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Copolymerization of 2,2-dimethyltrimethylene carbonate with tetramethylene urea: a new route to the polyurethane

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Copolymerization of equimolar amounts of 2,2-dimethyltrimethylene carbonate (DTC) with tetramethylene urea (TeU) results in a copolymer the microstructure of which depends on the reaction conditions and on the catalyst used. With *sec*-butyllithium, dibutylmagnesium and diethylzinc as a catalyst a nearly alternating copolymer, i.e. a polyurethane, was obtained. With dibutyldimethoxytin, *tris*(*sec*-butoxyaluminium), and *tetrakis*(*iso*-propoxytitanium) as a catalyst copolymers with carbonate, urea, and urethane groups were obtained. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: polyurethane; polycondensation; ring-opening copolymerisation)

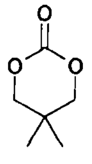
INTRODUCTION

In the early 1980s it was reported in the patent literature that lactams are anionically copolymerized with cyclic carbonates to result in a polymeric product which contains beside carbonate groups urethane and ester groups[1]. Similar products are obtained when polycarbonates are treated with ε-caprolactam in the presence of sodium lactamate[2,3].

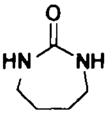
In our laboratory the copolymerization of equimolar amounts of 2,2-dimethyltrimethylene carbonate and ε-caprolactam was found to result a copolymer with alternating ester and urethane groups[4]. A mechanistic investigation of the reaction revealed that the polymer is produced in two consecutive reaction steps: first the polycarbonate is formed, then formally insertion of the ring-opened lactam moiety into the carbonate group occurs which leads to ester and urethane groups.

When these results are transferred to a monomer system comprising a cyclic carbonate and a cyclic urea in equimolar amounts a polyurethane of the AABB-typ is expected to be formed (see *Scheme 1*), where AA represents a diisocyanate and BB a diol respectively (AA represents a diamine and BB a bischloroformate).

This paper presents experimental results on the copolymerization of 2,2-dimethyltrimethylene carbonate (DTC) and tetramethylene urea (TeU) with dibutylmagnesium (Bu_2Mg) as initiator in the melt and in solution with N,N′-dimethylpropylene urea (DMPU) as the solvent. The influence of various parameters on the polymer yield, its molecular weight and its microstructure are discussed.



DTC



TeU

EXPERIMENTAL DETAILS

Starting materials and reagents used for the monomer synthesis were of high purity (analytical grade). 2,2-dimethyltrimethylene carbonate[5] (DTC) and tetramethylene urea[6,7] (TeU) were sublimed before use. Dibutylmagnesium (Bu_2Mg), 1.1 M solution in hexane (from Alfa), *tris*(*sec*-butoxyaluminium[$Al(O$*sec*$-Bu)_3$] (from Fluka) were used without further purification. All solvents were freshly distilled before use. Where necessary, the reactions were conducted in an inert gas atmosphere, for example, a nitrogen atmosphere. Nitrogen (from Linde) was passed over molecular sieves (4 Å), finely distributed potassium on aluminium oxide and over an activated copper catalyst (BTS, BASF) for purification.

Measurements

^1H n.m.r. and ^{13}C n.m.r. spectra were recorded on a Varian 300 FT-n.m.r. spectrometer at 300 MHz and 75 MHz, respectively. Deuterated solvents were used and tetramethylsilane (TMS) served as internal standard.

Gel permeation chromatography (GPC) analyses were carried out using a high pressure liquid chromatography pump, a refractive index detector and an ultraviolet detector. The eluting solvent was DMAc with 2.5 g/L LiBr and a flow rate of 0.5 mL/min. Four columns with PL-gel from Polymer Laboratories were applied: length of each column: 300 mm, diameter: 7.5 mm, diameter of gel particles: 5 μm, nominal pore widths: 100 Å, 500 Å, 10^3 Å, and 10^4 Å.

Viscosity measurements were carried out with a viscosimeter of Ostwald type (diameter = 0.7 mm) at 25 °C.

C,H,N elemental analyses were performed with a Carlo Erba MOD 1106 instrument.

Syntheses

Polycondensation of 1,4-diaminobutane with 2,2-dimethylpropandiol-bis-chloroformate. 0.88 g (10 mmol) of diaminobutane, 2.12 g (20 mmol) sodium carbonate and 0.3 g sodium lauryl sulfate were dissolved in 30 mL water

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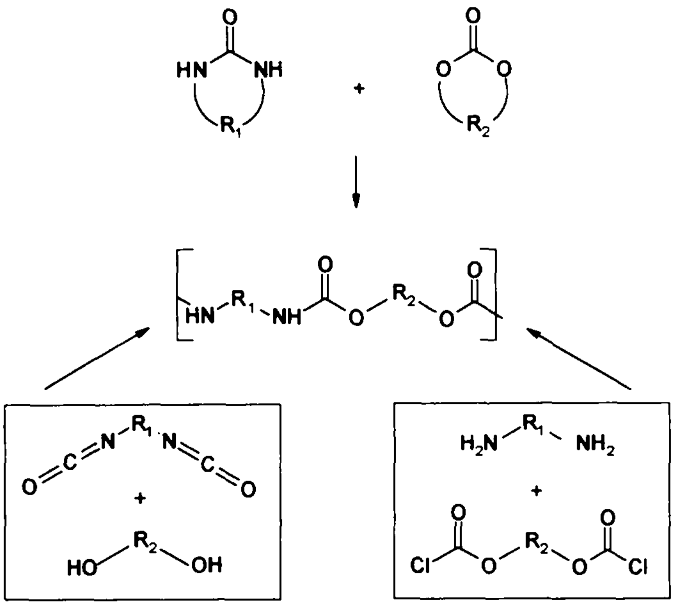


