Isocyanate-Free Route to Caprolactam-Blocked Oligomeric Isocyanates via Carbonylbiscaprolactam- (CBC-) Mediated End Group Conversion

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Received November 28, 2002; Revised Manuscript Received April 25, 2003

ABSTRACT: Blocked isocyanate functional oligomers and liquid rubbers are prepared by a novel, solvent-free carbonylbiscaprolactam (CBC) mediated end group conversion reaction of amine-terminated oligodimethylsiloxanes (PDMS) and oligopropyleneoxides (PPO), with molar masses varying between 400 and 3140 g/mol, and of hydroxy-terminated oligoethylene oxide (PEG), oligopropyleneoxide (PPO) and oligotetrahydrofuran (PTHF), with molar masses of around 1000 g/mol. The key reaction is the carbonylbiscaprolactam (CBC) mediated amino or hydroxy end group conversion yielding carbamoyl caprolactam functional polymers, without requiring addition of either phosgene or isocyanates. The quantitative CBC conversion of amine end groups occurred in bulk at 100 °C in the absence of catalysts, yielding *N*-carbamoyl caprolactam terminated oligomers and caprolactam (ring elimination, pathway RE). The reaction of hydroxy end groups at 100 to 150 °C in the presence of catalysts such as zirconium alcoholates, magnesium bromide or dibutyltindilaurate (DBTDL) produced *N*-carbamoyl caprolactam end groups via nucleophilic attack of the hydroxy group at one of the CBC caprolactam rings and subsequent ring opening (ring opening, pathway RO). The CBC reactions were monitored by means of ReactIR, ^{1}H NMR and ^{13}C NMR spectroscopy. The molecular masses of the oligomers and liquid rubbers with caprolactam-blocked isocyanate end groups were measured by means of MALDI−ToF mass spectroscopy and size exclusion chromatography (SEC). The thermal behavior and deblocking temperatures of the caprolactam-blocked isocyanates obtained were examined by means of thermogravimetric analysis (TGA).

1. Introduction

The property profiles of polyurethanes are tailored to meet the diversified demands of various industries. Traditional intermediates are di- and polyfunctional isocyanate resins, most of which are obtained via the phosgene-mediated conversion of the corresponding amines, or via the isocyanate-mediated conversion of the corresponding hydroxy-functional intermediates, respectively. Special safety and processing precautions are required for such reactions because phosgene and low molecular weight isocyanates are very toxic and very sensitive to the presence of water. Moreover, isocyanate-mediated oligomer formation via the conversion of polyols requires addition of a large excess of diisocyanates in order to prevent undesirable molar mass buildup via chain extension or premature gelation, especially in the case of multifunctional branched polyols and polyamines. The excess diisocyanate is either left in the resins or must be removed by vacuum stripping.

To circumvent problems related to the presence of free isocyanates, isocyanates are blocked by reacting them with various blocking groups. Deblocking can be induced thermally or by reacting blocked isocyanates with polyols. Comprehensive reviews on the chemistries and applications of blocked isocyanates were published by Wicks.[1,2] Today, the applications of blocked isocyanates range from automotive coatings to adhesives, sealants, paper and textile treatment, foams, rubbers, and reinforced plastics. Typical blocking reagents are bisulfites, which produce water-soluble blocked isocyanates, phenols, pyridinols, thiophenols, mercaptopyridines, mercaptans, oximes such as methyl ethyl ketoxime, amides, cyclic amides such as caprolactam, imidazoles, amidines, pyrazoles, 1,2,4-triazoles, and secondary amines. Another simple method of blocking an isocyanate represents the reversible formation of uretdiones by dimerization of isocyanates in the presence of trialkylphosphine catalysts.

Control on polymer structures and safety requirements are an important objective in polyurethane research and development. This makes it necessary to explore isocyanate- and phosgene-free routes to blocked isocyanates via end group conversion of amine and hydroxy end groups. Here we report the use of carbonylbiscaprolactam as a new very versatile, nontoxic reagent that can convert terminal as well as pendant hydroxy- and amine-groups of functional polymers into the corresponding caprolactam-blocked isocyanates without requiring the use of isocyanates.

2. Experimental Section

Materials. Carbonylbiscaprolactam (CBC, ALLINCO) was supplied by DSM and used as received (purity >99%). The prepolymers polytetrahydrofuran (PTHF, M_n = 1010 g/mol, bis(hydroxy) terminated, DuPont), poly(ethylene glycol) (PEG, M_n = 910 g/mol, bis(hydroxy) terminated, Merck), poly(propylene oxide) (PPO, M_n = 990 g/mol, bis(hydroxy) terminated, Aldrich), Jeffamines (M-600: M_n = 590 g/mol, mono(amine) terminated, D-400: M_n = 430 g/mol, bis(amine) terminated, D-2000: M_n = 1950 g/mol, bis(amine) terminated, all from Fluka and Aldrich), and poly(dimethylsiloxane) (PDMS, M_n = 3140 g/mol, bis(3-aminopropyl) terminated,

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10.1021/ma0258861 CCC: $25.00
Published on Web 06/07/2003

Table 1. Uncatalyzed Reactions of CBC with Isopropylenamine Terminated Oligopropyleneoxides (Jeffamines with M = Mono- and D = Difunctional) and with Bis(*N*-propyleneamine) Terminated Poly(dimethylsiloxane) (PDMS)[a]

reaction	oligomer	M_n (g/mol)	T (°C)	t (min)	CBC convn (%)
SMA353	Jeffamine M-600	560	100	15	83
				30	90
				60	95
SMA354	Jeffamine D-400	450	100	15	89
				30	95
				60	99
KS44	Jeffamine D-2000	1870	100	30	83
				60	89
				120	92
SMA340	PDMS($-NH_2$)$_2$	3140	100	30	100

[a] Molar ratio of CBC:NH_2 groups = 1:1.

Aldrich) were dried before use. The catalysts $MgBr_2$ from Aldrich and dibutyltin dilaurate (DBTDL) from Fluka were used without further purification. Zr(O−n-C_3H_7)$_4$ was available as 70 wt % solution in *n*-propanol from Aldrich. Toluene p.a. (Merck) and $CaCl_2$ (Grüssing) were also used as received.

