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Copolymers and Terpolymers of Tetramethylene Urea, γ-Butyrolactone, and Ethylene Carbonate or 1,2-Propylene Carbonate

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ABSTRACT: Tetramethylene urea (TeU) is successfully copolymerized with γ-butyrolactone (γBL), leading to an alternating poly(amide urethane) with alternating carbonyl-amino-tetramethylene-amino and carbonyl-trimethylene-oxy repeating units ($\bar{M}_n$ = 12 600; $\bar{M}_w$ = 21 100; $\bar{M}_n$ = 1.67) and with a T_m of 196.5 °C and a T_g of 36.4 °C. Small defects in the microstructure of the alternating poly(amide urethane) arise from the formation of TeU−TeU diads. Furthermore, TeU is successfully copolymerized with mixtures of γBL and ethylene carbonate (EC) or 1,2-propylene carbonate (PC). From NMR spectroscopic data of the terpolymers obtained, it is concluded that the reactivity of the five-membered cycles used increases in the following order: EC $\gg$ PC $\approx$ γBL. It is possible to increase the content of γBL repeating units in the poly[(TeU−γBL)-*stat*-(TeU−EC)] or poly[(TeU−γBL)-*stat*-(TeU−PC)] by increasing the fraction of γBL in the feed. ^{13}C NMR spectroscopy reveals that TeU−EC or TeU−PC and TeU−γBL units are randomly distributed in the polymer chain. This conclusion is supported by the thermal properties.

Introduction

In a previous paper, we described the successful synthesis of a polyurethane via copolymerization of tetramethylene urea (TeU), **1**, with 1,2-propylene carbonate (PC), **2**, and proposed a reaction mechanism based on ^{1}H NMR spectroscopic studies on a model compound. Furthermore, polyurethanes with randomly distributed TeU−EC and TeU−PC units and containing up to 54.2 mol % PC repeating units were prepared via copolymerization of TeU with PC and ethylene carbonate (EC), **3**. Studies on the copolymerization of TeU with mixtures of EC and PC showed that the reactivity of EC is approximately 5 times higher than that of PC.[1]

Besides EC and PC, γ-butyrolactone (γBL), **4**, is a five-membered cyclic monomer which does not homopolymerize because of the positive standard free energy change in the monomer−polymer equilibrium ($\Delta G°_{pol} >$ 0). A drastic change in the polymerization conditions, e.g., high-pressure, shifts the equilibrium to the side of polymer as shown by Zhulin et al.[2] and Korte et al.[3] (at pressure of 20 000 atm at 160 °C, PBL with $\bar{M}_n$ up to 3350 was obtained). Duda et al.[4] showed that it is possible to oligomerize γBL with aluminum isopropoxide trimer Al(O^{i}Pr)$_3$ to a mixture of linear oligomers up to the decamer. A review on the polymerization of γBL was recently published by Zhao et al.[5]

Furthermore, reports on the copolymerization of γBL are found in the literature.[6−19] Duda et al.[6] reported on the preparation of copolymers with ϵ-caprolactone (CL) with random structure and $\bar{M}_n$ up to 3×10^4, containing up to 43 mol % repeating units derived from γBL. Tada et al.[7] copolymerized γBL and β-propiolactone (βPL) with AlEt$_3$/H$_2$O as initiator and obtained up to 30 mol % γBL repeating units in the copolymer. The reported yields do not exceed 3%. Kricheldorf et al.[8] prepared copolymers of γBL and glycolide with yields up to 42% and containing up to 25 mol % of oxybutyroyl units via cationic polymerization with FeCl$_3$, BF$_3$·Et$_2$O, or FSO$_3$H as initiators. Fukuzaki et al.[9] prepared relatively low molecular weight polyesters from glycolic acid and γBL in the presence of water without catalysts at 200 °C in a nitrogen atmosphere. Furthermore, they reacted γBL with L-lactic acid (LA) at 200 °C in the absence of a catalyst and obtained poly(γBL-*co*-LA) with an oxybutyroyl unit content of up to 19 mol % and $\bar{M}_n \approx 2 \times 10^3$.[10] Tsuda et al.[11] prepared copolymers of γBL and CL with 3,3-bis(chloromethyl)oxacyclobutane via cationic polymerization with BF$_3$·Et$_2$O as a catalyst at 0 °C for 4 days. Ito et al.[12] obtained via cationic mechanism copolymers of βPL and γBL. Hori et al.[13] prepared high molecular weight copolymers ($\bar{M}_n$ up to 96 000) with an oxybutyroyl unit content of up to 35 mol % via copolymerization of γBL with (*R*)-β-butyrolactone initiated with 1-ethoxy-3-chlorotetrabutyldistannoxane. In an analogous way, Lee et al.[14] obtained oligomeric copolyesters with an oxybutyroyl unit content of up to 56 mol % via copolymerization of γBL with β-butyrolactone in the bulk with BF$_3$·Et$_2$O as a catalyst at room temperature. Various copolyesters with γBL content of up to 26 mol % and $\bar{M}_n$ up to 1.5×10^5 were synthesized by Nakayama et al.[15] via ring-opening polymerization of γBL with L-lactide, glycolide, βPL, δ-valerolactone (δVL), or CL with tetraphenyl tin as an initiator. Mas et al.[16] reported on the curing of diglycidyl ether bisphenol A with γBL and ytterbium triflate as a catalyst. Hou et al.[17,18] showed that the samarium(II) bis(aryloxide) complex Sm(OAr)$_2$(THF)$_3$ exerts an extremely high activity for the ring-opening polymerization of CL and δVL and the copolymerization of CL with γBL (copolyesters containing up to 22 mol % γBL units with $\bar{M}_n$ up to 12.9×10^4 were prepared). ^{1}H and ^{13}C NMR spectroscopic studies showed that in CL-γBL copolymers the γBL units all exist in an isolated form and the CL units all in blocks and, therefore, are different from any of the conventional alternating, block, or random copolymers. Fedtke et al.[19] studied the influence of the catalysts boron trifluoride *p*-methoxyaniline complex and BF$_3$·Et$_2$O in the cationic copolym-