Scheme 1 Routes to polyurethanes

and cooled to 10 °C. 2.29 g (10 mmol) of 2,2-dimethylpropandiol-bis-chloroformate in 25 mL dichloromethane were added and the mixture was stirred vigorously. After 5 min the polymer is isolated by precipitation in 450 mL iced water and filtration. The polymer was purified by reprecipitation from DMF solution into water. Yield 84%.

^{1}H n.m.r. (DMSO-d$_6$/TMS): $\delta = 0.86$ (s, 6H, 2CH$_3$), 1.37 (m, 4H, 2CH$_2$), 2.95 (m, 4H, 2CH$_2$NH), 3.73 (s, 4H, 2CH$_2$O), 7.09 (m, 2H, 2NH) ppm.

^{13}C n.m.r. (DMSO-d$_6$/TMS): $\delta = 21.22$ (CH$_3$, 2C), 26.67 (CH$_2$, 2C), 34.90 (C$_{quat}$, 1C), 39.83 (CH$_2$NH, 2C), 68.48 (CH$_2$O,2C), 156.23 (CO,2C) ppm.

$[C_{11}H_{20}N_2O_4]_n[244.29]_n$

Calc.: C 54.08 H 8.25 N 11.47; Found: C 53.93 H 8.22 N 11.10.

Ring-opening polymerization of tetramethylene urea.

(1) *In the melt*: 1.14 g (10 mmol) of tetramethylene urea (TeU), 10 μL (0.5 mmol) N-methoxycarbonyl-ε-caprolactam and 12 mg (0.5 mmol) NaH were heated to 180 °C for 1.5 h. The solid product was dissolved in 10 mL trifluoroacetic acid and precipitated in water. Yield 91%. Inherent viscosity $\eta_{inh} = 0.56$ dL g^{-1}(H$_2$SO$_4$ conc).

(2) *In solution*: 228 mg (2 mmol) TeU were heated in 1.1 mL DMF to 140 °C and treated with 0.1 mmol s-BuLi. After 48 h at 140 °C the cold reaction product was diluted with 2 mL DMF and precipitated into 50 mL water. Yield 35%.

^{1}H n.m.r.(CF$_3$COOD/TMS):δ = 1.78 (m, 4H, 2CH$_2$), 3.44 (m, 4H, 2CH$_2$NH) ppm.

^{13}C n.m.r. (CF$_3$COOD/TMS):δ = 27.57 (CH$_2$,2C), 43.26 (CH$_2$NH, 2C), 161.43 (CO, 2C) ppm.

Copolymerization of TeU with DTC.

(1) *In solution*: 0.52 g (4 mmol) DTC and 0.46 g (4 mmol) TeU in 1 mL DMPU were heated to 120 °C and treated with 0.04 mmol MgBu$_2$. After 48 h the polymerization was terminated by cooling to room temperature and 4 mL DMPU were added to the highly viscous product. The polymer was isolated by precipitation in water. Yield 78%.

(2) *In the melt*: 0.52 g (4 mmol) DTC and 0.46 g (4 mmol) TeU were polymerized with 0.04 mmol MgBu$_2$ as initiator at 140 °C for 24 h. The product was dissolved in 5 mL DMPU and precipitated into 100 mL water. Yield 63%.

The n.m.r. spectroscopic data were identical to those obtained by polycondensation of 1,4-diaminobutane with 2,2-dimethylpropandiol-*bis*-chloroformate.

Table 1 ^{1}H n.m.r. data of the TeU repeating unit in a TeU-DTC diad and a TeU-TeU diad. Solvent: DMSO-d$_6$, at 20 °C

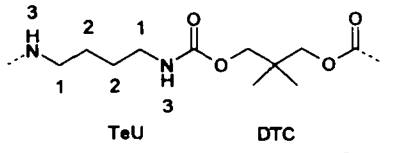
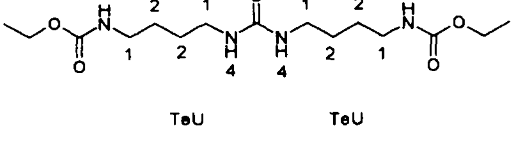
model compound	δ/ppm			
	1	2	3	4
	2.95	1.37	7.09	-
	2.94	1.33	7.06	5.75

Table 2 ^1H n.m.r. data of the DTC repeating unit in a DTC-DTC-DTC, TeU-DTC-DTC, and a TeU-DTC-TeU triad. Solvent: DMSO-d_6, at 20 °C and 100 °C (in parentheses)

