1}$  ( $\text{C}=\text{O}$ , chloroformate);  $1739\text{ cm}^{-1}$  ( $\text{C}=\text{O}$ , ester).  $^1\text{H-NMR}$  ( $\delta$ ,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ): 1.66 (m,  $-\text{CO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CO}-$ ), 2.35 (t,  $-\text{CO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CO}-$ ), 4.22 (t,  $-\text{CH}_2-\text{CH}_2-\text{O}-\text{CO}-\text{Cl}$ , 4 H), 4.26 (s,  $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$ ), 4.50 (t,  $-\text{CH}_2-\text{O}-\text{CO}-\text{Cl}$ , 4 H).  $^{13}\text{C-NMR}$  ( $\delta$ ,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ): 23.9 ( $-\text{CO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CO}-$ ), 33.3 ( $-\text{CO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CO}-$ ), 60.8 ( $-\text{CH}_2-\text{CH}_2-\text{O}-\text{CO}-\text{Cl}$ ), 61.8 ( $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$ ), 68.9 ( $-\text{CH}_2-\text{O}-\text{CO}-\text{Cl}$ ), 150.4 ( $-\text{O}-\text{CO}-\text{Cl}$ ), 172.6 ( $-\text{CH}_2-\text{O}-\text{CO}-\text{CH}_2-$ ).

$\alpha$ -(Chlorocarbonyloxyhexamethylene- $\omega$ -chlorocarbonyloxyhexamethylene (dimethyl) silicopoly (dimethylsiloxane) (**1c**). 50 g (21.7 mmol) of a 2310 mol. wt.  $\alpha$ -hydroxyhexamethylene- $\omega$ -hydroxyhexamethylene (dimethyl)silicopoly (dimethylsiloxane) (Tegomer H-Si 2311, Goldschmidt) were reacted as described for compound **1a**. 50.9 g (20.9 mmol) of **1c** were obtained. Yield: 97%. IR (film):  $1771\text{ cm}^{-1}$  ( $\text{C}=\text{O}$ ).  $^1\text{H-NMR}$  ( $\delta$ ,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ): 0.09 (m,  $-\text{O}-\text{Si}(\text{CH}_3)_2-\text{O}-$ ), 0.16 (m,  $-\text{CH}_2-\text{Si}(\text{CH}_3)_2-\text{O}-$ , 12 H), 0.55 (t,  $-\text{CH}_2-\text{Si}(\text{CH}_3)_2-\text{O}-$ , 4 H), 1.37 (m,  $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Si}(\text{CH}_3)_2-\text{O}-$ , 12 H), 1.73 (m,  $-\text{CH}_2-\text{CH}_2-\text{O}-\text{CO}-\text{Cl}$ , 4 H), 4.32 (t,  $-\text{CH}_2-\text{O}-\text{CO}-\text{Cl}$ , 4 H).  $^{13}\text{C-NMR}$  ( $\delta$ ,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ): 1.4 ( $-\text{O}-\text{Si}(\text{CH}_3)_2-\text{O}-$ ), 1.9 ( $-\text{CH}_2-\text{Si}(\text{CH}_3)_2-\text{O}-$ ), 18.8 ( $-\text{CH}_2-\text{Si}(\text{CH}_3)_2-\text{O}-$ ), 23.9 ( $-\text{CH}_2-\text{CH}_2-\text{Si}(\text{CH}_3)_2-\text{O}-$ ), 26.0 ( $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Si}(\text{CH}_3)_2-\text{O}-$ ), 29.3 ( $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-\text{CO}-\text{Cl}$ ), 33.8 ( $-\text{CH}_2-\text{CH}_2-\text{O}-\text{CO}-\text{Cl}$ ), 72.3 ( $-\text{CH}_2-\text{O}-\text{CO}-\text{Cl}$ ), 150.6 ( $-\text{O}-\text{CO}-\text{Cl}$ ).

POTM bis(carbonyl- $N$ ,  $N'$ -1,5-naphthalene diamine benzyl carboxylate) (**3a**). 8 g (3.75 mmol) of **1a** were dissolved in 50 ml of THF and added dropwise to a solution of 2.4 g (8.22 mmol) of **2** in 300 ml of THF and 1 mL (12.5 mmol) of pyridine. After reprecipitation, 9.2 g (3.48 mmol) of **3a** were obtained. Yield: 93%. IR (film):  $3276\text{ cm}^{-1}$  ( $\text{N}-\text{H}$ );  $1693\text{ cm}^{-1}$  ( $\text{C}=\text{O}$ ).  $^1\text{H-NMR}$  ( $\delta$ ,  $\text{d}_8\text{-THF}$ ,  $25^\circ\text{C}$ ): 1.58 (m,  $-\text{O}-\text{CH}_2-$

CH<sub>2</sub>—), 1.82 (m, —NH—CO—O—CH<sub>2</sub>—CH<sub>2</sub>—, 4 H), 3.36 (m, —O—CH<sub>2</sub>—), 4.17 (t; —NH—CO—O—CH<sub>2</sub>—, 4 H), 5.18 (s, —NH—CO—O—CH<sub>2</sub>—C—, 4 H), 7.36—7.53 (m, 14 H); 7.60 (d, 4 H), 7.90 (d, 4 H), 8.62 (s, —NH—CO—O—CH<sub>2</sub>—CH<sub>2</sub>—, 2 H), 8.77 (s, —NH—CO—O—CH<sub>2</sub>—C—, 2 H). <sup>13</sup>C-NMR (δ, d<sub>8</sub>-THF, 25°C): 27.1 (—NH—CO—O—CH<sub>2</sub>—CH<sub>2</sub>—), 27.3 (—NH—CO—O—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—), 27.6 (—O—CH<sub>2</sub>—CH<sub>2</sub>—), 65.4 (—NH—CO—O—CH<sub>2</sub>—), 67.0 (—NH—CO—O—CH<sub>2</sub>—C—), 71.0 (—NH—CO—O—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—), 71.3 (—O—CH<sub>2</sub>—), 118.5, 118.7, 119.9, 125.9, 126.0, 128.9, 129.0, 129.1, 135.3, 135.5, 138.1, 155.1 (—NH—CO—O—CH<sub>2</sub>—C—), 155.2 (—NH—CO—O—CH<sub>2</sub>—CH<sub>2</sub>—).

PEA bis(carbonyl-*N*, *N'*-1,5-naphthalene diamine benzyl carboxylate) (**3b**). 8 g (3.75 mmol) of **1b** were reacted with 2.4 g (8.22 mmol) of **2** as described for compound **3a**. After reprecipitation, 9.2 g (3.48 mmol) of **3b** were obtained. Yield: 93%. IR (film): 3346 (N—H), 1737 cm<sup>-1</sup> (C=O). <sup>1</sup>H-NMR (δ, d<sub>8</sub>-THF, 25°C): 1.62 (m, —CO—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—CO—), 2.31 (m, —CO—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—CO—), 4.22 (s, —O—CH<sub>2</sub>—CH<sub>2</sub>—O—), 4.25 (t, —NH—CO—O—CH<sub>2</sub>—CH<sub>2</sub>—), 4.32 (t, —NH—CO—O—CH<sub>2</sub>—), 5.18 (s, —NH—CO—O—CH<sub>2</sub>—C—, 4 H), 7.37—7.54 (m, 14 H), 7.61 (d, 4 H), 7.91 (d, 4 H), 8.64 (s, —NH—CO—O—CH<sub>2</sub>—CH<sub>2</sub>—, 2 H), 8.79 (s, —NH—CO—O—CH<sub>2</sub>—C—, 2 H). <sup>13</sup>C-NMR (δ, d<sub>8</sub>-THF, 25°C): 25.1 (—CO—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—CO—), 34.2 (—CO—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—CO—), 61.0 (—NH—CO—O—CH<sub>2</sub>—CH<sub>2</sub>—), 62.9 (—O—CH<sub>2</sub>—CH<sub>2</sub>—O—), 64.8 (—NH—CO—O—CH<sub>2</sub>—), 66.9 (—NH—CO—O—CH<sub>2</sub>—C—), 118.8, 120.0, 120.3, 126.1, 126.6, 128.7, 129.0, 129.2, 135.2, 135.3, 138.1, 155.0 (—NH—CO—O—CH<sub>2</sub>—C—), 155.1 (—NH—CO—O—CH<sub>2</sub>—CH<sub>2</sub>—), 173.1 (—CO—CH<sub>2</sub>—CH<sub>2</sub>—).

PDMS bis(carbonyl-*N*, *N'*-1,5-naphthalene diamine benzyl carboxylate) (**3c**). 8 g (3.29 mmol) of **1c** were reacted with 2.1 g (87.19 mmol) of **2** as described for compound **3a**. After reprecipitation, 8.6 g (2.92 mmol) of **3c** were obtained. Yield: 89%. 9.2 g (3.48 mmol) of **3c** were obtained. Yield: 93%. IR (film): 3278 (N—H), 1695 cm<sup>-1</sup> (C=O). <sup>1</sup>H-NMR (δ, d<sub>8</sub>-THF, 25°C): 0.01 (m, —O—Si (CH<sub>3</sub>)<sub>2</sub>—O—), 0.10 (m, —CH<sub>2</sub>—Si (CH<sub>3</sub>)<sub>2</sub>—O—, 12 H), 0.48 (t, —CH<sub>2</sub>—Si (CH<sub>3</sub>)<sub>2</sub>—O—, 4 H), 1.27 (m, —CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—Si (CH<sub>3</sub>)<sub>2</sub>—O—, 12 H), 1.63 (m, —NH—CO—O—CH<sub>2</sub>—CH<sub>2</sub>—, 4 H), 4.15 (t, —NH—CO—O—CH<sub>2</sub>—, 4 H), 5.19 (s, —NH—CO—O—CH<sub>2</sub>—C—, 4 H), 7.39—7.56 (m, 14 H), 7.63 (d, 4 H), 7.93 (d, 4 H), 8.60 (s, —NH—CO—O—CH<sub>2</sub>—CH<sub>2</sub>—, 2 H), 8.75 (s, —NH—CO—O—CH<sub>2</sub>—C—, 2 H). <sup>13</sup>C-NMR (δ, d<sub>8</sub>-THF, 25°C): 1.4 (—O—Si (CH<sub>3</sub>)<sub>2</sub>—O—), 2.0 (—CH<sub>2</sub>—Si (CH<sub>3</sub>)<sub>2</sub>—O—), 19.0 (—CH<sub>2</sub>—Si (CH<sub>3</sub>)<sub>2</sub>—O—), 24.1 (—CH<sub>2</sub>—CH<sub>2</sub>—Si (CH<sub>3</sub>)<sub>2</sub>—O—), 26.6 (—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—Si (CH<sub>3</sub>)<sub>2</sub>—O—), 30.1 (—NH—CO—O—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—), 34.1 (—NH—CO—O—CH<sub>2</sub>—CH<sub>2</sub>—), 65.5 (—NH—CO—O—CH<sub>2</sub>—), 67.2 (—NH—CO—O—CH<sub>2</sub>—C—), 118.5, 118.7, 119.9, 125.9, 126.0, 128.6, 129.0, 129.1, 135.4, 135.5, 138.1, 155.1 (—NH—CO—O—CH<sub>2</sub>—C—), 155.3 (—NH—CO—O—CH<sub>2</sub>—CH<sub>2</sub>—).