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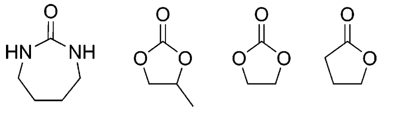


1 2 3 4

Figure 1. Structures of TeU, PC, EC, and γBL.

erization of phenyl glycidyl ether with γBL, yielding copolymers with low lactone content.

The present paper describes the copolymerization of TeU with γBL initiated with dibutylmagnesium (Bu_2Mg) and the copolymerization of TeU with mixtures of γBL and EC or PC. The microstructure of the polymers obtained is determined by means of NMR spectroscopy, the molecular weight and polydispersity index are determined by means of gel permeation chromatography (GPC), and the thermal properties are determined by means of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

Experimental Part

Materials. Starting materials and reagents used for the monomer synthesis and polymerizations were of high purity. *N*,*N*-Dimethylacetamide (DMAc, Acros Organics) and dibutylmagnesium (Bu_2Mg, Aldrich), 1.0 M solution in heptane, were used as received. γ-Butyrolactone (Acros Organics), ethylene carbonate (Acros Organics), and 1,2-propylene carbonate (Aldrich) were dried over calcium hydride and distilled in a vacuum before use. Tetramethylene urea[1] was subjected to sublimation before use. The synthesis of polyurethanes **9** and **16** is described elsewhere.[1] Where necessary, the reactions were conducted in a nitrogen atmosphere. Nitrogen (Linde) was passed over molecular sieves (4 Å) and finely distributed potassium on aluminum oxide for purification.

Measurements. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX-300 FT-NMR spectrometer at 300 and 75 MHz, respectively. Dimethyl sulfoxide (DMSO-d_6) was used as a solvent, and tetramethylsilane (TMS) served as internal standard.

Gel permeation chromatography (GPC) analyses were carried out on a high-temperature GPC at 80 °C (Polymer Laboratories PL-GPC210 with a Bischoff HPLC compact pump) using a refractive index detector (Polymer Laboratories). The eluting solvent was *N*,*N*-dimethylacetamide (DMAc) with 2.44 g L^{-1} LiCl and a flow rate of 0.8 mL min^{-1}. Four columns with MZ-DVB gel were applied: length of each column 300 mm, diameter 8 mm, diameter of gel particles 5 μm, nominal pore width 100, 100, 10^3, 10^4 Å. Calibration was achieved using polystyrene standards of narrow molecular weight distribution.

Differential scanning calorimetric (DSC) analyses were performed on a Netzsch DSC 204 in a nitrogen atmosphere. All samples were annealed for 1 h at a given temperature closely before their melting transition temperature. Heating and cooling rates of 10 K min^{-1} were applied. Calibration was achieved using indium standard samples.

Thermogravimetric analyses (TGA) were performed on a TG 209 C with a TA system controller TASC 414/4 from Netzsch. The measurements were performed in a nitrogen atmosphere with a heating rate of 10 K min^{-1}.

Syntheses. *Copolymerization of TeU with γBL.* TeU (279 mg, 2.44 mmol) and γBL (631 mg, 7.33 mmol) were heated to 100 °C; then Bu_2Mg (50 μL) was added, and the polymerization occurred within 24 h in a nitrogen atmosphere. The product was dissolved in DMAc (6 mL) and precipitated into water. The product was dried in a vacuum (10^{-2} mbar) at 50 °C. Yield: 409 mg (2.04 mmol, 84%). ^1H NMR (DMSO-d_6, 80 °C) (Figure 2): $\delta = 1.41$ (m, 4H, H-4, H-5), 1.77 (m, 2H, H-10), 2.12 (m, 2H, H-9), 3.01 (m, 4H, H-3, H-6), 3.93 (t, 2H, H-11, $^3J = 6.7$ Hz), 6.52 (m, 1H, H-2), 7.38 (m, 1H, H-7) ppm.

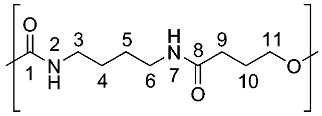


Figure 2. NMR assignments of poly(amide urethane).

^{13}C NMR (DMSO-d_6, 80 °C): $\delta = 24.63$ (C-10), 26.04/26.49 (C-4/C-5), 31.46 (C-9), 37.88 (C-6), 39.79 (C-3), 62.83 (C-11), 155.75 (C-1), 170.86 (C-8) ppm.

GPC (DMAc/LiCl): $\bar{M}_n = 12\,600$; $\bar{M}_w = 21\,100$; $\bar{M}_w/\bar{M}_n = 1.67$.

Copolymerization of TeU with Mixtures of EC and γBL. General procedure for the copolymerization of 1 equiv of TeU with 1 equiv of EC and *X* equiv of γBL, e.g., 3 equiv of γBL.