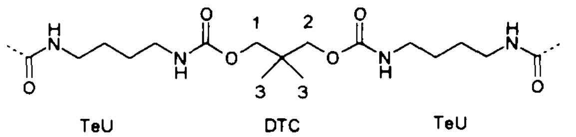
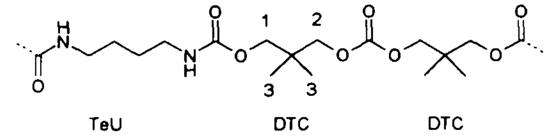
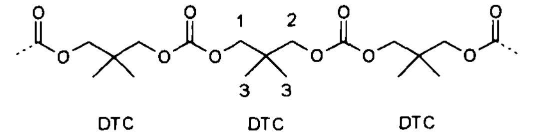
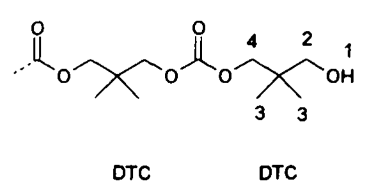
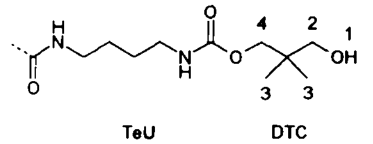
triad	δ/ppm 1	2	3
	3.74 (3.76)	3.74 (3.76)	0.87 (0.89)
	3.75 (3.77)	3.90 (3.92)	0.89 (0.91)
	3.92 (3.93)	3.92 (3.93)	0.92 (0.93)

Table 3 ^1H n.m.r. data of the DTC endgroup in a DTC-DTC diad and a TeU-DTC diad. Solvent: DMSO-d_6, at 20 °C and 100 °C (in parentheses)

endgroup	δ/ppm 1	2	3	4
	4.68 (4.27)	3.15 (3.18)	0.82 (0.84)	3.88 (3.90)
	4.52 (4.28)	3.16 (3.17)	0.81 (0.82)	3.72 (3.74)

n.m.r.-spectroscopic data of DTC and TeU repeating units in different diads, triads and model compounds.

(1) TeU-repeating unit in TeU-DTC-, and TeU-TeU diads (see *Table 1*).
(2) DTC-repeating units in DTC-DTC-DTC-, TeU-DTC-DTC-, and TeU-DTC-TeU triads (see *Table 2*).
(3) DTC-endgroups in a DTC-DTC diad and a TeU-DTC diad (see *Table 3*).

RESULTS AND DISCUSSION

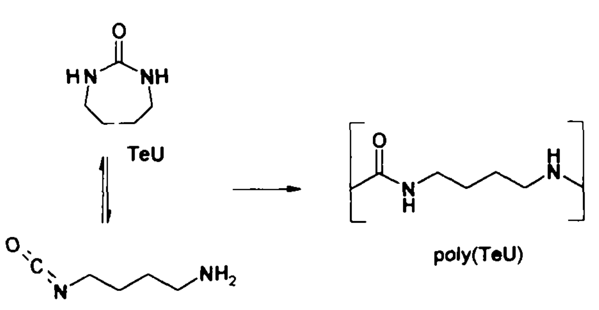
The ring-opening polymerization of DTC proceeds anionically or by insertion with a variety of initiating systems, e.g., sec-butyllithium (sec-BuLi)[8,9], dibutylmagnesium (Bu_2Mg)[10], sec-butoxyaluminium [$Al(Osec\text{-}Bu)_3$][11], diethylzinc (Et_2Zn)[12], and dibutyldimethoxytin [$Bu_2Sn(OMe)_2$][12]. The initiation reaction comprises the nucleophilic attack of the initiator at the carbonyl carbon, followed by an acyl oxygen cleavage and formation of the active species, an alcoholate. At this point it should be mentioned that weak nucleophiles like amines may also act as initiators.

The ring-opening polymerization of TeU was briefly mentioned in the literature[13] and was confirmed in our laboratory[14].

Poly(tetramethylene urea)[poly(TeU)] was obtained at 210 °C in a yield of 85% ($\eta_{inh} = 0.62$ dl.g^{-1} in H_2SO_4 conc.) in the absence of a catalyst. In the presence of, e.g., 5 mol% NaH and 5 mol% N-methoxycarbonyl-ε-caprolactam and at a temperature of 180 °C poly(TeU) was obtained in a yield of 91% ($\eta_{inh} = 0.56$ dl.g^{-1}/H_2SO_4 conc.). Polymerization of tetramethylene urea was catalyzed as well by sodium hydroxide (NaOH), sec-butyllithium (s-BuLi), potassium naphthalene, dibutylmagnesium ($MgBu_2$) and diethylzinc (Et_2Zn) while catalysts based on aluminium [$Al(OBu)_3$], tin[$Bu_2Sn(OMe)_2$ or Bu_2SnLau_2], and titanium [Ti(O-isoPr)$_4$] were not catalytically active. The polymerization of TeU was successfully performed also in DMF solution at 140 °C, however, the yield was only 35% when 5 mol% sec-BuLi was used as a catalyst. In the absence of a catalyst no conversion of TeU in solution was observed.