*POTM bis(carbonyl-N, N'-1,5-naphthalene diamine) (4a)*. 8.5 g (3.21 mmol) of **3a** were dissolved in 200 ml of THF. After adding 200 mg of Pd on charcoal (5%), the hydrogenation was carried out for 2 h at a temperature of 50 °C and 5 bar H<sub>2</sub>-pressure. After removing the catalyst by filtration, removing the solvent and reprecipitation, the product was freeze-dried. 7.2 g (3.03 mmol) of **4a** were obtained. Yield: 94%. IR (film): 3474, 3370, 3281 (N-H), 1738 cm<sup>-1</sup> (C=O). <sup>1</sup>H-NMR (δ, d<sub>8</sub>-THF, 25 °C): 1.58 (m, -O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.82 (m, -NH-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-, 4 H), 3.36 (m, -O-CH<sub>2</sub>-), 4.16 (t, -NH-CO-O-CH<sub>2</sub>-, 4 H), 5.65 (s, -NH<sub>2</sub>, 4 H), 6.66 (d, 2 H), 7.17 (t, 2 H), 7.31 (m, 4 H), 7.68 (d, 2 H), 7.82 (d, 2 H), 8.38 (s, -NH-CO-, 2 H). <sup>13</sup>C-NMR (δ, d<sub>8</sub>-THF, 25 °C): 27.1 (-NH-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-), 27.4 (-NH-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 27.4 (-O-CH<sub>2</sub>-CH<sub>2</sub>-), 65.4 (-NH-CO-O-CH<sub>2</sub>-), 71.0 (-NH-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 71.3 (-O-CH<sub>2</sub>-), 109.1, 111.0, 118.3, 119.4, 124.1, 125.0, 126.7, 129.0, 135.1, 145.5 (-C-NH<sub>2</sub>), 155.1 (-NH-CO-).

*PEA bis(carbonyl-N, N'-1,5-naphthalene diamine) (4b)*. 8.5 g (3.21 mmol) of **3b** were reacted as described for compound **4a**. After freeze-drying, 6.7 g (2.82 mmol) of **4b** were obtained. Yield: 88%. IR (film): 3460, 3365, 3263 (N-H), 1735 cm<sup>-1</sup> (C=O). <sup>1</sup>H-NMR (δ, d<sub>8</sub>-THF, 25 °C): 1.62 (m, -CO-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CO-), 2.31 (m, -CO-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CO-), 4.23 (s, -O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 4.26 (t, -NH-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-), 4.33 (t, -NH-CO-O-CH<sub>2</sub>-), 5.64 (s, -NH<sub>2</sub>, 4 H), 6.68 (d, 2 H), 7.18 (t, 2 H), 7.33 (m, 4 H), 7.70 (d, 2 H), 7.83 (d, 2 H), 8.40 (s, -NH-CO-, 2 H). <sup>13</sup>C-NMR (δ, d<sub>8</sub>-THF, 25 °C): 25.1 (-CO-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CO-), 34.2 (-CO-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CO-), 61.0 (-NH-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-), 62.9 (-O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 64.7 (-NH-CO-O-CH<sub>2</sub>-), 109.1, 110.9, 118.5, 119.5, 124.2, 125.1, 126.8, 129.2, 135.1, 145.7 (C-NH<sub>2</sub>), 155.3 (-NH-CO-), 173.3 (-CO-CH<sub>2</sub>-CH<sub>2</sub>-).

*PDMS bis(carbonyl-N, N'-1,5-naphthalene diamine) (4c)*. 8.2 g (2.78 mmol) of **3c** were reacted as described for compound **4a**. After freeze-drying, 6.7 g (2.5 mmol) of **4c** were obtained. Yield: 90%. IR (film): 3458, 3358, 3267 (N-H), 1740 cm<sup>-1</sup> (C=O). <sup>1</sup>H-NMR (δ, d<sub>8</sub>-THF, 25 °C): 0.01 (m, -O-Si (CH<sub>3</sub>)<sub>2</sub>-O-), 0.10 (m, -CH<sub>2</sub>-Si (CH<sub>3</sub>)<sub>2</sub>-O-, 12 H), 0.49 (t, -CH<sub>2</sub>-Si (CH<sub>3</sub>)<sub>2</sub>-O-, 4 H), 1.28 (m, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-Si (CH<sub>3</sub>)<sub>2</sub>-O-, 12 H), 1.64 (m, -CH<sub>2</sub>-CH<sub>2</sub>-O-CO-Cl, 4 H), 4.15 (t, -CH<sub>2</sub>-O-CO-Cl, 4 H), 5.66 (s, -NH<sub>2</sub>, 4 H), 6.65 (d, 2 H), 7.16 (t, 2 H), 7.28 (m, 4 H), 7.67 (d, 2 H), 7.81 (d, 2 H), 8.35 (s, -NH-CO-, 2 H). <sup>13</sup>C-NMR (δ, d<sub>8</sub>-THF, 25 °C): 1.4 (-O-Si (CH<sub>3</sub>)<sub>2</sub>-O-), 2.0 (-CH<sub>2</sub>-Si (CH<sub>3</sub>)<sub>2</sub>-O-), 19.0 (-CH<sub>2</sub>-Si (CH<sub>3</sub>)<sub>2</sub>-O-), 24.1 (-CH<sub>2</sub>-CH<sub>2</sub>-Si (CH<sub>3</sub>)<sub>2</sub>-O-), 26.6 (-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-Si (CH<sub>3</sub>)<sub>2</sub>-O-), 30.1 (-NH-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 34.1 (-NH-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-), 65.3 (-NH-CO-O-CH<sub>2</sub>-), 109.0, 110.9, 118.4, 119.4, 124.1, 125.0, 126.7, 129.1, 135.1, 145.6 (C-NH<sub>2</sub>), 155.2 (-NH-CO-).

*POTM bis(carbonyl-N, N'-1,5-naphthalene diamine carbonyloxypentamethyleneoxycarbonyl-N, N'-1,5-naphthalene diamine (3,5-di-tert-butyl) benzyl carboxylate) (6a)*. 3.5 g (1.47 mmol) of **4a** were dissolved in 300 mL of THF and 1 mL (12.5 mmol) of pyridine and reacted with 1.9 g (3.26 mmol) of **5**, which was added in the solid state, as described for compound **3a**. After reprecipitation, 4.6 g (1.33 mmol) of **6a** were obtained. Yield: 90%. IR (film): 3378 (N-H), 1695 cm<sup>-1</sup> (C=O). <sup>1</sup>H-NMR (δ, d<sub>8</sub>-THF, 25 °C): 1.32 (s, -C-C(CH<sub>3</sub>)<sub>3</sub>-, 36 H), 1.57 (m, -O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.72 (m, -CO-O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-

CH<sub>2</sub>-O-CO-, 8 H), 1.81 (m, -NH-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-, 4 H), 3.35 (m, -O-CH<sub>2</sub>-), 4.16 (t, -NH-CO-O-CH<sub>2</sub>-, 4 H), 4.24 (m, -CO-O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O-CO-, 8 H), 5.16 (s, -NH-CO-O-CH<sub>2</sub>-C-, 4 H), 7.16-7.27 (m, 4 H), 7.30 (m, 4 H), 7.41 (m, 8 H), 7.76-7.98 (m, 14 H), 8.59 (s, -NH-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-, 6 H), 8.74 (s, -NH-CO-O-CH<sub>2</sub>-C-, 2 H). <sup>13</sup>C-NMR (δ, d<sub>8</sub>-THF, 25°C): 25.7 (-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O-CO-), 27.1 (-NH-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-), 27.3 (-NH-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 27.6 (-O-CH<sub>2</sub>-CH<sub>2</sub>-), 31.9 (-C-C(CH<sub>3</sub>)<sub>3</sub>), 35.5 (-C-C(CH<sub>3</sub>)<sub>3</sub>), 65.2 (-NH-CO-O-CH<sub>2</sub>-), 65.4 (-NH-CO-O-CH<sub>2</sub>-), 66.8 (-NH-CO-O-CH<sub>2</sub>-C-), 71.0 (-NH-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 71.3 (-O-CH<sub>2</sub>-), 118.6, 118.7, 120.1, 120.3, 121.9, 122.1, 122.6, 123.5, 125.8, 126.0, 128.7, 128.9, 129.1, 134.2, 135.5, 136.2 (-O-CH<sub>2</sub>-C-), 150.8 (-O-CH<sub>2</sub>-C-), 155.2 (-NH-CO-O-CH<sub>2</sub>-C-), 155.3 (-NH-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-). PEA bis[carbonyl-N, N'-1,5-naphthalene diamine] carbonyloxypentamethyleneoxycarbonyl-N, N'-1,5-naphthalene diamine (3,5-di-tert-butyl)benzyl carboxylate] (**6b**). 3.5 g (1.47 mmol) of **4b** were dissolved in 300 ml of THF and 1 ml (12.5 mmol) of pyridine and reacted with 1.9 g (3.26 mmol) of **5**, which was added in the solid state, as described for compound **3a**. After reprecipitation, 4.4 g (1.27 mmol) of **6b** were obtained. Yield: 86%. IR (film): 3349 (N-H), 1740 cm<sup>-1</sup> (C=O). <sup>1</sup>H-NMR (δ, d<sub>8</sub>-THF, 25°C): 1.33 (s, -C-C(CH<sub>3</sub>)<sub>3</sub>, 36 H), 1.61 (m, -CO-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CO-), 1.72 (m, -CO-O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O-CO-, 8 H), 2.30 (m, -CO-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CO-), 4.23 (m, -CO-O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O-CO-, 8 H), 4.25 (t, -O-CH<sub>2</sub>-CH<sub>2</sub>-O-, 4 H), 4.27 (s, -O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 4.33 (t, -NH-CO-O-CH<sub>2</sub>-, 4 H), 5.17 (s, -NH-CO-O-CH<sub>2</sub>-C-, 4 H), 7.16-7.27 (m, 4 H), 7.30 (m, 4 H), 7.41 (m, 8 H), 7.76-7.98 (m, 14 H), 8.61 (s, -NH-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-, 6 H), 8.76 (s, -NH-CO-O-CH<sub>2</sub>-C-, 2 H). <sup>13</sup>C-NMR (δ, d<sub>8</sub>-THF, 25°C): 25.1 (-CO-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CO-), 25.8 (-NH-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-), 31.7 (-C-C(CH<sub>3</sub>)<sub>3</sub>), 34.2 (-CO-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CO-), 35.3 (-C-C(CH<sub>3</sub>)<sub>3</sub>), 61.0 (-NH-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-), 62.9 (-O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 64.8 (-NH-CO-O-CH<sub>2</sub>-), 65.2 (-NH-CO-O-CH<sub>2</sub>-), 66.9 (-NH-CO-O-CH<sub>2</sub>-C-), 118.7, 118.9, 120.2, 120.4, 122.0, 122.2, 122.7, 123.6, 125.9, 126.1, 128.8, 129.0, 129.2, 134.3, 135.6, 136.3 (-O-CH<sub>2</sub>-C-), 150.9 (-O-CH<sub>2</sub>-C-), 155.3 (-NH-CO-O-CH<sub>2</sub>-C-), 155.4 (-NH-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-), 173.0 (-CO-CH<sub>2</sub>-CH<sub>2</sub>-).