TeU (478 mg, 4.19 mmol), EC (369 mg, 4.19 mmol), and γBL (1.08 g, 12.57 mmol) were heated to 100 °C; then Bu_2Mg (50 μL) was added, and the polymerization occurred within 24 h in a nitrogen atmosphere. The product was dissolved in DMAc (6 mL) and precipitated into water. The product was dried in a vacuum (10^{-2} mbar) at 50 °C. Yield: 674 mg (3.34 mmol, 80%) (Figure 3).

^1H NMR (DMSO-d_6): $\delta = 1.36$ (m, H-4, H-5, H-15, H-16), 1.76 (m, H-10), 2.10 (t, H-9, $^3J = 6.8$ Hz), 2.95 (m, H-3, H-6, H-14, H-17), 3.89 (m, H-11), 4.08 (s, H-20, H-21), 6.73/6.81 (m, H-$2_{(Z)}$, H-$13_{(Z)}$, H-$18_{(Z)}$), 7.05/7.19 (m, H-$2_{(E)}$, H-$13_{(E)}$, H-$18_{(E)}$), 7.81 (m, H-7) ppm.

^{13}C NMR (DMSO-d_6): $\delta = 25.12$ (C-10), 26.58/26.98/26.85 (C-4, C-5, C-15, C-16), 31.81 (C-9), 38.31 (C-6), 39.79 (C-3, C-14, C-17), 62.50 (C-11, C-20, C-21), 156.16 (C-12, C-19), 156.44 (C-1), 171.54 (C-8) ppm.

GPC (DMAc/LiCl): $\bar{M}_n = 12\,800$; $\bar{M}_w = 22\,200$; $\bar{M}_w/\bar{M}_n = 1.73$.

General procedure for the copolymerization of 1 equiv of TeU with *X* equiv of PC and *Y* equiv of γBL, e.g., 1 equiv of PC and 1 equiv of γBL.

TeU (497 mg, 4.36 mmol), PC (445 mg, 4.36 mmol), and γBL (375 mg, 4.36 mmol) were heated to 100 °C; then Bu_2Mg (50 μL) was added, and the polymerization occurred within 24 h in a nitrogen atmosphere. The product was dissolved in DMAc (6 mL) and precipitated into water. The product was dried in a vacuum (10^{-2} mbar) at 50 °C. Yield: 619 mg (2.97 mmol, 68%) (Figure 4).

^1H NMR (DMSO-d_6): $\delta = 1.13$ (d, H-22, $^3J = 6.4$ Hz), 1.35 (m, H-4, H-5, H-15, H-16), 1.74 (m, H-10), 2.10 (t, H-9, $^3J = 6.7$ Hz), 2.94 (m, H-3, H-6, H-14, H-17), 3.91 (m, H-11, H-21), 4.79 (m, H-20), 6.73/6.75 (m, H-$2_{(Z)}$, H-$13_{(Z)}$, H-$18_{(Z)}$), 7.07/7.18 (m, H-$2_{(E)}$, H-$13_{(E)}$, H-$18_{(E)}$), 7.81 (m, H-7) ppm.

^{13}C NMR (DMSO-d_6): $\delta = 16.79$ (C-22), 25.11 (C-10), 26.57–27.01 (C-4, C-5, C-15, C-16), 31.81 (C-9), 38.31 (C-6), 40.07 (C-3, C-14, C-17), 63.29 (C-11), 65.96 (C-21), 68.24 (C-20), 155.80 (C-19), 156.11 (C-12), 156.40 (C-1), 171.48 (C-8) ppm.

GPC (DMAc/LiCl): $\bar{M}_n = 19\,300$; $\bar{M}_w = 35\,400$; $\bar{M}_w/\bar{M}_n = 1.83$.

Results and Discussion

In previous papers we reported the successful synthesis of polyurethanes via nonisocyanate methods, e.g., the copolymerization of TeU with EC, with 2,2-dimethyltrimethylene carbonate, or with PC.[1,20,21] The result of all copolymerization reactions is a polyurethane with alternating carbonyl-amino-tetramethylene-amino and ethylene carbonate, 2,2-dimethyltrimethylene carbonate, or propylene carbonate repeating units.

Furthermore, to cover a wide range of properties, polymers with different functional groups were synthesized and characterized in our group, e.g., poly(ester amide)s,[22–26] poly(amide urethanes),[27,28] and poly(amide urea)s and poly(amide urethane urethane)s.[29] The properties of these polymers are determined not only by the building blocks but also by the concentration and by the distribution—random or regular—of the functional groups.

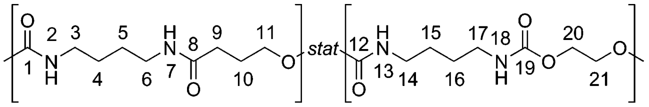


Figure 3. NMR assignments of poly[(TeU−γBL)-*stat*-(TeU−EC)].

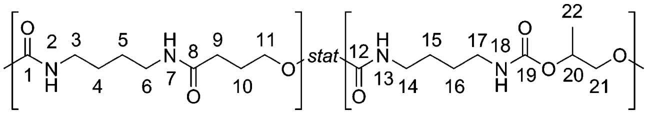
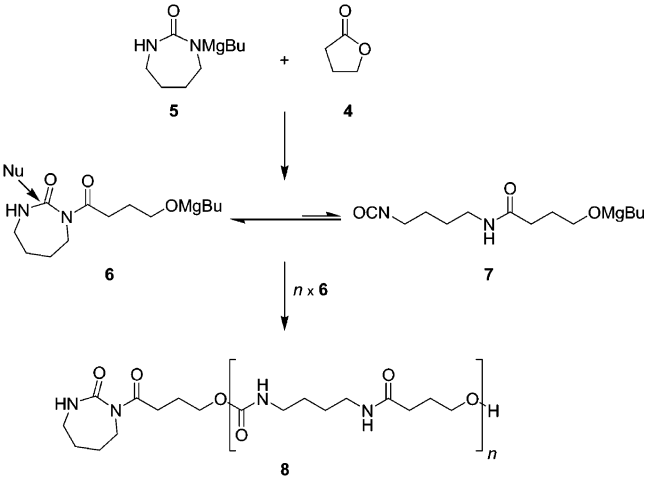


Figure 4. NMR assignments of poly[(TeU−γBL)-*stat*-(TeU−PC)].

