Cationic Ring-Opening Polymerization of Tetramethylene Urethane

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ABSTRACT: The cationic ring-opening polymerization of tetramethylene urethane (TeU; systematic name, hexahydro-1,3-oxazepin-2-one, (**1**)) in the melt at 67 °C with methyl trifluoromethanesulfonate (TfOMe) as the initiator yields poly(tetramethylene urethane) (poly(TeU), (**6**)) with a regular microstructure. This [5]-polyurethane is a semicrystalline material with a T_g of 47 °C and a T_m of 209.5 °C. The reaction proceeds via an active chain end mechanism with a protonated cyclic endo iminocarbonate as the active species. The propagation step involves nucleophilic attack of the carbonyl oxygen of the monomer at the endocyclic methylene group adjacent to the oxygen atom of the active species. The propagation rate constant was 4.2×10^{-4} L·mol^{-1}·s^{-1}. The polymerization of tetramethylene urethane is accompanied by termination reactions; however, transfer reactions and backbiting reactions were not observed. Thermodynamic data support the ring-opening mechanism and the thermal stability (lack of ring-closing depolymerization and/or backbiting reactions).

Introduction

The ring-opening polymerization of cyclic urethanes has scarcely been mentioned in the scientific literature of the past years. In a US patent of the American Cyanamide Co. the synthesis and ring-opening polymerization of trimethylene urethane (TU; systematic name, tetrahydro-2H-1,3-oxazin-2-one) and of tetramethylene urethane (TeU, systematic name, hexahydro-1,3-oxazepin-2-one) was mentioned.[1] Hall and Schneider[2] reported on the ring-opening polymerization of TU in the presence of sodium hydride and *N*-acetyl-ϵ-caprolactam. No details on the polymer structure or polymerization mechanism were reported. Our laboratory recently studied the polymerization mechanism of the cationic ring-opening polymerization of TU.[3,4] The thermodynamics of TU, its polymerization in bulk, and of poly(TU) were studied by Lebedev et al. with special emphasis on the polymerization/depolymerization equilibrium.[5] In addition, we have investigated the synthesis and properties of block copolymers comprising poly(TU) and poly(THF) blocks obtained by cationic ring-opening polymerization.[6] The cationic ring-opening polymerization of TU and the sequential copolymerization of THF and TU employing methyl trifluoromethanesulfonate (TfOMe, methyl triflate) as a typical monofunctional initiator and trifluoromethanesulfonic acid anhydride (Tf_2O, triflic anhydride) as a typical bifunctional initiator yielded poly(TU) and block copolymers poly(THF)-*block*-poly(TU) and poly(TU)-*block*-poly(THF)-*block*-poly(TU) with regular microstructure of the respective blocks.

This paper reports kinetic, thermodynamic, and mechanistic aspects of the cationic ring-opening polymerization of tetramethylene urethane (TeU) with methyl triflate as initiator in bulk, as well as the characterization of the resulting [5]-polyurethane.

Experimental Part

Materials. 4-Amino-1-butanol (Aldrich, 98%), benzyl chloroformate (Fluka, 95%), and phenyl chloroformate (Fluka, >97%) were used as received. Before polymerization, TeU was sublimed at 52 °C and 10^{-2} mbar. The initiators TfOMe (Fluka, >97%), Tf_2O (Fluka, >98%) and $BF_3 \cdot OEt_2$ (Fluka, purum) were used without further purification. The monomer, initiators, and purified reagents were stored under nitrogen. Nitrogen was passed over molecular sieves (4 Å), finely distributed potassium on aluminum oxide, and BTS catalyst (from BASF) for purification.

Measurements. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker DPX-300 spectrometer at 300, 75, and 282 MHz, respectively. DMSO-d_6 and CD_2Cl_2 were used as solvents. Chemical shifts are given in ppm against TMS or $CFCl_3$ as internal standard.

DSC was measured on a Perkin-Elmer DSC-7 (heating and cooling rate: 20 K/min; calibration achieved using indium standard samples).

C, H, N elemental analyses were performed with a Carlo Erba MOD 1106 instrument. Thermogravimetric analysis (TGA) was performed with a Netzsch TG 209 instrument with a TA-System controller TASC 412/2 (heating rate: 20 K/min) The measurements were performed in air.

Gel permeation chromatography (GPC) was carried out at room temperature using an ERC HPLC pump and a Melz refractive index detector. Hexafluoro-2-propanol (HFIP) containing 0.01 M CF_3COONa served as the eluting solvent. The measurements were performed at a flow rate of 0.5 mL/min. A mixed bed column (Jordi DVB gel) was applied: length 500 mm, diameter 10 mm, diameter of the gel particles 5 μm, and pore sizes of 100−10^5 Å. Calibration was achieved using poly(methyl methacrylate) standards of narrow molecular weight distribution from Polymer Standard Service Mainz.

Preparation of Tetramethylene Urethane (TeU, 1). (a) 4-Benzyloxycarbonylimino-1-butanol (3). Benzyl chloroformate (51.8 mL, 363 mmol) and 4 N NaOH (300 mL, 1.20 mol) were added simultaneously under stirring at 0 °C to a solution of 4-amino-1-butanol (**2**) (29.4 g, 330 mmol) in 2 N NaOH (150 mL, 300 mmol). The resulting suspension was stirred for 30 min and brought to pH 5 with concentrated HCl. The solid was separated by filtration, washed with water, and dried. After removal of the solvent, a colorless solid was obtained. Yield: 89%. Mp: 81 °C.

^{1}H NMR (DMSO-d_6): $\delta = 7.38{-}7.29$ (m, 5H, CH_{arom}), 7.24 (tr, 1H, NH), 5.01 (s, 2H, $PhCH_2$), 4.41 (tr, 1H, OH), 3.38 (m, 2H, $CH_2{-}O$), 2.99 (m, 2H, $CH_2{-}N$), 1.42 (m, 4H, $CH_2{-}CH_2$) ppm.