With respect to the mechanism of the uncatalyzed polymerization of TeU, an equilibrium of the cyclic urea with ω-aminobutyl isocyanate was suggested at higher temperature which upon polyaddition results in poly(tetramethylene urea) (Reaction 1). The rate constant for the thermal dissociation was determined to be $k_1 = 50.3 \cdot 10^3$ min^{-1} at 139.5 °C[15].

For the catalyzed polymerization of TeU a mechanism analogous to that proposed for the polymerization of ε-caprolactam is conceivable.



(1)

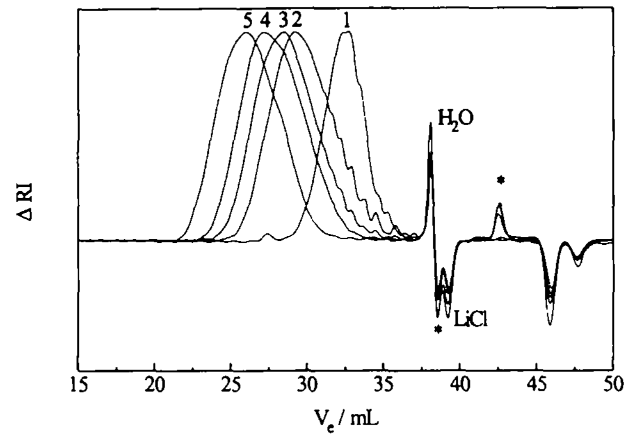


Figure 1 GPC traces of DTC/TeU copolymers of different molecular weights. For conditions of preparation see *Table 5*, Nos. 1–5; *, unknown peaks

Copolymerization of DTC and TeU. In order to test the catalytic activity of different initiating systems for the copolymerization of DTC and TeU an equimolar mixture of the monomers is treated in DMPU solution with initiator and reacted for 48 h at 120 °C. The polymer is isolated by precipitation in water analyzed by means of n.m.r. and GPC (see *Table 4*). The quality of the catalyst is primarily estimated by the concentration of urethane groups as compared to carbonate or urea groups in the copolymer but also by the molecular weight and the yield of the copolymer obtained. In all experiments the concentration of urea groups is at the limit of detection ($< 5\%$); high concentrations of urethane groups ($> 95\%$) are obtained with $MgBu_2$, $ZnEt_2$ and s-BuLi as catalyst. Less effective with respect to high concentrations of urethane groups are the catalysts based on tin, aluminium and titanium, which are also less effective in the homopolymerization of TeU.

The initial monomer concentration has an influence on the polymer yield and the number average molecular weight of the copolymer. For otherwise equal initial conditions, with increasing monomer concentration (see *Table 5*, Nos. 1–5) an increase in the molecular weight of the copolymer is observed. GPC analysis of the reaction products reveals (*Figure 1*, c.f. *Table 5*) that no cyclic oligomers are present in the reaction mixture as were observed when the polymer was prepared by polycondensation of $ClCO\text{-}O\text{-}CH_2\text{-}C(CH_3)_2\text{-}CH_2\text{-}O\text{-}COCl$ with α,ω-diaminobutane. The copolymerization of DTC and TeU at temperatures between 80 and 140 °C (*Table 5* Nos. 6–9) revealed that at $T < 100$ °C the polymerization of TeU is handicapped as is reflected by a lower urethane/carbonate ratio, lower yield,

Table 4 Copolymerization of DTC and TeU in DMPU[a] with various catalysts; characterization of the copolymer

No.	Catalyst[b]	U/C[c] mol/mol	$\bar{M}_n$[d]	$\bar{M}_w/\bar{M}_n$[d]	yield[e] wt%
1	$MgBu_2$	96/4	19000	2.4	78
2	$ZnEt_2$	96/4	16000	2.1	64
3	sec-BuLi	96/4	13000	1.8	61
4	$Bu_2Sn(OMe)_2$	78/22	11000	1.9	55
5	without	52/48	10000	1.8	51
6	$Al(Osec\text{-}Bu)_3$	52/48	6000	1.5	41
7	$Ti(OisoPr)_4$	26/74	6000	1.7	39

[a] Polymerization conditions: $[M]_o = [DTC]_o + [TeU]_o = 50$ wt%; $[DTC]_o/[TeU]_o = 1$ mol/mol, $T = 120$ °C, $t = 48$ h.
[b] $[catalyst]_o = 1$ mol% with respect to DTC
[c] Ratio urethane/carbonate groups in the copolymer as determined from ^1H n.m.r. data; contents of urea groups $< 5\%$ were neglected
[d] Determined from GPC in DMAc/LiBr with polystyrene standards
[e] Polymer obtained after precipitation in water

Table 5 Copolymerization of equimolar amounts of DTC and TeU in DMPU with $MgBu_2$ at various conditions; characterization of the copolymer