Scheme 1. Proposed Mechanism of TeU/γBL Copolymerization: Formation of an Alternating Poly(amide urethane)



γ-Butyrolactone, a five-membered lactone which does not homopolymerize, is a readily available and cheap monomer which excellently fits our strategy toward the synthesis of polyurethanes via non-isocyanate ways and at the same time toward the preparation of polymers with different functional groups. For these purposes, TeU was copolymerized with γBL in the presence of dibutylmagnesium (Bu$_2$Mg) as a catalyst leading to an alternating poly(amide urethane), as will be shown later. The polymers obtained are interesting materials for coating applications because they possess good adsorption properties on different types of surfaces and do not yellow.

Copolymerization of TeU with γBL. Copolymerization of TeU **1** with γBL (**4**) in the presence of dibutylmagnesium (Bu$_2$Mg) as a catalyst in the melt at 100 °C results in an alternating copolymer ($\bar{M}_n$ = 12 600; $\bar{M}_w$ = 21 000; $\bar{M}_w/\bar{M}_n$ = 1.67) with the microstructure of a poly(amide urethane) **8**. Scheme 1 illustrates the proposed mechanism for the copolymerization of TeU with γBL. Bu$_2$Mg does not initiate the homopolymerization of TeU nor of γBL under the reaction conditions applied. However, in the presence of Bu$_2$Mg a mixture of TeU and γBL is converted into a polymer. We presume that TeU reacts initially with Bu$_2$Mg to form the salt **5** in which the nucleophilicity of the nitrogen is enhanced, and the reaction between activated TeU and γBL is made possible. Ring-opening leads to the AB monomer **6**. The equilibrium between compound **6** and its isocyanato compound **7** is completely shifted to the side of compound **6** at 100 °C as was shown by means of ^{1}H NMR spectroscopic investigations on a model compound.[1] Nucleophilic attack of the alcoholate oxygen at the endocyclic carbonyl carbon of **6** results in polymer **8** under ring-opening.

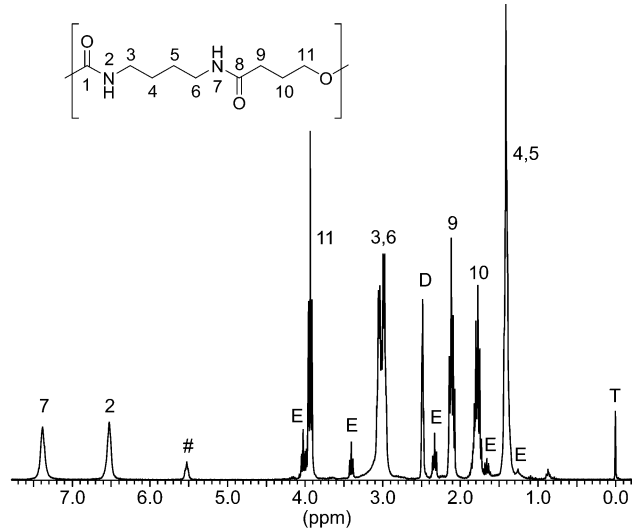


Figure 5. ^{1}H NMR spectrum of poly(amide urethane) **8** in DMSO-d_6 at 80 °C (T = TMS; E = end group; D = DMSO; # = TeU−TeU diad).

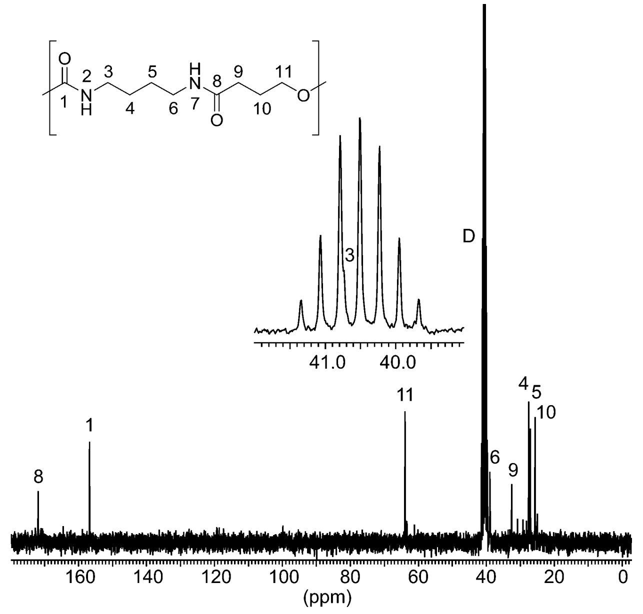


Figure 6. ^{13}C NMR spectrum of poly(amide urethane) **8** in DMSO-d_6 at 80 °C (D = DMSO).