End Group Conversions with CBC. Amine-terminated oligomers such as mono-, di-, and tri-isopropyleneamine-terminated oligopropyleneoxides (Jeffamine) and bis(*n*-propylene-amine) terminated poly(dimethylsiloxane) (PDMS) were reacted in bulk with CBC at 100 °C without catalyst.

Reaction of CBC with Jeffamines. The Jeffamines were dried by stirring for 16 h at 60 °C in oil pump vacuum. For example, 10.08 g (40 mmol) of CBC was reacted with 22.4 g (40 mmol) of Jeffamine M-600 (M_n = 560 g/mol). CBC and the Jeffamine were mixed together and then stirred under argon for the duration of 1 h at 100 °C. To remove the caprolactam formed, the product mixture was dissolved in 40 mL of toluene and extracted three times with 30 mL of an aqueous solution of $CaCl_2$ (40 g/L). After drying (4 d, 50 °C, oil pump vacuum), 23.89 g (85%) of a slightly yellow liquid was obtained. Properties are listed in Table 1.

Reaction of CBC with Diamine-Terminated Oligodimethylsiloxane (PDMS). A mixture of 1.84 g (7.32 mmol) of CBC and 11.5 g (3.66 mmol) of PDMS (M_n = 3140 g/mol) was stirred under argon for 30 min at 100 °C. At certain time intervals, samples were removed from the reaction. The caprolactam formed was removed by extracting three times with an aqueous solution of $CaCl_2$ (40 g/L). After drying (60 °C, 2 d, oil pump vacuum) 9.66 g (77%) of a slightly yellow liquid was obtained. Reaction conditions and polymer properties are listed in Table 1.

Dihydroxy-terminated oligomers such as PTHF, PEG, and PPO with molecular masses of around 1000 g/mol were reacted in bulk with CBC at 100 and 150 °C in the absence and the presence of the catalysts Zr(OR)$_4$, $MgBr_2$, and DBTDL. The reactions were carried out under argon on a 50 g scale. The resulting oligomers were dried by stirring for 1 h at 100 °C at oil pump vacuum. In a typical experiment, the Zr−alcoholate-catalyzed reaction of CBC with PTHF is described below.

Reaction of CBC with PTHF in the Presence of a Zr—Alcoholate Catalyst. First, 16.75 g (66.5 mmol) of CBC, 33.25 g (32.9 mmol) of PTHF and 0.224 mL (0.234 g) of a 70 wt % solution of Zr(O−C_3H_7)$_4$ in *n*-propanol (i.e., 0.5 mmol of Zr(O−C_3H_7)$_4$, 0.75 mol % with respect to CBC) were employed. The Zr−propylate solution was added to 5 g of the PTHF, and then the *n*-propanol was removed by stirring for 30 min at 80 °C in oil pump vacuum. The CBC was dissolved in the remaining PTHF and was heated to the reaction temperature. Subsequently the PTHF-catalyst-mixture was added via a syringe. The reaction was stirred for a given time at the reaction temperature and stopped by cooling to room temperature. The reaction was monitored with a ReactIR, and the products were analyzed by ^{1}H and ^{13}C NMR spectroscopy. Reaction conditions and properties are listed in Tables 2 and 3.

Characterization. The reaction products were identified, and the CBC and end group conversions were determined by means of ^{1}H and ^{13}C NMR spectroscopy (Bruker ARX 300, 300 and 75 MHz, respectively) and with ReactIR spectroscopy (Mettler, Applied Systems, ReactIR1000). The molecular masses were measured with SEC (Knauers Mikrogelset A22, $CHCl_3$, 30 °C, with UV/RI and low angle laser light scattering detectors, calibration vs PS standards) and MALDI−ToF mass spectrometry (Bruker REFLEX 2, reflex mode, dithranol matrix, LiBr and KCl as cationizing agent). The thermal behavior of the caprolactam-blocked oligomers was measured with TGA (Netzsch STA 409).

3. Results and Discussion

The carbonylbiscaprolactam (CBC) represents an activated derivative of carbonic acid. It is a nontoxic (LD_{50} > 2000 mg/kg) white crystalline product that melts at 118 °C. The CBC is readily obtained by reacting phosgene with caprolactam. This route to CBC was pioneered in 1956 by Meyer, who used CBC together with hexamethylenediamine to produce low molecular weight ureas and amides with rather ill-defined structures.[3] In 1962 Fawcett et al. reported that CBC was obtained as a byproduct when they studied the reaction of caprolactam with COF_2.[4] In 1967, the synthesis of CBC as an intermediate for the synthesis of lysine was disclosed in a Japanese patent.[5] As difunctional *N*-acyllactam, CBC was used successfully as activator for the anionic ring-opening polymerization of various lactams.[6−10] In 1996, BASF claimed the use of a large variety of heterocyclic substances, among them CBC, as activators for organic peroxides in washing and bleaching agents.[11] Since 2000, DSM and others have filed patents concerning the preparation of CBC and its use as coupling agent, chain extender, or cross-linker.[12−19]

As illustrated in Scheme 1, there exist two very different reaction pathways for CBC reaction with nucleophiles: first, the ring elimination (pathway RE) associated with caprolactam formation, and second, ring opening (pathway RO), which does not produce caprolactam as side-product. The reaction pathway RE is typical for the reaction of phosgene and many other phosgene derivatives such as carbonyldiimidazole. According to pathway RE the reaction of CBC with amines (R−XH in Scheme 1 is R−NH_2) affords formation of either *N*-carbamoyl caprolactam and caprolactam or ureas, accompanied by elimination of both caprolactam molecules. In contrast, CBC also offers the opportunity of nucleophilic attack at the carbonyl group of the caprolactam ring followed by ring opening (pathway RO). In pathway RO no caprolactam is eliminated. One-fold ring opening converts hydroxy groups into ester-functional *N*-carbamoyl caprolactams. Two-fold ring opening yields polyesterureas. The reaction pathway RO represents a very special feature of CBC chemistry and is very attractive with respect to reduced emission of low volatile organic compounds such as caprolactam. The predominance of reaction pathway RO with respect to pathway RE depends primarily upon the choice of the nucleophile and is also affected by catalyst addition and reaction conditions. Both reaction pathways are very attractive with respect to the end group conversion of hydroxy- and amine-terminated oligomers and the in situ formation of reactive oligomers containing caprolactam-blocked isocyanate end groups without requiring the addition of either phosgene or isocyanates during end group conversion. The end group conversion of amine- and hydroxy-terminated oligomers was investi-

