Cationic Ring-Opening Polymerization of Trimethylene Urethane: A Mechanistic Study

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ABSTRACT: The cationic ring-opening polymerization of trimethylene urethane (TU; systematic name, tetrahydro-2*H*-1,3-oxazin-2-one, (**1**)) in the melt at 100 °C with methyl trifluoromethanesulfonate (TfOMe), trifluoromethanesulfonic acid (TfOH), and $BF_3 \cdot OEt_2$ as initiators yields poly(trimethylene urethane) (poly(TU), (**2**)) with a uniform microstructure. The reaction mechanism is examined for TfOMe and TfOH as initiators. According to NMR spectroscopic results, with both initiators the polymerization proceeds via an active chain end mechanism with protonated cyclic endo iminocarbonates (**5**) as active species. The propagation step involves a nucleophilic attack of the active species at the monomer followed by a double isomerization process and regeneration of the active species. The polymerization kinetics was investigated yielding a polymerization rate constant of 4.2×10^{-4} $L \cdot mol^{-1} \cdot s^{-1}$ for the TfOMe-initiated process. Comparison of the kinetic data of the TfOMe- and the TfOH-initiated polymerizations reveals a qualitative and quantitative difference. On the basis of ion trapping experiments this difference is interpreted in terms of deviating initiation mechanisms. It is shown that the polymerization of trimethylene urethane is accompanied by termination and transfer reactions. A transfer mechanism implying termination in a subsequent step is proposed.

Introduction

The ring-opening polymerization of cyclic derivatives of carbonic acid has attracted attention over the past 10 years, especially with regard to cyclic carbonates. A large variety of products has been synthesized, employing the six-membered carbonate dimethyltrimethylene carbonate (systematic name, 5,5-dimethyl-1,3-dioxan-2-one) as a monomer, ranging from the homopolymer and block copolymers to statistical copolymers. The polymerization with anionic initiators was characterized with respect to the identity of the active species and the polymerization kinetics.[1]

The polymerization of cyclic urethanes as another family of cyclic derivatives of carbonic acid, however, has only been rarely investigated in the past 40 years, although it would be an interesting alternative for the preparation of polyurethanes without the involvement of isocyanates or phosgene (in the preceding step). An early report by Drechsel[2] demonstrated that polymers are obtained by polymerization of cyclic urethanes, e.g., trimethylene urethane (TU; systematic name, tetrahydro-2*H*-1,3-oxazin-2-one, (**1**)) and tetramethylene urethane (systematic name, hexahydro-1,3-oxazepin-2-one), with anionic and cationic initiators. Hall and Schneider[3] showed that the six membered TU (**1**) polymerizes in the presence of NaH and traces of *N*-acetyl-ϵ-caprolactam. Details on the polymer structure or polymerization mechanisms, however, were not disclosed by either one of the cited authors. There are only a few additional publications covering the field of the polymerization of cyclic urethanes,[4] and to the best of our knowledge, mechanistic details up to now are unknown. In a recent study on the polymerization of cyclic six-membered urethanes and the depolymerization of the respective polyurethanes we reported that upon polymerization of TU (**1**) poly(trimethylene urethane) (**2**) is obtained with a uniform microstructure employing methyl trifluoromethanesulfonate (TfOMe) as a typical cationic initiator.[5] In contrast to this result the anionic and pseudoanionic polymerization of TU with different initiators leads to polymers containing urea and carbonate linkages besides urethane linkages.[6]

In the present communication we report a detailed investigation on the synthetic and mechanistic aspects of the cationic polymerization of trimethylene urethane which was chosen as an example of a polymerizable cyclic urethane. The polymerization mechanism is examined for two different initiators, e.g., trifluoromethanesulfonic acid (TfOH) and methyl trifluoromethanesulfonate (TfOMe).

Experimental Part

Materials. Trimethylene urethane (TU, **1**) was prepared according to ref 5; before use TU was sublimed at 78 °C and 10^{-2} mbar. The monomer was kept in a nitrogen atmosphere after sublimation. TfOMe (>99% purity), TfOH (99% purity) (both from Aldrich), and $BF_3 \cdot OEt_2$ (from Fluka) were stored under nitrogen and normally used without further purification. For comparison in ion trapping experiments TfOH was additionally dried over P_2O_5 and distilled under nitrogen. 2-Methoxy-5,6-dihydro-4*H*-1,3-oxazinium triflate (**3a**) was prepared according to ref 5. Triphenylphosphine (from Aldrich) was sublimed at 10^{-2} mbar. Potassium acetate (from Merck) was dried at 10^{-2} mbar for 4 days. Acetic acid was distilled over P_2O_5 in a nitrogen atmosphere. All purified reagents were stored under nitrogen after the purification procedure. Solvents were dried by conventional methods and distilled under nitrogen. The solvents were stored in an inert gas atmosphere after distillation. Nitrogen (from Linde) was passed over molecular sieves (4 Å), finely distributed potassium on aluminum oxide, and BTS catalyst (from BASF) for purification.

Measurements. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AC 300 or a Varian VXR 300 FT NMR spectrometer at 300 MHz and 75 MHz, respectively. ^{19}F-NMR at 282 MHz and ^{31}P NMR spectra at 121 MHz were recorded using a Bruker AC 300 instrument, both in proton-decoupled modes. $CDCl_3$, CD_2Cl_2, and perdeuterated dimethyl sulfoxide (DMSO-d_6) were used as solvents. For ^1H NMR and ^{13}C NMR spectroscopic results chemical shifts are given in ppm against TMS as an internal standard, for the ^{19}F NMR spectroscopic results $CFCl_3$ was used as an internal standard. Chemical shifts of ^{31}P NMR spectroscopic measurements are given with

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respect to 85% H_3PO_4 as an external standard. 507-PP Wilmad sample tubes were used, diameter 5 mm, length 175 mm.

High-resolution mass spectrometric investigations were performed by employing a Finnegan MAT 95 instrument. IR spectra were recorded with a Perkin-Elmer 283 B instrument. DSC was measured on a Perkin-Elmer DSC 7 (calibration using indium standard samples), and C, H, N elemental analyses were performed with a Carlo Erba MOD 1106 instrument.

Gel permeation chromatography was carried out using an ERC-64 HPLC pump, an ERC-7215 ultraviolet detector (measurements at 264 nm), and a Waters 410 refractive index detector. *N*,*N*-Dimethylacetamide (DMAc) containing 2.50 $g{\cdot}L^{-1}$ LiBr (from Fluka) served as the eluting solvent. The measurements were performed at a flow rate of 0.5 $mL{\cdot}min^{-1}$. A combination of four columns containing PL gel from Polymer Laboratories (polystyrene gel) was applied: length of the columns, 300 mm; diameter, 7.5 mm, diameter of the gel particles, 5 μm; nominal pore widths, 100 Å, 500 Å, 1000 Å, 10 000 Å. A guard column of 50 mm length and 8 mm diameter containing polystyrene gel of 5 μm particle diameter and 100 Å nominal pore width from Polymer Standard Sevice (Mainz, Germany) was installed before the main columns. The GPC was run at a column temperature of 80 °C. Calibration was achieved using polystyrene standards of narrow molecular weight distribution from Polymer Standard Service. The calibration curve was determined by a semilogarithmic plot of the peak molar mass (M_P) vs elution volume (V_e).

Preparation of 1-(Methoxycarbonyl)iminopropane. To a solution of 0.6 g (9.5×10^{-4} mol) of dibutyltin dilaurate in 50 mL of methanol was added 15 mL (0.16 mol) of propyl isocyanate at room temperature. After 2 h excess methanol was evaporated and the residue was distilled at 20 mbar (bp 65 °C). A colorless liquid is obtained. Yield: 65%.