The ^{1}H NMR spectrum of the purified polymer **8** in DMSO-d_6 at 80 °C (Figure 5) shows the resonance lines of the CH$_2$ groups of the TeU repeating units at δ = 1.41 ppm and δ = 3.01 ppm, and the characteristic shifts for the NH proton of the urethane and amide group at δ = 6.52 ppm and δ = 7.38 ppm, respectively. Furthermore, the spectrum reveals an almost 1:1 ratio of TeU and γBL repeating units, although a 3-fold excess of γBL was used in the monomer feed. The small deviation from the 1:1 ratio of TeU and γBL repeating units is caused by the formation of TeU−TeU diads (δ = 5.52 ppm). The resonance lines of the γBL repeating units are found at δ = 1.77 ppm ($-COCH_2CH_2-$), δ = 2.12 ppm ($-COCH_2-$), and δ = 3.93 ppm ($-CH_2O-$).

The ^{13}C NMR spectrum of polymer **8** (Figure 6), which usually gives more insight into the microstructure of copolymers and, in particular, the signals of the carbonyl carbons which are sensitive to sequence effects, shows

Table 1. γBL Content, Yield, Molecular Weight, and Polydispersity of the Polymers with EC in the Feed

polymer	equivalents TeU	 EC	 γBL	γBL content,[a] mol %	yield, %	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
8	1		3	100	84	12 600	21 100	1.67
9	1	3		0	79	8 600	12 500	1.46
10	1	1	1	16.2	68	11 400	18 600	1.63
11	1	1	2	27.0	54	8 200	12 000	1.46
12	1	1	3	33.2	80	12 800	22 200	1.73
13	1	1	4	35.1	58	10 700	16 900	1.58
14	1	1	5	38.3	37	8 100	12 200	1.50
15	1	1	10	*b*		4 300	7 100	1.66

[a] γBL content = r.u.(γBL)/[r.u.(γBL) + r.u.(EC)] × 100%; r.u. = repeating unit. [b] Polymer **15** cannot be isoltated by precipation of a DMAc solution into water. GPC results were obtained from the raw material.

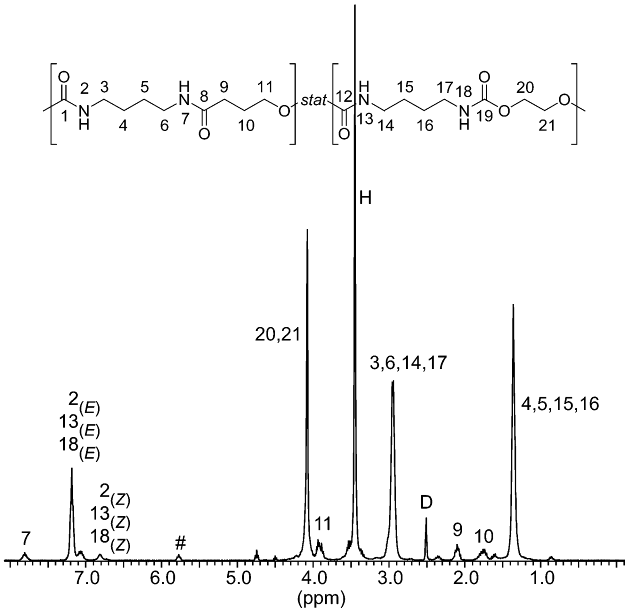


Figure 7. ^{1}H NMR spectrum of poly[(TeU−γBL)-*stat*-(TeU−EC)] **10** from TeU (1 equiv), EC (1 equiv), and γBL (1 equiv) in DMSO-d_6 (D = DMSO; H = water; # = TeU−TeU diad).

single resonance lines, confirming the uniform microstructure. The carbonyl carbon signals are found at $\delta = 155.75$ ppm (urethane linkage) and $\delta = 170.86$ ppm (amide linkage). Also, single resonance lines are found for the methylene carbons of the TeU repeating units at $\delta = 26.04$ ppm, $\delta = 26.49$ ppm, $\delta = 37.88$ ppm, and $\delta = 39.79$ ppm. The methylene carbons of the γBL repeating units are found at $\delta = 24.63$ ppm, $\delta = 31.46$ ppm, and $\delta = 62.83$ ppm. It should be mentioned that the chemical shifts of the $-OCONHCH_2CH_2-$ and $-CONHCH_2CH_2-$ carbons of the TeU repeating units differ slightly, but no clear assignment can be made.

Copolymerization of TeU with Mixtures of γBL and EC. The copolymerization of 1 equiv of TeU with a mixture of 1 equiv of γBL and 1 equiv of EC in the presence of dibutylmagnesium (Bu_2Mg) as a catalyst in the melt at 100 °C results in poly[(TeU−γBL)-*stat*-(TeU−EC)] with randomly distributed carbonyl-amino-tetramethylene-amino, carbonyl-trimethylene-oxy, carbonyl-amino-tetramethylene-amino, and ethylene carbonate repeating units ($\bar{M}_n = 11\,400$; $\bar{M}_w = 18\,600$; $\bar{M}_w/\bar{M}_n = 1.63$). The γBL content in the terpolymer was calculated from the ^{1}H spectrum (Figure 7). The signal intensity of the amide proton ($I_{(\gamma BL)}$, $\delta = 7.6-8.0$ ppm) which is indicative of γBL repeating units in the terpolymer was compared with the signal intensity of the urethane protons (I, $\delta = 6.5-7.45$ ppm) which is indicative of γBL and EC repeating units in the terpolymer. It should be mentioned that each NH resonance signal of the urethane groups is split into two signals (*E* and *Z* conformers) because of conformational restrictions around the CO−N bond (this phenomenon is not observed at higher temperatures; cf. Figure 5). The γBL content in the terpolymer is calculated according to the following equation:

$$\text{mol \% } \gamma\text{BL} = \frac{I_{(\gamma \text{BL})}}{I_{(\gamma \text{BL})} + \dfrac{I - I_{(\gamma \text{BL})}}{2}} \times 100 \qquad (1)$$

Although the ratio of γBL and EC in the feed was 1:1, only 16.2 mol % of γBL was incorporated in the polymer, showing that the reactivity of EC is much higher than that of γBL.