Table 2. Functionalization Reactions of PTHF (M_n = 1010 g/mol), PEG (M_n = 910 g/mol) and PPO (M_n = 990 g/mol) with CBC (Molar Ratio of −OH:CBC = 1:1)[a]

							% of CBC converted into					
reaction	oligomer	catalyst	[catalyst] (mol %)	[catalyst] (wt %)	T (°C)	t (min)	1x RO[b]	1x RE[b]	urethane	2x RE[b]	Σ	OH convn (%)
SMA224	PTHF	none	0	0	200	75	0	33	13	17	63	93
SMA223		$Zr(OR)_4$	0.75	0.33	100	120	82	0	0	6	88	94
SMA225		$Zr(OR)_4$	0.75	0.33	150	20	85	0	0	6	91	97
SMA236		$MgBr_2$	0.75	0.18	100	120	0	0	0	0	0	0
SMA238		$MgBr_2$	0.75	0.18	150	70	65	15	4	6	90	100
SMA231		DBTDL	0.5	0.42	100	170	8	0	0	4	12	16
SMA231		DBTDL	0.5	0.42	150	50	18	0	11	7	36	54
SMA315	PEG	$Zr(OR)_4$	0.75	0.33	100	120	75	0	5	7	87	90
SMA316		$Zr(OR)_4$	0.75	0.33	150	20	85	0	10	3	98	100
SMA322		$MgBr_2$	0.75	0.18	150	70	79	4	9	4	96	99
SMA323	PPO	$Zr(OR)_4$	0.75	0.33	150	20	86	0	7	0	93	99
SMA324		$MgBr_2$	0.75	0.18	150	20	23	0	11	0	34	45
						70	36	0	32	0	68	99

[a] No urea was found under the reaction conditions applied. [b] RO = ring opening; RE = ring elimination.

Table 3. Molar Mass Distribution of PTHF and Its CBC Reaction Products, As Determined by Means of Size Exclusion Chromatography (SEC)

sample	catalyst	T (°C)	t (min)	M_n (g/mol)	M_w (g/mol)	M_w/M_n
PTHF				1670	3290	2.0
SMA223	$Zr(OR)_4$	100	120	3470	5700	1.6
SMA225	$Zr(OR)_4$	150	20	3000	5190	1.7
SMA238	$MgBr_2$	150	70	4630	7845	1.7
SMA231	DBTDL	150	50	2130	3400	1.6

gated using spectroscopic methods including ReactIR spectroscopy.

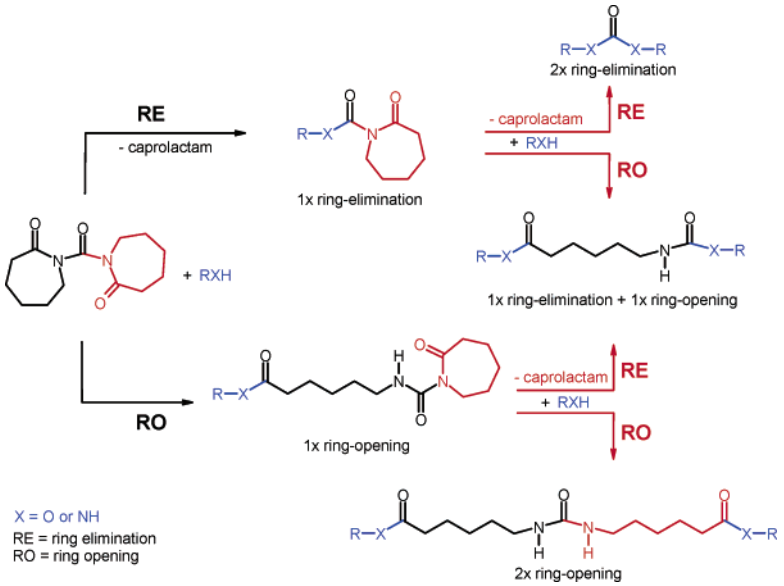
Reactions of CBC with Amine-Terminated Oligomers. Amine-terminated oligomers such as the bis-(*n*-propylene-amine)-terminated oligodimethylsiloxane (PDMS) and the mono-, di- and tri- isopropylene-amine-terminated oligopropyleneoxide (also known under the trade name of Jeffamine) were reacted with CBC in bulk at 100 °C. Reaction conditions and properties are listed in Table 1. According to the spectroscopic studies the reaction of CBC with amine groups proceeds in the absence of catalyst exclusively via the ring elimination mechanisms shown as pathway RE in Scheme 1. The *N*-carbamoyl caprolactam end groups are equivalent to the corresponding reaction products of the isocyanate with caprolactam. The byproduct caprolactam can be removed by means of vacuum stripping, thin film evaporation or extraction using an aqueous 4 wt % calcium chloride solution. Interestingly, as evidenced by the absence of urea groups, the *N*-carbamoyl caprolactam is obtained in almost quantitative yield without any indication of elimination of the second caprolactam ring. Thus, although during the synthesis blocked isocyanates and amines are present simultaneously, no sign of the consecutive reaction forming ureas was noted, meaning that the reaction is very selective. This reaction does not require excess CBC and is a very clean stoichiometric end group conversion. The end group conversion of the isopropylene-amine-terminated oligopropyleneoxides (Jeffamines) is displayed in Scheme 2.