^{13}C NMR (DMSO-d_6): $\delta = 156.03$ (C═O, 1C), 137.25, 128.25, 127.63 (C_{arom}, 6C), 65.01 ($PhCH_2$, 1C), 60.36 ($CH_2{-}O$, 1C), 40.24 ($CH_2{-}N$, 1C), 29.70 and 26.07 ($CH_2{-}CH_2$, 2C) ppm.

(b) 4-Benzyloxycarbonylimino-1-phenoxycarbonyloxybutane (4). A solution of phenyl chloroformate (42.0 mL, 335 mmol) in dry THF (80 mL) was added to a solution of 4-benzyloxycarbonylimino-1-butanol (**3**) (65.0 g, 291 mmol) in

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Table 1. Kinetic Data of the TeU Bulk Polymerization at 67 °C with TfOMe as Initiator[a]

$[M]_0/[I]_0$	10^{-2} $[I]_0$, mol·L^{-1}	10^5 $k[P^*]$, s^{-1}	10^4 k, L·mol^{-1}·s^{-1}
20	50.2	21.64	4.31
50	20.0	11.28	5.64
75	13.4	4.03	3.00
100	10.0	3.83	3.84

[a] The monomer density at 67 °C was determined to be ρ_{TeU}(67 °C) = 1.156 g/cm^3; the monomer concentration in bulk was calculated to be $[M]_0 = 10.04$ mol/L.

dry THF (508 mL) and dry pyridine (35.2 mL, 437 mmol) at 50 °C. After 12 h of stirring at 50 °C, the suspension was cooled to room temperature, pyridine hydrochloride was filtered off, and the solvent was distilled off in vacuo. The residue was treated with dry Et_2O and residual pyridine hydrochloride was removed by filtration. After removal of the solvent, a colorless solid was obtained. Yield: 97%. Mp 57−58 °C.

^{1}H NMR (DMSO-d_6): $\delta = 7.58-7.28$ (m, 10H, CH_{arom}), 7.24 (m, 1H, NH), 5.03 (s, 2H, $PhCH_2$), 4.20 (tr, 2H, CH_2-O), 3.05 (m, 2H, CH_2-N), 1.70−1.63 and 1.55−1.48 (m, 4H, CH_2-CH_2) ppm.

^{13}C NMR (DMSO-d_6): $\delta = 156.09$ and 153.02 (C=O, 2C), 150.70, 137.19, 129.64/129.51, 128.27/127.66, 126.01, and 121.19 (C_{arom}, 12C), 68.13 (CH_2-O, 1C), 65.09 ($PhCH_2$, 1C), 39.90 (CH_2-N, 1C), 25.65 and 25.35 (CH_2-CH_2, 2C) ppm.

(c) Tetramethylene Urethane (1). A solution of 4-benzyloxycarbonyl-imino-1-phenoxycarbonyloxybutane (**4**) (20.0 g, 58.2 mmol) in dry THF (3 wt % solution) and freshly prepared Pd black was hydrogenated in a glass ampule under a H_2 pressure of 1 bar. After complete conversion (dc control) the catalyst was removed by filtration and the solvent was distilled off in vacuo. The residue was purified by column chromatography using silica gel, Merck (70−230 mesh, 60 Å) as the stationary phase and ethyl acetate/ethanol (6:4 v/v) as the eluent followed by sublimation at 53 °C and 10^{-2} mbar. Yield: 84%. Mp: 60−62 °C.

^{1}H NMR (DMSO-d_6): $\delta = 7.13$ (br.s, 1H, NH), 3.98 (tr, 2H, CH_2-O), 2.96 (m, 2H, CH_2-N), 1.79−172 and 1.61−1.54 (m, 4H, CH_2-CH_2) ppm.

^{13}C NMR (DMSO-d_6): $\delta = 160.25$ (C=O, 1C), 68.94 (CH_2-O, 1C), 41.29 (CH_2-N, 1C), 29.02 and 26.92 (CH_2-CH_2, 2C) ppm.

Anal. Calcd for $C_5H_9NO_2$ (115.13): C, 52.16; H, 7.88; N, 12.17. Found: C, 51.75; H, 7.54; N, 11.79.

Ring-Opening Polymerization of Tetramethylene Urethane. General Procedure. All glass vessels were heated in vacuo prior to use, filled with inert gas, and handled in a stream of dry inert gas. The monomer was weighed under nitrogen directly into the reaction vessel, and the initiator was added at room temperature. For polymerization the closed reaction vessel was heated to 67 °C in a preheated oil bath under permanent stirring. The polymerization was terminated by cooling to room temperature followed by maceration of the crushed product with CH_2Cl_2.

Poly(tetramethylene urethane). Synthesis of Sample No. 5 in Table 2. Tetramethylene urethane (0.46 g, 4.0 mmol) and TfOMe (9.4 mg, 5.7×10^{-2} mmol) were polymerized for 12 h at 67 °C. The polymerization was terminated by cooling to room temperature followed by maceration of the crushed product with CH_2Cl_2 (10 mL). Yield: 85%.

GPC in HFIP/0.01 M CF_3COONa: $M_n = 3700$, $M_w = 8200$, $Q = M_w/M_n = 2.23$.

$T_m = 209.5$ °C (as determined by DSC); $T_g = 47$ °C (as determined from calorimetric measurements).

^{1}H NMR (DMSO-d_6, 100 °C): $\delta = 6.54$ (br s, 1H, NH), 3.95 (tr, 2H, CH_2-O), 3.01 (q, 2H, CH_2-N,), 1.52 (m, 4H, CH_2-CH_2) ppm. $CH_3-O-CO-N$ end group: $\delta = 3.55$ (s).

^{13}C NMR (DMSO-d_6, 100 °C): $\delta = 155.80$ (C=O, 1C), 62.95 (CH_2-O, 1C), 39.63 (CH_2-N, 1C), 25.72 and 25.58 (CH_2-CH_2, 2C) ppm.

From end group analysis an M_n value of 6700 was calculated.