To increase the concentration of γBL in the polymer, the fraction of γBL in the feed was constantly increased. The γBL content in the terpolymer as calculated from the ^{1}H NMR spectra according to eq 1 increases with increasing concentration of γBL in the feed up to a maximum of 38.3 mol % (Table 1). The formation of large sequences of TeU−EC is excluded as will be shown later (section Thermal Properties).

The microstructure of the terpolymers was analyzed by means of ^{13}C NMR spectroscopy which is sensitive to sequence effects. Figure 8 (**I** at room temperature; **II** at 100 °C) shows as an example the carbonyl carbon signals of poly[(TeU−γBL)-*stat*-(TeU−EC)], **13** (35.1 mol % γBL). At room temperature, four sequences are assumed to be responsible for the carbonyl carbon resonance around 156 ppm (signals C and D). The sequence TeU−EC−TeU−EC absorbs at the highest field (156.16 ppm; signal C). Furthermore, three sequences (signal D), i.e., TeU−γBL−TeU−EC, TeU−EC−TeU−γBL, and TeU−γBL−TeU−γBL, which at the time cannot be assigned are expected. In addition, signal D shows a splitting of the signals because of conformational restrictions of the polymer chain. Signal A (171.54 ppm) is assigned to the carbonyl carbon of the amide group. Occasionally, a small signal B is observed at 172.60 ppm, which is assumed to be due to the carbonyl carbon of the ester group of a TeU−γBL−γBL sequence. **II** shows that at 100 °C the carbonyl carbon signals are shifted to higher field. However, the conformational restrictions are not eliminated.

According to GPC analysis, poly[(TeU−γBL)-*stat*-(TeU−EC)] shows moderate molecular weights ($8100 < \bar{M}_n < 12\,800$; $12\,000 \le \bar{M}_w < 22\,200$) and unimodal elution curves ($1.46 < \bar{M}_w/\bar{M}_n < 1.73$) (Table 1). It should be mentioned that polymers **8**−**14** precipitate after a certain monomer conversion has been reached. Polymer **15** could not be precipitated from a DMAc solution into

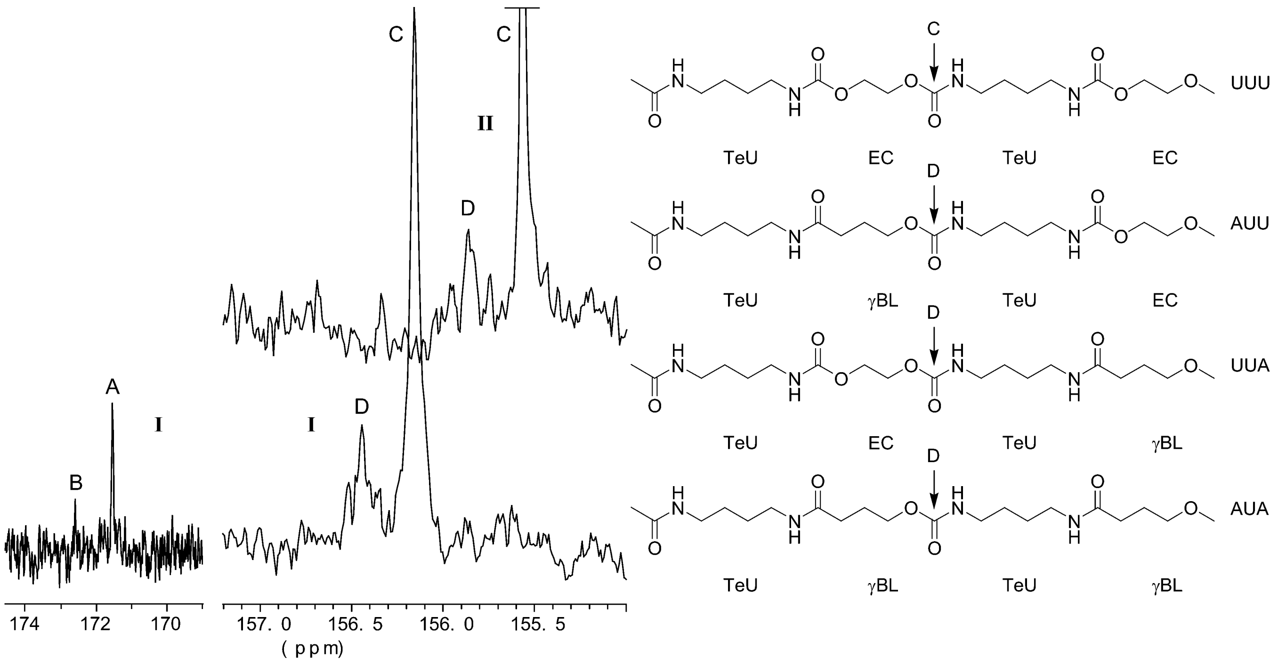


Figure 8. ^{13}C NMR spectrum of poly[(TeU−γBL)-*stat*-(TeU−EC)] **13**; **I** at room temperature, **II** at 100 °C (four sequences were taken into consideration: UUU, AUU, UUA, AUA).