The CBC conversions of amine end groups were monitored by ReactIR spectroscopy and by ^1H and ^{13}C NMR spectroscopy. Figure 1 shows the ReactIR spectra of the uncatalyzed bulk reaction of CBC with Jeffamine M-600 at 100 °C. The CBC conversion was calculated from the area of the amide II band at 1520 cm^{-1}. The calibration of this method was carried out by correlating the band area at the end of the reaction with the final CBC conversion, as measured by means of ^1H NMR spectroscopy. It can be seen in Figure 2 that the reaction rate of CBC with amines is quite high. The ^1H NMR spectra of caprolactam blocked isocyanate functionalized Jeffamine and PDMS are shown in Figures 3 and 4. The conversions were calculated from the integrals of the ^1H NMR-signals of the caprolactam blocked isocyanate (3.93, 2.62 ppm), caprolactam (3.11, 2.39 ppm) and CBC (3.8, 2.45 ppm).

The CBC conversion with time depends on the nulceophilicity of the amine and the amine concentration. As is apparent from Table 1 and Figures 1 and 2, the amine conversion is very high and quantitative at appropriate reaction times. For the diamine Jeffamine D-400, the conversion amounted 99% after 1 h, whereas for M-600, 95% was reached after 1 h. The reaction with Jeffamine D-2000 yielded only 89% after 1 h and 92% after 2 h. This is in accord when taking into account the different concentrations of the amine end groups, which is 4.44 mmol/g for D-400, 1.79 mmol/g for M-600, and only 1.07 mmol/g for D-2000. In comparison to the CBC reactions of the Jeffamines, the reaction of CBC with diamine-terminated oligodimethylsiloxane (PDMS) was considerably faster and gave quantitative conversion in less than 1 h, although the PDMS amine concentration was only 0.64 mmol/g. Most likely, this remarkable difference in reactivity is closely associated with the nucleophilicity of the amine end groups. The isopropylene−amine end groups of the Jeffamines are sterically more hindered and less nucleophilic with respect to the *n*-propylene−amine end groups of PDMS. Higher steric hindrance requires either higher temperatures or longer reaction times, respectively, to achieve quantitative conversion of the end groups. The ReactIR analysis of Jeffamine reactions performed at different temperatures allowed the determination of the activation enthalpy of the CBC amine end group conversion which was found to be 55.2 kJ/mol.

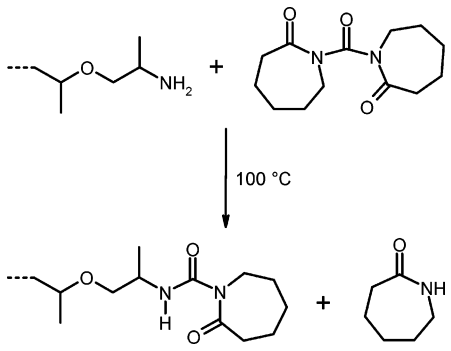
Reactions of CBC with Polyols. To examine the possibility of forming *N*-carbamoyl caprolactam from hydroxy-terminated oligomers via the ring opening mechanism (pathway RO in Scheme 1), the reactions of α,ω-dihydroxy-terminated polyols such as oligoethylene oxide (PEG), oligopropylene oxide (PPO), and oligotetrahdyrofuran (PTHF) were investigated. The reaction with CBC was performed in bulk at 100, 150,

Scheme 1. Reactions of Carbonylbiscaprolactam (CBC) with Nucleophiles[a]



[a] Pathway RE: Ring elimination mechanism associated with caprolactam formation. Pathway RO: Ring opening reaction of the CBC caprolactam ring.

Scheme 2. CBC Reaction with Amine End Groups of Isopropylenamine-Terminated Oligopropyleneoxides (Jeffamine) According to the Ring Elimination Mechanism



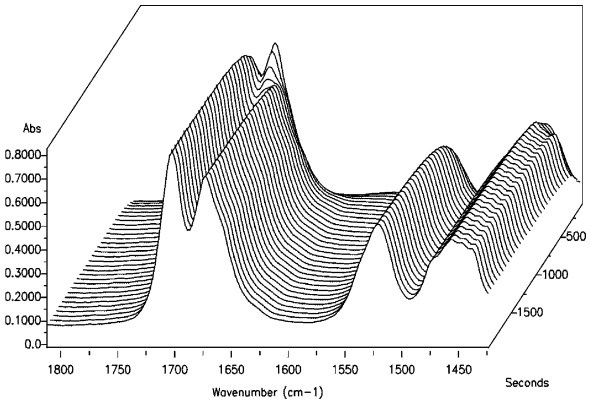


Figure 1. ReactIR spectra of reaction of CBC with Jeffamine M-600 at 100 °C (SMA353) in the absence of catalyst. In back: CBC, bands at 1708 and 1684 cm^{-1}. In front: 95% *N*-carbamoyl caprolactam termninated Jeffamine, bands at 1706, 1673, and 1520 cm^{-1}.

and 200 °C in the absence and in the presence of catalysts such as $Zr(OR)_4$, $MgBr_2$, and dibutyltindilaurate (DBTDL). The reaction compositions and the product properties are summarized in Tables 2 and 3. An unexpected effect of the catalyst addition was discovered. In the absence of catalyst the reaction of CBC proceeded mainly via ring elimination pathway

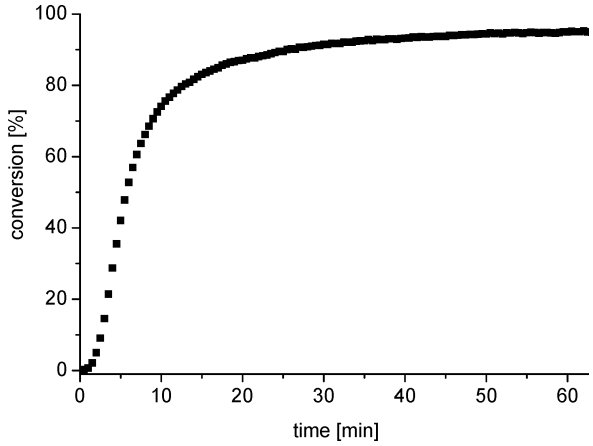


Figure 2. CBC conversion to blocked isocyanates as a function of time. The reaction of CBC with Jeffamine M-600 was carried out at 100 °C in bulk without catalyst. After 60 min, 95% of the amine end groups of the Jeffamine were transferred into caprolactamblocked isocyanates. The conversion was determined by ReactIR spectroscopy (evaluation of the amide II band at 1520 cm^{-1}, calibration with ^1H NMR spectroscopy).