^{1}H NMR (DMSO-d_6/room temperature): $\delta = 7.03$ (br signal, 0.9 H, NH); 6.74 (br signal, 0.1 H, NH), two conformers; 3.51 (s, 3H, CH_3–O); 2.94 (q, $^3J = 6.5$ Hz, 2H, CH_2–N); 1.40 (sext, 2H, $^3J = 7.2$ Hz, CH_2–C); 0.82 (tr, 3H, $^3J = 7.4$ Hz, CH_3) ppm.

^{13}C NMR (DMSO-d_6/room temperature): $\delta = 156.9$ (C=O, 1C), 51.1 (CH_3–O, 1C), 42.3 (CH_2–NH, 1C), 22.9 (CH_2, 1C), 11.2 (CH_3, 1C) ppm.

Preparation of *N*-Propyl Trimethylene Urethane (4). To a solution of 2.43 g (0.024 mol) of TU in 40 mL of 1,2-dimethoxyethane under inert gas was added an equimolar amount of a solution of sodium dihydronaphthylide in 1,2-dimethoxyethane at 0 °C. 1-Propyl-*p*-toluenesulfonate (5.13 g, 0.024 mol) was added to the resulting suspension, and the mixture was heated to 90 °C for 48 h. Precipitated salt was filtered off, and the solvent was evaporated. The residue was dissolved in 60 mL of water/methanol 85:15 (v/v) and washed thrice with 35 mL of hexane. After the solvent was evaporated, the residue was dissolved in 30 mL of ether and the ether phase was washed thrice with 10 mL of saturated aqueous NaCl solution. The organic layer was dried over $MgSO_4$, the solvent was evaporated and the residue was distilled at 10^{-2} mbar (bp 72–76 °C). A colorless liquid was obtained. Yield: 28%.

^{1}H NMR (DMSO-d_6/room temperature): 4.14 (m, 2H, CH_2–O), 3.26 (tr, 2H, $^3J = 6.1$ Hz, *exo*-CH_2-N), 3.16 (m, 2H, *endo*-CH_2-N), 1.92 (m, 2H, *endo*-CH_2), 1.50 (hex, 2H, $^3J = 7.3$ Hz, *exo*-CH_2), 0.84 (tr, 3H, $^3J = 7.4$ Hz, CH_3) ppm.

^{13}C NMR (DMSO-d_6/room temperature): 152.6 (C=O, 1C), 66.1 (CH_2–O, 1C), 50.1/44.6 (*exo-/endo*-CH_2–N, 2C), 21.9/19.8 (*exo-/endo*-CH_2, 2C), 10.9 (CH_3, 1C) ppm.

IR ($CDCl_3$): 2970 (m), 2940 (m), 2900 (w), 2880 (m), 1680 (vs), 1490 (s), 1450 (m), 1435 (m), 1390 (w), 1295 (w), 1265 (s), 1210 (m), 1205 (m), 1150 (m), 1105 (s) cm^{-1}.

High-resolution MS for $C_7H_{13}NO_2$: calcd (*m*/*e*) 143.09463 (M^+); found (*m*/*e*) 143.09446 (M^+).

Ring-Opening Polymerization of Trimethylene Urethane, General Procedure. All glass vessels were heated under vacuum prior to use, filled with inert gas and handled in a stream of dry inert gas. The monomer (**1**) was weighed under nitrogen directly into the prepared reaction vessels, and the initiator (TfOMe, TfOH, $BF_3{\cdot}OEt_2$) was added in bulk at room temperature using a syringe technique. For polymerization the closed reaction vessel was heated to 100 °C in a pretempered oil bath under permanent stirring while the monomer melts. During polymerization the polymer precipitated from the melt. The polymerization was terminated by cooling and dissolution of the product in DMAc. The polymer was isolated by precipitation in methanol. After a reaction time of about 24 h the usual workup afforded a polymer yield of 48–77% (cf. Table 1). The analytical data presented below refer to a sample which was prepared by polymerization of TU using TfOMe as initiator.

$[C_4H_7NO_2]_n$ $(101.104)_n$ Calc: C, 47.52; H, 6.98 N, 13.85; O, 31.65. Found: C, 47.42; H, 6.94; N, 13.84.

^{1}H NMR (DMSO-d_6/room temperature): 7.14 (br tr, 0.9H, $^3J = 5.0$ Hz, NH); 6.80 (br signal, 0.1H, NH), two conformers; 3.93 (tr, 2H, $^3J = 6.4$ Hz, CH_2–O); 3.02 (q, 2H, $^3J = 6.2$ Hz, CH_2–N); 1.66 (p, 2H, $^3J = 6.7$ Hz, CH_2); 3.51 (s, CH_3–O, end group) ppm.

^{13}C NMR (DMSO-d_6/room temperature): 156.2 (C=O, 1C), 61.4 (CH_2–O, 1C), 37.1 (CH_2–N, 1C), 29.1 (CH_2, 1C) ppm.

^{1}H NMR (DMSO-d_6/80 °C): 6.72 (br signal, ≤1H, NH), 3.96 (tr, 2H, $^3J = 6.5$ Hz, CH_2–O), 3.04 (q, 2H, $^3J = 6.3$ Hz, CH_2–N), 1.66 (p, 2H, $^3J = 6.7$ Hz, CH_2), 3.53 (s, CH_3–O, end group) ppm.

^{13}C NMR (DMSO-d_6/80 °C): 156.3 (C=O, 1C), 61.7 (CH_2–O, 1C), 37.5 (CH_2–N, 1C), 29.4 (CH_2, 1C) ppm.

IR (KBr): 3302 (br, s), 3078 (w), 2965 (w), 1684 (vs), 1551 (s), 1479 (w), 1445 (w), 1369 (sh), 1338 (w), 1277 (sh), 1259 (s), 1155 (m), 1098 (w), 1035 (m) cm^{-1}.

Study of the Initiation of the Cationic Polymerization of TU. With TfOMe as Initiator. In an NMR tube a solution of TU (**1**) (1.35 $mol{\cdot}L^{-1}$) in $CDCl_3$ or in CD_2Cl_2 was placed in a nitrogen atmosphere. TfOMe (10 mol %) was added, the tube was sealed, and the reagents were mixed by shaking. The tube was kept at room temperature (22 °C), and the progress of the reaction was monitored by ^{1}H NMR and ^{19}F NMR spectroscopy.

With TfOH as Initiator. In an NMR tube a solution of 75 mg (7.4×10^{-4} mol) TU (**1**) in 0.75 mL of $CDCl_3$ was placed in a nitrogen atmosphere at room temperature. The reagents were mixed, the tube was sealed, and the product was examined by ^{1}H NMR and ^{19}F NMR spectroscopy.

Investigation of the Active Species of the Propagation Reaction. NMR Spectroscopic Investigation in Solution. In a typical procedure 234 mg (2.32×10^{-3} mol) of TU (**1**) was polymerized with TfOMe or TfOH at a monomer to initiator ratio of $[M]_0/[I]_0 = 10$ at 100 °C. The polymerization was terminated by cooling after an appropriate reaction time: For the TfOMe-initiated process the reaction time was 5 and 10 min; in the case of the TfOH-initiated process the polymerization was carried out for 20 and 40 min after the monomer crystals melted. The product was dissolved in CD_2Cl_2 and studied by ^{1}H NMR and ^{19}F NMR spectroscopy. The following analytical data refer to the active chain ends.

(i) TfOMe-Initiated Process. ^{1}H NMR (CD_2Cl_2): 10.7 (br signal, ≈1H, NH), 4.74 (m, 2H, *endo*-CH_2–O), 4.41 (tr, $^3J = 5.9$ Hz, *exo*-CH_2–O), 3.51 (m, 2H, CH_2–NH), 2.17 (m, 2H, CH_2) ppm. ^{19}F NMR (CD_2Cl_2): −79.3 ppm.