POTM bis(carbonyl-N, N'-1,5-naphthalene diamine) carbonyloxypentamethyleneoxycarbonyl-N, N'-1,5-naphthalene diamine (**7a**). 4.2 g (1.21 mmol) of **6a** were reacted as described for compound **4a**. After freeze-drying, 3.1 g (1.04 mmol) of **7a** were obtained. Yield: 86%. IR (film): 3623, 3544, 3376 (N-H), 1737 cm<sup>-1</sup> (C=O). <sup>1</sup>H-NMR (δ, d<sub>8</sub>-THF, 25°C): 1.59 (m, -O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.74 (m, -CO-

O—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—O—CO—, 8 H), 1.85 (m, —NH—CO—O—CH<sub>2</sub>—CH<sub>2</sub>—, 4 H), 3.37 (m, —O—CH<sub>2</sub>—), 4.18 (t, —NH—CO—O—CH<sub>2</sub>—, 4 H), 4.25 (m, —CO—O—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—O—CO—, 8 H), 5.66 (s, —NH<sub>2</sub>, 4 H), 6.67 (d, 2 H), 7.15—7.90 (m, 22 H), 8.39 (s, —NH—CO—O—CH<sub>2</sub>—CH<sub>2</sub>—, 2 H), 8.61 (s, —NH—CO—O—CH<sub>2</sub>—CH<sub>2</sub>—, 4 H). <sup>13</sup>C-NMR (δ, d<sub>8</sub>-THF, 25°C): 25.6 (—CO—O—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—O—CO—), 27.0 (—NH—CO—O—CH<sub>2</sub>—CH<sub>2</sub>—), 27.2 (—NH—CO—O—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—), 27.5 (—O—CH<sub>2</sub>—CH<sub>2</sub>—), 65.1 (—NH—CO—O—CH<sub>2</sub>—), 65.4 (—NH—CO—O—CH<sub>2</sub>—), 70.9 (—NH—CO—O—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—), 71.2 (—O—CH<sub>2</sub>—), 108.3, 110.5, 117.0, 119.0, 120.4, 122.1, 123.9, 123.9, 126.5, 127.4, 128.5, 129.9, 133.5, 134.2, 145.3 (—C—NH<sub>2</sub>), 155.0 (—NH—CO—), 155.2 (—NH—CO—).

PEA bis(carbonyl-*N*, *N'*-1,5-naphthalene diamine carbonyloxyltetramethyleneoxycarbonyl-*N*, *N'*-1,5-naphthalene diamine) (**7b**). 4.2 g (1.21 mmol) of **6b** were reacted as described for compound **4a**. After freeze-drying, 3 g (1.01 mmol) of **7b** were obtained. Yield: 83%. IR (film): 3620, 3539, 3371 (N—H), 1735 cm<sup>-1</sup> (C=O). <sup>1</sup>H-NMR (δ, d<sub>8</sub>-THF, 25°C): 1.61 (m, —CO—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—CO—), 1.73 (m, —CO—O—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—O—CO—, 8 H), 2.31 (m, —CO—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—CO—), 4.22 (m, —CO—O—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—O—CO—, 8 H), 4.24 (m, —CO—O—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—O—CO—, 8 H), 4.25 (t, —O—CH<sub>2</sub>—CH<sub>2</sub>—O—, 4 H), 4.31 (t, —NH—CO—O—CH<sub>2</sub>—, 4 H), 5.65 (s, —NH<sub>2</sub>, 4 H), 6.66 (d, 2 H), 7.14—7.88 (m, 22 H), 8.38 (s, —NH—CO—O—CH<sub>2</sub>—CH<sub>2</sub>—, 2 H), 8.60 (s, —NH—CO—O—CH<sub>2</sub>—CH<sub>2</sub>—, 4 H). <sup>13</sup>C-NMR (δ, d<sub>8</sub>-THF, 25°C): 25.1 (—CO—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—CO—), 25.7 (—NH—CO—O—CH<sub>2</sub>—CH<sub>2</sub>—), 31.6 (—C—C(CH<sub>3</sub>)<sub>3</sub>), 34.1 (—CO—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—CO—), 61.0 (—NH—CO—O—CH<sub>2</sub>—CH<sub>2</sub>—), 62.9 (—O—CH<sub>2</sub>—CH<sub>2</sub>—O—), 64.8 (—NH—CO—O—CH<sub>2</sub>—), 65.1 (—NH—CO—O—CH<sub>2</sub>—), 66.9 (—NH—CO—O—CH<sub>2</sub>—C—), 120.2, 108.3, 110.5, 117.0, 119.0, 120.4, 122.1, 123.9, 123.9, 126.5, 127.4, 128.5, 129.9, 133.5, 134.2, 145.3 (—C—NH<sub>2</sub>), 155.0 (—NH—CO—), 155.3 (—NH—CO—), 173.0 (—CO—CH<sub>2</sub>—CH<sub>2</sub>—).

POTM elastomer PEU-0. 1 g (0.47 mmol) of **1a**, dissolved in 50 mL of THF, were added dropwise to a solution of 74.2 mg (0.47 mmol) of NDA in 100 mL of THF and 0.5 mL (6.25 mmol) of pyridine. After reprecipitation, 0.8 g of PEU-0 were obtained. IR (film): 3292 (N—H), 1694 cm<sup>-1</sup> (C=O). <sup>1</sup>H-NMR (δ, d<sub>8</sub>-THF, 25°C): 1.59 (m, —O—CH<sub>2</sub>—CH<sub>2</sub>—), 1.84 (m, —NH—CO—O—CH<sub>2</sub>—CH<sub>2</sub>—), 3.38 (m, —O—CH<sub>2</sub>—), 4.19 (t, —NH—CO—O—CH<sub>2</sub>—), 7.45 (t), 7.87 (m), 8.61 (s, —C—NH—CO—). <sup>13</sup>C-NMR (δ, d<sub>8</sub>-THF, 25°C): 27.1 (—NH—CO—O—CH<sub>2</sub>—CH<sub>2</sub>—), 27.3 (—NH—CO—O—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—), 27.6 (—O—CH<sub>2</sub>—CH<sub>2</sub>—), 65.6 (—NH—CO—O—CH<sub>2</sub>—), 71.0 (—NH—CO—O—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—), 71.2 (—O—CH<sub>2</sub>—), 118.5, 120.0, 126.0, 128.9, 135.6 (—C—NH—CO—), 155.3 (—C—NH—CO—).

PEA elastomer PAU-0. 2 g (0.94 mmol) of **1b**, dissolved in 50 mL of THF, were added dropwise to a solution of 148.1 mg (0.94 mmol) of NDA in 100 mL of THF and 0.5 mL (6.25 mmol) of pyridine. After reprecipitation, 1.8 g of PAU-0 were obtained. IR (film): 3341 (N—H), 1736 cm<sup>-1</sup> (C=O). <sup>1</sup>H-NMR (δ, d<sub>8</sub>-THF, 25°C): 1.63 (m, —CO—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—CO—), 2.32 (m, —CO—CH<sub>2</sub>—CH<sub>2</sub>—

CH<sub>2</sub>-CH<sub>2</sub>-CO-), 4.23 (s, -O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 4.26 (t, -NH-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-),  
 4.33 (t, -NH-CO-O-CH<sub>2</sub>-), 7.46 (t), 7.88 (m), 8.62 (s, -C-NH-CO-). <sup>13</sup>C-NMR (δ, d<sub>8</sub>-THF, 25°C): 25.1 (-CO-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CO-), 34.2 (-CO-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CO-), 61.0 (-NH-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-), 62.8 (-O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 64.8 (-NH-CO-O-CH<sub>2</sub>-), 119.0, 120.3, 126.1, 128.9, 135.2 (-C-NH-CO-), 155.1 (-C-NH-CO-), 173.1 (-CO-CH<sub>2</sub>-CH<sub>2</sub>-).

*PDMS elastomer PSU-0*. 2.29 g (0.94 mmol) of **1c**, dissolved in 50 mL of THF, were added dropwise to a solution of 148.1 mg (0.94 mmol) of NDA in 100 mL of THF and 0.5 mL (6.25 mmol) of pyridine. After reprecipitation, 1.9 g of PSU-0 were obtained. IR (film): 3305 (N-H), 1697 cm<sup>-1</sup> (C=O). <sup>1</sup>H-NMR (δ, d<sub>8</sub>-THF, 25°C): 0.02 (m, -O-Si (CH<sub>3</sub>)<sub>2</sub>-O-), 0.10 (m, -CH<sub>2</sub>-Si (CH<sub>3</sub>)<sub>2</sub>-O-, 12 H), 0.49 (t, -CH<sub>2</sub>-Si (CH<sub>3</sub>)<sub>2</sub>-O-, 4 H), 1.29 (m, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-Si (CH<sub>3</sub>)<sub>2</sub>-O-, 12 H), 1.65 (m, -NH-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-, 4 H), 4.15 (t, -NH-CO-O-CH<sub>2</sub>-, 4 H), 7.44 (t), 7.85 (m), 8.60 (s, -C-NH-CO-). <sup>13</sup>C-NMR (δ, d<sub>8</sub>-THF, 25°C): 1.5 (-O-Si (CH<sub>3</sub>)<sub>2</sub>-O-), 2.1 (-CH<sub>2</sub>-Si (CH<sub>3</sub>)<sub>2</sub>-O-), 19.1 (-CH<sub>2</sub>-Si (CH<sub>3</sub>)<sub>2</sub>-O-), 24.3 (-CH<sub>2</sub>-CH<sub>2</sub>-Si (CH<sub>3</sub>)<sub>2</sub>-O-), 26.7 (-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-Si (CH<sub>3</sub>)<sub>2</sub>-O-), 30.2 (-NH-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 34.2 (-NH-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-), 65.6 (-NH-CO-O-CH<sub>2</sub>-), 118.5, 119.8, 125.9, 128.7, 135.5 (-C-NH-CO-), 155.2 (-C-NH-CO-).

*POTM elastomers PEU-1 (10a), PEU-2 (11a), PEU-3 (12a) and PEU-4 (13a)*.

The bischloroformates, dissolved in 20 mL of THF, were added dropwise to the solutions of the diamine compounds in 100 mL of THF and 0.5 mL (6.25 mmol) of pyridine. PEU-1: 90.3 mg (0.42 mmol) of **8** and 1 g (0.42 mmol) of **4a**. PEU-2: 216.8 mg (0.42 mmol) of **9** and 1 g (0.42 mmol) of **4a**. PEU-3: 72.1 mg (0.34 mmol) of **8** and 1 g (0.34 mmol) of **7a**. PEU-4: 173 mg (0.34 mmol) of **9** and 1 g (0.34 mmol) of **7a**. After reprecipitation, the polymers were obtained.

IR (film): 3294 (N-H), 1695 cm<sup>-1</sup> (C=O). <sup>1</sup>H-NMR (δ, d<sub>8</sub>-THF, 25°C): 1.58 (m, -O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.72 (m, -NH-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.84 (m, -NH-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-), 3.36 (m, -O-CH<sub>2</sub>-), 4.18 (t, -NH-CO-O-CH<sub>2</sub>-), 4.24 (m, -NH-CO-O-CH<sub>2</sub>-), 7.41-7.56 (m), 7.86 (m), 8.60 (s, -C-NH-CO-). <sup>13</sup>C-NMR (δ, d<sub>8</sub>-THF, 25°C): 25.8 (-NH-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-), 27.1 (-NH-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-), 27.3 (-NH-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 27.6 (-O-CH<sub>2</sub>-CH<sub>2</sub>-), 65.3 (-NH-CO-O-CH<sub>2</sub>-), 65.6 (-NH-CO-O-CH<sub>2</sub>-), 71.0 (-O-CH<sub>2</sub>-), 71.3 (-O-CH<sub>2</sub>-), 118.7, 120.3, 126.3, 129.2, 135.8 (-C-NH-CO-), 155.4 (-C-NH-CO-).

*PEA elastomers PAU-1 (10b), PAU-2 (11b), PAU-3 (12b) and PAU-4 (13b)*.