Table 2. Polymerization of TeU in Bulk with Electrophilic Initiators at 67 °C, Giving Initial Conditions, Monomer Conversion, and Polymer Characterization[a]

no.	I	$[M]_0/[I]_0$	t/h	$M_{n,th}$[b]	M_n[c]	Q[c]	M_n[d]	X_p[e]/%
1	TfOMe	20	0.25	1357	1200	2.04	1070	59
2	TfOMe	20	1.5	2116	1800	1.68	1310	92
3	TfOMe	50	1.5	4485	3000	2.19	3300	78
4	TfOMe	50	21	5175	3500	1.93	6100	90
5	TfOMe	75	12	7331	3700	2.23	6700	85
6	TfOMe	100	1.5	4370	3800	2.08	4400	38
7	TfOMe	100	6	6095	4300	2.28	8300	53
8	TfOMe	100	25	8740	5200	2.19	11 200	76
9	Tf_2O	50	22	5577	1500	2.37	n.d.[f]	97
10	$BF_3 \cdot OEt_2$	50	22	5347	2000	3.57	n.d.[f]	93

[a] The polymer was purified by maceration with CH_2Cl_2 prior to analysis. [b] $M_{n,th} = [M]_0/[I]_0 \times X_p \times 115$ (with X_p being the monomer conversion). [c] Determined by GPC in HFIP/0.01 M CF_3COONa, PMMA standards (with Q being the polydispersity index). [d] Determined by end group analysis (^{1}H NMR spectroscopy). [e] Determined gravimetrically (with X_p being the polymer yield). [f] No well-defined end group was detected in ^{1}H NMR.

Anal. Calcd for $[C_5H_9NO_2]_n$ $(115.13)_n$: C, 52.16; H, 7.88; N, 12.17. Found: C, 51.78; H, 7.95; N, 11.86.

For quantitative combustion, addition of V_2O_5 as a catalyst was required.

Preparation of 2-Methoxy-4,5,6,7-tetrahydro-1,3-oxazepinium Trifluoromethanesulfonate. TfOMe (0.89 g, 5.4 mmol) was added to a solution of tetramethylene urethane (0.62 g, 5.4 mmol) in CH_2Cl_2 (4.2 mL) at −78 °C. The mixture was stirred for 2 h at −78 °C and then allowed to warm to room temperature during 12 h. The solvent was evaporated in vacuo, and the residual oil was analyzed by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy.

^{1}H NMR ($CD_2Cl_2/CFCl_3$): $\delta = 9.67$ (br s., 1H, NH), 4.87 (tr, 2H, CH_2-O), 4.07 (s, 3H, CH_3-O), 3.62 (q, 2H, CH_2-N), 2.15 and 2.04 (m, 4H, CH_2-CH_2) ppm.

^{13}C NMR ($CD_2Cl_2/CFCl_3$): $\delta = 165.61$ (C=O, 1C), 123.00 (F_3C, 1C), 78.54 (CH_2-O, 1C), 59.50 (CH_3-O, 1C), 43.24 (CH_2-N, 1C), 26.92 and 24.45 (CH_2-CH_2, 2C) ppm.

^{19}F NMR ($CD_2Cl_2/CFCl_3$): $\delta = -79.53$ ppm.

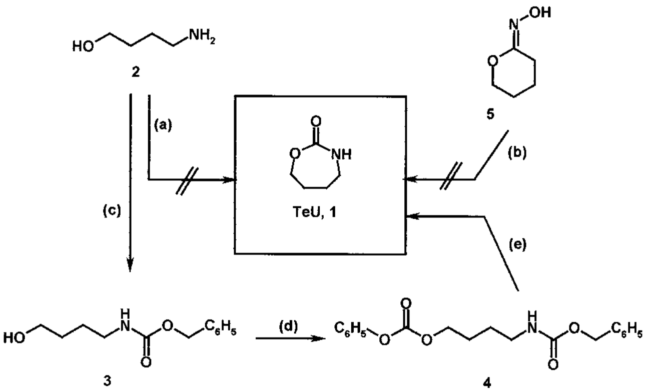
Polymerization of TeU with TfOMe as Initiator. Termination with Potassium Acetate/Acetic Acid. Tetramethylene urethane (0.51 g, 4.4 mmol) and TfOMe (14.4 mg, 8.7×10^{-2} mmol) were polymerized for 15 min at 67 °C. The polymerization was terminated by addition of a solution of KOAc (0.58 g, 5.9 mmol) in AcOH (3.6 g, 60 mmol). After an additional 15 min of stirring at 67 °C, the solvent was removed in vacuo. The residue was macerated with water, and the polymer was filtered off, dried, and analyzed by means of ^{1}H NMR spectroscopy.

^{1}H NMR (DMSO-d_6, 100 °C): The end groups show resonances at $\delta = 1.99$ ($-O-OC-CH_3$) and at $\delta = 3.55$ ppm ($-NH-CO-O-CH_3$). The intensity ratio of the resonance lines is 1.

Qualitative NMR Spectroscopic Study of the Stability of the Active Species. A solution of TeU (100 mg, 0.87 mmol) in dry CD_2Cl_2 (0.75 mL) was treated in an NMR tube with a solution of TfOMe (213.3 mg, 1.3 mmol) in dry CD_2Cl_2 (0.75 mL). The NMR tube was cooled with liquid N_2, evacuated and sealed. At selected times, ^{1}H NMR spectra were recorded (cf. Figure 6).

Kinetic Investigation of the TeU Polymerization with TfOMe as Initiator. The polymerization of TeU was carried out at 67 °C with different monomer/initiator ratios: $[M]_0/[I]_0$ = 20, 50, 75, and 100. Each point in the first-order plot and in the M_n vs conversion plot represents an experiment. After selected reaction times, the polymerization was terminated by cooling to room temperature. The conversion was determined gravimetrically, and the number-average molecular weight was determined by ^{1}H NMR spectroscopy (end group analysis). Additional information on the polydispersity (Q) and number-average molecular weight was obtained from GPC in HFIP. The results of the kinetic data are summarized in Table 1.

Scheme 1. Synthesis of Tetramethylene Urethane[a]



[a] Key: (a) $(C_6H_5O)_2CO$, 140−150 °C, 0.25 mol % $Bu_2Sn(OMe)_2$; (b) according to ref 1; (c) $C_6H_5CH_2OCOCl$, NaOH, 0 °C; (d) C_6H_5OCOCl, Py, THF, 50 °C; (e) Pd/H_2, THF, room temperature.

