

Synthesis and Application of 3,5-Di-*tert*-butylbenzyl chloroformate for the Protection of Amino Functions and the Improvement of Solubility in Polyurethane Synthesis

Gunter Festel* ¹⁾

Bayreuth, Lehrstuhl Makromolekulare Chemie II der Universität

Claus D. Eisenbach

Stuttgart, Institut für Technische Chemie II der Universität

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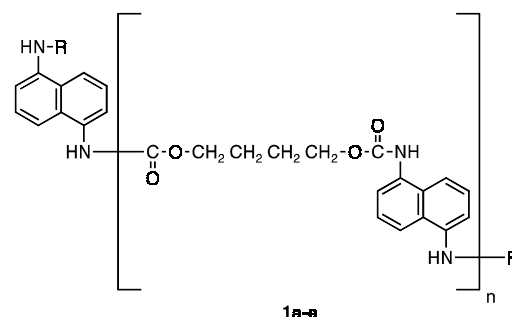
Abstract. The benzyloxycarbonyl (BOC) group was used for the protection of amino functions in the stepwise synthesis of molecularly uniform oligourethanes based on 1,5-naphthalene diamine (NDA) as well as polyurethane (PUR) elastomers with molecularly uniform NDA-based hard segments. Whereas the poor solubility of the BOC terminated key intermediates **5** in solvents suitable for condensation reactions of oligourethane building blocks in the planned synthesis route prevented the employing of this convenient protective group, the modified 3,5-di-*tert*-butyl substituted BOC (3,5-

di-*t*BBOC) group was found to significantly improve of the solubility of the compounds **16**. This allowed the stepwise building-up of oligourethane model compounds and of telechelic hard segments precursors **18**. Furthermore, due to the better solubility, the 3,5-di-*t*BBOC protective group also led to considerable improvement of the purification of intermediate products **13b** by liquid chromatography as compared to the purification of corresponding BOC terminated compounds **13a**.

Segmented polyurethane (PUR) elastomers based on 1,5-naphthalene diisocyanate (NDI) are of considerable technological relevancy [1–4]. Molecularly uniform oligourethanes with methyl urethane and 4-methoxybutyl urethane end groups (**1b,c**, Scheme 1) as well as PUR elastomers with molecularly uniform hard segments served as model compounds for the detailed analysis of the structure-property relationships of these materials [5–7].

Starting with 1,5-naphthalene diamine (NDA) and 1,4-butanediol (BDO), oligourethanes **1** with one to five NDA/BDO repeating units were built-up in a stepwise procedure. The urethane linkage was formed by condensation of amines with chloroformates, which were obtained by the reaction of an alcohol with phosgene. The chloroformateamine condensation reaction had considerable advantages over the addition of an alcohol to an isocyanate, as chloroformates are less sensitive to moisture than isocyanates; furthermore, one can take advantage of the higher activity of the amino group as compared to the hydroxyl function [8], and therefore, the chloroformate route is preferred to the reaction of carbamic acid chlorides with alcohols [9].

A basic requirement for obtaining molecular uniformity in the condensation reaction of basically bifunction-



1	R	n=1	n=2	n=3
a	-H	20	22	18
b				
c				
d				
e		19	21	17

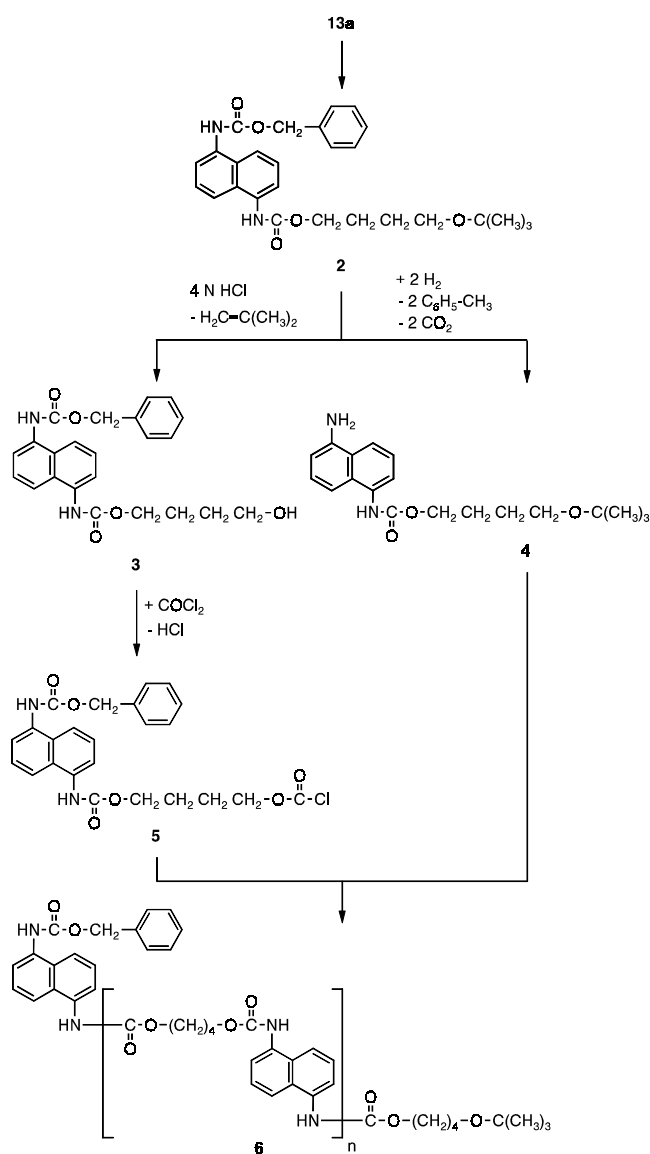
Scheme 1 Molecularly uniform oligourethanes **1** with various end groups; n = number of NDA/BDO repeating units