No.	$[MgBu_2]$[a] mol%	$[M]_o^b$ wt%	T °C	t h	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]	yield[d] in wt%	U/C[e]
1	1	10	120	24	3.000	1.2	27	n.d.
2	1	20	120	24	6.000	1.5	76	n.d.
3	1	33	120	24	9.000	1.5	90	n.d.
4	1	50	120	24	18.000	1.5	82	n.d.
5	1	66	120	24	20.000	1.6	78	n.d.
6	1	50	80	48	15.000	2.2	67	88/9
7	1	50	100	48	19.000	2.4	72	93/4
8	1	50	120	48	19.000	2.4	78	91/4
9	1	50	140	48	18.000	2.5	74	88/4
10	0.5	50	120	48	22.000	2.1	78	90/4
11	1	50	120	48	19.000	2.1	74	90/4
12	5	50	120	48	17.000	2.1	n.d.	86/3

[a] concentration of $MgBu_2$ with respect to DTC
[b] $[M]_o = [DTC]_o + [TeU]_o = 50$ wt%; $[DTC]_o/[TeU]_o = 1$ mol/mol
[c] determined from GPC in DMAc/LiBr with polystyrene standards
[d] polymer obtained after precipitation in water
[e] ratio of urethane/carbonate groups in the copolymer as determined from ^1H n.m.r. data; the difference to 100% are urea groups

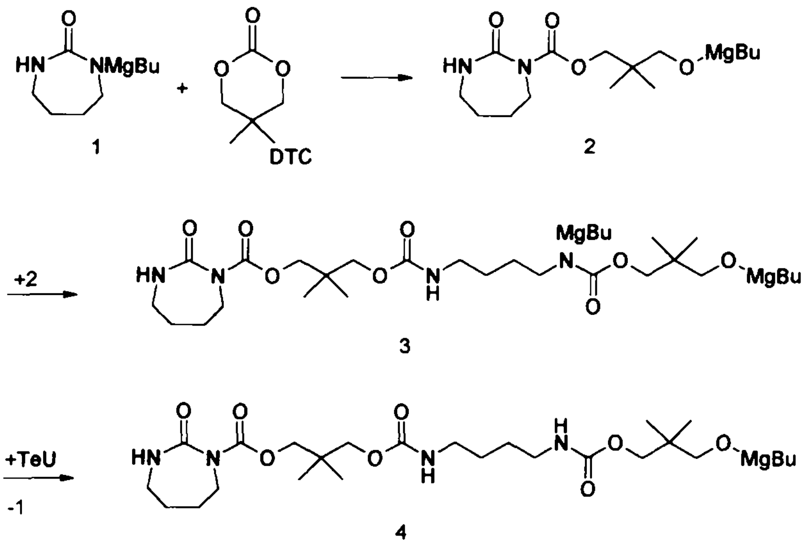
and lower molecular weight. At a temperature of 140 °C the polymerization of TeU is enhanced (higher urea content of the copolymer). With respect to the polymerization time the most striking effect is the increase of the ratio $\bar{M}_w/M_n$ (*Table 5* runs 4 and 8). This effect can be explained by transurethanization reactions. The polymerization is also influenced by the concentration of $MgBu_2$ used as catalyst (*Table 5* runs 10–12). An increase in catalyst concentration from 0.5 mol% to 1 mol% results in a slight decrease in the molecular weight; further increase of catalyst concentration leads to a partially crosslinked product.

The analysis of the microstructure of a copolymer with equal molar concentration of the repeating units (see below) reveals that upon copolymerization of DTC with TeU an alternating copolymer is obtained and not a random one. For the mechanism of copolymerization a priori two alternatives were taken into consideration[16](see *Scheme 2* and *Scheme 3*).

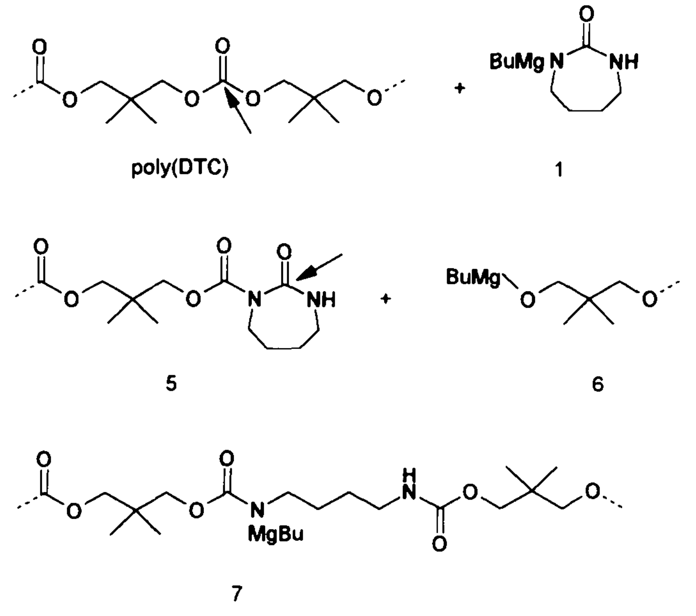
In *Scheme 2* Bu_2Mg reacts first with TeU with formation of a nucleophilic (TeU) active species. Upon reaction with DTC the resulting adduct shows two oppositely activated chain ends: an electrophilic TeU moiety and a nucleophilic (DTC) alcoholate. Intermolecular reaction of this species in a ring-opening way results in a chain extension; the new chain ends, however, are identical with the old ones. The intermediate reacts with TeU and regenerates the electrophilic TeU moiety.