Model Compounds. *N*-Methoxycarbonylpyrrolidine. Pyrrolidine (5.69 g, 80.0 mmol) in dry THF (30 mL) was slowly added to a solution of methyl chloroformate (3.78 g, 40.0 mmol) in dry THF (190 mL) at 0 °C (N_2). The mixture was stirred at room temperature for 16 h. Pyrrolidine hydrochloride was removed by filtration and the solvent was evaporated in vacuo. The residue was dissolved in diethyl ether (150 mL) and was washed with 5% HCl, saturated $NaHCO_3$ solution, and water. The organic phase was dried on $MgSO_4$. The solvent was evaporated in vacuo. The solvent was evaporated in vacuo, and the residue was analyzed by ^1H and ^{13}C NMR spectroscopy. Yield: 60%.

^1H NMR (CD_2Cl_2): δ = 3.66 (s, 3H, CH_3−O), 3.33 (tr, 4H, CH_2−N), 1.86 (tr, 4H, CH_2) ppm.

^{13}C NMR (CD_2Cl_2): δ = 156.14 (C=O, 1C), 52.66 (CH_3−O, 1C), 46.67 (CH_2−N, 2C), 26.34/25.80 (CH_2, 2C) ppm.

***N*-Methoxycarbonylpyrrolidinium Trifluoromethanesulfonate.** Trifluoromethanesulfonic acid (58 mg, 0.39 mmol) in CD_2Cl_2 (0.2 mL) was added under nitrogen to a solution of *N*-methoxycarbonylpyrrolidine (50 mg, 0.39 mmol) in CD_2Cl_2 (0.4 mL). The NMR analysis after 15 min revealed the following results.

^1H NMR (CD_2Cl_2): δ = 14.31 (s, 1H, NH^+), 4.00 (s, 3H, CH_3−O), 3.57 (m, 4H, CH_2−N), 2.01 (m, 4H, CH_2) ppm.

^{13}C NMR (CD_2Cl_2): δ = 158.50 (C=O, 1C), 120.69 (CF_3, 1C), 57.49 (CH_3−O, 1C), 48.68 (CH_2−N, 2C), 25.75 (CH_2, 2C) ppm.

2-Hydroxy-4,5;6,7-tetrahydro-1,3-oxazepinium Trifluoromethanesulfonate ($TeU^*CF_3SO_3H$). Trifluoromethanesulfonic acid (58 mg, 0.39 mmol) in CD_2Cl_2 (0.2 mL) was added under nitrogen to a solution of TeU (45 mg, 0.39 mmol) in CD_2Cl_2 (0.4 mL). The NMR analysis after 15 min revealed the following results.

^1H NMR (CD_2Cl_2): δ = 13.55 (br s, 1H, NH^+), 8.55 (br s, 1H, OH), 4.61 (tr, 2H, CH_2−O), 3.51 (m, 2H, CH_2−N), 2.13 (m, 2H, CH_2−CH_2−O), 1.99 (m, 2H, CH_2−CH_2−N) ppm.

^{13}C NMR (CD_2Cl_2): δ = 166.71 (C=O, 1C), 120.70 (CF_3, 1C), 76.36 (CH_2−O, 1C), 43.70 (CH_2−N, 1C), 27.71 (CH_2−CH_2−O, 1C), 25.15 (CH_2−CH_2−N, 1C) ppm.

Results and Discussion

Monomer Synthesis. Five- and six-membered cyclic urethanes were prepared starting with the corresponding amino alcohol and diphenyl carbonate at temperatures above 100 °C and with $Bu_2Sn(OMe)_2$ as catalyst; the cyclic urethanes were isolated by sublimation.[4,7,8] Treatment of 4-amino-1-butanol (**2**) with diphenyl carbonate under these conditions, however, results in [5]-polyurethane without a trace of TeU (**1**). The route to the monomer described in the literature[1] starting with the hydroxamic acid **5** failed (Scheme 1). Access to TeU was achieved by using protecting groups technique common in peptide chemistry.[7] TeU was obtained by the three step synthesis outlined in Scheme 1 in an overall yield of 73% with a melting point of 60−62 °C.

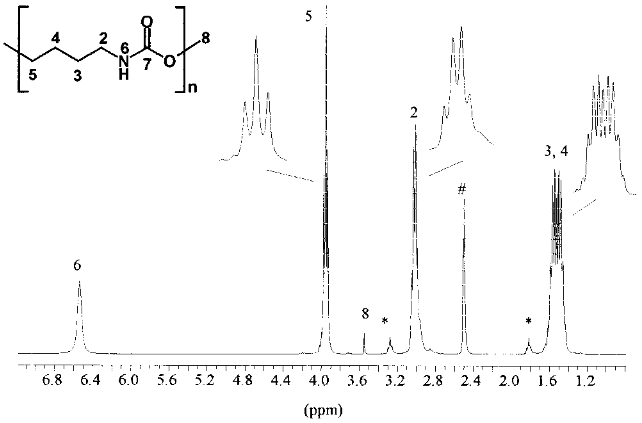
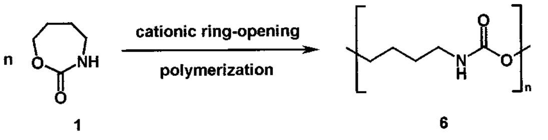


Figure 1. ^1H NMR spectrum of poly(TeU) in DMSO-d_6 at 100 °C. Key: (#) DMSO; (*) resonance of N-substituted pyrrolidine end groups.