RE, similar to the reaction pathways established for phosgene and other carbonic acid derivatives such as carbonyldiimidazole and similar to the reaction with amines. In the absence of ring opening, CBC conversion of hydroxy groups gave mainly *N*-carboxylate caprolactam (denoted as 1*x* ring elimination in Table 2) in conjunction with urethane and carbonate, both of which result from subsequent reaction of the *N*-carboxylate caprolactam with hydroxy groups. In sharp contrast, catalyst addition promoted reaction pathway RO involving ring opening of one or even two of the CBC caprolactam rings. While the tin catalyst DBTDL was less effective, zirconium alcoholate and Lewis acids such as magnesium bromide gave high conversion and predominant ring opening (cf. Table 2). This ring-opening reaction of CBC with hydroxy-terminated oligomers represents a very attractive new, isocyanate-free route to blocked isocyanates derived from polyols!

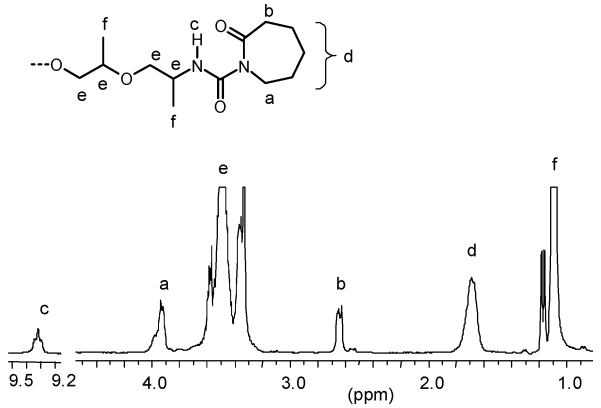


Figure 3. ^{1}H NMR spectrum of the caprolactam-blocked isocyanate derived from CBC and the isopropyleneamine terminated oligopropyleneoxide (Jeffamine M-600). Reaction conditions: 100 °C, 60 min, and conversion = 95%.

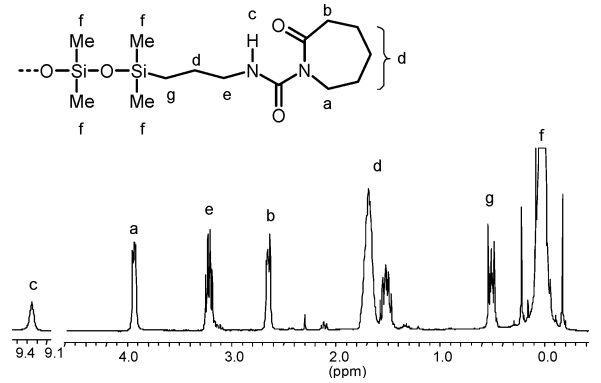


Figure 4. ^{1}H NMR spectrum of the caprolactam-blocked isocyanate derived from CBC and the bis(propyleneamine)-terminated poly(dimethylsiloxane).

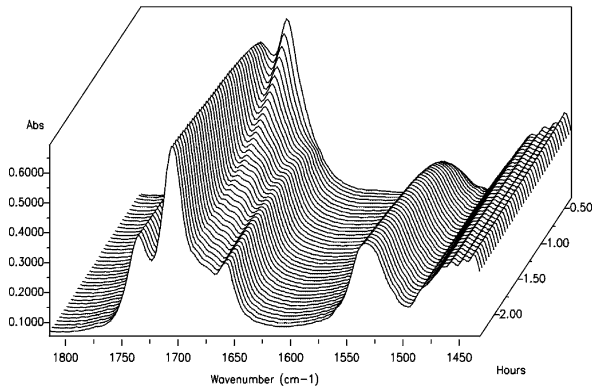


Figure 5. ReactIR spectra of the reaction of CBC with PTHF, catalyzed by 0.75 mol % $Zr(OR)_4$ with respect to CBC at 100 °C (SMA223). In back: CBC, bands at 1706 and 1673 cm^{-1}. In front: product mixture containing 82% 1*x* ring-opened CBC, bands at 1735, 1705, 1656, and 1536 cm^{-1}.

The reactions of CBC with polyols were also monitored by means of ReactIR. Typical ReactIR traces are displayed in Figure 5. The conversion of CBC with hydroxy groups to produce caprolactam-blocked isocyanate end groups was calculated from the area under the amide II band at 1536 cm^{-1}. The calibration of this method was accomplished by correlating the final conversion, as determined by ^{1}H NMR spectroscopy, with the area of this IR band at the end of the reaction. A typical ^{1}H NMR spectrum of a CBC reaction with a polyol is displayed in Figure 6.