The bischloroformates, dissolved in 20 mL of THF, were added dropwise to the solutions of the diamine compounds in 100 mL of THF and 0.5 mL (6.25 mmol) of pyridine. PAU-1: 90.3 mg (0.42 mmol) of **8** and 1 g (0.42 mmol) of **4b**. PAU-2: 216.8 mg (0.42 mmol) of **9** and 1 g (0.42 mmol) of **4b**. PAU-3: 72.1 mg (0.34 mmol) of **8** and 1 g (0.34 mmol) of **7b**. PAU-4: 173 mg (0.34 mmol) of **9** and 1 g (0.34 mmol) of **7b**. After reprecipitation, the polymers were obtained.

IR (film): 3338 (N-H), 1735 cm<sup>-1</sup> (C=O). <sup>1</sup>H-NMR (δ, d<sub>8</sub>-THF, 25°C): 1.64 (m, -CO-

CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CO-), 1.73 (m, -CO-O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O-CO-), 2.33 (m, -CO-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CO-), 4.24 (m, -CO-O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O-CO-), 4.25 (t, -O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 4.27 (s, -O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 4.34 (t, -NH-CO-O-CH<sub>2</sub>-), 7.41-7.56 (m), 7.86 (m), 8.60 (s, -C-NH-CO-). <sup>13</sup>C-NMR (δ, d<sub>8</sub>-THF, 25°C): 25.2 (-CO-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CO-), 25.9 (-NH-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-), 34.3 (-CO-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CO-), 61.1 (-NH-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-), 62.9 (-O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 64.9 (-NH-CO-O-CH<sub>2</sub>-), 65.4 (-NH-CO-O-CH<sub>2</sub>-), 119.2, 120.4, 126.2, 129.0, 135.3 (-C-NH-CO-), 155.1 (-C-NH-CO-), 173.2 (-CO-CH<sub>2</sub>-CH<sub>2</sub>-).

PDMS elastomers PSU-1 (10c) and PSU-2 (11c).

The bischloroformates, dissolved in 20 mL of THF, were added dropwise to the solutions of the diamine compounds in 100 mL of THF and 0.5 mL (6.25 mmol) of pyridine. PSU-1: 66.7 mg (0.31 mmol) of **8** and 1 g (0.31 mmol) of **4c**. PSU-2: 159.7 mg (0.31 mmol) of **9** and 1 g (0.31 mmol) of **4c**. After reprecipitation, the polymers were obtained.

IR (film): 3302 (N-H), 1694 cm<sup>-1</sup> (C=O). <sup>1</sup>H-NMR (δ, d<sub>8</sub>-THF, 25°C): 0.01 (m, -O-Si (CH<sub>3</sub>)<sub>2</sub>-O-), 0.08 (m, -CH<sub>2</sub>-Si (CH<sub>3</sub>)<sub>2</sub>-O-), 0.47 (t, -CH<sub>2</sub>-Si (CH<sub>3</sub>)<sub>2</sub>-O-), 1.28 (m, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-Si (CH<sub>3</sub>)<sub>2</sub>-O-), 1.64 (m, -NH-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.72 (m, -NH-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-), 4.14 (t, -NH-CO-O-CH<sub>2</sub>-), 4.24 (t, -NH-CO-O-CH<sub>2</sub>-), 7.39-7.55 (m), 7.84 (m), 8.58 (s, -C-NH-CO-). <sup>13</sup>C-NMR (δ, d<sub>8</sub>-THF, 25°C): 1.5 (-O-Si (CH<sub>3</sub>)<sub>2</sub>-O-), 2.1 (-CH<sub>2</sub>-Si (CH<sub>3</sub>)<sub>2</sub>-O-), 19.1 (-CH<sub>2</sub>-Si (CH<sub>3</sub>)<sub>2</sub>-O-), 24.3 (-CH<sub>2</sub>-CH<sub>2</sub>-Si (CH<sub>3</sub>)<sub>2</sub>-O-), 25.8 (-NH-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-), 26.7 (-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-Si (CH<sub>3</sub>)<sub>2</sub>-O-), 30.2 (-NH-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 34.2 (-NH-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-), 65.4 (-NH-CO-O-CH<sub>2</sub>-), 65.6 (-NH-CO-O-CH<sub>2</sub>-), 118.6, 119.9, 126.1, 128.8, 135.6 (-C-NH-CO-), 155.3 (-C-NH-CO-).

## Sample characterization

Polymer films were casted from THF (PEU-n, n = 0, 1; PAU-n, n = 0, 1; PSU-n, n = 0, 1), trifluoroacetic acid (PEU-n, n = 2-4), DMA (PAU-n, n = 2-4) and dioxane (PSU-2).

GPC measurements were made with a chromatograph Waters 150°C (styragel columns with pore sizes 10<sup>5</sup>, 10<sup>4</sup>, 10<sup>3</sup> and 500 Å; pressure 70 bar; flow rate 1 mL/min; sample concentration 10 mg/mL; PEU-n and PAU-n; DMA as solvent, temperature 60°C; PSU-n; THF as solvent, temperature 25°C).

NMR spectra were recorded on a Bruker AC 250-Spectrometer at 250 MHz (<sup>1</sup>H-NMR) and 62.9 MHz (<sup>13</sup>C-NMR) using tetramethylsilane as internal standard.

IR measurements were made with a FTIR spectrometer Bio-Rad Digilab Division 3240-SPC FTS-40 (PEU-n and PAU-n; film from DMA on CaF<sub>2</sub>; PSU-n; film from dioxane on NaCl). For temperature-dependent FT-IR investigations the heatable measuring cell Specac PIN 21500 was used (film from DMA on Si-weaver; heating rate 1°C/min; measurement technically attainable temperature 230°C).

Melting points and heats of fusion were measured on a Perkin Elmer DSC-7 with film samples (sample weight 5 mg; heating and cooling rate 20°C/min; N<sub>2</sub>-atmosphere).

Thermogravimetric analysis measurements were obtained with a Simultaneous Thermoanalytical Apparatus Netzsch STA 409 with film samples (sample weight 10 mg; heating rate 10°C/min; N<sub>2</sub>-atmosphere).

Dynamic mechanical measurements were carried out with a Brabender torsion pendulum by using polymer

films of  $60 \times 10 \times 0.5$  mm in size. Starting with a temperature of  $-130^\circ\text{C}$  (PEU-n) and  $-100^\circ\text{C}$  (PAU-n), respectively, the samples were heated with  $1^\circ\text{C}/\text{min}$  (frequency 1 Hz).

## Results and discussion

### Synthesis

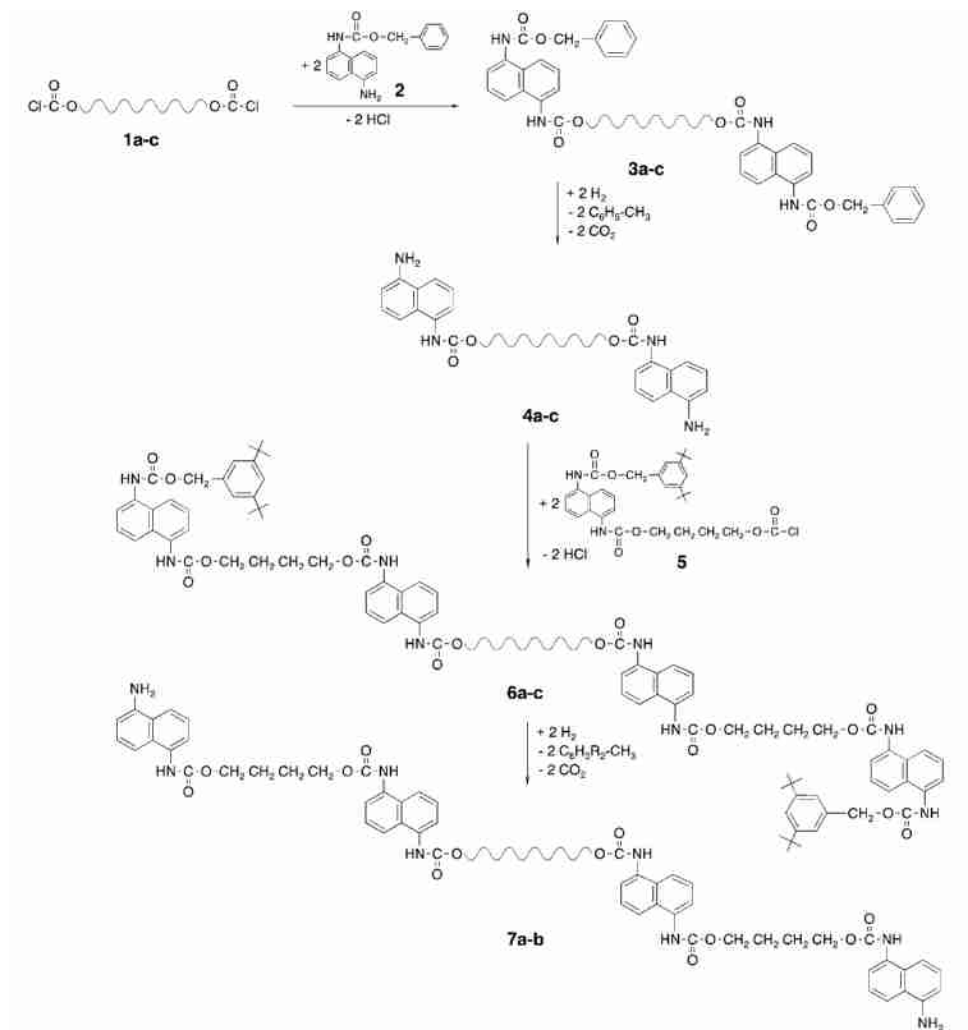
The segmented PUR elastomers with molecularly uniform NDI/BDO hard segments have been synthesized in a stepwise procedure to form the urethane linkage by the condensation reaction of chloroformates with amino groups, because this route has more advantages compared to the addition of hydroxyl compounds to isocyanates. Due to the bifunctionality of the starting material 1,5-naphthalene diamine (NDA), the carbobenzyloxy (CBO) group, which was introduced by reaction with benzyl chloroformate and removed by hydrogenolysis in the presence of a catalyst, was used as the protection group for the amino function.

The usual method to synthesize elastomers with monodisperse hard segments by condensation of polyol bis-chloroformates with amino terminated, molecularly uniform hard segment precursors, was hindered by the poor solubility of the amino terminated NDI/BDO oligourethanes. Nevertheless, the synthesis was made possible by the double-sided elongation of polyether, polyester and polysiloxane polyols with naphthalene units by reaction of the polyol bischloroformates **1a-c** with mono-CBO protected NDA **1** and the subsequent hydrogenolytical removal of the CBO groups. The amino terminated prepolymers **4a-c** were obtained (scheme 1; the letters a, b and c stand for the respective different soft segments; a = POTM, b = PEA, c = PDMS). Thus, advantage could be taken of the high solubility of the soft segment building units in suitable solvents, like tetrahydrofuran (THF).