Polymerization of TeU and Characterization of Poly(TeU). Tetramethylene urethane (**1**) was polymerized in bulk at temperatures above the melting point of the monomer with a variety of nucleophilic initiators, i.e., $Ti(OiPr)_4$, Bu_2Mg, and K−naphthalene.[7] NMR spectroscopic analysis, however, revealed that the polymeric product does not have a regular microstructure with head-to-tail linkages between repeating units. The fractions of head-to-head (tail-to-tail) units varies with the initiator. This means that urea and carbonate groups are also present. The resonance line of the urea-NH (δ = 5.55 ppm) was used to quantify the head-to-head linkages. In contrast to the results obtained with nucleophilic initiators, polymerization of TeU with electrophilic initiators ($Et_2O{\cdot}BF_3$, TfOMe, Tf_2O) yields a polymer with a regular microstructure (eq 1). The polymer precipitates during melt polymerization and is insoluble at room temperature in most solvents. NMR analysis was performed in DMSO at 100 °C and GPC analysis in a 0.01 M solution of CF_3COONa in hexafluoro-2-propanol (HFIP). The GPC results strongly depend on the concentration of added salt and therefore no absolute information on the molecular weight is obtained. The M_n values obtained by GPC are lower than the data obtained from ^1H NMR end group analysis. GPC analyses of [6]- and [7]-polyurethane in DMAc and HFIP further result polydispersity values which are higher than 2.[7]



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Polymerizations performed with the electrophilic initiators at different monomer/initiator ratios (Table 2) demonstrate that M_n increases with increasing $[M]_0/[I]_0$ ratio. The deviations from a linear relationship results from the heterogeneous course of the polymerization.

The ^1H NMR spectrum (Figure 1) reveals that all repeating units are connected head-to-tail, and that only one series of resonance lines is observed. The urea-NH resonance at δ = 5.55 ppm is not observed, thus head-to-head connected repeating units are excluded. The

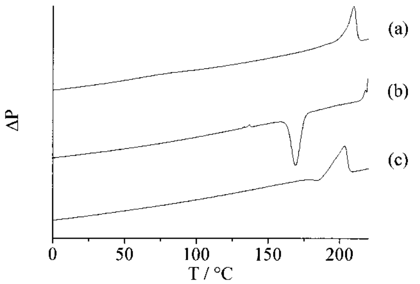


Figure 2. DSC curves of poly(TeU) for sample no. 5 of Table 2: (a) first heating; (b) cooling; (c) second heating. Heating rate 20 K/min.

Table 3. DSC Data of Poly(TeU)[a]

heating cycle[b]	T_{cr}/°C	ΔH_{cr}/J·g^{-1}	T_m/°C	ΔH_m/J·g^{-1}
first heating			209.5	100.3
cooling	169.3	−92.8		
second heating			203.0	78.0

[a] Sample no. 5 of Table 2. [b] Heating and cooling rate: 20 K/min.

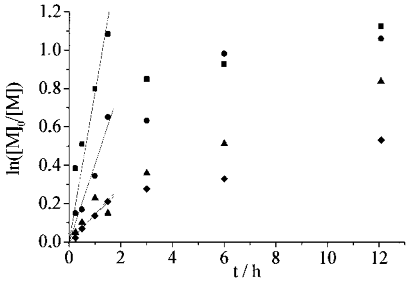


Figure 3. First-order kinetic plot of the polymerization of TeU with TfOMe as initiator at 67 °C in bulk: (■) $[TeU]_0/[I]_0 = 20$; (●) $[TeU]_0/[I]_0 = 50$; (▲) $[TeU]_0/[I]_0 = 75$; (◆) $[TeU]_0/[I]_0 = 100$.

singlet at $\delta = 3.55$ was assigned to the methyl urethane end group and was used for the calculation of the number-average molecular weight. The two resonance lines at $\delta = 3.25$ and 1.80 ppm were assigned to N-substituted pyrrolidine end groups. Their origin will be discussed in connection with the stability of the active species and the polymerization mechanism. The ^{13}C NMR data (cf. Experimental Part) support the proposed regular microstructure of [5]-polyurethane.

Poly(TeU) is a semicrystalline material with a glass transition temperature of 47 °C[9] and a melting point of 209.5 °C. The endotherm at the melting transition may show a peak with a shoulder at lower temperature (Figure 2) or two unresolved peaks. Thus, [5]-polyurethane may show two crystalline modifications. This interpretation is supported by calorimetric measurements performed in the laboratory of Lebedev.[9]

The polymer melt crystallizes on cooling at 169.3 °C. The DSC data are summarized in Table 3. The high value for the melting enthalpy indicates that poly(TeU) is highly crystalline.

The thermal stability of [5]-polyurethane was determined by thermogravimetric analysis: a 5% mass loss is observed at 275 °C, 50% mass loss at 324 °C, and 95% mass loss at 341 °C. These data indicate a higher thermal stability than that of corresponding [*m*,*n*]-polyurethanes.

Kinetic Aspects. The kinetic analysis of the reaction was performed for four monomer/initiator ratios: $[M]_0/[I]_0 = 20$, 50, 75, and 100. Each point in the first order plot (Figure 3) represents one experiment. The first order plot is linear only in the beginning of the reaction. For this part of the reaction a propagation rate constant of 4.2×10^{-4} L·mol^{-1}·s^{-1} was obtained from the apparent rate constant under consideration of the monomer density at 67 °C (ρ_{TeU}(67 °C) = 1.156 g/cm^3).[7] For short reaction times − i.e., for the linear part of the first-order plot − the ratio $[I]_0/[P^*] = 1$ (where $[P^*]$ is the concentration of the active species). The deviation from linearity in the first-order plot at longer reaction times is indicative of termination reactions. For high initiator concentrations ($[M]_0/[I]_0 = 20$ or 50) the linear relationship in the first-order plot applies up to 90% monomer conversion while for lower initiator concentrations ($[M]_0/[I]_0 = 75$ or 100) deviations from linearity become evident at 50% monomer conversion. This is explained by the instability of the active species leading to chain termination. At decreasing initiator concentration the polymerization rate decreases and the extent of chain termination increases. A plot of the number-average molecular weight vs conversion is linear for all monomer/initiator ratios studied (Figure 4) indicating that no transfer and no backbiting occurs. The lack of backbiting reactions further results from the absence of cyclic oligomers in the reaction product.