(ii) TfOH-Initiated Process. ^{1}H NMR (CD_2Cl_2): 10.58 (br signal, NH), 4.70 (m, *endo*-CH_2–O), 4.36 (tr, 6Hz, *exo*-CH_2–O), 3.45 (m, CH_2–NH), 2.11 (m, CH_2) ppm. ^{19}F NMR (CD_2Cl_2/$CFCl_3$): −79.3 ppm.

NMR Spectroscopic Investigations in Situ. TU (446 mg, 4.41×10^{-3} mol) was placed in an NMR tube in a nitrogen atmosphere. TfOMe (10 mol %) was added, and the mixture was heated until a homogeneous melt was achieved. A coaxial insert (from Wilmad) containing DMSO-d_6 (ensuring a lock signal) was placed into the tube which was sealed afterward. The polymerization of TU was then investigated by ^{1}H NMR and ^{19}F NMR spectroscopy at a temperature of 100 °C.

Ion Trapping with PPh_3. The polymerization of TU (**1**) was performed at 100 °C using 1.01 mol % initiator (TfOMe or TfOH). After an appropriate polymerization time a 2.50 molar excess of PPh_3 (with regard to the initiator) was added in an inert gas atmosphere while stirring was continued and the product was kept at 100 °C.

Table 1. Results and Conditions of the Cationic Polymerization of TU (1) at 100 °C in the Melt

no.	initiator	$[M]_0^a/[I]_0$	t_{pol}^b/h	M_n^c	M_w/M_n^c	yield^d/%
1	TfOMe	297	53	32 600	2.46	77
2	"	198	21.25	27 600	1.87	69
3	"	99	6.10	18 900	1.41	57
4	"	"	22	22 000	1.98	71
5	TfOH	297	53	31 200	2.21	64
6	"	198	20.5	32 500	2.00	53
7	$BF_3{\cdot}OEt_2$	198	20.75	34 800	1.91	48
8	TU·TfOMe	116	24	22 400	2.06	65

[a] Mole ratio monomer/initiator. [b] Time of polymerization. [c] Fraction insoluble in MeOH; MW according to GPC in DMAc/2.50 g·L^{-1} LiBr. [d] After precipitation in methanol.

(i) UV Tracing of the Active Chain End. The terminating reagent was added after 2 h (TfOMe) or 3.9 h (TfOH) of polymerization, and the product was stirred for an additional 7.5 min at 100 °C. Samples were drawn and investigated by means of GPC.

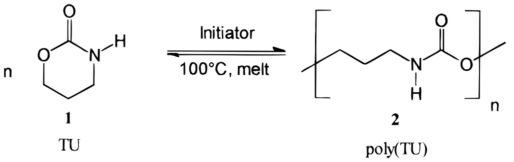
(ii) Qualitative and Quantitative Determination of the Active Species. The polymerization was terminated and stirred at 100 °C at least for an additional 20 min (cf. Table 5). Samples were drawn and transferred to NMR tubes under nitrogen. The samples were dissolved in DMSO-d_6 and examined by ^{31}P NMR spectroscopy. ^{31}P NMR (DMSO-d_6): 25.3 ppm.

Termination with Potassium Acetate/Acetic Acid. Trimethylene urethane was polymerized at 100 °C using 2.0 mol % TfOMe. After an appropriate time (cf. Table 6) a solution of potassium acetate (KOAc) in acetic acid (HOAc) containing 15 wt % KOAc was added in a large excess ($[KOAc]_0/[TfOMe]_0 > 75$) and the polymer was dissolved in the terminating reagent at 115 °C. The homogeneous solution was kept at this temperature for an additional 10 min. The polymer was precipitated in methanol and examined by means of ^{1}H NMR spectroscopy.

Kinetics. The polymerization of TU was carried out at 100 °C and at different monomer to initiator ratios with TfOMe and TfOH as initiators. The start of the polymerization was taken after the melting of the monomer crystals had taken place. Samples were drawn in a stream of dry nitrogen at different reaction times while the reaction vessel was kept at 100 °C. The conversion was determined by means of GPC measurements and integration of the refractive index detector signal on the basis of quantitative calibration curves for monomer and polymer.

Results and Discussion

The polymerization of TU was carried out to yield poly(trimethylene urethane) (poly(TU)) with a uniform microstructure in a cationically initiated process (eq 1).



(1)

1
TU

2
poly(TU)

TfOH, TfOMe, and $BF_3{\cdot}OEt_2$ (as examples of Brønsted acids, strong alkylating agents, and Lewis acids, respectively) were employed as initiators. The polymerization proceeds at 100 °C in the melt in the course of several hours up to days. In the beginning the reaction mixture is homogeneous; later the polymer precipitates from the melt. The synthetic results are summarized in Table 1. After 1 day polymer yields of 48−77% are obtained by precipitation in methanol; the rest of the mixture consists of unreacted monomer. At long reaction times (120 h, 100 °C) conversions up to 95% can be achieved in the bulk process. The yields obtained with TfOMe as initiator are considerably higher than those obtained with the acid and the Lewis acid under comparable conditions, while the molecular weights mostly are higher, employing the latter two initiators (see runs 6 and 7 compared with run 2). The MWD are monomodal for all runs; however, polydispersities are rather large for reaction times exceeding several hours, indicating that the cationic polymerization of TU is not a “living” process.

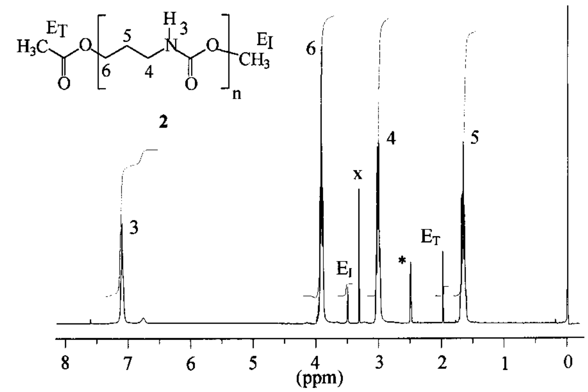


Figure 1. ^{1}H NMR spectrum of poly(TU). Solvent: DMSO-d_6 Key: (*) DMSO; (x) H_2O. Initiator: TfOMe; termination with KOAc/HOAc.

TU did not polymerize in a 15 wt % solution in nitromethane at 95 °C and a molar ratio of $[TU]_0/[TfOMe]_0 = 50$. This behavior is presumably of thermodynamic origin; the polymerization step, which is reversible in the melt,[5] becomes unfavorable in the diluted state and the polymerization does not proceed under the applied conditions. For a detailed discussion of the thermodynamics of TU polymerization see ref 7.

The ^{1}H NMR spectrum of poly(TU) obtained from a TfOMe-initiated polymerization process which was terminated by dissolution in a 15 wt % solution of potassium acetate (KOAc) in glacial acetic acid (HOAc) is presented in Figure 1 and discloses the constitutionally uniform structure of the polyurethane. The NH resonance around $\delta \approx 7$ ppm is split into two signals at room temperature due to conformational restrictions around the CO−N bond. At 80 °C only one signal is observed for the NH proton in poly(TU) (**2**).[5] A small resonance line at $\delta = 3.51$ ppm (E_I) is attributed to a methyl urethane end group. The assignment of this signal is made by comparison with the ^{1}H NMR spectrum of a model compound; $H_3CCH_2CH_2NHCOOCH_3$ shows a resonance line for the OCH_3 protons at $\delta = 3.51$ ppm in DMSO-d_6. The methyl urethane end group is introduced in the initiating step since the respective resonance line is absent in the spectra of polymers which were prepared by employing TfOH or $BF_3{\cdot}OEt_2$ as initiators. Another signal of low intensity at $\delta = 1.99$ ppm is attributed to an acetate end group (E_T) formed in the termination reaction of the active species with an acetate anion. At low polymerization times (e.g., 2.5 h in the present case) the integrals of the acetate signals and methyl urethane signals are of equal magnitude. Acetate end groups are also observed in polymers formed in TfOH-initiated polymerizations which are terminated with KOAc/HOAc.