In *Scheme 3*, polymerization of DTC occurs first followed by a transfer of the active species to TeU. This nucleophilic TeU species reacts with a carbonate moiety of the poly(DTC) chain, induces a chain cleavage and generates two oppositely activated chain ends – a nucleophilic TeU chain end and an electrophilic alcoholate. Intermolecular reaction of these two fragments generates a new molecule in which formally a TeU is inserted into a DTC-DTC diad with formation of two urethane groups. At the same time a new TeU active species is generated by deprotonation of TeU.

Copolymerization experiments of DTC and TeU in



Scheme 2 Copolymerization mechanism of DTC and TeU in the sense of a step growth polymerization (proposal 1)



Scheme 3 Copolymerization mechanism of DTC and TeU in the sense of a formal insertion of TeU into a poly(DTC) chain (proposal 2)

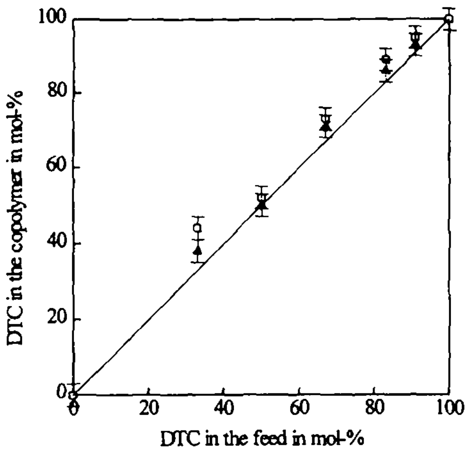


Figure 2 Copolymerization diagram of DTC and TeU. For conditions of preparation see *Table 6*: -▲- Nos. 1–5, -□- No. 6–10

DMPU at 120 °C with $MgBu_2$ as initiator reveals that DTC polymerizes first with formation of a polycarbonate sequence. Later when TeU is consumed the concentration of carbonate groups in the polymer decreases and that of urethane groups increases; at the same time some urea groups appear. After 24 h both monomers are consumed to > 95% and the molar ratio of carbonate/urethane/urea is 0.1/1/0.05.

As support for the interpretation of this experimental result living poly(DTC) was prepared via polymerization of DTC in THF with $MgBu_2$ as initiator ($\bar{M}_n = 30000$); then TeU was added, the solvent was removed and the reaction was continued in the melt at 140 °C. The composition of the reaction mixture was followed by quantitative analysis of the content of carbonate, urethane and urea groups (n.m.r. measurements) and by the determination of the molecular weight of the polymer (GPC measurements). The time dependent analysis of the polymer shows a similar behaviour as was observed in solution copolymerization, a