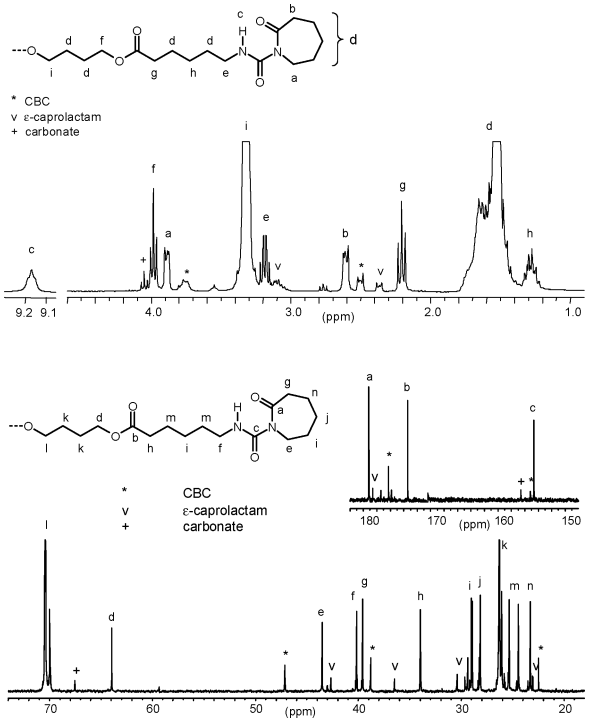


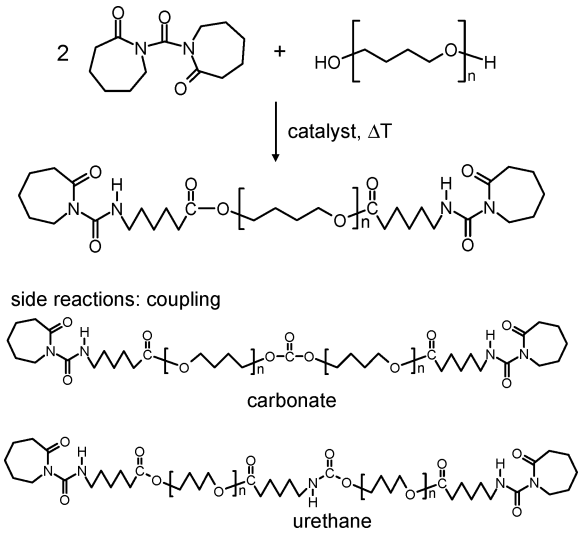
Figure 6. ^{1}H and ^{13}C NMR spectra of the caprolactam-blocked isocyanate derived from PTHF, synthesized in the presence of Zr−alcoholate (0.75 mol % Zr with respect to CBC) at 100 °C (composition: 82% caprolactamblocked isocyanate, 6% carbonate, 12% ϵ-caprolactam, and 12% CBC (all with respect to total amount of CBC employed as educt)).

In the absence of catalyst addition the thermal reaction of CBC with PTHF at 200 °C yielded after 75 min 33% *N*-carboxylate caprolactam terminated PTHF obtained via elimination of one caprolactam (values are with respect to the employed amount of CBC) together with 17% carbonate via 2-fold caprolactam elimination and 13% urethane via caprolactam elimination followed by ring opening. In the absence of catalyst no ring opening of the caprolactam rings of CBC with hydroxy groups occurred! This is strong experimental evidence that thermal reaction of CBC caprolactam ring proceeds exclusively via the ring elimination pathway (pathway RE in Scheme 1). According to Table 2, the total conversion of CBC amounted only to 63% in that case. For stoichiometric reasons (CBC:hydroxy end group molar ratio of 1 mol:1 mol !), the total conversion of the CBC cannot reach 100% when a part of CBC reacts twice with hydroxy groups. The total conversion of the hydroxy end groups was 93%.

When catalyst was added, the reactivity of CBC increased drastically. In the presence of catalyst the predominant reaction is ring opening according to pathway RO, thus producing the ester-functional *N*-carbamoyl caprolactam, which is equivalent to a blocked isocyanate end group. The obtained *N*-carbamoyl caprolactam can react with hydroxy groups either via ring elimination or ring opening, thus producing either urethane or urea, respectively. Predominantly urea formation was observed when using sodium or potassium alcoholates at room temperature. Also carbonates were encountered as minor side products, formed via the 2-fold ring elimination reactions according to pathway RE.

Scheme 3 shows the catalytic reaction of CBC with PTHF. In this reaction, catalyzed by $Zr(OR)_4$ at 100 °C,

Scheme 3. Reaction of CBC with PTHF Producing *N*-Carbamoyl Caprolactam End Groups, Equivalent to Caprolactam-Blocked Isocyanates, via Catalytic Ring Opening Reactions[a]



[a] Minor side reactions represent molar mass build up via carbonate chain extension resulting from ring elimination reactions.

82% of the CBC was converted after 120 min via the 1*x* ring opening pathway into *N*-carbamoyl caprolactam (caprolactam-blocked isocyanate). This corresponds to a hydroxy conversion of 94%. At 150 °C, 85% (with respect to CBC) *N*-carbamoyl caprolactam was formed already after 20 min. This corresponds to a hydroxy end group conversion of 97%. Carbonate was formed in both reactions to a small extent of only 6% (with respect to the amount of CBC employed). Carbonate byproduct formation is tolerated in many applications, since it is associated with the chain extension reaction which does not affect end group functionality. The Lewis acidic catalyst $MgBr_2$ showed almost no activity as catalyst at 100 °C However, at 150 °C it yielded 65% (with respect to CBC) of the *N*-carbamoyl caprolactam via the 1*x* ring-opening reaction (pathway RO). This corresponds to 100% conversion of the hydroxy groups. Here byproducts were found to be 15% of *N*-carboxylate caprolactam (1*x* ring elimination), 4% urethane and 6% carbonate (all with respect to CBC). In comparison to $Zr(OR)_4$, $MgBr_2$ was less active and somewhat less selective. In Figure 7, the addition of $Zr(OR)_4$ and $MgBr_2$ catalysts is compared with respect to the CBC conversion and formation of the ester-functional *N*-carbamoyl caprolactam. Clearly, the zirconium catalyst is more active than the magnesium catalyst, especially at lower temperatures.

The data of the reactions of CBC with PEG and with PPO are summarized in Table 2 as well. The CBC reactions with PEG proceeded similarly to reactions of CBC with PTHF. $Zr(OR)_4$ catalysis led to 75% or 85% of *N*-carbamoyl caprolactam via 1*x* ring opening at 100 or 150 °C, respectively. $MgBr_2$ catalysis led also to a product distribution quite similar to the CBC/PTHF reaction. Main product was *N*-carbamoyl caprolactam via 1*x* ring opening, byproducts were urethane, *N*-carboxylate caprolactam via 1*x* ring elimination, and carbonate. The reactions SMA323 and SMA324 listed in Table 2 confirm that the $Zr(OR)_4$ catalyst is also more effective than $MgBr_2$ for PPO containing the less reactive secondary hydroxy end groups. The reaction of