The ^{13}C NMR spectrum of the polyurethane provides additional proof of the proposed microstructure since only the expected resonance lines are observed (cf. Experimental Part).

DSC (Figure 2) shows on the first heating a glass transition which is very weak. In a detailed thermo-

Table 2. Thermal Data of Poly(TU) According to DSC (No. 1, M_n = 27 600;[a] Nos. 2 and 3, M_n = 14 400[a])

no.	thermal history	T_g[b]/°C	ΔC_p/J·g^{-1}·K^{-1}	T_{cr}/°C	T_m/°C	ΔH_m/J·g^{-1}
1	first heating[c]	26	0.12		140.3/166.9	74.0
2	first heating[c]				136.3/165.6	4.9/71.0
3	second heating[c,d]	15	14.9	120.0	164.0	n.d.

[a] According to GPC in DMAc/2.50 g·L^{-1} LiBr (polystyrene calibration). [b] Lebedev[7] determines T_g = 25 °C. [c] First heating: −30 to +180 °C/20 K·min^{-1}. Cooling: +180 to −30 °C/20 K·min^{-1}. [d] Sample did not show crystallization upon cooling.

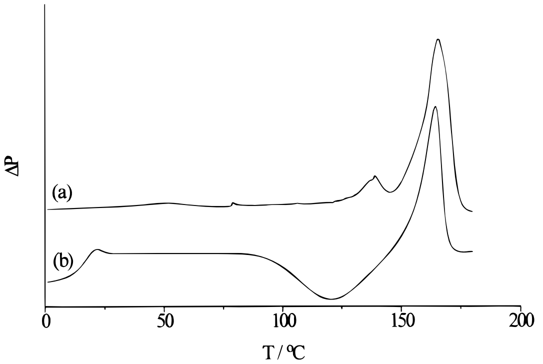


Figure 2. DSC of poly(TU) (nos. 2 and 3 of Table 2): (a) first heating; (b) second heating.

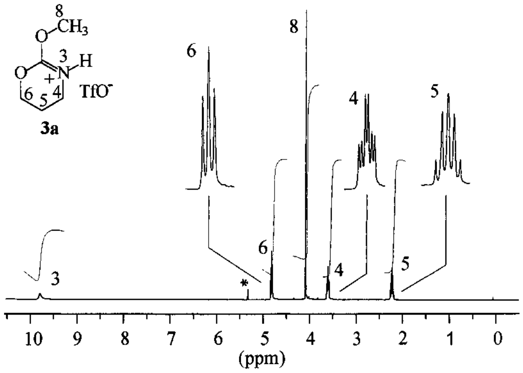
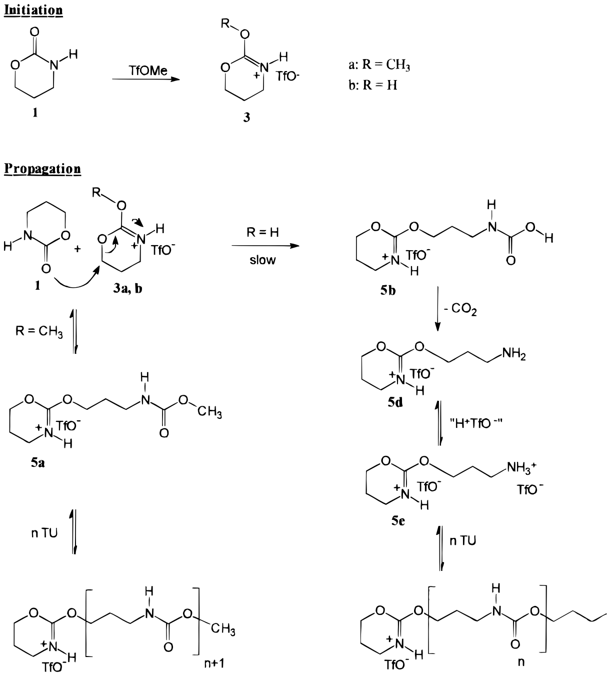


Figure 3. ^{1}H NMR spectrum of 2-methoxy-5,6-dihydro-4*H*-oxazinium trifluoromethanesulfonate (**3a**) in CD_2Cl_2: (*) $CHDCl_2$.

Scheme 1. Mechanism of the Cationic Polymerization of TU Initiated with TfOMe and TfOH



dynamic study on another poly(TU) sample Lebedev et al. found a glass transition at 25 °C.[7] Upon the second heating a pronounced glass transition is observed at 15 °C. For melting of the polymer crystals two seperated peaks are observed on the first heating. Upon the second heating a broad exotherm is found with a minimum at 120 °C which is attributed to the crystallization of the polymer. The crystallization peak interferes with the melting endotherm of the polymer crystals appearing at 164 °C. Upon the second heating only one melting endotherm is observed. The thermal data of poly(TU) according to DSC are summarized in Table 2.

Mechanistic Studies. The Active Species: Initiation. The initiation reaction was studied in solution at room temperature. Since TU does not polymerize under these conditions, it is ensured that only the primary step of the reaction between initiator and monomer is observed.

In the reaction of TU (**1**) with TfOMe the salt of a cyclic endo iminocarbonate, e.g., 2-methoxy-5,6-dihydro-4*H*-1,3-oxazinium trifluoromethanesulfonate (**3a**), is formed by methylation of the carbonyl oxygen of TU (Scheme 1). When a small excess of TfOMe is used, the adduct **3a** is isolated in almost quantitative yield as a crystalline solid, the structure of which is identified by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy as well as elemental analysis.[5] The ^{1}H NMR spectum of **3a** (Figure 3) shows the typical signals for six-membered iminiocarbonate at δ = 4.80, 3.59, and 2.22 ppm for the methylene protons and at δ = 9.77 ppm for the NH^+ proton. In the presence of a 9-fold excess of TU the chemical shift of the resonance of the NH^+ proton is shifted toward δ = 10.8 ppm. The most conclusive proof of the ionic structure of the adduct is provided by ^{19}F NMR spectroscopy, a method which has been already applied by several authors in connection with polymerizations initiated with derivatives of TfOH.[8] In CD_2Cl_2 the ^{19}F NMR spectrum of **3a** consists of a resonance line at δ = −79 ppm which is in the range of chemical shifts of typical anionic TfO^- fragments (TfO^- $HNEt_3^+$ shows a resonance at δ = −78.9 ppm), while the ^{19}F resonance of the covalent TfOMe appears at δ = −74.8 ppm.

The initiation with TfOMe proceeds rapidly compared with the polymerization even at room temperature in CD_2Cl_2 solution. At a monomer concentration of 1.35 mol·L^{-1} and a ratio $[M]_0/[I]_0$ = 10 the initiation reaction is already completed after 12 min according to ^{1}H NMR and ^{19}F NMR spectroscopy.

The assumption that the adduct **3a** is the primarily formed species in the TfOMe-initiated TU polymerization is supported by the fact that it is successfully used as an initiator to yield a polymer which, according to NMR spectroscopic results, is identical to that formed in the TfOMe-initiated process (cf. Table 1, no. 8).