¹⁾ Present Address: Bayer AG, D-51368 Leverkusen, Germany

al compounds is that one functional group of the bifunctional educts NDA and BDO is protected before each condensation reaction, as it is extremely difficult to remove the oligomeric by-products. Therefore, the *tert*-butyl (*t*B) group was used for protecting the hydroxyl functions and the benzyloxycarbonyl (BOC) group for amino functions. The BOC group was introduced by Bergmann in the 1930's for the protection of amino functions in the peptide synthesis [10]. Today, the BOC group is widely used as amino protective group in various types of syntheses [11]. The BOC protective group for the amino function has also been successfully employed in the controlled syntheses of oligourethanes, including NDA/BDO model compounds. This protective group is well suited for the protection of amino groups in the stepwise building-up of molecularly uniform oligourethanes by the chloroformateamine condensation reaction, because it can be removed selectively and quantitatively by hydrogenolysis, and without any decomposition of the urethane group [12].

The characteristic features of the stepwise and sequential building-up of the oligourethanes by using selectively removable protective groups are illustrated in the reaction Scheme 2 (cf. ref. [12]). A key building block is the molecule **2** on top of Scheme 2, which actually represents one repeat unit of an oligourethane with a BOC protected amino function and a *tert*-butyl protected hydroxyl function. The reaction sequence shows the extension of the starting diprotected compound **2** by one repeat unit to give **6** with $n=1$; the higher oligomers are synthesized accordingly either by stepwise chain extension of *N*- or *O*-terminal activated oligomers **6** by one repeating unit (employing **5** or **4**, respectively), or by the condensation of oligomers **6** with one activated (deblocked) end group.

A problem in the realization of the planned synthesis route as shown in Scheme 2 was that the NDA-based oligourethanes – due to the rigid structure of the naphthalene core – had a very low solubility in the organic solvents suitable for the different synthetic steps. As a consequence, the stepwise building-up of model compounds involving the cleavage of the BOC group, and the subsequent reactions could only be carried out for oligomers with a maximum of 2 NDA/BDO repeating units, and only in very small quantities. In order to overcome this problem, the solubility of the BOC terminated building blocks had to be improved. Thus the 3,5-di-*tert*-butyl substituted BOC (3,5-di-*t*BBOC) group, which had already been employed in the peptide synthesis for the protection of amino functions, was selected; this group can be easily cleaved by moderately acidic hydrolysis [16–18], and the *tert*-butyl substitution is known to have a solubility increasing effect. This modified protective group could be employed in the oligourethane synthesis analogously to the conventional BOC group, and the solubility of the (oligomeric) build-



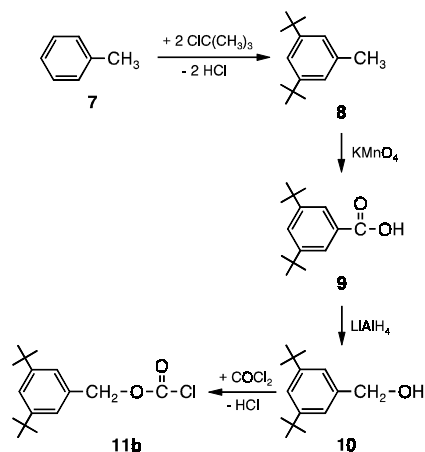
Scheme 2 General reaction scheme for the sequential synthesis of molecularly uniform oligourethanes by using protective groups for the amino and hydroxyl function; the bracket in **6** indicates the repeating unit, and $n=1$ in this example. The detailed synthesis of corresponding oligourethanes based on methylene biphenyl [13], methylene bis(4,4'-cyclohexyl) [14] and N(H)RN(H) piperazinyl [15] is described elsewhere

ing blocks was substantially improved due to the *tert*-butyl group effect.

In this paper we describe the preparation of the 3,5-di-*tert*-butylbenzyl chloroformate reagent, its employing to protect the amino group of building blocks and oligourethanes, and the removal of 3,5-di-*t*BOC. The detailed synthesis and characterization of the molecularly uniform oligourethanes and the different PUR elastomers with molecularly uniform hard segments containing the naphthalene diurethane constitutional unit is given elsewhere [6, 7].