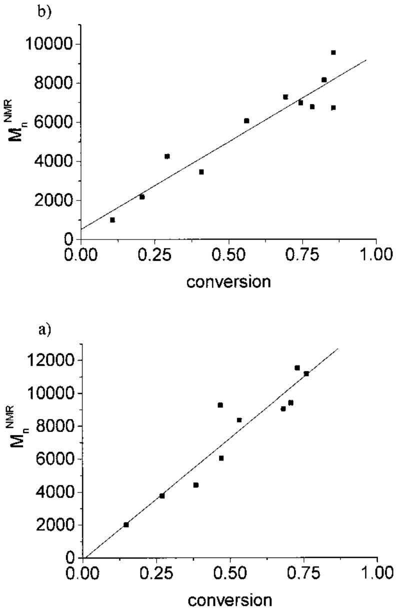
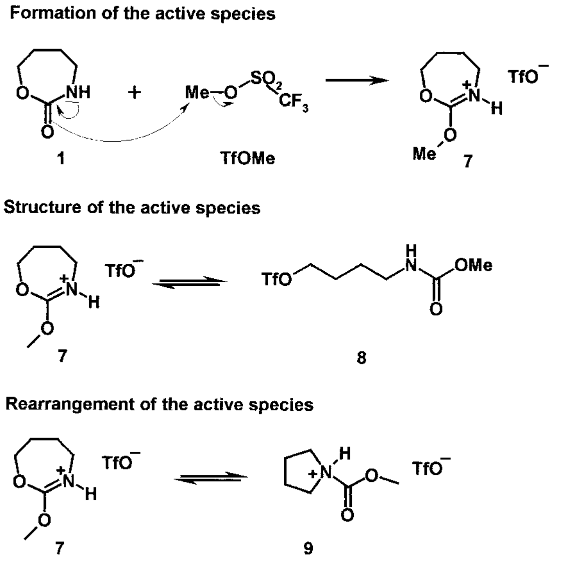


Figure 4. Molecular weight M_n as a function of conversion in the polymerization of TeU initiated with TfOMe at 67 °C in bulk: (a) $[TeU]_0/[I]_0 = 100$; (b) $[TeU]_0/[I]_0 = 75$.

Formation and Stability of the Active Species. The active species are formed by reaction of equimolar amounts of TeU with TfOMe in CH_2Cl_2 solution (Scheme 2). Under these conditions no propagation is observed. The active species **7** could not be obtained in crystalline form. ^{1}H NMR analysis of the crude product (Figure 5) reveals the complete conversion of the starting materials and the characteristic resonances of the active species. No resonance is observed at $\delta = 4.24$ ppm for TfOMe. The assignment of the resonance lines of the active species **7** is supported by the data obtained for the active species in the polymerization of trimethylene urethane (TU) as shown in Table 4. The origin of the unassigned signals of low intensity in Figure 5 will be discussed later in connection with the stability of the active species.

The ^{13}C and ^{19}F NMR data of the CF_3SO_3 fragment give information on whether the active species is ionic

Scheme 2. Formation, Structure, and Stability of the Active Species 7



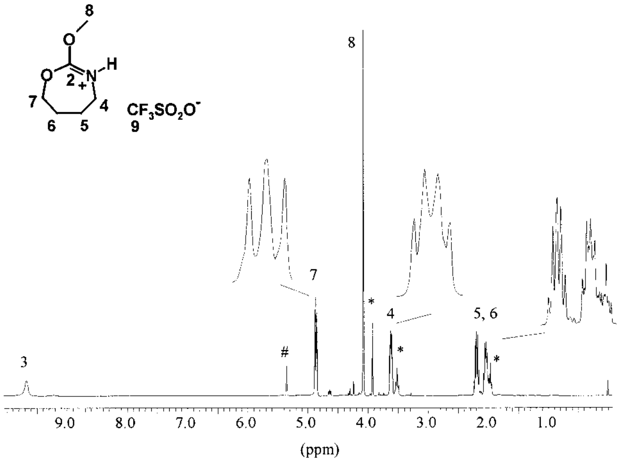


Figure 5. ^{1}H NMR spectrum of 2-methoxy-4,5−6,7-tetrahydro-oxazepinium trifluoromethanesulfonate (**7**) in CD_2Cl_2. Key: (#) CD_2Cl_2; (∗) resonance of *N*-methoxycarbonylpyrrolidinium trifluoromethanesulfonate.

Table 4. ^{1}H and ^{13}C NMR Data of the Active Species of TeU (7) and of the Active Species of Trimethylene Urethane (TU) for Comparison Reasons

active species	NH^+	C=O	CH_2O	OCH_3	CH_2-N	$CF_3SO_3^-$
		^{1}H NMR Data[a]				
TeU	9.67		4.87	4.07	3.62	
TU	9.77		4.80	4.07	3.59	
		^{13}C NMR Data[a]				
TeU		165.61	78.54	59.50	43.24	123.00
TU		160.30	73.10	58.60	38.90	120.80

[a] NMR spectral data in CD_2Cl_2; δ values in ppm.

(structure **7**) or covalent (structure **8**). The chemical shifts clearly reveal the ionic nature of the active species **7** upon comparison with the chemical shifts of $Et_3NH^+TfO^-$ (an ionic species) and TfOMe (a covalent species): $\delta = 123.0$ and -79.5 ppm for the active species **7**, $\delta = +120.7$ and -78.9 ppm for $Et_3NH^+TfO^-$ and $\delta = +117.2$ and -75.5 ppm for TfOMe. The chemical shifts observed for the active species **7** and $Et_3NH^+TfO^-$ are similar.