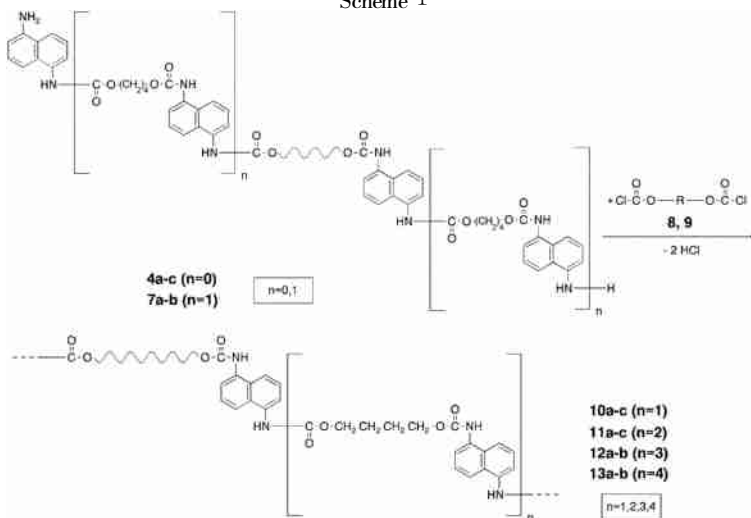
Using again the same procedure, reaction with mono protected NDA and cleavage of the protecting group, prepolymers **6a-c** with 2 naphthalene units at each end of the polyols were accessible. The solubility of these compounds was improved by employing the mono-modified-CBO protected NDA **5**, i. e. by using a modified CBO protective group, the 3,5-di-*tert*-butyl benzyloxycarbonyl group<sup>[14]</sup>. After cleavage of the protective groups, amino terminated precursors **7a-b** with POTM and PEA soft segments were obtained. However, it was not possible to get the corresponding polysiloxane based prepolymer, because the GPC analysis of the compound after the hydrogenolytical cleavage of the modified-CBO protective group showed the partial decomposition of the PDMS chain. In the last step, the synthesis of PUR elastomers with up to 4 NDI/BDO repeating units in the hard segment chain was made possible by the polycondensation reaction of the precursors **4a-c** and **7a-b** with the bischloroformates **8** and **9**, after determination of the content of amino end groups by ultra violet spectroscopy and titration (scheme 2; the synthesis of the polyol bischloroformates as well as the compounds **2** and **5** will be described elsewhere<sup>[15]</sup>).

The molar masses of the polymers (equivalent to polystyrene standards) were determined by gel-permeation chromatography (GPC), whereby smaller amounts of the polyether and polyester elastomers could be dissolved in N,N-dimethylacetamide (DMA) and the polysiloxane polymers were soluble in THF. Because of the poor solubility of the naphthalene bisurethane units, solving more material for the preparation of polymer films (used for the thermal and mechanical investigations), was the main difficulty for the characterization of the synthesized model elastomers. THF was a suitable solvent for the different types of polymers with up to only 1 repeating unit. DMA was used for the hard segment richer polyester elastomers PAU-n ( $n = 2-4$ ) and dioxane for the compound PSU-2, whereby solving was only possible by strong heating.

Trifluoroacetic acid, which solved the hard as well as the soft segments, could be employed as sole solvent for the polyether based elastomers PEU-n ( $n = 2-4$ ) with more than 1 NDI/BDO repeating unit. However, after solving several times, the GPC analysis showed a decomposition of the polymer (Fig. 1), making it impossible to use the synthesized material for more than one investigation. Further GPC measurements of the oligomeric DMU model compounds and the pure POTM soft segment showed, that the decomposition of the



Scheme 1



Scheme 2

polymers took place at the polyether polyol, while the urethane group remained stable.

## Microphase separation

The amount of microphase separation, i.e. the degree of physical crosslinking, was evaluated by the shift of the soft phase glass transition temperature  $T_g$  in differential scanning calorimetry (DSC) measurements in the low temperature region. It is known, that the building-in of the soft segments in PUR elastomers leads to a rise of the soft phase  $T_g$ <sup>[16~18]</sup>; the higher the amount of microphase separation, the smaller the increase of the glass transition temperature. While the  $T_g$  of a 350000 mol·wt· POTM (the very high molecular weight was chosen because of the lower influence of the hydroxyl end groups) was measured at  $-84^\circ\text{C}$ , the DSC traces of the polyether based elastomers PEU-*n* (2000 mol·wt· POTM with  $T_g = -78^\circ\text{C}$ ) showed the soft phase  $T_g$  at temperatures in the region of  $-65^\circ\text{C}$  (Fig. 2), about  $20^\circ\text{C}$  higher than the glass transition of the pure soft segments. The elastomer PEU-0 with only isolated naphthalene units in the soft phase showed the glass transition at  $-62^\circ\text{C}$ , the same temperature calculated for non-phase separation. This indicated, that the isolated naphthalene bisurethane units were unable to form segregated hard segments and were, therefore, completely dissolved in the soft segment matrix.

For comparison, the  $T_g$  values of the corresponding MDI based elastomers (2000 mol·wt· POTM) were almost in the same temperature region as the NDI based elastomers<sup>[19]</sup>, but the elastomers based on tt HMDI showed distinctly lower glass transition temperatures<sup>[20]</sup> (Tab. 1). For example, the  $T_g$  of the POTM soft phase at the NDI-PEU-2 was determined to be about  $-67^\circ\text{C}$  compared with  $-75^\circ\text{C}$  at the tt HMDI-PEU-2, thus indicating a better phase separation when employing tt HMDI as diisocyanate component.

The building-in of the 2 other types of soft segments also led to a significant shift of the glass transition temperatures. While the pure 2000 mol·wt· PEA polyol showed the  $T_g$  at  $-54^\circ\text{C}$ , the corresponding NDI based polyester elastomers PAU-*n* were characterized at values in the region of  $-40^\circ\text{C}$ . The  $T_g$  of the polysiloxane elastomers PSU-*n* (2300 mol·wt· PDMS), which was around  $-114^\circ\text{C}$ , shifted about  $11^\circ\text{C}$  to higher temperatures compared to the pure 2300 mol·wt· PDMS ( $T_g = -125^\circ\text{C}$ ). Generally, the glass transition region became broader and shifted slightly to lower temperatures at all types of elastomers with a rising number of NDI/BDO repeating units in the hard segments, showing that the phase separation increased with increasing hard segment length. Based on the measured soft segment glass transition temperatures  $T_{g(ss)}$ , the amount of hard segments solubilized in the soft phase  $x_2$ , and these values related to the stoichiometric hard segment content  $x_2/x_{hs}$ , were calculated for all investigated polymers<sup>[21]</sup>.

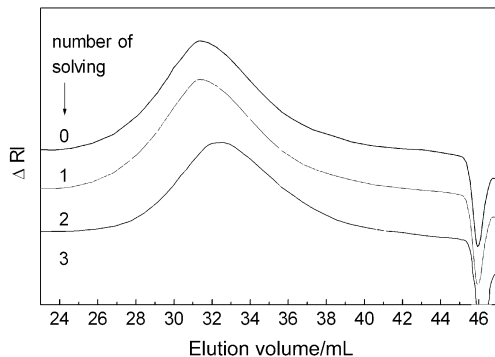


Fig. 1 GPC curves of different times in trifluoroacetic acid solvated samples of the polyether elastomer PEU-2 (DMA as solvent)

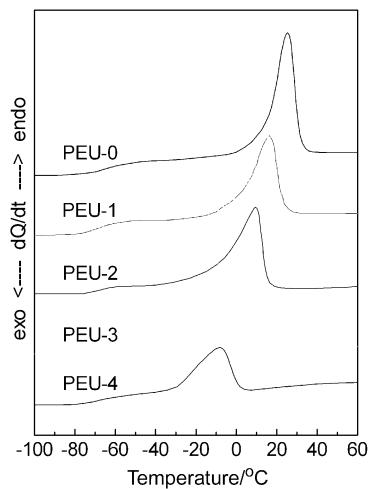


Fig. 2 DSC curves of the polyether elastomers PEU-*n* in the low temperature region (second heating; heating rate  $20^\circ\text{C}$ )

The microphase separation was also investigated by Fourier-transform infrared (FTIR) spectroscopical

measurements of the hydrogen bonding behaviour. The typical PUR is extensively hydrogen bonded, the donor being the NH group of the urethane linkage. The hydrogen bond acceptor may be in either the carbonyl of the urethane hard segments or the ester carbonyl group of polyester soft segments and the ether O atom of polyether soft segments, respectively. Most of the CO groups were hydrogen bonded, giving a peak at  $1695\text{ cm}^{-1}$ , and so indicating hard-hard segment interactions in segregated hard segment domains. Non-bonded CO groups, absorbed at the higher frequency of  $1735\text{ cm}^{-1}$ , were due to isolated hard segments which were dissipated in the soft segment matrix. As expected, the PEU-0 showed no absorption of hydrogen bonded CO groups, thus confirming that this polymer was completely homogeneous (Fig. 3).

In the case of the other elastomers, the absorption at  $1695\text{ cm}^{-1}$  and the ratio of hydrogen bonded to non-bonded CO groups, respectively, increased with a rising hard segment length, indicating a higher amount of microphase separation. When investigating the polyester elastomers, problems arose using this method, because the absorption of the PEA carbonyl groups lay in the region of  $1735\text{ cm}^{-1}$  and added to the absorption of non-bonded CO groups. For that reason, the amount of hydrogen bonded CO groups  $x_{\text{C=O}\cdots\text{H}}$  was much lower and a comparison with the results, obtained at the polyether and polysiloxane elastomers, was not possible.

Values regarding the microphase separation, obtained by means of the described DSC and IR measurements, are shown in Tab. 1 together with those of corresponding MDI and tHMDI based polyether elastomers. The DSC results indicated, that the polyester soft segments led to a lower phase separation in comparison to the building-in of the POTM. The observed behaviour was caused by very strong interactions between the urethane NH groups and the polyester carbonyls due to hydrogen bonding, so that the PEA soft segments showed a larger affinity to the hard segments than to the polyether soft segments. The best phase separation was achieved by the building-in of the PDMS due to the unpolar PDMS soft segments.

Compared with corresponding polyether elastomers based on MDI, the microphase separation of NDI elastomers was more enhanced at a similar number of repeating units, resulting in higher melting points and higher heats of fusion. Polyether elastomers based on tHMDI showed the best phase separation, indicating that there is a higher hard-soft segment incompatibility in that case. As in the case of the different soft segments, the respective segregation behaviour can be explained by the strength of the hydrogen bonds of the urethane NH groups to the soft segment O atom. With increasing hydrogen bond strength, the interaction between hard and soft segments increased and the phase separation decreased<sup>[22, 23]</sup>.

## Softening behaviour

The melting of the soft segments was observed in DSC measurements in the mid temperature region. The polyether elastomers PEU-n showed the melting of the POTM segments in the range from  $25^\circ\text{C}$  (PEU-0) to  $-8^\circ\text{C}$  (PEU-4) (Fig. 2). The melting of the PEA soft segments occurred in each case at temperatures about  $25^\circ\text{C}$  higher (PAU-0;  $49^\circ\text{C}$ , PAU-4;  $27^\circ\text{C}$ ). The shift of the melting peaks to lower temperatures with an increasing hard segment length indicated a decreasing size of the soft segment crystallites with a growing hard segment volume share. The soft segment melting also occurred in the first heating. The polysiloxane soft segments were completely amorphous and showed no tendency to crystallize, so that soft segment melting could not be observed at the PSU-n polymers.