Results and Discussion

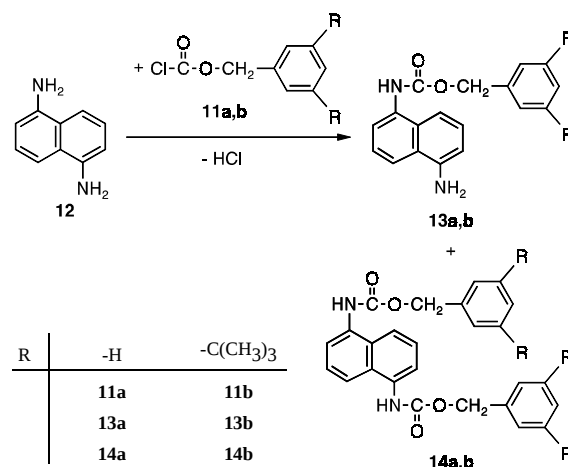
3,5-Di-*tert*-butylbenzyl chloroformate was synthesized in a 4-step reaction (Scheme 3). Starting with toluene (7), the *tert*-butyl groups were introduced by Friedel-Crafts-alkylation with *tert*-butyl chloride and AlCl_3 . As both the 4-mono- and the 3,5-disubstituted products were obtained in this reaction, 3,5-di-*tert*-butyltoluene (8) was removed from 4-*tert*-butyltoluene by distillation [19]. The oxidation of the methyl group to the carboxyl function was carried out with potassium permanganate under basic conditions in pyridine [20, 21]. 3,5-Di-*tert*-butylbenzoic acid (9) was reduced to 3,5-di-*tert*-butylbenzyl alcohol (10) by the reaction with lithium aluminum hydride in tetrahydrofuran (THF). In the last step, 3,5-di-*tert*-butylbenzyl chloroformate (11b) was formed by reaction of 10 with phosgene. 11b was used without further purification by distillation, because benzyl chloroformates could explosively decompose during heating.



Scheme 3 Synthesis of 3,5-di-*tert*-butylbenzyl chloroformate **11b** in a 4-step reaction

The synthesis of the single protected NDA with either the conventional BOC or the 3,5-di-*t*BBOC is shown in the Scheme 4. The course of the reaction was similar for benzyl chloroformate **11a** and the di-*tert*-butyl substituted reagent **11b**. The condensation reaction of NDA **12** with an equimolar amount of **11a** or **11b** at 0 °C in CH_2Cl_2 and using Na_2CO_3 to neutralize the HCl gave the single protected benzyl-*N*-1,5-naphthalene diamine carboxylate **13a** or the 3,5-di-*tert*-butylbenzyl-*N*-1,5-naphthalene diamine carboxylate **13b** as the main reaction product. Besides, unreacted NDA as well as the bisurethanes **14a,b** (benzyl- or 3,5-di-*tert*-butylbenzyl-*N,N'*-1,5-naphthalene diamine dicarboxylate) were also present in the reaction mixture. The pure monoprotected **13a** or **13b** were obtained by purification of the crude reaction product by flash chromatography over a silica gel column. Different toluene/metha-

nol, toluene/THF and cyclohexane/THF solvent mixtures were tested as eluent, whereby the best results were obtained with toluene/THF 10:1 v/v.



Scheme 4 Synthesis of the single protected **13a** and double reacted **14a** BOC NDA derivative as well as the corresponding single protected **13b** and double reacted **14b** 3,5-di-*t*BBOC compounds

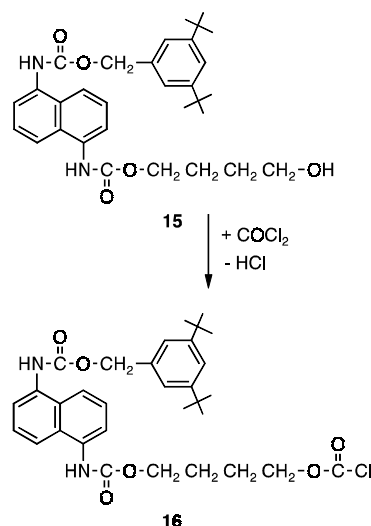
One advantage of using the 3,5-di-*t*BBOC instead of the conventional BOC group is the more efficient chromatographical isolation of the single protected product **13b**, which is partially due to the solubility enhancing effect of the *tert*-butyl substituents. Whereas in the case of the BOC group **13a** only 2 g of the crude reaction product could be given on the column due to its relatively low solubility, the purification of **13b** with the 3,5-di-*t*BBOC protective group could be carried out in 10 g quantities (the crude reaction product was solved in 100 ml of toluene/THF 10:1, given on the column and flashed with toluene/THF 10:1; diameter of the column 7 cm, height of silica gel 25 cm).

The differences of the R_f -values between NDA **12**, single protected **13** and double reacted **14** product as determined by thin-layer chromatography was significantly larger for the *tert*-butyl substituted system as compared to the corresponding BOC terminated compounds. The R_f -values of the starting material NDA and the reaction products, according to Scheme 4 and determined by thin-layer chromatography (toluene/THF 10:1 v/v as solvent), are as follows: NDA **12** 0.26, single BOC protected NDA **13a** 0.31, double BOC substituted NDA **14a** 0.55, single 3,5-di-*t*BBOC protected NDA **13b** 0.40 and double 3,5-di-*t*BBOC substituted NDA **14b** 0.79. As a result of both the increased solubility in the eluent and the higher resolution in the chromatographical purification, the overall yield of **13b** was distinctly higher (42%) than the yield of **13a** (33%). A comparison of the solubility of oligourethanes **1** with

the same number of repeating units but different end groups (amino, methyl urethane, 4-methoxybutyl urethane, BOC and 3,5-di-*t*BBOC) showed that the BOC terminated oligourethanes **1d** had the lowest solubility. Even in the case of oligourethanes with only two NDA units (**1** with $n=1$) the solubility of the compounds with the conventional BOC protective group **1d** was so poor that it could be dissolved only under heating in very polar solvents such as *N,N*-dimethylformamide, *N,N*-dimethylacetamide, and dimethyl sulfoxide. Therefore, the reactions for the synthesis of oligomers with $n>1$ following Scheme 2 were not possible using the BOC protective group because of the insolubility of the oligourethanes in appropriate solvents. However, these reactions could be carried out when introducing the 3,5-di-*t*BBOC group. This is illustrated in the following in detail for three examples.