The reaction of TU with TfOH (Scheme 1) in solution at a ratio $[M]_0/[I]_0$ = 10 leads to the protonation of the monomer according to ^{19}F NMR spectroscopy in $CDCl_3$ since only a resonance line at δ = −79.0 ppm is observed (the acid TfOH shows a ^{19}F resonance at δ = −76.3 ppm in the same medium). In the ^{1}H NMR spectrum the

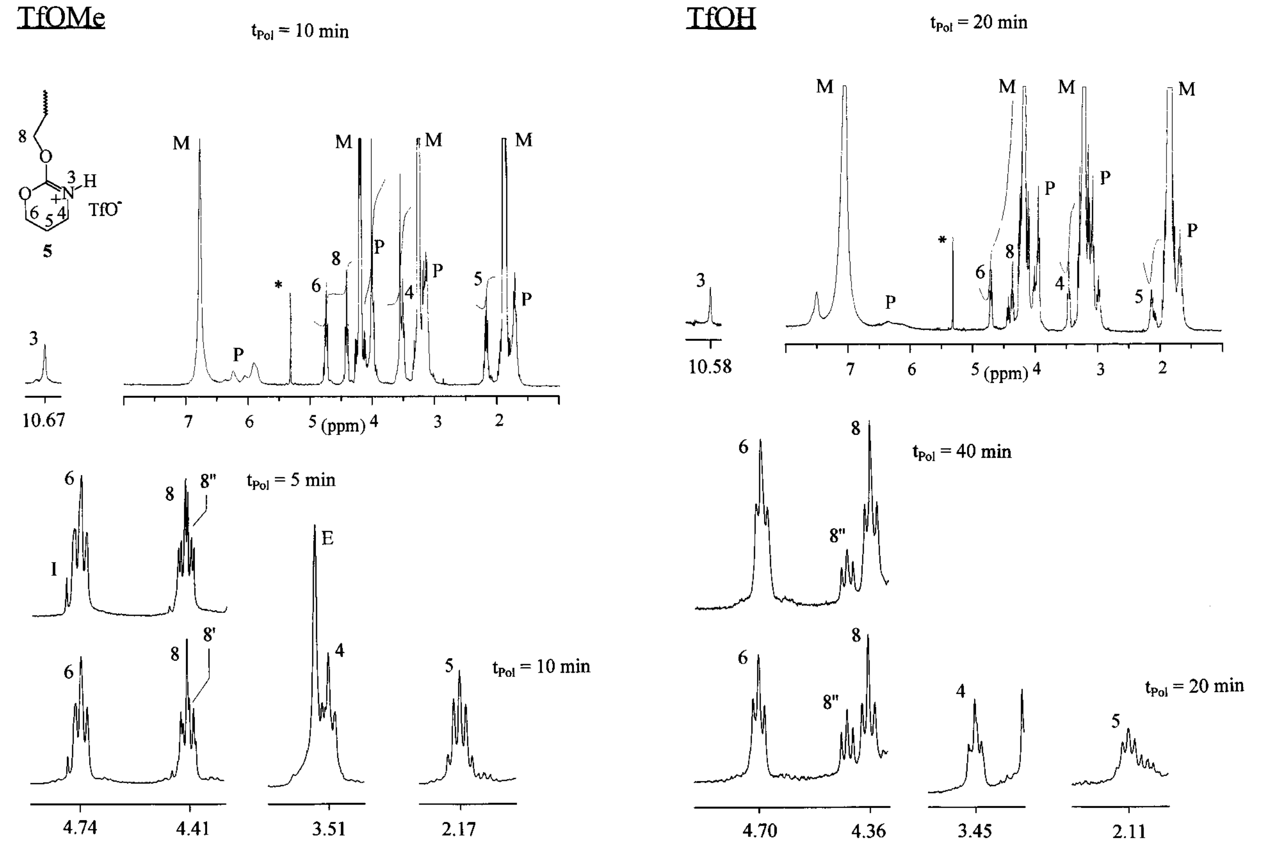


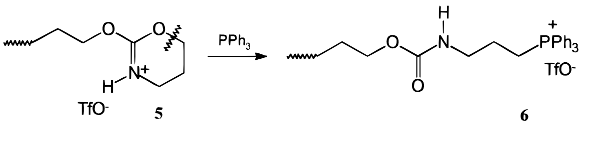
Figure 4. ^{1}H NMR spectra of active poly(TU) initiated with TfOMe and TfOH in CD_2Cl_2: (*) $CHDCl_2$; E, *O*-methyl urethane end group; P, polymer; M, monomer; I, **3a**. Polymerization conditions: $[TU]_0/[TfOMe]_0 = 10$, $T = 100$ °C, $t_{pol} = 10$ min and 5 min; $[TU]_0/[TfOH]_0 = 10$, $T = 100$ °C, $t_{pol} = 20$ and 40 min.

protonation is detected by a downfield shift of all resonance lines of TU by 0.07−0.10 ppm due to rapidly exchanging protons. Following the results of Olah and Calin[9] and Le Questrel et al.[10] who investigated the protonation of several open-chain urethanes, it seems to be reasonable to assume the protonation of the carbonyl oxygen of the monomer. Thus an adduct **3b** is formed.

The Active Species: Propagation. The active species of the propagation reaction is directly identified by means of ^{1}H NMR and ^{19}F NMR spectroscopy. Since most solvents for poly(TU) (e.g., DMSO, DMAc, HOAc) are terminating reagents, the polymerization is carried out only for a short time at a ratio $[M]_0/[I]_0 = 10$ so that a low molecular weight polymer is formed which is soluble in CD_2Cl_2, an inert solvent for the active species. For TfOMe and TfOH as initiators analogous results are obtained. The ^{1}H NMR spectra of both products are presented in Figure 4 and clearly demonstrate that the active species is formed by a six-membered cyclic iminiocarbonate end group **5**. The resonance lines of the ring methylene protons appear at nearly the same chemical shifts as in the spectra of **3a** (within 0.07 ppm) which serves as a model compound for the active chain end. The signals referring to the NH^+ proton appear at $\delta = 10.7$ ppm (TfOMe initiated polymerization) and $\delta = 10.6$ ppm (TfOH initiated polymerization). In the case of the TfOMe-initiated process the resonance lines of the active chain end interfere with those of unreacted **3a** (signals marked by "I") which is present in the mixture due to the short reaction time. A triplett at $\delta = 4.43$ ppm (TfOMe) or $\delta = 4.36$ ppm (TfOH) is attributed to the exo methylene protons (resonance 8). Besides the resonance 8, multiplets 8′ (TfOMe, Figure 4a) and 8″ (TfOH, Figure 4b) are found, the intensities of which are dependent on the polymerization time and hence on conversion. Considering that during short polymerization times only oligomers are formed, these signals are attributed to end groups. The ^{19}F NMR spectra of both polymerization products show a resonance line at $\delta = -79.3$ ppm. This result is an additional proof of the ionic structure of the active species.

An insight into the structure of the active species under polymerization conditions, i.e., at 100 °C in the melt, is gained at low conversion by in situ NMR spectroscopy. In this case the polymerization is performed in an NMR spectrometer. Under these conditions the monomer melt serves as a solvent and the lock signal is ensured by an external sample of DMSO-d_6. This method was applied for the TfOMe-initiated process. Qualitatively, identical signals are observed in the ^{1}H NMR spectrum as in solution NMR and it is concluded that also in the melt the active species is formed by iminiocarbonates **5a,b** (cf. Scheme 1).