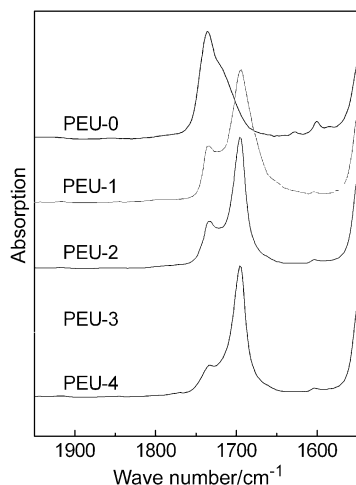


Fig. 3 FTIR spectra of the polyether elastomers PEU-n (CO region)

Table-1 Amount of microphase separation of the polyether elastomers PEU-n with NDI, MDI and ttHMDI hard segments as well as the NDI based polyester and polysiloxane elastomers PAU-n and PSU-n, determined by means of DSC and IR spectroscopic investigations

|               | $T_g(ss)^{a)}$<br>in °C | $x_2^{b)}$<br>in % | $x_2/x_{hs}^{c)}$<br>in % | $x_{C=O\cdots H}^{d)}$<br>in % |
|---------------|-------------------------|--------------------|---------------------------|--------------------------------|
| NDI-PEU-0     | -62                     | —                  | —                         | —                              |
| NDI-PEU-1     | -67                     | 6.4                | 31.6                      | 73                             |
| NDI-PEU-2     | -67                     | 5.7                | 19.8                      | 81                             |
| NDI-PEU-3     | -66                     | 5.5                | 15.4                      | 85                             |
| NDI-PEU-4     | -66                     | 5.0                | 12.1                      | 89                             |
| MDI-PEU-1     | -67                     | 11.1               | 48.9                      | 51                             |
| MDI-PEU-2     | -69                     | 10.0               | 31.5                      | 74                             |
| MDI-PEU-3     | -71                     | 8.5                | 21.9                      | 81                             |
| MDI-PEU-4     | -67                     | 9.6                | 21.5                      | 77                             |
| ttHMDI-PEU-01 | -76                     | 3.9                | 17.2                      | 75                             |
| ttHMDI-PEU-02 | -75                     | 4.2                | 13.2                      | 85                             |
| NDI-PAU-0     | -28                     | —                  | —                         | —                              |
| NDI-PAU-1     | -38                     | 7.0                | 34.5                      | 19                             |
| NDI-PAU-2     | -38                     | 6.3                | 21.6                      | 23                             |
| NDI-PAU-3     | -39                     | 5.3                | 14.8                      | 29                             |
| NDI-PAU-4     | -40                     | 4.5                | 10.8                      | 35                             |
| NDI-PSU-0     | -101                    | —                  | —                         | —                              |
| NDI-PSU-1     | -113                    | 7.0                | 34.5                      | 77                             |
| NDI-PSU-2     | -114                    | 6.3                | 21.6                      | 86                             |

a) Soft segment glass transition temperature; b) Share of hard segments in the soft phase; c) Share of hard segments in the soft segment phase related to the stoichiometric hard segment content; d) Share of hydrogen bonded CO groups related to total CO groups.

DSC measurements of the hard segment melting behaviour of the polyether elastomers PEU-n showed a rise in the melting temperatures with an increasing hard segment length from 168/203°C (PEU-1) to 234/245°C (PEU-4) (Fig. 4). The length of the hard segments fixed the upper limit of the extension of the hard segment crystals in chain direction. It has to be taken in consideration, that the crystal size effect played an important role due to the small hard segment lengths<sup>[24,25]</sup>. Clear differences in the softening behaviour between the elastomers with several soft segments were recorded. The PAU-n showed lower melting points and heats of fusion (Fig. 5A). The highest melting points and heats of fusion were obtained with polysiloxane elastomers PSU-n (Fig. 5B). Apart from the influence of the melting entropy, the melting point was determined essentially by the interactions between the hard segments as well as the interactions between hard and soft segments. The melting temperature of the crystalline hard segment domains determined the heat resistance of the elastomers and the transition to the thermoplastic deformability.

Multipeak behaviour was observed at all investigated samples, whereby after annealing experiments, only one peak normally appeared at a higher melting temperature, i.e. the crystal packing order increased upon annealing. This observation could be explained by the crystallization behaviour of the hard domains. The hard

segment chains engaged in the crystal displaced one another, thus forming a larger and rugged phase interface. With a rising surface of the microcrystallites, the surface energy increased and was responsible for a decrease of the melting points of the crystallites. The size distribution of the microcrystallites, formed at the casting of the polymer films from solution, was quite a distance away from the thermodynamic equilibrium and drew nearer to it during the annealing process. Annealing at higher temperatures, loosened the crystal lattice and led to an improvement of the hard segment packing and a better order of the domains<sup>[26]</sup>. Therefore, it was possible to form thermodynamically favourable crystals with a better order and smaller surface. A partial decomposition of the hard segments also occurred, due to a decrease in the heat of fusion after annealing; e.g., the value of the PEU-1 at 9.6 J/g was distinctly lower than the heat of fusion before annealing.

Compared with polyether elastomers based on MDI<sup>[19]</sup> and ttHMDI<sup>[20]</sup>, the NDI elastomers showed the highest melting points and heats of fusion (Tab. 2, first heating of the samples crystallized from solution) (NDI-PEU-1:  $T_m = 168^\circ\text{C}$ ,  $H_m = 13.4 \text{ J/g}$ ; MDI-PEU-1:  $T_m = 112^\circ\text{C}$ ,  $\Delta H_m = 1.8 \text{ J/g}$ ; ttHMDI-PEU-1:  $T_m = 129^\circ\text{C}$ ,  $\Delta H_m = 12 \text{ J/g}$ ). The here discussed investigations regarding the amount of microphase separation showed that the influence of the different diisocyanates is partly due to the ratio of hard-hard segment and hard-soft segment interactions, i.

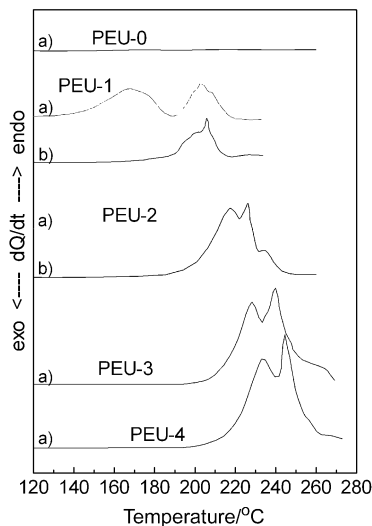


Fig. 4 DSC curves of the polyether elastomers PEU-*n*: a) first heating, b) heating after 15 min annealing at 185°C (PEU-1) and 190°C (PEU-2) (heating rate 20°C/min)

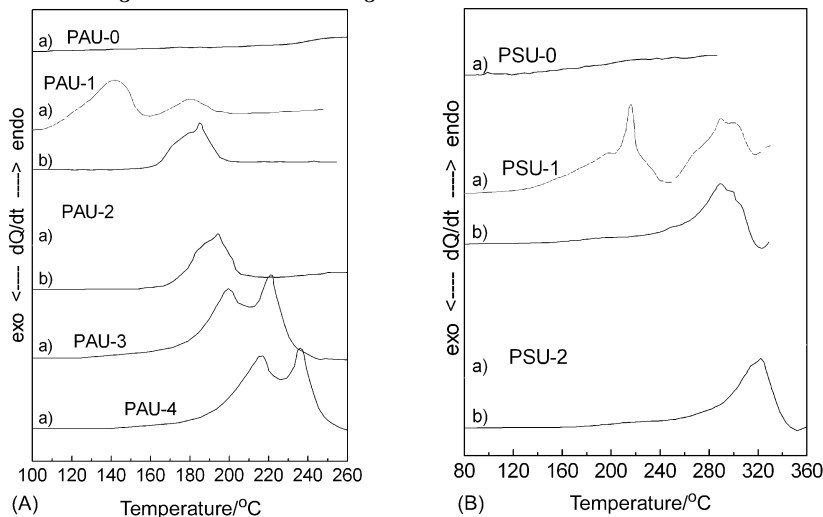


Fig. 5 DSC curves of A) the polyester elastomers PAU-*n*: a) first heating, b) heating after 15 min annealing at 160°C (PAU-1) and 175°C (PAU-2) (heating rate 20°C/min); and B) the polysiloxane elastomers PSU-*n*: a) first heating, b) heating after 15 min annealing at 245°C (PSU-1) and 270°C (PSU-2) (heating rate 20°C/min)

e. the degree of hydrogen bonding. But there are also some other factors which explain the special behaviour of the NDI based system. The high values of melting points and heats of fusion were mostly attributed to strong intermolecular interactions between the naphthalene-butanediol units which, combined with the rigid structure of the system, might result in a denser packing of the NDI/BDO hard segments.

## Thermal stability

Thermogravimetric analysis measurements of the elastomers with 1 NDI/BDO repeating unit in the hard segment and polyether, polyester and polysiloxane soft segments showed a mass reduction beginning at 250°C, independent of the type of soft segment (Fig. 6). Based on this, the stability limit of the hard segment domains was determined at about 250°C. However, the DSC measurements on annealed samples showed that decomposition at lower temperatures must occur. Therefore, the thermal stability of the hydrogen bonds was investigated by studying the NH and CO absorption at temperature-dependent FTIR measurements<sup>[27]</sup>.

The NH and CO region as a function of the temperature at the polyether elastomer PEU-1 showed that polyurethanes are characterized in the same way as polyamides<sup>[28]</sup>, by specific temperature-dependent changes. At 30°C virtually all of the NH and most of the CO groups are hydrogen bonded, giving peaks at 3280 cm<sup>-1</sup> for the bonded NH and 1695 cm<sup>-1</sup> for the bonded CO groups (Fig. 7). Non-bonded NH and CO groups, absorbing at higher frequencies with much lower intensity, can be used to monitor hydrogen bond disruption. The NH peak disappeared rapidly at temperatures above 180°C. At 200°C, hydrogen bonded carbonyl groups were no longer observed, indicating a rapid decomposition, after the first hydrogen bonds had started to dissolve. Corresponding measurements of the PEU-2 showed the solving of the hydrogen bonds starting at 200°C, i.e. the thermal stability increased with an increasing hard segment length.

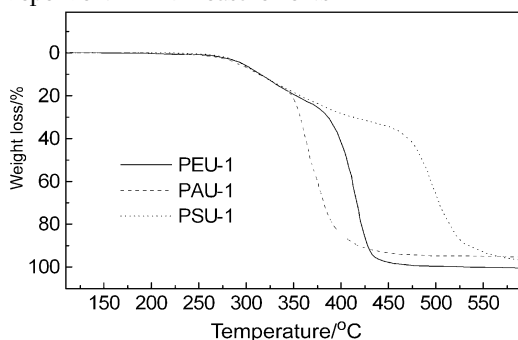


Fig. 6 Thermogravimetric analysis curves of the elastomers with 1 NDI/BDO repeating unit in the hard segment and polyether, polyester and polysiloxane soft segments (heating rate 10°C/min; N<sub>2</sub>-atmosphere)

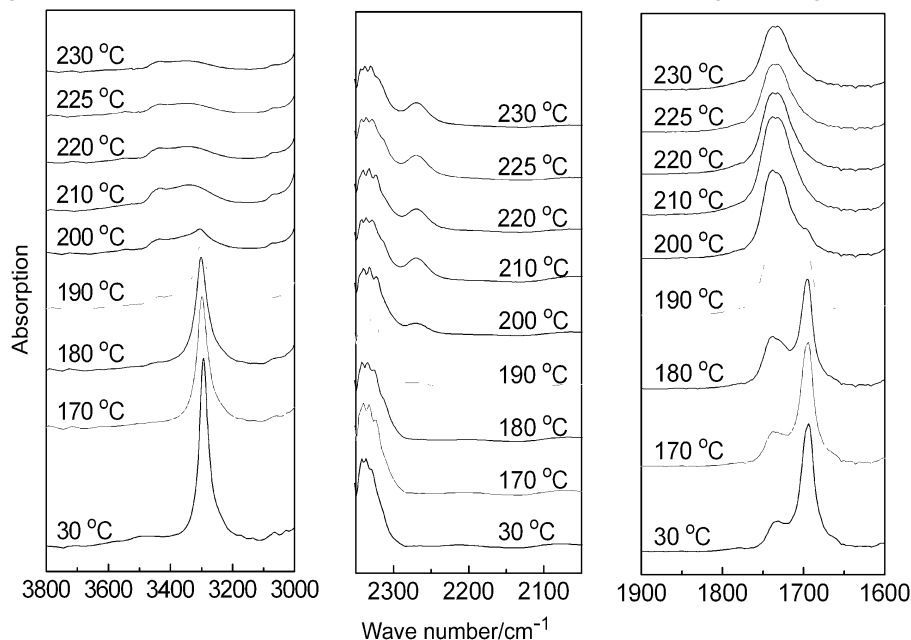


Fig. 7 Temperature-dependent FTIR spectra of the polyether elastomer PEU-1 (NH, NCN and CO region)

The appearance of retrourethanization reactions of the urethane linkage (urethane  $\rightarrow$  isocyanate + alcohol)  
(C)1994-2022 China Academic Journal Electronic Publishing House. All rights reserved. <http://www.cnki.net>

hol) was studied by the detection of free NCO groups at the cleavage temperature. The NCO absorption was observed at the polyether urethane PEU-1 beginning at a temperature of 180°C (Fig. 7), which corresponded to the FTIR measurements of the NH and CO groups. Therefore, the stability limit of the hard segment domains in the PEU-1 was determined at 180°C. DSC measurements showed, that although the crystal order of the hard domains increased by annealing, there is the danger of decomposition processes at temperatures above 180°C. At even higher temperatures, decomposition reactions are already in progress to a large extent, so that the results of the investigations regarding the melting behaviour have to be interpreted with caution. Generally, only opinions regarding the melting behaviour of the solution-crystallized samples are possible, as melting-crystallized samples already exhibit changes in their chemical structure.