First, the phosgenation, which was necessary to obtain chloroformates by the reaction of an alcohol with phosgene, could be carried out more easily using the 3,5-di-*t*BBOC group, as the solubility was higher in suitable solvents. Due to the sufficient difference in reactivity of the two carbonyl chloride functions of phosgene, the forming of carbonate by-products was avoided. As an example, Scheme 5 shows the reaction of (3,5-di-*tert*-butyl) benzyl (4-hydroxy) butyl-*N,N'*-1,5-naphthalene diamine dicarboxylate **15** with phosgene to form the 3,5-di-*tert*-butylbenzyl 4-chloroformyloxybutyl-*N,N'*-1,5-naphthalene diamine dicarboxylate **16** which was an important building block for the synthesis of the higher oligomeric model compounds as already explained in Scheme 2; the conversion of **15** to **16** in Scheme 5 corresponds to the conversion of **3** to **5** in Scheme 2.

The phosgenation in good solvents for urethanes such as *N,N*-dimethylformamide and *N,N*-dimethylacetamide



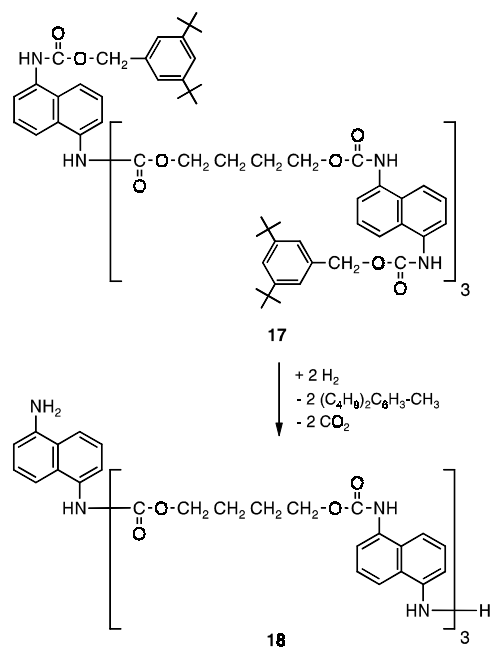
Scheme 5 Formation of the NDA building unit **16** with a 3,5-di-*t*BBOC protected amino and a reactive chloroformate end group by phosgenation of the corresponding alcohol **15**

was not possible, because they react with phosgene and with chloroformates [22]. Dimethyl sulfoxide is non-phosgene reactive [23], but this solvent could introduce traces of sulphur, so that the hydrogenation with the Pd catalyst (removal of amine protective group, *e.g.*, conversion of **2** into **4**, Scheme 2) would fail. Therefore, the phosgenation could only be carried out in non-phosgene reactive solvents like chloroform, THF or 1,4-dioxane, and the latter turned out to be the best solvent. The alcohol **15** was treated with the fivefold excess of phosgene at 0 °C. Because of the melting point of 1,4-dioxane of 12 °C, it is advantageous to use a 9:1 v/v 1,4-dioxane/THF-mixture for this reaction. While only 0,3 g of the alcohol **3** (Scheme 2), dissolved in 1 l of 1,4-dioxane, could be treated using the conventional BOC group, the 3,5-*tert*-butyl substituted BOC in **15** allowed to run the phosgenation of the tenfold higher concentration.

Another example is the conversion of the end group protected oligourethane **1d** or **1e** (Scheme 1) into the α,ω -diamino oligourethane building block (**1a**, Scheme 1) which can be employed for the synthesis of segmented polyurethanes with molecularly uniform hard segments (cf. Ref. [12]). The oligourethane with 3 NDA/BDO repeating units and BOC end groups (**1d** with $n=3$, Scheme 1) was insoluble in solvents suitable for the catalytical hydrogenation; therefore the removal of the BOC protecting group (see conversion of **2** into **4**, Scheme 2) could not be carried out accordingly. The analogous tetramethylene bis {5-[4-[5-(3,5-di-*tert*-butyl benzyloxy carbonyl)-1,5-naphthalene diamine-1-yl carbonyloxy]butoxy carbonyl]-1,5-naphthalene diamine-1-carboxylate} (**17**) (**1e** with $n=3$, Scheme 1) was sufficiently soluble in DMA so that a cleavage of the protective groups at 10 bar H_2 -pressure and a temperature of 80 °C was possible (Scheme 6). The solubility of the resulting amino terminated tetramethylene bis {5-[4-(1,5-naphthalene diamine-1-yl carbonyloxy) butoxycarbonyl]-1,5-naphthalene diamine-1-carboxylate} (**18**) (**1a** with $n=3$, Scheme 1) was even better than that of **17**.