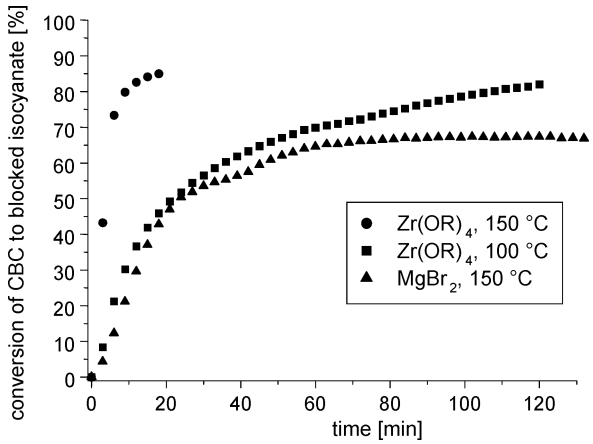


Figure 7. CBC conversion as a function of time. The reactions of CBC with PTHF were catalyzed by 0.75 mol % (with respect to CBC) $Zr(OR)_4$ at 150 °C and 100 °C (SMA225 and SMA223) and by 0.75 mol % (with respect to CBC) $MgBr_2$ at 150 °C (SMA238). The conversion was determined by ReactIR spectroscopy (evaluation of the amide II band at 1536 cm^{-1}, calibration with ^1H NMR spectroscopy).

SMA323, catalyzed by $Zr(OR)_4$ at 150 °C, gave complete CBC conversion already after 20 min and yielded 86% of the ester-functional *N*-carbamoyl caprolactam via 1*x* ring opening, whereas SMA234, catalyzed by $MgBr_2$ at the same temperature, needed 70 min for reaching a CBC conversion of 68%. The reaction mixture obtained in the presence of $MgBr_2$ contained similar amounts of the *N*-carbamoyl caprolactam and urethane. Again, the addition of $MgBr_2$ appears to be much less effective than $Zr(OR)_4$ with respect to the catalytic formation of the ester-functional *N*-carbamoyl caprolactam via ring opening of exclusively one of the CBC caprolactam rings.

Characterization of the Oligomers with Caprolactam-Blocked Isocyanate End Groups. Several of the oligotetrahydrofurans with caprolactam-blocked isocyanate end groups, prepared by reacting CBC with PTHF, were analyzed by means of MALDI−ToF mass spectroscopy.

The MALDI−ToF spectra of the samples produced in the absence and presence of various catalysts are displayed in Figure 8. In the spectrum of SMA223 (PTHF/2 CBC/$Zr(OR)_4$/100 °C) the three main signals correspond to bis(*N*-carbamoyl caprolactam)-terminated PTHF, obtained via conversion of both hydroxy end groups according to the 1*x* ring-opening reaction. No signal of residual PTHF or PTHF containing only one *N*-carbamoyl caprolactam end group were detected. Clearly, as byproduct carbonate-mediated chain extension occurred.

For MALDI−ToF spectrum of SMA238 (PTHF/2 CBC/$MgBr_2$/150 °C) a very similar signal pattern was observed, although three additional weak signals indicate the occurrence of other side reactions which were not identified. In contrast to the spectra of oligomers produced in the presence of catalysts, the spectrum of SMA224 (PTHF/2 CBC/no catalyst/200 °C) was very different and confirmed the predominant formation of the bis(*N*-carboxylate caprolactam)-terminated PTHF, resulting from caprolactam elimination occurring at both chain ends. The MALDI−ToF measurements are in accord with the above-mentioned measurements performed by means of ^1H NMR and ReactIR spectroscopy: In the absence of catalysts, CBC mainly reacts with hydroxy end groups via the ring elimination reaction (pathway RE), thus producing *N*-carboxylate

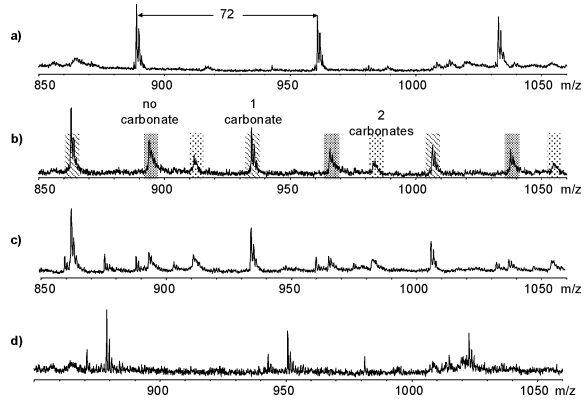


Figure 8. MALDI−ToF mass spectra of (a) PTHF and (b) its reaction products with CBC from reaction SMA223, catalyzed by $Zr(OR)_4$, and (c) SMA238, catalyzed by $MgBr_2$, and (d) the corresponding reaction product obtained in the absence of catalyst. The signals in parts b and c belong to PTHF with two blocked isocyanate end groups (ring-opening reaction) and 0, 1, or 2 carbonate units in the chain (2*x* ring elimination reaction). The signals of part d belong to bis(*N*-carboxylate caprolactam)-terminated PTHF (1*x* ring elimination reaction).

caprolactam together with carbonate and urethane via elimination or opening of the other ring. In contrast, the catalyst addition promoted ring opening of mainly one caprolactam ring of CBC, thus producing *N*-carbamoyl caprolactam end groups, which are equivalent to caprolactam-blocked isocyanates. In comparison to the $Zr(OR)_4$ catalyst, the $MgBr_2$ catalyst is somewhat less active and less selective. In the presence of catalyst the CBC-mediated end group conversion proceeds smoothly and is accompanied by formation of small amounts of carbonates.

In addition to MALDI−ToF mass spectrometry also the size exclusion chromatography (SEC) was applied to examine molar masses and molar mass distributions. The polymers obtained in the reactions SMA223 and SMA238 were analyzed by SEC in $CHCl_3$ solution at 30 °C using linear polystyrene as molar mass standard. The results are listed in Table 3. The *N*-carbamoyl caprolactam terminated PTHF obtained exhibited somewhat higher molar masses with respect to that of PTHF starting material. This is due to the end group formation via CBC reaction and also to chain extension, e.g., via carbonate formation. In fact, molar mass buildup was less pronounced for *N*-carbamoyl caprolactam blocked PTHF prepared in the presence of the $Zr(OR)_4$ catalyst than in the presence of $MgBr_2$ catalyst, due to more molar mass buildup via carbonate chain extension as side reaction.