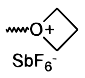
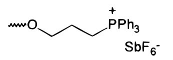
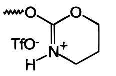
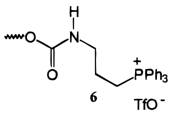
Termination with PPh$_3$. The termination of the cationic polymerization using triphenylphosphine was developed by Penczek et al.[11] who coined the term "ion trapping". In the present case the termination of the polymerization of TU (**1**) with triphenylphosphane leads to triphenylalkylphosphonium end groups **6** (eq 2). This



(2)

result is confirmed by ^{31}P NMR spectroscopy. Only one resonance line at $\delta = 25.3$ ppm (for the TfOMe-initiated

Table 3. ^{31}P-NMR Spectroscopic Data of Some Trapping Products of Cationic Species with PPh$_3$

No.	Active species	Trapping product	Solvent	δ / ppm	Lit.
1			CD_2Cl_2	23.8	11a
2	$H_3CCO^+ SbF_6^-$	$H_3CCOPPh_3^+ SbF_6^-$	CD_2Cl_2	10.1	11b
3	TfOMe	$H_3CPPh_3^+ TfO^-$	DMSO-d_6	23.8	
4	 5	 6	DMSO-d_6	25.3	

process) and at $\delta = 25.2$ ppm (for the TfOH initiated process) is observed besides the resonance of excess PPh$_3$. The small difference of the chemical shifts in the two trapping experiments is considered to be due to the concentration effect.

In Table 3 the ^{31}P NMR chemical shifts of some trapping products are listed and compared with values taken from the literarure. According to ^{31}P NMR spectroscopic data no acylphosphonium ions are formed because no resonance in the range of $\delta = 10$ ppm is observed. These results disclose that the active species **5** reacts with an incoming nucleophile by *O*-alkyl scission, a sort of reactivity which is known to be typical of salts of iminocarbonates as described in the literature.[12] A reaction between PPh$_3$ (or other nucleophiles) and the *exo*-methylene group of the iminiocarbonate function of **5** is also possible. The product, however, is indistinguishable from that of the reaction between PPh$_3$ and the respective *endo*-methylene group. The *exo*-reactivity of iminiocarbonates is revealed in a termination experiment which is performed after 15 min of the polymerization initiated with TfOMe. At this time the polymerization mixture still contains a portion of **3a**. In the termination products besides phosphonium ions **6** ($\delta = 25.3$ ppm) also methyltriphenylphosphonium ions are observed by ^{31}P NMR spectroscopy at $\delta = 23.8$ ppm. The latter are formed by reaction of PPh$_3$ with the *exo*-methyl group of **3a**.

In Figure 5 the GPC traces (UV and RI detector traces) of the trapping products of the polymerizations initiated with TfOMe and TfOH are compared with those of the polymerization product before addition of PPh$_3$. Before addition of PPh$_3$ the polymer fractions do not show UV absorption, while afterward strong UV absorptions are observed. Thus, since the triphenylphosphonium group serves as a UV-absorbing tracer for the active species, it is demonstrated for both initiators, TfOMe and TfOH, that the polymerization follows an active chain end mechanism because the active species is found in the polymer fraction.

Polymerization Mechanism with TfOMe. The polymerization mechanism of the cationic ring-opening polymerization of TU initiated with TfOMe is outlined in Scheme 1. In the first propagation step a monomer molecule (**1**) nucleophilically attacks at the primary adduct **3a** formed in the initiation reaction of TfOMe and TU in the α-position to the ring oxygen atom. Here the carbonyl oxygen atom of TU is the center of the highest nucleophilicity. The adduct **3a** reacts via *O*-alkyl scission and the iminiocarbonate function is isomerized to form a methyl urethane end group while an iminiocarbonate is regnerated at the active chain end. The active chain **5a** grows by addition of further monomer to result in poly(TU).

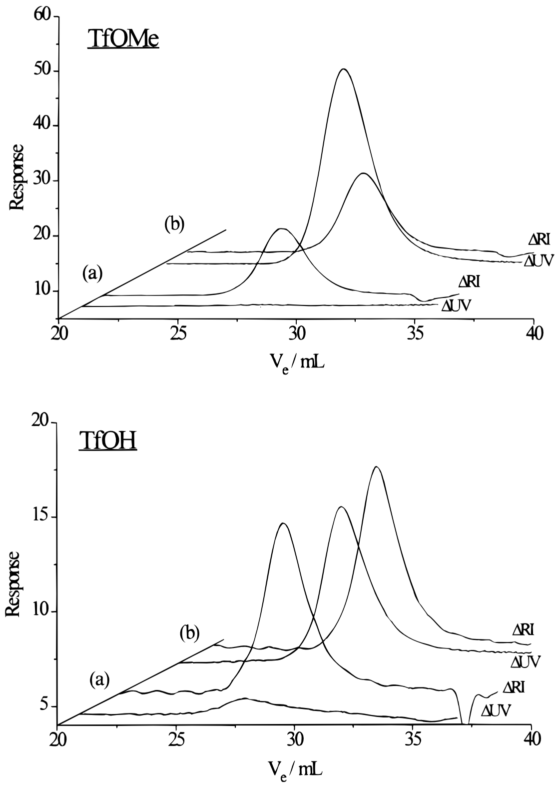


Figure 5. GPC traces of poly(TU) initiated with TfOMe and TfOH employing PPh$_3$ as a trapping reagent (b) compared with poly(TU) before addition of PPh$_3$ (a) (differential refractive index (ΔRI) and ultraviolet (UV) detectors). Polymerization conditions: $[TU]_0/[I]_0 = 100$, $T = 100$ °C, $t_{pol} = 2$ h. Termination reaction conditions: $[PPh_3]_0/[I]_0 = 2.50$, $T = 100$ °C, $t_{term} = 7.5$ min.

With TfOH as the initiator the same propagation reaction takes place; however, a variation in the initiation reaction pathway is obseved, which has significant consequences for the reaction kinetics (cf. below).

Kinetical Aspects. In Figure 6 the pseudo-first-order plots of the TfOMe- and the TfOH-initiated polymerizations are presented for different ratios $[M]_0/[I]_0$. For short reaction times (up to 7 h) with both initiators the polymerization proceeds according to a pseudo-first-order rate law. At longer reaction times deviations are observed. A qualitative difference between the TfOMe- and TfOH-initiated polymerizations is found in the initiation phase. While in the TfOMe case the regression lines start from the origin, in the case of the TfOH-initiated process an induction period of about 1 h is observed which is explained by slow initiation of the chain reaction. The apparent (first-order) rate constants disclose a quantitative difference between the two initiators (Table 4). At identical initiator concentrations the TfOH-initiated process is slower by a factor of 1.91−1.71 than the TfOMe-initiated process in the range where the pseudo-first-order rate law is fulfilled.

Based on the density of the monomer melt at 100 °C which was determined to be $\rho_{TU}(100\ °C) = 1.186$ kg·L^{-1} the rate constants are calculated for the TfOMe-initiated polymerization to range from 3.94×10^{-4} to 4.42×10^{-4} L·mol^{-1}·s^{-1}.