In the context of the removal of the BOC or 3,5-di-*t*BBOC protective group by catalytical hydrogenation it has to be mentioned that in NDA based compounds, for a successful cleavage, it was necessary to purify the starting NDA material (**12**) from sulphur by twice recrystallizing the derivative *N,N'*-bis(benzylidene)-1,5-naphthalene diamine (which was obtained by on reacting of **12** with benzaldehyde) from 1,4-dioxane [7]. Even small amounts of sulphur, which originated from the technical synthesis of **12**, contaminated the catalyst required for the hydrogenolytical cleavage of the BOC or 3,5-di-*t*BBOC group to such an extend that almost no conversion occurred.

The complete and selective cleavage of the BOC as well as of the 3,5-di-*t*BBOC protective group could be verified by 1H NMR spectroscopic analysis, as it is ex-



Scheme 6 Cleavage of the 3,5-di-*t*BBOC protective group of the oligourethane **17** (1d with 3 NDA/BDO) repeating units by hydrogenolysis to give the oligourethane diamine **18** (**1a** with $n=3$)

emplarily shown for the 3,5-di-*t*BBOC terminated tetramethylene bis [5-(3,5-di-*tert*-butyl benzyloxy carbonyl)-1,5-naphthalene diamine-1-carboxylate] **19** with one NDA/BDO repeating unit (**1e** with $n=1$, Scheme 1). The signals of the *tert*-butyl protons at $\delta = 1.29$ (h), the methylene protons of the benzyl group at $\delta = 5.17$ (e) and the urethane NH group of the 3,5-di-*t*BBOC group at $\delta = 9.66$ (d), which are characteristic for the 3,5-di-*t*BBOC group (Figure 1a), disappeared after the hydrogenolytical removal, and the amino end groups were detected by the signal at $\delta = 5.66$ (d) (Figure 1b). The ^{13}C NMR spectrum of the corresponding tetramethylene bis (1,5-naphthalene diamine-1-carboxylate) **20** (**1a** with $n=1$, Scheme 1) no longer showed the peaks of the *tert*-butyl carbon atoms at $\delta = 31.6$ and 34.8 and the methyl carbon atom of the benzyl group at $\delta = 66.7$.

IR spectroscopical analysis also showed the successful cleavage of the 3,5-di-*t*BBOC group. While the absorption of the NH vibration at the 3,5-di-*t*BBOC terminated 4-[5-(3,5-di-*tert*-butyl benzyloxy carbonyl)-1,5-naphthalene diamine-1-yl carbonyloxy]butyl-*N,N'*-1,5-naphthalene diamine dicarboxylate **21** with 2 NDA/BDO repeating units (**1e** with $n=2$, Scheme 1) was seen at 3290 cm^{-1} (Figure 2a), the 4-(1,5-naphthalene diamine-1-yl carbonyloxy) butyl-*N,N'*-1,5-naphthalene diamine dicarboxylate **22** with amino end groups (**1a** with $n=2$, Scheme 1) showed the peak at 3370 cm^{-1} (Figure 2b). The peak of the CO group was shifted from 1700 to 1740 cm^{-1} .

Finally, the synthesis of the PUR elastomers with mo-

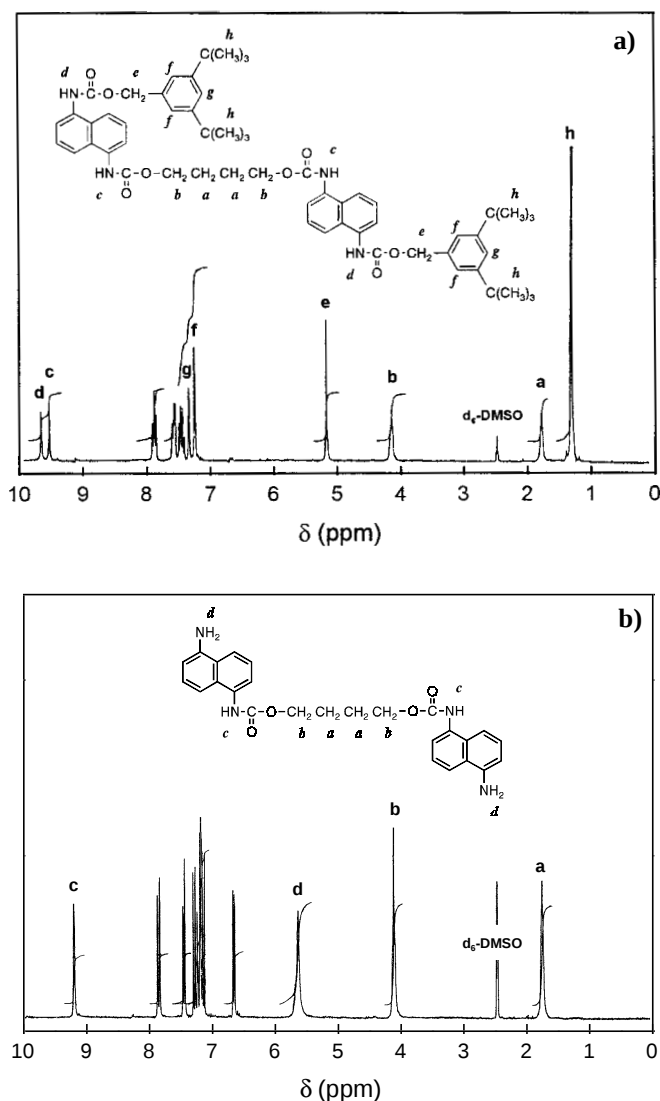


Fig. 1 ^1H NMR spectra ($\text{d}_6\text{-DMSO}$ as solvent) of a) the 3,5-di-*t*BBOC terminated compound **19** (oligourethane **1e** with $n=1$) and b) the corresponding amino terminated compound **20** (oligourethane **1a** with $n=1$) after cleavage of the protective group