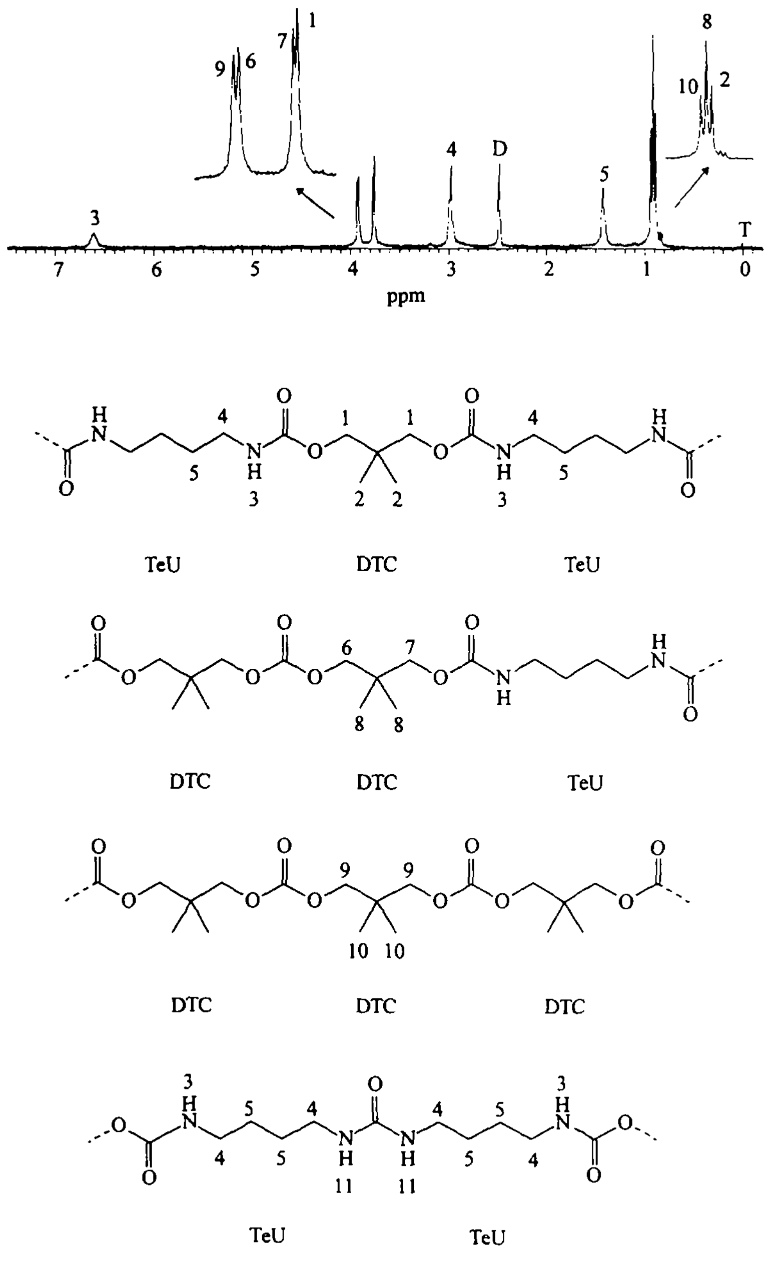


Figure 3 ^1H n.m.r. spectrum of a DTC/TeU copolymer (molar ratio DTC:TeU = 2.7); assignment of the characteristic resonance lines to specific triads or diads. Solvent: DMSO; T = 100 °C. For conditions of preparation see *Table 5*, No. 8; Key: T for TMS, D for DMSO

decrease in the content of carbonate groups, an increase in the content of urethane groups and a low concentration of urea groups. However, the reaction in the melt is slower than in solution.

The results obtained by GPC analysis reveal first a drastic decrease of the molecular weight to $\bar{M}_n = 9000$ and then a slow increase to a final value of $\bar{M}_n = 13000$. Obviously, the reaction of the TeU with the carbonate groups of the polymer is much faster than the intermolecular reaction of the polymeric fragments. In an analogous reaction of living poly(DTC) with ε-caprolactam this (strong) decrease in molecular weight was not observed[4].

The role of the catalyst in this reaction is essential since a change to an Al-active site—initiation of the DTC polymerization with Al(O*sec*-Bu)$_3$—does not result in a copolymer.

Synthesis of DTC/TeU-copolymers of variable composition; determination of the microstructure by means of n.m.r.-spectroscopic analysis. In the following the microstructure of the copolymer obtained by copolymerization of variable amounts of DTC with TeU will be discussed. The analytical method for the determination of the microstructure is ^{1}H- and ^{13}C n.m.r. spectroscopy. Copolymerization experiments were performed in DMPU solution (24 h, 120 °C) and in the melt (24 h, 120 °C) with molar ratios of $[DTC]_0/[TeU]_0$ in the range from 10/1 to 0.5/1. The polymers were isolated by precipitation in water and then analyzed spectroscopically.

As is shown in Tab. 6 the composition of the copolymer corresponds to a large extent to the monomer composition in the feed, for both the copolymerization in solution and in the melt. At high $[DTC]_0/[TeU]_0$ ratios, however, the deviation is larger than for equimolar amounts of the monomers and larger for the experiments in the melt than for those in DMPU solution. These results are summarized in *Figure 2*; for $[DTC]_0/[TeU]_0 \neq 1$ the copolymer exhibits a higher DTC content than in the feed.

^{1}H n.m.r. spectroscopic analysis of the TeU-DTC and TeU-TeU diads (see experimental part of *Table 1*) reveals that the methylene protons of the TeU moieties are not sensitive to structural changes in their vicinity; no significant difference in the chemical shift of the protons of the four CH$_2$ groups of the TeU moiety are observed. A clear evidence for TeU-DTC resp. TeU-TeU diads comes only from the different chemical shifts of the protons of the urethane NH ($\delta = 7.06$ ppm) and urea NH ($\delta = 5.75$ ppm) groups. The situation is different for the DTC moiety; the protons of the CH$_2$O groups show clearly different chemical shifts for TeU-DTC and DTC-DTC diads (see experimental part of *Table 2*), e.g. $\delta = 3.74$ ppm for a TeU-DTC and $\delta = 3.90$ ppm for a DTC-DTC diad.

Figure 3 shows the ^{1}H n.m.r. spectrum of a DTC/TeU copolymer with a DTC/TeU ratio 2.7 and a urethane/carbonate ratio of U/C = 46/54. The assignment of the resonance lines was made with the aid of model compounds and other copolymer samples with different DTC/TeU ratios. The absence of TeU-TeU diads results from the absence of a resonance line at $\delta = 5.75$ ppm.

From small resonance lines which appear in ^{1}H n.m.r. spectra of polymers with low molecular weight it is concluded that only DTC end groups are present, the chemical shift of which depends on the penultimate repeating unit (see experimental part of *Table 3*).

Additional evidence for the microstructure of the DTC/TeU copolymers comes from ^{13}C n.m.r. spectroscopy.