Table 2. γBL Content, Yield, Molecular Weight, and Polydispersity of the Polymers with PC in the Feed

	equivalents							
polymer	TeU	PC	γBL	γBL content,[a] mol %	yield, %	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
16	1	3		0	49	12 200	18 400	1.50
17	1	1	1	47.8	68	19 300	35 400	1.83
18	1	1	2	62.4	14	9 100	10 200	1.12
19	1	2	1	27.4	28	11 100	14 200	1.28

[a] γBL content = r.u.(γBL)/[r.u.(γBL) + r.u.(PC)] × 100%; r.u = repeating unit.

water (GPC results were obtained from the raw material).

Copolymerization of TeU with Mixtures of γBL and PC. The results obtained for the copolymerization of TeU with a 1:1 mixture of EC and PC (leading to a PC content of 19.6 mol %)[1] and with a 1:1 mixture of EC and γBL (leading to a γBL content of 16.2 mol %) led to the preliminary conclusion that the reactivity of the three five-membered cyclic monomers increases in the following order: EC ≫ PC ≈ γBL.

To investigate the reactivity between PC and γBL, 1 equiv of TeU was copolymerized with a mixture of 1 equiv of PC and 1 equiv of γBL in the presence of dibutylmagnesium (Bu_2Mg) as a catalyst in the melt at 100 °C, resulting in the random terpolymer poly[(TeU−γBL)-*stat*-(TeU−PC)] ($\bar{M}_n = 19\,300$; $\bar{M}_w = 35\,400$; $\bar{M}_w/\bar{M}_n = 1.83$). The γBL content in the terpolymer was calculated from the ^1H NMR spectrum according to eq 1.

A γBL content of 47.8 mol % confirms that the reactivity of γBL is similar to that of PC. To increase the content of γBL in the terpolymer, 2 equiv of γBL was used in the feed. The opposite was done to decrease the γBL content (Table 2).

Figure 9 shows the carbonyl carbon signals of poly[(TeU−γBL)-*stat*-(TeU−PC)] **17**−**19**. By comparing **I**−**III**, it is evident that signal D (156.40 ppm), which increases or decreases with increasing (**II**) or decreasing (**III**) γBL content, has to be assigned to the carbonyl carbon of the TeU−γBL urethane group. Signals C and E in a 1:1 ratio are assigned to the carbonyl carbon of the TeU−PC urethane groups; because of the different orientation of the PC repeating units, a carbonyl carbon signal is observed at 156.11 ppm (signal C), which corresponds to $-NHCOOCH_2CH(CH_3)O-$, and at 155.80 ppm (signal E), which corresponds to $-NHCOOCH(CH_3)CH_2O-$. This assignment was made after comparing the chemical shift of the carbonyl carbon of the TeU−EC urethane group (156.16 ppm) with that of TeU−PC urethane group. Furthermore, signal A (171.48 ppm) is assigned to the carbonyl carbon of the amide group. A small signal B is observed in **II** at 172.50 ppm, and it is assumed that this signal has to be assigned to the carbonyl carbon of the ester group of a TeU−γBL−γBL sequence. Having a closer look at the resonance lines, a small peak around signal D, in particular in figure **II**, is observed. It is likely that because of the relatively high γBL content, signal D1 has to be assigned to the urethane carbonyl carbon of a TeU−γBL−TeU−γBL sequence.

According to GPC analysis, poly[(TeU−γBL)-*stat*-(TeU−PC)] shows moderate molecular weights ($9100 < \bar{M}_n < 19\,300$; $10\,200 \le \bar{M}_w < 35\,400$) and unimodal elution curves ($1.12 < \bar{M}_w/\bar{M}_n < 1.83$) (Table 2). It should be mentioned that the low yield of polymers **18** and **19** is because of the removal of low molecular weight material upon fractionation.

Thermal Properties. The thermogravimetric analysis of the poly(amide urethane) **8** shows that it is stable up to approximately 210 °C; then it begins to decompose in three steps to form volatile products (at 247.6, 277.4, and 303.4 °C). Polyurethanes **9** (100 mol % EC) and **16** (100 mol % PC) decompose with a first maximum at 265.9 and 266.3 °C, respectively.[1]

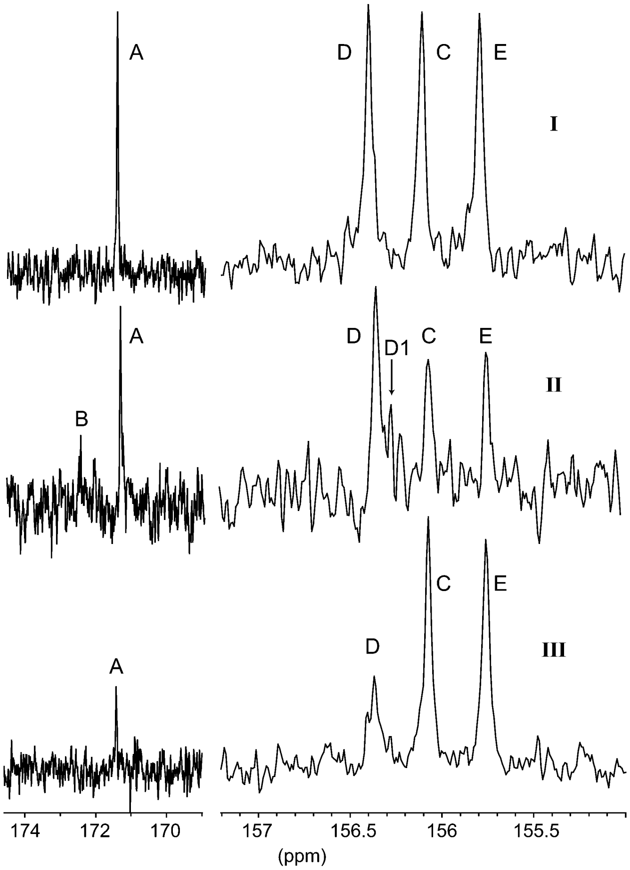


Figure 9. ^{13}C NMR spectrum of poly[(TeU−γBL)-*stat*-(TeU−PC)] **17**−**19** (**I** = 47.8 mol % γBL; **II** = 62.4 mol % γBL; **III** = 27.4 mol % γBL).