lecularly uniform hard segments was also more efficient when using the 3,5-di-*t*BBOC group instead of the BOC group. The usual method to synthesize model elastomers with monodisperse hard segments by condensation of polyol bischloroformates with amino terminated, molecularly uniform hard segment precursors **1a** (Scheme 1) was severely restricted by the limited solubility of the amino terminated oligourethanes with more than 2 NDA/BDO repeating units. However, the synthesis could be realized by employing an α,ω -amino naphthalene urethane telechelic prepared from polyether, polyester or polysiloxane polyols by reaction of the polyol bischloroformates with single BOC protected NDA **13a** and the subsequent hydrogenolytical remov-

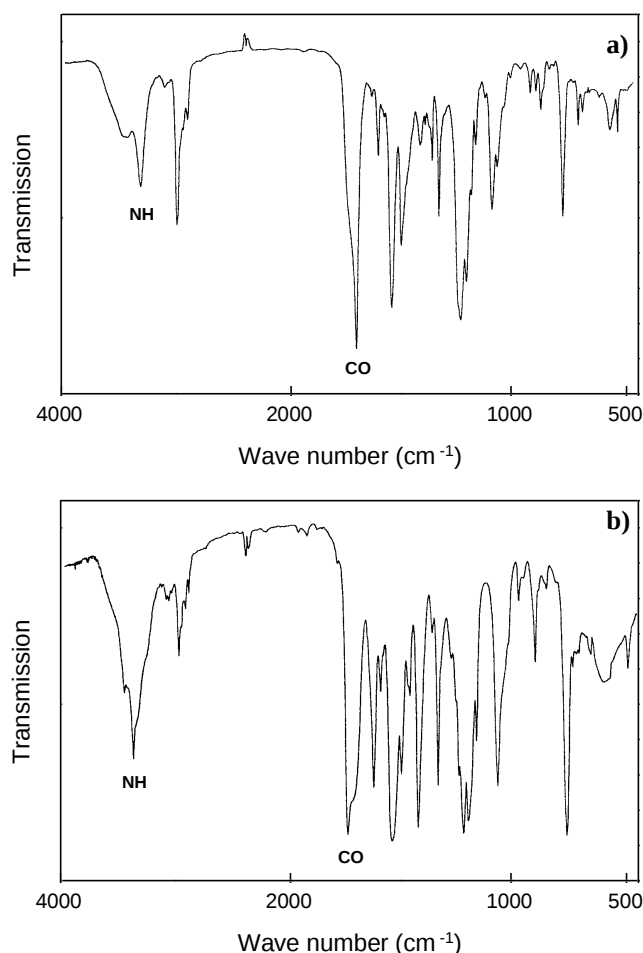


Fig. 2 IR spectra (KBr) of a) the 3,5-di-*t*BBOC terminated compound **21** (oligourethane **1e** with $n=2$) and b) the corresponding amino terminated compound **22** (oligourethane **1a** with $n=2$) after cleavage of the protective group

al of the BOC groups; further reacting of this NDA urethane terminated polyol with **16**, whereby the solubility was improved by employing the 3,5-di-*t*BBOC protective group and subsequent deblocking, amino terminated prepolymers with 2 naphthalene units at each end of the polyols were accessible. The polycondensation reaction of such diamino telechelics representing polyols carrying a full hard segment repeating unit at both ends with suitable bischloroformates (e.g. of BDO or hydroxybutylurethane terminated hard segment building blocks), PUR elastomers with up to 4 NDA/BDO repeating units in the molecularly uniform hard segment were obtained [5].

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Experimental

Silica gel layers Polygram Sil G/UV₂₅₄ from Macherey-Nagel (size 4×8 cm) were used for thin-layer chromatography (toluene/THF 10:1 as eluent). – Flash chromatography was carried out with a column filled with silica gel 60 from Fluka (diameter 7 cm, height of silica gel 25 cm) and 0.4 bar N₂-pressure (toluene/ THF 10:1 as solvent). – ¹H NMR and ¹³C NMR spectra were recorded at 25 °C on a Bruker AC 250 spectrometer at 250 MHz and 62.9 MHz, respectively, using tetramethylsilane as internal standard. – IR measurements were made with a FTIR spectrometer Bio-Rad Digilab Division 3240-SPC FTS-40. – NDA was provided by Bayer, all other chemicals were from Fluka.