### Dynamic mechanical properties

The temperature dependence of the storage modulus  $G'$  and the loss factor  $\delta$  of the polyether elastomers PEU-*n* are depicted in Fig. 8. All samples of the homologous series of polymers revealed a similar change in the storage modulus and the loss factor when going through the glass-rubber transition of the soft segment with the drop in  $G'$  starting at -80°C and the loss peak maximum at about -55°C. But there are clear differences in the following courses. The slope of the storage modulus curve at temperatures above the soft segment glass transition increased with growing hard segment content. The temperature range of the elastomeric behaviour, which is reflected in the relatively constant modulus in the plateau region up to the final drop associated with hard domain softening, increased with a growing hard segment length and hard segment content, respectively, and showed in the same way an increasing level of the storage modulus (Tab. 3). This is characteristic of an incompatible system whereby the hard segment domains behave as active filler particles and act as reinforcement. The glass transition temperature is shifted to higher values with increasing hard segment length, thus indicating an increasing amount of solubilized hard segment in the soft segment matrix.

The comparison of the polyether elastomers with hard segments based on different diisocyanates is also very interesting (Fig. 9A). Depending on the diisocyanate compound, the specimens of the POTM based elastomers PEU-2 with 2 repeating units in the hard segment exhibited a different dynamic mechanical behaviour. The ttHMDI based elastomer showed the lowest loss peak maximum with -64°C<sup>[20]</sup>, indicating the best phase separation and confirming the results obtained by DSC and IR measurements.

The slow decay of the storage modulus from just above the glass transition temperature up to higher temperatures by NDI-PEU-2 is distinctly clearer in comparison to the MDI and even ttHMDI based elastomers. This indicates a pronounced soft segment crystallinity which is due to relatively pure soft segments in NDI-PEU-2 and ttHMDI-PEU-2 (Fig. 9B), and results from the high incompatibility of the soft segment and hard segment polymer chains in these polymers. MDI-PEU-2 showed no soft segment crystallinity in the modulus curves, indicating a small amount of mixing of hard and soft segments which disturbed the soft segment crystallinity to a large extent, but left the overall morphology of a 2-phase system intact.

The height of the storage modulus and especially the temperature range of the elastomeric behaviour of the MDI-PEU-2 was much smaller compared with the 2 other samples<sup>[19]</sup>. The temperature difference between the melting of the hard segment microcrystallite based on different diisocyanates is similar to that observed by DSC (Tab. 2). The lower melting point of the MDI bisurethane units caused a shift in the softening of the hard do-

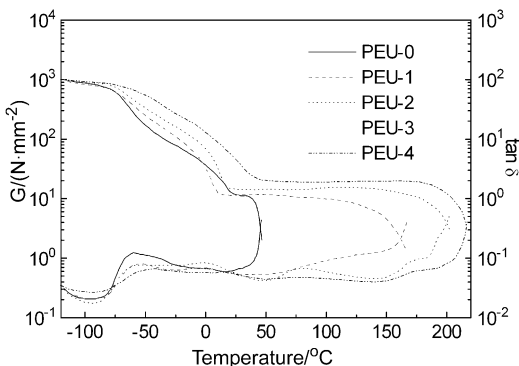


Fig. 8 Dynamic mechanical properties of the polyether elastomers PEU-*n*

Table.1 Dynamic mechanical behaviour of the polyether elastomers PEU-n with NDI, MDI and ttHMDI hard segments as well as the NDI based polyester elastomers PAU-n

|               | $\tan \delta_{\max}^{\text{a)}}$<br>in $^{\circ}\text{C}$ | $G'$ at $25^{\circ}\text{C}^{\text{b)}}$<br>in $\text{N}/\text{mm}^2$ | $G'$ at $50^{\circ}\text{C}^{\text{c)}}$<br>in $\text{N}/\text{mm}^2$ | $\text{Tr}^{\text{d)}}$<br>in $^{\circ}\text{C}$ | $\text{Te}^{\text{e)}}$<br>in $^{\circ}\text{C}$ |
|---------------|-----------------------------------------------------------|-----------------------------------------------------------------------|-----------------------------------------------------------------------|--------------------------------------------------|--------------------------------------------------|
| NDI-PEU-00    | −60                                                       | 11.5                                                                  | —                                                                     | —                                                | 47                                               |
| NDI-PEU-01    | −55                                                       | 11.6                                                                  | 11.7                                                                  | 13—122                                           | 166                                              |
| NDI-PEU-02    | −56                                                       | 14.4                                                                  | 14.4                                                                  | 20—152                                           | 203                                              |
| NDI-PEU-03    | −48                                                       | 24.1                                                                  | 16.9                                                                  | 40—170                                           | 209                                              |
| NDI-PEU-04    | −45                                                       | 45.2                                                                  | 20.2                                                                  | 45—180                                           | 216                                              |
| MDI-PEU-01    | −50                                                       | 4.3                                                                   | 2.5                                                                   | —                                                | 99                                               |
| MDI-PEU-02    | −34                                                       | 7.1                                                                   | 6.2                                                                   | —                                                | 119                                              |
| ttHMDI-PEU-01 | −64                                                       | 5.2                                                                   | 4.4                                                                   | 18—122                                           | 119                                              |
| ttHMDI-PEU-02 | −63                                                       | 12.1                                                                  | 12.0                                                                  | 7—138                                            | 166                                              |
| NDI-PAU-01    | −33                                                       | 29.7                                                                  | 18.4                                                                  | 39—148                                           | 159                                              |
| NDI-PAU-02    | −32                                                       | 44.1                                                                  | 21.4                                                                  | 42—159                                           | 176                                              |
| NDI-PAU-03    | −30                                                       | 53.7                                                                  | 28.8                                                                  | 47—168                                           | 180                                              |
| NDI-PAU-04    | −27                                                       | 70.3                                                                  | 37.4                                                                  | 51—169                                           | 184                                              |

a) Temperature of the loss peak maximum; b) Storage modulus at 25°C; c) Storage modulus at 50°C; d) Temperature range of the relatively constant modulus in the plateau region; e) End temperature.

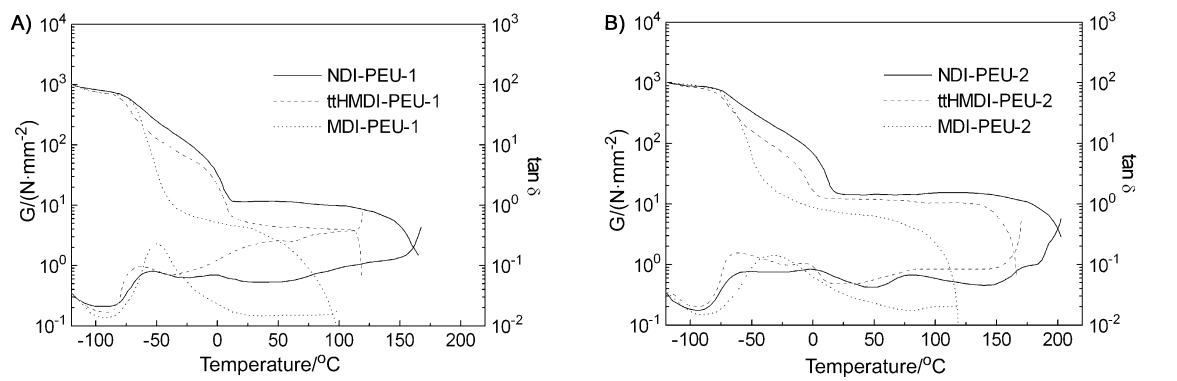


Fig. 9 Dynamic mechanical properties of A) polyether elastomers with different diisocyanate components and 1 diisocyanate/BDO repeating unit; and B) polyether elastomers with different diisocyanate components and 2 diisocyanate/BDO repeating units

mains to a lower temperature which consequently led to a smaller temperature range of the elastomeric behaviour of the MDI elastomers. This again is an indication of the solubilized hard segments in the soft segment in the MDI-PEU-2. The amount of solubilized hard segment is not segregated and therefore does not contribute to the modulus plateau and the heat resistance of the polymer.

In the service temperature range of the elastomers, the NDI system showed the highest storage modulus value  $G'$  over the broadest temperature range. This indicates a higher and less temperature-dependent stiffness and a better hard domain stability of the NDI based hard segments compared to the MDI and ttHMDI based systems. In addition to the function as thermoreversible crosslinks, crystallized hard segments also act as a reinforcing filler. Comparing the NDI and ttHMDI elastomers, the higher modulus of the NDI-PEU-2 could be attributed to the greater effective filler content induced by the staggered packing of the NDI hard segments.