The quantitative evaluation of the ^{31}P NMR spectroscopic results from the ion trapping experiments utilizing PPh$_3$ as a trapping reagent reveals that the differ-

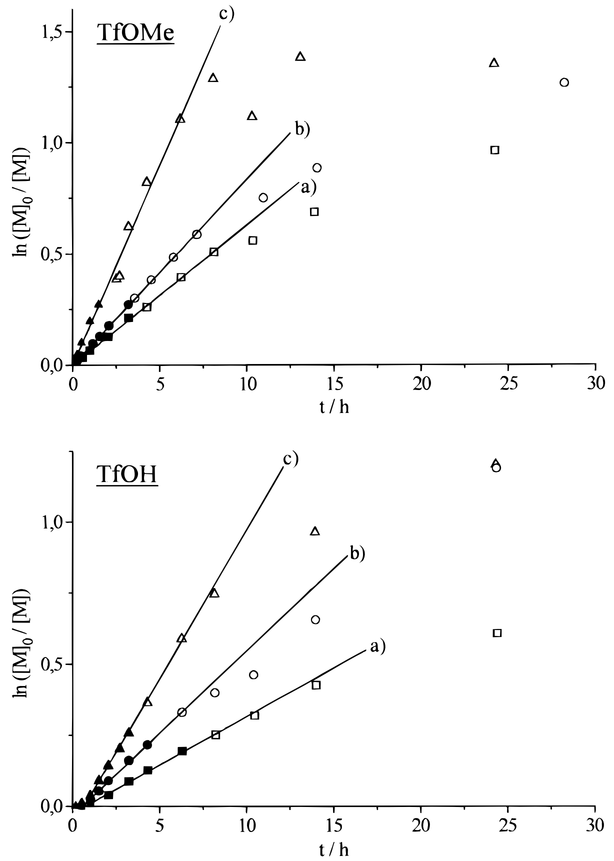


Figure 6. First-order kinetic plots of the polymerization of TU with TfOMe and TfOH, respectively, at 100 °C in bulk: (a) $[TU]_0/[I]_0$ = 297; (b) $[TU]_0/[I]_0$ = 198; (c) $[TU]_0/[I]_0$ = 99; (solid symbols) homogeneous melt; (open symbols) optically heterogeneous system.

Table 4. Kinetic Data of the Polymerization of TU in the Melt at 100 °C, $[M]_0$ = 11.73 mol·L^{-1}

initiator	$[M]_0{}^a$/ $[I]_0$	$10^2[I]_0{}^b$/ mol·L^{-1}	$t_0{}^c$/h	$10^5k[P^*]^d$/ s^{-1}	10^4k^e/ L·mol^{-1}·s^{-1}
TfOMe	297	3.95		1.75	4.42
"	198	5.87		2.33	3.94
"	99	11.87		5.00	4.22
TfOH	297	3.95	1.14	0.92	n.d.
"	198	5.87	0.95	1.31	n.d.
"	99	11.87	0.83	2.94	n.d.

[a] Mole ratio monomer/initiator. [b] Initial concentration of initiator. [c] Zero of the regression line calculated for the range of linearity. [d] Pseudo-first-order rate constant. [e] Rate constant.

ence of the apparent rate constants of the acid- and the ester-initiated polymerizations stems from a different concentration of the active species in the respective polymerization mixtures. In Table 5 the ratios of the concentrations of actually trapped active species [P*] to added initiator $[I]_0$ are summarized for polymerizations which were terminated at low conversions of TU. The results disclose that in the TfOMe-initiated process about 90% of the initially added ester is present after the polymerization time regarded, while after a comparable time (at the end of the induction period) in the TfOH-initiated case slightly less than half of the added initiator has effectively formed active species.

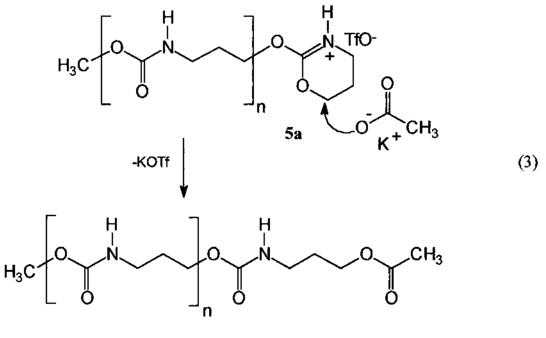
Polymerization Mechanism with TfOH. A monomer molecule **1** attacks the protonated form of TU (**3b**) in the α-position to the ring oxygen atom and **3b** reacts via *O*-alkyl scission (Scheme 1). An iminiocarbonate function at the active chain end and a carbamic acid end group are formed (**5b**). This reaction, which is the real initiation of the chain reaction, is slow compared with the propagation reaction, and thus an induction period appears. The carbamic acid group in **5b** is not stable under the reaction conditions and loses CO_2, forming an amino end group (**5d**) which binds a proton from the reaction mixture to result in **5e**. Thus in each initiation step one potential active species is consumed. With the assumption that the decarboxylation and acid/base reactions are much faster than the first propagation step, at the end of the initiation phase half of the initially added protons are bound in ammonium groups (**5e**). The postulated mechanism correlates well with the ^{1}H NMR spectrum of the TfOH-initiated active chain shown in Figure 4b, which shows a broad signal at 7.5 ppm which is absent in the TfOMe-initiated case. According to its chemical shift, this signal can be interpreted as an ammonium proton resonance.

Table 5. Fraction of Active Species at Different Reaction Times for the Polymerization of TU Initiated by TfOMe and TfOH, Respectively, as Determined by Ion Trapping with PPh_3 and ^{31}P NMR Analysis (Polymerization and Termination at 100 °C)

no.	initiator	t_{pol}/min^a	t_{term}/min^b	$[P^*]/[I]_0{}^c$
1	TfOMe^d	70	20	0.90
2	"^{d}	70	40	0.89
3	TfOH^d	75	20	0.47
4	"^{d}	150	20	0.42
5	"^{e}	120	20	0.47
6	"^{e}	120	60	0.49

[a] Time of polymerization. [b] Time of termination. [c] Ratio of trapped active species to initially applied initiator. [d] Commercial initiator without further purification. [e] TfOH distilled over P_2O_5 under nitrogen.

Stability of the Active Species. In the present case the ion-trapping method is not applicable for the determination of the concentration of active species at high conversion since no homogeneous mixture can be achieved between the solid trapping reagent and the solidified polymerization product (good solvents for the polymer tend to react with the active species). In the case of the TfOMe-initiated polymerization the actual fraction of active species compared with the amount of applied initiator in the course of the polymerization reaction is investigated by termination of the polymerization employing KOAc in glacial acetic acid solution as a trapping reagent, in which HOAc serves as a solvent also for poly(TU) at elevated temperatures. During termination, acetate end groups are formed (eq 3), a type of reaction which has been reported in the literature.[13]



(3)

Methyl urethane end groups and acetate end groups are detected by ^{1}H NMR spectroscopy in the purified polymer (Figure 1a). It is shown, by time dependent monitoring of the molecular weight of the polymer fraction and the ratio of the integral of the acetate signal

Table 6. Fraction of the Active Species at Different Reaction Times for the Polymerization of TU Initiated with TfOMe as Determined by End Capping with KOAc/HOAc and ^{1}H NMR Analysis (T_{pol} = 100 °C, $[M]_0/[I]_0$ = 50, T_{term} = 115 °C)

no.	t_{pol}/h^a	$[KOAc]_0/[I]_0$^{b}	$[P^*]/[I]_0$^{c}
1	2.6	75	0.9
2	24.1	140	0.4
3	72	75	0.1

[a] Time of polymerization. [b] Molar ratio of trapping reagent KOAc to initially applied initiator. [c] Molar ratio of actually trapped active species to initially applied initiator.