Benzyl (4-tert-butoxy)butyl-N,N'-1,5-naphthalene diamine dicarboxylate (2)

3 g (10.2 mmol) of **13a** were dissolved in 100 ml of THF and 1.5 ml (18.8 mmol) of pyridine. After adding a solution of 2.5 g (12 mmol) of 4-*tert*-butoxybutyl chloroformate in 50 ml of THF dropwise at –78 °C and warming up to room temperature, the solution was stirred for 8 h. After evaporating the solvent, washing with methanol and drying, the product was recrystallized from 20 ml of THF. Yield 4.2 g (88%) with *m.p.* 148 °C. – IR (KBr): ν/cm^{-1} = 3299 (m), 1694 (s). – ¹H NMR (250 MHz, d₆-DMSO): δ/ppm = 1.12 (s, 9H, –O–C(CH₃)₃), 1.61 (m, 4H, –O–CH₂–CH₂–CH₂–), 3.32 (t, 2H, –CH₂–O–C(CH₃)₃), 4.12 (t, 2H, –CO–O–CH₂–CH₂–), 5.18 (s, 2H, –O–CH₂–C=), 7.34–7.52 (m, 7H), 7.61 (t, 2H), 7.90 (d, 2H), 9.50 (s, 1H, –NH–CO–O–CH₂–CH₂–), 9.68 (s, 1H, –NH–CO–O–CH₂–C=). – ¹³C NMR (62.9 MHz, d₆-DMSO): δ/ppm = 25.8 (–CO–O–CH₂–CH₂–CH₂–), 26.7 (–CO–O–CH₂–CH₂–), 27.4 (–O–C(CH₃)₃), 60.5 (–CH₂–O–C(CH₃)₃), 64.4 (–CO–O–CH₂–CH₂–), 65.9 (–O–CH₂–C=), 71.9 (–CH₂–O–C(CH₃)₃), 119.8, 120.0, 121.5, 125.2, 125.3, 127.8, 127.9, 128.4, 128.9, 134.0, 134.1, 136.9, 154.8 (–CO–O–CH₂–C=), 155.0 (–CO–O–CH₂–CH₂–).

Benzyl (4-hydroxy)butyl-N,N'-1,5-naphthalene diamine dicarboxylate (3)

A mixture of 4 g (8.6 mmol) of **2**, 100 ml of dioxane and 20 ml of 4N HCl were refluxed for 8 h under an argon atmosphere. After cooling, 4N NaOH was added, until the solution was alkaline. The dioxane was evaporated, and the product was filtered off, washed with a lot of water, dried and recrystallized from 50 ml of THF. Yield: 2.9 g (84%) with *m.p.* 178 °C. – IR (KBr): ν/cm^{-1} = 3294 (m), 1695 (s). – ¹H NMR (250 MHz, d₆-DMSO): δ/ppm = 1.61 (m, 4H, –O–CH₂–CH₂–CH₂–), 3.45 (t, 2H, –CH₂–OH), 4.13 (t, 2H, –CO–O–CH₂–CH₂–), 5.19 (s, 2H, –O–CH₂–C=), 7.36–7.53 (m, 7H), 7.61 (t, 2H), 7.90 (d, 2H), 9.50 (s, 1H, –NH–CO–O–CH₂–CH₂–), 9.68 (s, 1H, –NH–CO–O–CH₂–C=). – ¹³C NMR (62.9 MHz, d₆-DMSO): δ/ppm = 25.7 (–CO–O–CH₂–CH₂–), 29.1 (–CO–O–CH₂–CH₂–), 60.7 (–CH₂–OH), 64.7 (–CO–O–CH₂–CH₂–), 66.2 (–CH₂–C=), 120.1, 120.3, 121.9, 125.7, 128.2, 128.7, 129.2, 134.1, 134.3, 137.1, 155.1 (–CO–O–CH₂–C=), 155.4 (–CO–O–CH₂–CH₂–).

4-tert-Butoxybutyl-N-1,5-naphthalene diamine carboxylate (4)

200 mg of Pd on charcoal (5%) were added to a solution of

5 g (10,8 mmol) of **2** in 200 ml of THF. The reaction mixture was treated under stirring with H_2 at 50 °C for 2 h at an initial pressure of 5 bar. The catalyst was removed by filtration, the solvent evaporated and the product recrystallized from 100 ml of THF. Yield 3.2 g (91%) with *m.p.* 69 °C. – IR (KBr): ν/cm^{-1} = 3370 (m), 1736 (s). – 1H NMR (250 MHz, d_6 -DMSO): δ/ppm = 1.13 (s, 9H, $-C(CH_3)_3$), 1.60 (m, 4H, $-O-CH_2-CH_2-$), 3.32 (t, 2H, $-CH_2-O-C(CH_3)_3$), 4.10 (t, 2H, $-NH-CO-O-CH_2-$), 5.61 (s, 2H, $-NH_2$), 6.70 (d, 1H), 7.16–7.28 (m, 2H), 7.33 (d, 1H), 7.49 (d, 1H), 7.88 (d, 1H), 9.12 (s, 1H, $-NH-CO-O-CH_2-$). – ^{13}C NMR (62,9 MHz, d_6 -DMSO): δ/ppm = 25.9 ($-O-CH_2-CH_2-CH_2-$), 26.7 ($-O-CH_2-CH_2-$), 27.5 ($-C(CH_3)_3$), 60.5 ($-CH_2-O-C(CH_3)_3$), 64.3 ($-O-CH_2-CH_2-$), 72.0 ($-C(CH_3)_3$), 107.9, 110.4, 119.5, 121.3, 123.1, 123.5, 126.6, 129.5, 133.7, 144.9 ($C=NH_2$), 155.1 ($-NH-CO-O-CH_2-$).