Samples of dihydroxy-terminated and of the corresponding bis(*N*-carbamoyl caprolactam)-terminated PTHF were analyzed by means of thermogravimetric analysis (TGA) in order to examine their thermal degradation behavior in view of the deblocking temperatures indicating the decomposition of the *N*-carbamoyl caprolactam into free caprolactam and isocyanate. As a function of isocyanate type and catalysts, the deblocking temperature of conventional caprolactam-blocked isocyanates is known to vary from 160 to 200 °C.[1] At temperatures above 300 °C, PTHF depolymerizes, thus yielding THF. The ceiling temperature for the depolymerization of PTHF with active end groups is approximately 80 °C. It is well-known that metal ions such as Zr^{4+} or Mg^{2+} can promote chain scission and subsequent depolymerization via an unzipping reaction.

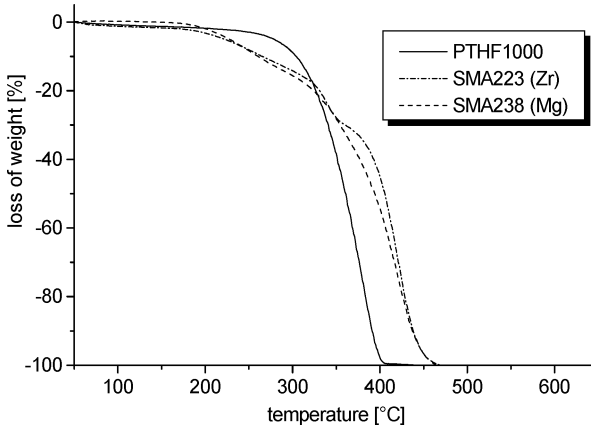


Figure 9. Thermogravimetric analysis of PTHF and the corresponding caprolactamblocked isocyanate, synthesized in the presence of Zr−alcoholate (SMA223) and $MgBr_2$ (SMA238) as catalysts.

Figure 9 displays the temperature-dependent weight loss of dihydroxy- and bis(*N*-carbamoyl caprolactam)-terminated PTHF. The dihydroxy-terminated PTHF degraded in a single step with an onset degradation temperature of around 270 °C. For the bis(*N*-carbamoyl caprolactam)-terminated PTHF, prepared via CBC-mediated end group conversion of dihydroxy-terminated PTHF in the presence of zirconium and magnesium catalysts, the degradation process exhibited two different steps. Above 180 °C the weight loss of approximately 20% is likely to be associated with the thermal deblocking of the end groups, involving formation of caprolactam and isocyanate. The magnesium and zirconium catalyst addition appeared to have little influence on this deblocking temperature. The thermal degradation of the bis(*N*-carbamoyl caprolactam)-terminated PTHF occurred at a higher temperature of 320 °C compared with only 270 °C for the dihydroxy-terminated PTHF. This increase of thermal stability is likely to be associated with isocyanurate ring formation resulting from trimerization of the isocyanate intermediates resulting from the deblocking reaction.

4. Conclusions

The stoichiometric end group conversion of amine- and hydroxy-terminated oligomers by means of the nontoxic carbonylbiscaprolactam (CBC) represents a very convenient phosgene- and isocyanate-free route to the preparation of a wide range of bis- and poly(*N*-carbamoyl caprolactam)-terminated oligomers which are equivalent to caprolactam-blocked isocyanate resins. A great variety of oligomers and reactive liquid rubbers with caprolactam-blocked isocyanate end groups are readily available in solvent-free CBC-mediated end group conversion reactions and do not require safety precautions typical for handling toxic isocyanates. The CBC-mediated end group conversion in bulk can be controlled via end group type and catalyst addition. In the absence of catalysts, amine end group react exclusively via ring elimination (pathway RE), thus producing *N*-carbamoyl caprolactam-terminated oligomers which are equivalent to caprolactam-blocked isocyanate-terminated oligomers. This reaction proceeds smoothly at elevated temperatures around 100 °C.

In contrast to other derivatives of carbonic acid such as carbonyldiimidazole, CBC offers new opportunities for tailoring reactive oligomers via selective ring-open-

ing reaction of either exclusively one or both CBC caprolactam rings. The ring-opening reaction (pathway RO) was demonstrated for the CBC-mediated end group conversion of hydroxy-functional oligomers. Only in the presence of catalysts such as alcoholates or Lewis acids, ring opening of the CBC caprolactam ring occurs, thus producing ester-functional *N*-carbamoyl caprolactams. It would be rather difficult to produce such oligomers via phosgenation because the conventional synthesis would require formation of aminocapronic acid esters of the hydroxy-terminated oligomers followed by phosgenation. The catalytic promotion of ring opening reduces the caprolactam emission during the reaction, thus reducing volatile organic compounds. The formation of chelating complexes with catalysts represents the key to control the reactivity of both carbonyl groups of the CBC caprolactam rings independently. While sodium alcoholates catalyze ring opening of both CBC caprolactam rings to form ester ureas, the addition of zirconium alcoholate or magnesium halides promote the predominant formation of ester-functional *N*-carbamoyl caprolactam resulting from mainly ring opening of only one CBC caprolactam ring. As a function of the catalyst choice and reaction temperatures it is possible to reduce the amount of carbonate formed via the ring elimination mechanism. The selective ring opening of the CBC caprolactam rings is very effective for the coupling reactions without emission of caprolactam. The very versatile CBC mediated hydroxy and amine group conversion uses stoichiometric amounts of CBC and can be applied to end groups as well as amine and hydroxy groups attached to the main and side chains.

In conclusion, the isocyanate-free routes to caprolactam-blocked isocyanates via the CBC mediated hydroxy and amine group conversions offer new opportunities for polymer diversification and formation of reactive oligomers in applications ranging from coatings, adhesives, and sealants to special isocyanate-free polyurethanes and polyureas useful in biomedical applications. Since CBC is nontoxic, such reactions can be performed in conventional processing equipment at elevated temperatures using polymer melts or polymer solutions, respectively. Since various other functional groups are tolerated, it is possible to prepare a large variety of new functional polymers with tailor-made property profiles.

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MA0258861