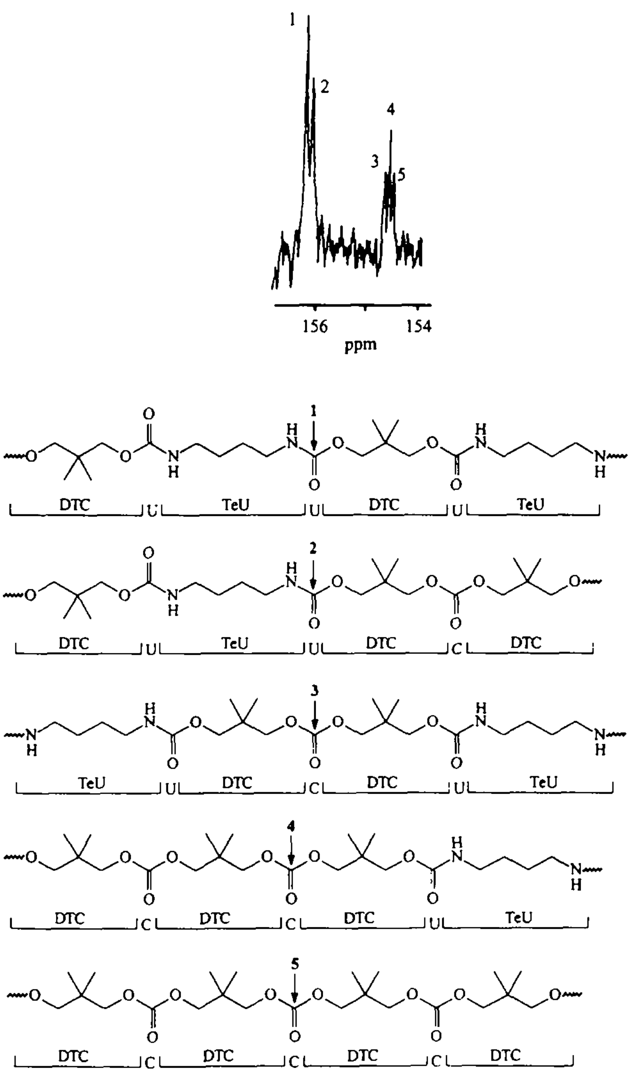


Figure 4 ^{13}C n.m.r. spectrum of the carbonyl region of a DTC/TeU copolymer (molar ratio DTC:TeU = 2.7); assignment of the characteristic resonance lines to specific triads. Solvent: DMSO; T = 100 °C; for conditions of preparation see *Table 6*, No.8

Table 6 Copolymerization of DTC and TeU: dependence of the microstructure of the copolymer on the monomer ratio in the feed (molar ratios)

No.	$[DTC]_0/[TeU]_0$[c]	[DTC]/[TeU][d]	U_t/C/U_r[e]
1[a]	10	13	14/86/0
2[a]	5	6.4	27/73/0
3[a]	2	2.5	57/43/0
4[a]	1	1	91/4.5/4.5
5[a]	0.5	0.6	71/0/29
6[b]	10	21	9/91/0
7[b]	5	8.4	21/79/0
8[b]	2	2.7	54/46/0
9[b]	1	1.1	87/9/4
10[b]	0.5	0.8	83/0/17

[a] polymerization conditions: t = 48 h, T = 120 °C, solvent: DMPU, $[DTC]_0 + [TeU]_0$ = 50 wt%, $[MgBu]_0$: 1 mol% with respect to DTC

[b] polymerization conditions: t = 48 h, T = 120 °C, in the melt, $[MgBu]_0$: 1 mol% with respect to DTC

[c] molar ratio of DTC to TeU in the feed

[d] molar ratio of the repeating units DTC and TeU in the copolymer, as determined by ^{1}H n.m.r. spectroscopy

[e] ratio of urethane (U_t), to carbonate (C), to urea (U_r) groups, resp. DTC-TeU, DTC-DTC, and TeU-TeU diads as determined from ^{1}H n.m.r. spectroscopy

Figure 4 shows the carbonyl region of the ^{13}C n.m.r. spectrum of a DTC/TeU copolymer (*Table 6*, No. 8) with two sets of resonance lines, one centered at $\delta = 154.5$ ppm for carbonate carbons and one centered at $\delta = 156$ ppm for urethane carbons.

For the carbonate groups three resonance lines are expected, i.e., for a sequence CCC, UCU and CCU resp. UCC which are expected to be identical. For the urethane groups only two resonance lines are expected, i.e., UUU, and CUU (the sequence CUC is not possible). The assignment of these combinations to the chemical shifts observed was made by means of copolymers with a compositional gradient: $\delta = 154.50$ ppm for CCC, $\delta = 154.59$ ppm for CCU resp. UCC, $\delta = 154.67$ ppm for UCU, $\delta = 156.10$ ppm for UUC resp. CUU and $\delta = 156.23$ ppm for UUU. In addition, when urea groups are present an additional resonance line is expected at $\delta = 157.98$ ppm.

CONCLUSIONS

This paper describes the preparation of rather specific nearly alternating copolymers of 2,2-dimethyltrimethylene carbonate and tetramethylene urea by polymerization of an equimolar mixture of the monomers. The result of this polymerization is a polyurethane. The mechanism comprises a complex reaction sequence in which the carbonate and urea groups of the monomer are converted into urethane groups by a formal insertion of the ring-opened urea moiety into carbonates groups.

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