Benzyl 4-chloroformyloxybutyl-N,N'-1,5-naphthalene diamine dicarboxylate (5)

0,2 g (0,5 mmol) of **3**, dissolved in 700 ml of dioxane was slowly added dropwise into 0,5 ml (6,8 mmol) of phosgene under ice cooling and stirred for 2 h at room temperature. The excess phosgene was removed by heating up to 50 °C in a water bath, and the remaining product was dried. Cleaning of the chloroformate by distillation was not possible, as benzyl chloroformates could explosively decompose during heating. Yield 0.2 g (84%) with *m.p.* 156 °C. – IR (KBr): ν/cm^{-1} = 3296 (m), 1780 (s), 1699 (s). – 1H NMR (250 MHz, $CDCl_3$): δ/ppm = 1.80 (m, 4H, $-O-CH_2-CH_2-$), 4.23 (t, 2H, $-O-CH_2-CH_2-$), 4.31 (t, 2H, $-CH_2-O-C(CH_3)_3$), 5.24 (s, 2H, $-O-CH_2-C=$), 7.36–7.53 (m, 7H), 7.61 (t, 2H), 7.90 (d, 2H), 9.48 (s, 1H, $-NH-CO-O-CH_2-CH_2-$), 9.65 (s, 1H, $-NH-CO-O-CH_2-C=$). – ^{13}C NMR (62,9 MHz, $CDCl_3$): δ/ppm = 25.1 ($-CH_2-CH_2-O-CO-Cl$), 30.3 ($-NH-CO-O-CH_2-CH_2-$), 64.6 ($-NH-CO-O-CH_2-$), 68.1 ($-O-CH_2-C=$), 71.5 ($-CH_2-O-CO-Cl$), 120.1, 120.3, 121.9, 125.7, 128.2, 128.7, 129.2, 134.1, 134.3, 137.1, 155.1 ($-NH-CO-O-CH_2-C=$), 155.4 ($-NH-CO-O-CH_2-CH_2-$).

Benzyl-N,N'-1,5-naphthalene diamine dicarboxylate (14a)

After dissolving 3 g (19 mmol) of **12** in 300 ml of CH_2Cl_2 , a solution of 8,2 g (48 mmol) of **11a** in CH_2Cl_2 and 50 ml of 1M Na_2CO_3 solution were added dropwise at 0 °C. After warming up to room temperature, the mixture was stirred for 8 h. The CH_2Cl_2 phase was separated from the water phase and dried with Na_2SO_4 . The CH_2Cl_2 was evaporated, and the crude product dried. For the purification by flash chromatography 2 g were solved in 100 ml of toluene/THF 10:1, given on the column and flashed with toluene/THF 10:1. After 500 ml, 100 ml fractions were taken. The composition of the fractions was controlled by thin-layer chromatography. After evaporating the solvent, the product was recrystallized from 150 ml of THF. Yield: 7 g (86%) with *m.p.* 250 °C. – IR (KBr): ν/cm^{-1} = 3268 (m), 1690 (s). – 1H NMR (250 MHz, d_6 -DMSO): δ/ppm = 5.18 (s, 4H, $-O-CH_2-$), 7.29–7.52 (m, 10H), 7.50 (d, 2H), 7.60 (d, 2H), 7.88 (s, 2H, $-NH-CO-$), 9.66 (s, 2H, $-NH-CO-$). – ^{13}C NMR (62,9 MHz, d_6 -DMSO): δ/ppm = 66.2 ($-CH_2-$), 120.2 ($-NH-C= -CH=CH-$), 121.8 ($-NH-C= -CH=$), 125.6 ($-NH-C= -CH= -CH-CH=$), 128.0,

128.1, 128.6, 129.2 ($-NH-C= -CH=CH-CH=C-$), 134.1 ($-NH-C=$), 137.0, 155.1 ($-NH-CO-O-$).

3,5-Di-tert-butylbenzyl-N,N'-1,5-naphthalene diamine dicarboxylate (14b)

3 g (19 mmol) of **12**, dissolved in 300 ml of CH_2Cl_2 , 13.6 g (48 mmol) of **11b** and 90 ml of a 1M Na_2CO_3 solution were reacted as described for compound **14a**. Yield 10.3 g (84%) with *m.p.* 203 °C. – IR (KBr): ν/cm^{-1} = 3282 (m), 1697 (s). – 1H NMR (250 MHz, d_6 -DMSO): δ/ppm = 1.26 (s, 36H, $(CH_3)_3C-$), 5.15 (s, 4 H, $-O-CH_2-$), 7.24 (d, 4H, $(CH_3)_3C-C= -CH=C-$), 7.34 (s, 2H, $(CH_3)_3C-C= -CH=C-$), 7.45 (t, 2H, $-NH-C= -CH=CH-$), 7.56 (d, 2H), 7.88 (d, 2H), 9.64 (s, 2H, $-NH-CO-$). – ^{13}C NMR (62.9 MHz, d_6 -DMSO): δ/ppm = 31.4 ($(CH_3)_3C-$), 34.6 ($(CH_3)_3C-$), 66.7 ($-CH_2-$), 120.3, 121.5, 121.9, 122.0, 125.4, 134.2, 136.2 ($-O-CH_2-C=$), 150.7 ($-C= -C(CH_3)_3$), 155.1 ($-NH-CO-O-$).

The synthesis and experimental data of the other presented compounds **8–11b**, **13a,b** and **15–22** have been described elsewhere [6, 7].

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Address for correspondence:
Dr. Gunter Festel
c/o Bayer AG
Bayerwerk, K 10
D-51368 Leverkusen
E-mail: Gunter.Festel@web.de