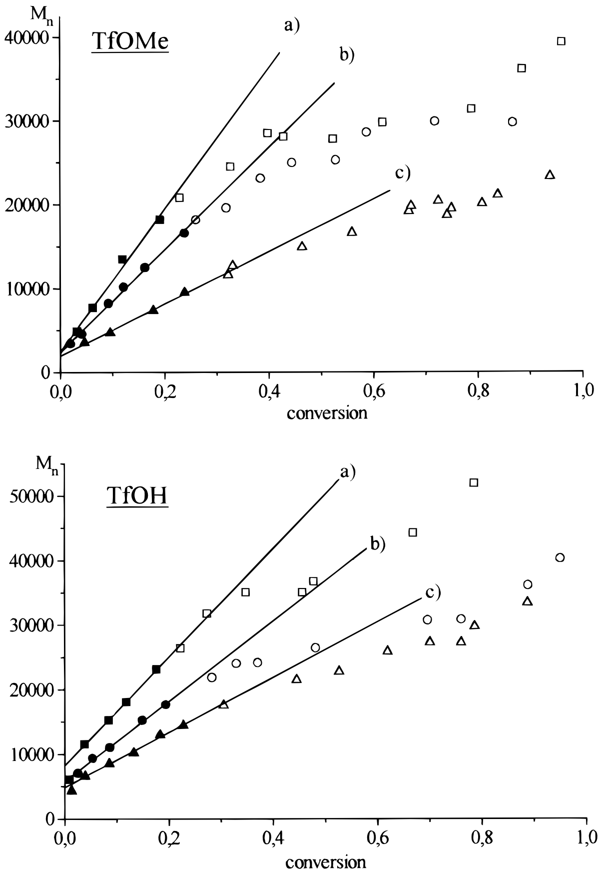


Figure 7. Molecular weight M_n as a function of conversion in the polymerization of TU initiated with TfOMe and TfOH, respectively, at 100 °C in bulk: (a) $[TU]_0/[I]_0$ = 297; (b) $[TU]_0/[I]_0$ = 198; (c) $[TU]_0/[I]_0$ = 99; (solid symbols) homogeneous melt; (open symbols) optically heterogeneous system.

to that of the methyl urethane signal in the ^{1}H NMR spectrum [AcO−]/[MeO−] that acetate groups are not introduced by simple insertion of the reagent into the polymer chain. Thus the integral of the ^{1}H NMR spectroscopic signal of the acetate end group is a measure for the actual concentration of active species [P*] in the polymerization mixture, and that of the methyl urethane end groups is a measure for the concentration of applied initiator $[I]_0$. In Table 6 the ratios $[P^*]/[I]_0$ are given for different polymerization times. The presented data indicate that the cationic polymerization of TU is accompanied with intrinsic termination reactions because the ratio $[P^*]/[I]_0$ decreases drastically in the course of 72 h from a value of 0.9 to 0.1.

Transfer Reaction/Termination. In Figure 7 M_n of the polymer fraction is plotted as a function of conversion *p* for the TfOMe- and the TfOH-initiated polymerization of TU. At low conversion linear traces of the function $M_n(p)$ are observed at all chosen conditions. In the TfOMe case the regression lines start from $M_n \approx 2500$, a value which is possibly an artifact of the GPC method applied (polystyrene calibration). In the TfOH case the lines start from $M_n(p{=}0)$ = 5000 to 8000 which is due to slow initiation. At higher conversion M_n deviates from the linear curves. Since neither in the polymerization products (before workup) nor in the mother liquors of the workup procedures are products of back-biting reactions observed (which would also explain a lowering of M_n compared with an expected straight line for a living process), it is concluded that transfer reactions take place during the polymerization.

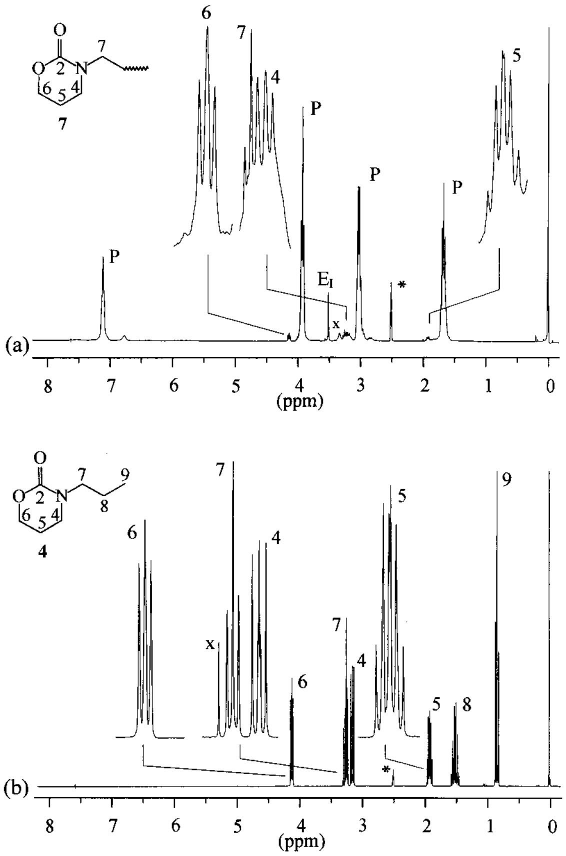
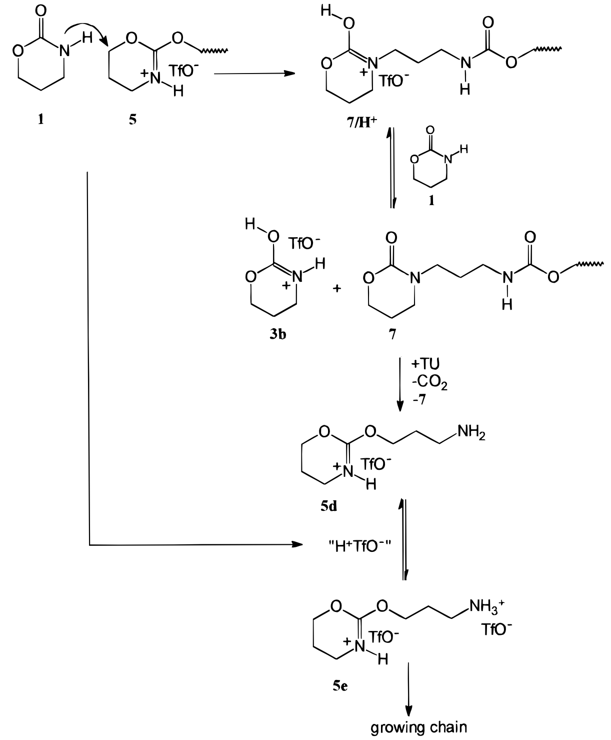


Figure 8. ^{1}H NMR spectra of (a) poly(TU) from a synthesis with high conversion of TU (polymerization conditions: $[TU]_0/[TfOMe]_0$ = 20, *T* = 100 °C, t_{pol} = 4 days) and (b) model compound *N*-propyl trimethylene urethane. Solvent: DMSO-d_6. Key: (*) DMSO; (x) H_2O; E$_I$, methyl urethane end group.

The ^{1}H NMR spectrum of a poly(TU) prepared by polymerization of TU at high conversion of monomer and low ratio $[M]_0/[I]_0$ (Figure 8) shows signals which are attributed to end groups of an *N*-alkyl trimethylene urethane structure **7**. The assignments were made by comparison with the spectrum of a model compound (*N*-propyl trimethylene urethane, **4**). These end groups are not observed at low conversion, and it is concluded that their appearance is directly related to transfer reactions. In Scheme 2 we propose a mechanism which explains chain transfer as well as termination reactions, the latter being a direct consequence of the former. The urethane group of monomer **1** acts as an ambident nucleophile; while in the propagation reaction the carbonyl oxygen is the nucleophile, in the transfer and termination reaction the nitrogen atom serves as a nucleophilic center. Reaction of monomer **1** with the active species **5** leads to the N-alkylated−O-protonated iminocarbonate structure **7/H$^+$**. Transfer of the proton

Scheme 2. Mechanism of Chain Transfer and Termination in the Cationic Polymerization of TU Initiated with Derivatives of TfOH



to excess monomer **1** leads to **3b** and **7**; the latter represents a dead chain, and the first may initiate a new chain in the sense depicted in Scheme 2. Hence each chain transfer directly leads to termination of another chain.

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