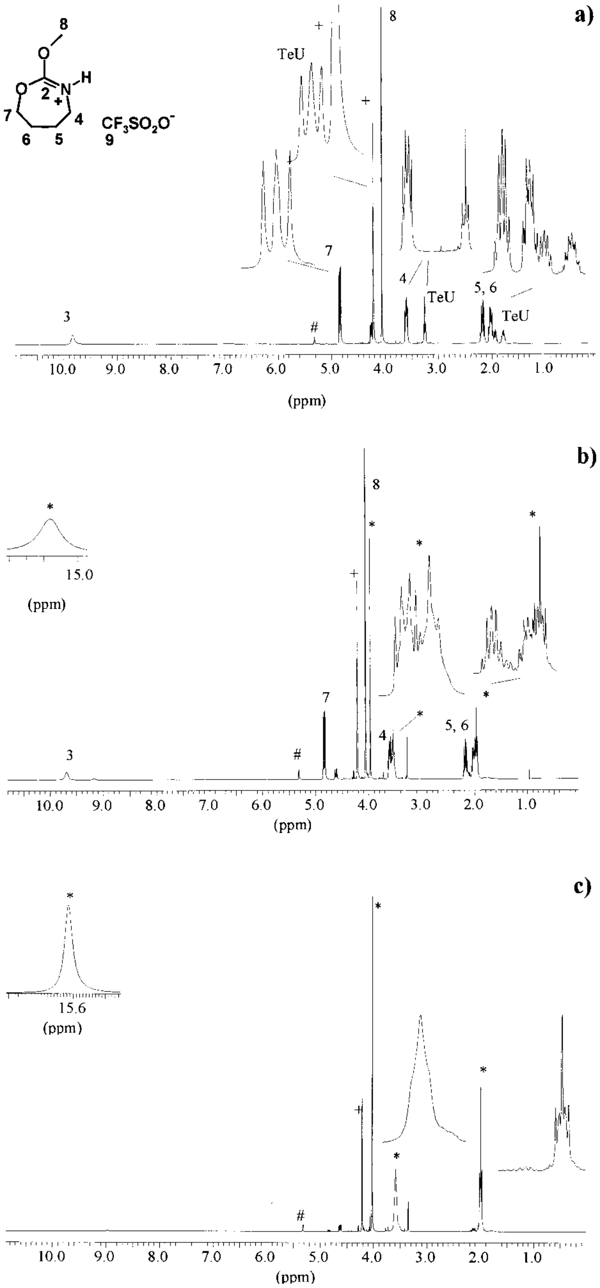


Figure 6. Formation and stability of the active species **7** in CD_2Cl_2. Initial conditions: $[TeU]_0/[TfOMe]_0 = 0.67$: (a) $t_1 = 1$ h; (b) $t_2 = 22$ h; (c) $t_3 = 10$ d. Key: (#) CD_2Cl_2; (∗) *N*-methoxycarbonylpyrrolidinium trifluoromethanesulfonate (**9**); (+) methyl trifluoromethanesulfonate (TfOMe).

To assign the signals of low intensity in Figure 5 we studied the stability of the active species in CD_2Cl_2 solution at room temperature starting with TeU and TfOMe (molar ratio of 0.67) in an evacuated sealed NMR tube. After 1 h (Figure 6a) the NMR spectrum shows the typical resonance lines of the active species (δ = 9.67, 4.87, 4.07, 3.62, 2.15, and 2.04 ppm), the monomer (δ = 4.25, 3.25, 1.95, and 1.75 ppm) and of TfOMe (δ = 4.24 ppm). After 3 h, all the monomer is consumed, and the resonances of the active species and of excess TfOMe are the only main resonances. The resolution of the signals decreases within the next few hours, and after 22 h (Figure 6b), additional resonances for the decomposition product appear at δ = 3.63 and 2.00 ppm in a ratio of 1:1 and at δ = 4.02 and 15.62 ppm. Complete conversion of the active species is observed after 10 d; beside the resonance of excess TfOMe, four new resonances are observed (Figure 6c). The structure of the final product was determined to be *N*-methoxycarbonylpyrrolidinium trifluoromethanesulfonate (**9**) by com-

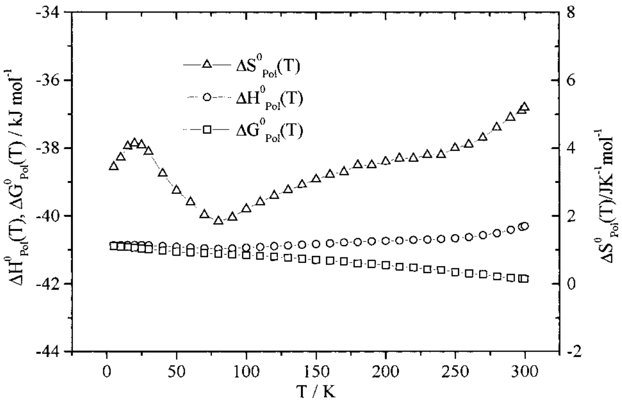


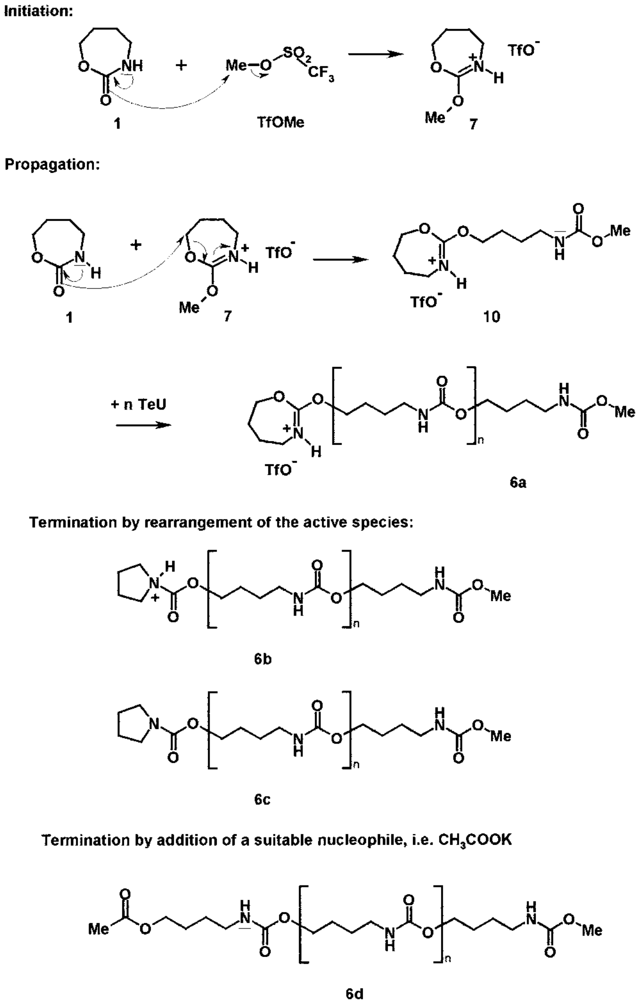
Figure 7. Enthalpy, entropy, and Gibbs function change in ring-opening polymerization of tetramethylene urethane to poly(tetramethylene urethane) with uniform microstructure (data obtained from calorimetric measurements).