**Table-2** Melting behaviour of the polyether elastomers PEU-n with NDI, MDI and ttHMDI hard segments as well as the NDI based polyester and polysiloxane elastomers PAU-n and PSU-n

|               | $T_m$ (ss) <sup>a)</sup><br>in °C | $T_{m1}$ (hs) <sup>b)</sup><br>in °C | $\Delta H_{m1}$ <sup>b)</sup><br>in J/g | $T_{m2}$ (hs) <sup>c)</sup><br>in °C | $\Delta H_{m2}$ <sup>c)</sup><br>in J/g | $T_{m^*}$ (hs) <sup>d)</sup><br>in °C | $\Delta H_{m^*}$ <sup>d)</sup><br>in J/g |
|---------------|-----------------------------------|--------------------------------------|-----------------------------------------|--------------------------------------|-----------------------------------------|---------------------------------------|------------------------------------------|
| NDI-PEU-00    | 25                                | —                                    | —                                       | —                                    | —                                       | —                                     | —                                        |
| NDI-PEU-01    | 16                                | 168                                  | 13.4                                    | 203                                  | 9.8                                     | 206                                   | 9.6                                      |
| NDI-PEU-02    | 10                                | 214                                  | 18.2                                    | 223                                  | 19.9                                    | 218, 226                              | 30.4                                     |
| NDI-PEU-03    | 3                                 | 228                                  | 24.4                                    | 240                                  | 23.2                                    | —                                     | —                                        |
| NDI-PEU-04    | −8                                | 234                                  | 32.8                                    | 245                                  | 26.9                                    | —                                     | —                                        |
| MDI-PEU-01    | —                                 | 112                                  | 1.8                                     | —                                    | —                                       | —                                     | —                                        |
| MDI-PEU-02    | —                                 | 131                                  | 8.2                                     | 147                                  | —                                       | —                                     | —                                        |
| MDI-PEU-03    | —                                 | 175                                  | 18.1                                    | —                                    | —                                       | —                                     | —                                        |
| MDI-PEU-04    | —                                 | 181                                  | 14.2                                    | —                                    | —                                       | —                                     | —                                        |
| ttHMDI-PEU-01 | —                                 | 129                                  | 12                                      | —                                    | —                                       | —                                     | —                                        |
| ttHMDI-PEU-02 | —                                 | 180                                  | 36                                      | —                                    | —                                       | —                                     | —                                        |
| NDI-PAU-00    | 49                                | —                                    | —                                       | —                                    | —                                       | —                                     | —                                        |
| NDI-PAU-01    | 42                                | 142                                  | 6.5                                     | 180                                  | 3.2                                     | 285                                   | 7.3                                      |
| NDI-PAU-02    | 36                                | 156                                  | 8.4                                     | 191                                  | 4.7                                     | 294                                   | 8.3                                      |
| NDI-PAU-03    | 31                                | 200                                  | 6.2                                     | 222                                  | 5.7                                     | —                                     | —                                        |
| NDI-PAU-04    | 27                                | 216                                  | 7.8                                     | 237                                  | 6.2                                     | —                                     | —                                        |
| NDI-PSU-00    | —                                 | —                                    | —                                       | —                                    | —                                       | —                                     | —                                        |
| NDI-PSU-01    | —                                 | 218                                  | 38.0                                    | 290                                  | 27.7                                    | 289                                   | 20.8                                     |
| NDI-PSU-02    | —                                 | 238                                  | 49.7                                    | 313                                  | 35.4                                    | 322                                   | 32.2                                     |

a) Soft segment melting temperature (second heating; heating and cooling rate 20°C/min); b) Hard segment melting temperature and heat of fusion of the first peak (first heating; heating rate 20°C/min); c) Melting temperature and heat of fusion of the second peak (first heating; heating rate 20°C/min); d) Melting temperature and heat of fusion after 15 min annealing at the temperatures, which are stated at Fig. 4-5.

Fig. 10 shows the storage moduli of the PAU-n, which are constant over a broad temperature range. Compared to polyether elastomers with a similar number of repeating units, the polyester elastomers had, as expected, higher storage moduli. After the melting of the soft segments, an almost horizontal plateau region with an increasing level of the storage modulus at a growing hard segment length and hard segment content, respectively (Tab. 3) is observed. The amount of soft segment crystallization decreases with increasing hard segment length and hard segment content due to partially reduced phase segregation. Increasing hard segment content leads to an increasing amount of solubilized hard segment in the soft segment and therefore overcomes the effect of increasing segregation with increasing hard segment length. The glass transition temperature is shifted to higher values with increasing hard segment length, thus also indicating an increasing amount of solubilized hard segment in the soft segment matrix.

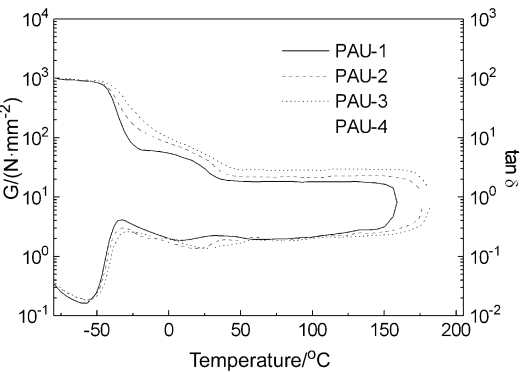


Fig. 10 Dynamic mechanical properties of the polyester elastomers PAU-n

evated temperatures (which was consistent with the temperatures of the hard segment melting in the DSC), was smaller for the PEA based samples than for the POTM based samples. This fact is related to the different ratio of hard-hard segment and hard-soft segment interactions in these polymers.

## Conclusions

The, by means of protecting groups, stepwise synthesized segmented PUR elastomers with molecularly uniform hard segments were suitable model elastomers for detailed investigations of the structure-properties-relations of technologically relevant NDI based elastomers. With the help of the well-defined hard segments, it was shown that the thermal and mechanical properties of these polymers were decisively influenced by the hard segment morphology. This morphology was dependent on both the crystallization behaviour of the naphthalene bisurethane units and the interactions between the NDI based hard and soft segments. These studies were completed by further investigations on molecularly uniform NDI/BDO oligourethanes, at which the hard segment properties were observed without the influence of the soft segments<sup>[15]</sup>.

## Reference :

- [ 1 ] Bayer O. *Angew Chem.* 1947, 59, 257.
- [ 2 ] Estes G M, Seymour R W, Cooper S L. *Macromolecules*, 1971, 4, 452.
- [ 3 ] Bonart R. *Angew Makromol Chem.* 1977, 58/59, 259.
- [ 4 ] Noshay A, McGrath J E. *Block Copolymers*. Academic Press, New York 1977, p. 365.
- [ 5 ] Meckel W, Goyert W, Wieder W. *Thermoplastic Polyurethane Elastomers*, in: *Thermoplastic Elastomers*, Legge N R, Holden G and Schroeder H E, Eds., Carl Hanser, München 1987, p. 13 ff.
- [ 6 ] Prolingheuer E C, Lindsey J J, Kleimann H. *J Elastomers Plast*, 1989, 21, 100.
- [ 7 ] Kogelnik H J, Huang H H, Barnes M, Meichsner R. *J Elastomers Plast*, 1991, 23, 314.
- [ 8 ] Prolingheuer E C, Barnes J M, Kopp R, Seggern E. *Rubber Plast News*, 1992, 21, 15.
- [ 9 ] Festel G, Eisenbach C D. *Polym Prepr (Am Chem Soc, Div Polym Chem)*, 1996, 37/1, 535.
- [ 10 ] Eisenbach C D, Baumgartner M, Günter C. *Polym Prepr (Am Chem Soc, Div Polym Chem)*, 1985, 26/2, 7.
- [ 11 ] Eisenbach C D, Baumgartner M, Günter C. *Polyurethane Elastomers with Monodisperse Segments and their Model Precursors; Synthesis and Properties*, in: *Advances in Elastomers and Rubber Elasticity*, Lal J und Mark J E, Eds, Plenum, New York 1986, p. 51 ff.
- [ 12 ] Eisenbach C D, Heinemann T, Ribbe A, Stadler E, Thaufelder H. *Polym Prepr (Am Chem Soc, Div Polym Chem)*, 1993, 34/1, 83.
- [ 13 ] Eisenbach C D, Ribbe A, Günter C. *Macromol Rapid Commun*, 1994, 15, 395.
- [ 14 ] Festel G, Fischer K, Eisenbach C D. *Macromol Chem Phys*, 1997, 198, 3105.
- [ 15 ] Festel G, Eisenbach C D. *Macromol Chem Phys*, 1998, 199, 1365.
- [ 16 ] Lipatov Y S. *Rubber Chem Technol*, 1968, 41, 537.
- [ 17 ] Dequatre C, Camberlin Y, Pillot C, Pascault J P. *Angew Makromol Chem.* 1978, 72, 11.
- [ 18 ] Camberlin Y, Gol J, Pascault J P. *Angew Makromol Chem*, 1981, 95, 67.
- [ 19 ] Günter C. Doctor thesis, Universität Freiburg, 1986.
- [ 20 ] Steinlein C. Doctor thesis, Universität Bayreuth, 1995.
- [ 21 ] MacKnight W J, Yang M, Kajiyama T. *Polym Prepr (Am Chem Soc, Div Polym Chem)*, 1968, 9/1, 860.
- [ 22 ] Song Y M, Chen W C, Yu T L, Linliu K, Tseng Y H. *J Appl Polym Sci*, 1998, 62, 827.
- [ 23 ] Lee D K, Tsai H B. *J Appl Polym Sci*, 2000, 75, 167.
- [ 24 ] Goyert W, Hespe H. *Kunststoffe*, 1978, 68, 819.
- [ 25 ] Bonart R, Morbitzer L, Rinke H. *Kolloid-Z Z Polym*, 1970, 240, 807.
- [ 26 ] van Bogart J W C, Bluemke D A, Cooper S L. *Polymer*, 1981, 22, 1428.
- [ 27 ] Tang Z G, Teoh S H. *J Appl Polym Sci*, 2004, 91, 3088.
- [ 28 ] Siesler H W, Holland-Moritz K. *Infrared and Raman Spectroscopy of Polymers*, Marcel Dekker, New York, 1980.

## 1,5-萘二异氰酸酯与 1,4-丁二醇基为基质的 多嵌段聚氨酯弹性体的合成与性能

**摘要:** 利用 1,5-萘二异氰酸酯(NDI)和 1,4-丁二醇(BDO)为均匀硬质分子单体,与不同软质分子单体(聚醚、聚酯、聚硅氧烷)缩合制备多嵌段聚氨酯弹性体,详细研究了硬嵌段相(NDI)弹性体的结构与性能间的关系,发现随着硬嵌段相长度的增加,或者氨基甲酸酯中胺基与聚醚、聚酯、聚硅氧烷中软段氧原子间氢键的减弱,都导致微相分离程度的增加,造成聚合物熔点和熔化热的升高。硬嵌段相熔化的多峰行为是由于形成了 NDI/BDO 半微晶区,在退火时转变为更加有序的结晶微区,当温度高于 180℃时,由于氢键的断裂,NDI/BDO 硬嵌段发生分解反应,该过程源于不很有序的硬嵌段半结晶微区。当温度高于 250℃时,发生快速的分解。在动态力学行为方面,NDI 基聚醚弹性体比其它硅氧烷基的弹性体展示了更高的硬嵌段区的稳定性,同时,在使用温度范围内,也显示出最高的储能模量值,表明刚性对温度的依赖性,以及 NDI/BDO 硬嵌段中活性填料的显著影响。

**关键词:** 聚氨酯弹性体; 亚萘基二异氰酸酯; 链段聚氨基甲酸酯; 单分散性硬链段; 结构与性能之间的关系

(上接 21 页)

- [56] Nogales A, Hsiao B S, Somani R H. *Polymer*, 2001, 42; 5247.
- [57] Ito H, Minagawa K, Takimoto J, Tada K. *International Polymer Processing XI*, 1996, 4; 363.
- [58] Kulkarni J A, Beris A N. *J Rheol*, 1998, 42; 971.
- [59] Bushman A C, McHugh A J. *J Polym Sci Polym Phys*, 1996, 34; 2393.
- [60] Doufas A K, Dairanieh I S, McHugh A J. *Polym Eng Sci*, 1995, 35(15); 1222.
- [61] Zuidema. *Flow Induced Crystallization of Polymers*, Eindhoven; Technische Universiteit Eindhoven, 2000.
- [62] Eder G, Janeschitz-Kriegl H, in: H E H Meijer(Ed.)·*Materials Science and Technology: Polymer Processing*, Vol 18, Wiley, Weinheim, 1998 (Chapter 5).

## Nonisothermal Crystallization Kinetics of Polymers

ZOU Xiao-xuan, DAI Wen-li, TIAN Ji-bo

(College of Chemistry, Xiangtan University, Xiangtan 411105, China)

**Abstract:** This paper reports the development on models of nonisothermal crystallization kinetic of polymers, especially in nonisothermal quiescent crystallization and shear-induced crystallization, and also discusses some chief models.

**Key words:** Nonisothermal; Kinetics; Crystallization; Model