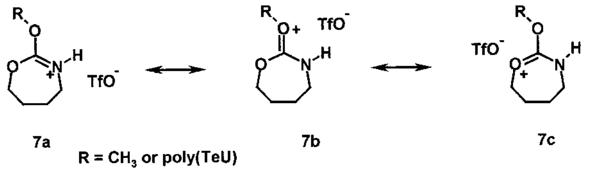
parison with an authentic sample (cf. Experimental Part).

Thermodynamic Aspects. Calorimetric measurements of TeU and poly(TeU) were performed between 0 and 300 K in order to determine the Gibbs function of polymerization $\Delta G^0_{\mathrm{pol}}$.[9] The molar polymerization enthalpy $\Delta H^0_{\mathrm{pol}}$(cr; p. cr) (the physical state of the monomer is crystalline, cr, that of the polymer is partial crystalline, p. cr) over the whole temperature range is nearly constant ($\Delta H^0_{\mathrm{pol}} = -40$ kJ/mol) while polymerization entropy $\Delta S^0_{\mathrm{pol}}$ is equal to 2−5 J/(mol·K). As a result, the Gibbs function of polymerization $\Delta G^0_{\mathrm{pol}}$(cr, p. cr) ≈ -42 kJ/mol (Figure 7). From these data a ceiling temperature of polymerization of ~1000 K (≈727 °C) was estimated. Such a high ceiling temperature indicates the high stability of the polymer with respect to ring-closing depolymerization. Thus, before ring-closing depolymerization occurs the urethane groups will be cleaved randomly. The results of the calorimetric measurements agree with the experimental results: (i) The polymerization of TeU occurs under very mild conditions just above the melting point. (ii) Upon thermal degradation no ring-closing depolymerization is observed.

Mechanistic Aspects. The mechanism of the cationic ring-opening polymerization of TeU was studied for TfOMe as initiator. Because of the high polymerization rate and the insolubility of TeU oligomers, the active species in the propagation reaction were not directly observed by NMR spectroscopy. On the basis of the experimental results, the following mechanism is proposed for the initiation, propagation and termination reaction (Scheme 3). The polymerization follows an activated chain end mechanism in which the monomer-initiator adduct **7** forms the active species. In the propagation step the carbonyl oxygen of the monomer **1**—the nucleophilic species—reacts with the endocyclic methylene group adjacent to the oxygen atom in the active species **7**—the electrophilic counterpart. During propagation an oxazepinium trifluoromethanesulfonate end group as in **6a** is formed as the active species. The polymerization is terminated by rearrangement of the active species or by addition of a nucleophilic species, such as acetate anions. The rearrangement of the active species leads to a pyrrolidinium trifluoromethanesulfonate end group as in **6b**, which is unable to further react with TeU. This rearrangement, however, is much slower than the propagation reaction. Workup finally leads to a poly(TeU) with a pyrrolidine end group as in **6c**. Termination by addition of potassium acetate in glacial acetic acid leads to a poly(TeU) with an acetate end group **6d**. This last reaction supports our assumption of the ionic nature of the active species. The alkyl−oxygen cleavage in the active species induced by the acetate nucleophile was explained by Miyamoto and Saegusa.[10] The delocalization of the positive charge over all heteroatoms of the active species **7a** ↔ **7b** ↔ **7c** induces a high electron deficiency in the endocyclic and exocyclic CH_2O- groups. However, due to the ring strain the probability of an endocyclic nucleophilic attack is preferred. Theoretical calculations are required to reveal the contribution of the immonium salt **7a** and the oxonium salts **7b** and **7c** to the real charge distribution.

Scheme 3. Mechanism of the Cationic Ring-Opening Polymerization of TeU with TfOMe as Initiator





The concentration of the two end groups in the absence of transfer and termination reactions should be equal. The ^{1}H NMR spectrum (Figure 8) shows a poly(TeU) in which the resonances of the end groups at $\delta = 1.99$ ppm (CH_3COO^-) and at $\delta = 3.55$ ppm ($CH_3O-CO-NH$) have the same intensity, which demonstrates that

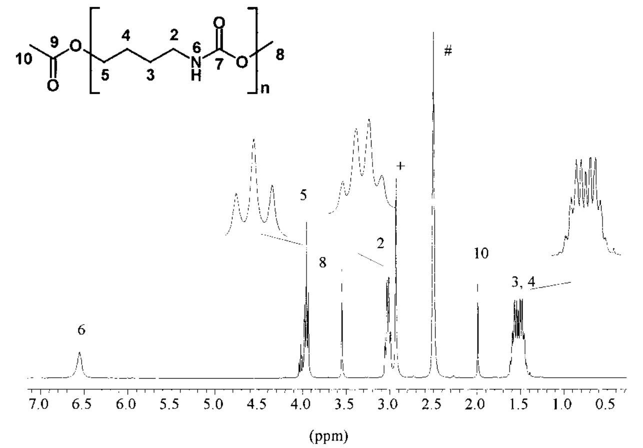


Figure 8. ^{1}H NMR spectrum of poly(TeU) (**6d**) in DMSO-d_6 at 100 °C. Key: (#) DMSO; (+) H_2O.

the ratio of active chain concentration to initial initiator concentration is 1, as in a living polymerization. In addition, the spectrum shows no pyrrolidine end groups.

Conclusions

The cationic ring-opening polymerization of TeU occurs with a high rate at 67 °C. The kinetic data of the polymerization support the absence of transfer reactions (see Figure 4) and the occurrence of termination reactions after more than 50% of the monomer is consumed (see Figure 3). On the basis of these results a controlled copolymerization leading to block copolymers should be possible by sequential cationic polymerization.

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