The thermogravimetric analyses of the poly[(TeU−γBL)-*stat*-(TeU−EC)] **10**−**14** and poly[(TeU−γBL)-*stat*-(TeU−PC)] **17**−**19** show that they are stable up to approximately 210 °C; then they begin to decompose in three steps to form volatile products (at approximately 252, 260, and 304 °C). It should be mentioned that the first and second maximum are often depicted as one maximum with a shoulder. TGA analyses show that the thermal stability of the terpolymers **10**−**14** or **17**−**19** is between those of poly(amide urethane) **8** and polyurethanes **9** or **16**. However, thermal stability is only slightly affected by the terpolymer composition. The first two maxima are assigned to the elimination of γBL and EC or PC and the formation of a polyurea. The third maximum is assigned to the fragmentation of the newly formed polyurea. The intramolecular elimination of cycles is known from literature. For example, Berti et al.[30] showed that a bisphenol A polycarbonate is obtained after intramolecular elimination of EC from an alternating EC/bisphenol A polycarbonate copolymer. In the past, our group proved experimentally that cyclic ethylene urea and propylene urea, but not tetramethylene urea, are formed in an intramolecular reaction from an alternating poly(amide urea).[29] However, the three-step decomposition of poly(amide urethane) **8** cannot be explained at this moment; TGA experiments in combination with mass spectroscopy should be done to explain this result.

In Figure 10, a typical DSC curve is shown for poly[(TeU−γBL)-*stat*-(TeU−EC)] **12** as an example after annealing the sample. Before annealing, DSC traces show small endotherm peaks at $T < T_m$ which on annealing disappear. The heating run shows a glass transition at 33.3 °C and a sharp melting transition at 203.2 °C.

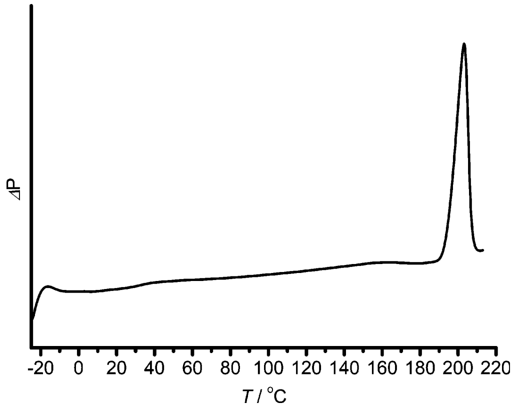


Figure 10. DSC curve of poly[(TeU−γBL)-*stat*-(TeU−EC)] **12**.

Table 3. DSC Results of Polymers 8−19 after Annealing

polymer	γBL content,[a] mol %	T_g, °C	T_m, °C	ΔH_m, J g^{-1}
8	100	36.4	196.5	19.8
9	*b*	35.7	203.1	72.1
10	16.2	36.8	203.5	42.7
11	27.0	33.1	201.5	48.8
12	33.2	33.3	203.2	61.1
13	35.1	30.0	202.5	48.3
14	38.3	40.1	198.8	45.9
15	*c*			
16	*d*	51.4	143.9	37.6
17	47.8	50.2	176.7	31.1
18	62.4	30.3	166.7	35.5
19	27.4	42.5	152.2	35.5

[a] For polymers **8**−**14**: γBL content = r.u.(γBL)/[r.u.(γBL) + r.u.(EC)] × 100%; for polymers **16**−**19**: γBL content = r.u.(γBL)/[r.u.(γBL) + r.u.(PC)] × 100%; r.u. = repeating unit. [b] 100 mol % EC. [c] Polymer cannot be isolated. [d] 100 mol % PC.

Table 3 shows DSC results of poly(amide urethane) **8**, polyurethanes **9** and **16**, poly[(TeU−γBL)-*stat*-(TeU−EC)] **10**−**14**, and poly[(TeU−γBL)-*stat*-(TeU−PC)] **17**−**19**. It should be noted that all samples were annealed for 1 h at a given temperature closely before their melting transition temperature.

Poly(amide urethane) **8** (100 mol % γBL) exerts a T_m of 196.5 °C. The melting enthalpy is low (19.8 J g^{-1}), indicating that poly(amide urethane) **8** is a material with low degree of crystallinity. Polyurethane **9** (100 mol % EC) exerts a T_m of 203.1 °C and shows a high melting enthalpy (72.1 J g^{-1}). Furthermore, Table 3 shows that the poly[(TeU−γBL)-*stat*-(TeU−EC)] **10**−**14** are highly crystalline materials.

Figure 11 shows that T_m is not affected by the terpolymer composition. EC and γBL are both five-membered rings with the difference that one oxygen of the carbonate group is substituted by a carbon atom, leading to an ester group. Therefore, the difference in the terpolymer composition is merely one atom, and thus, T_m is not affected by the terpolymer composition. It should be mentioned that all values are within a 2.5% limit from the straight line.

In addition, the glass transition temperature of poly(amide urethane) **8** (36.4 °C) does not significantly differ from polyurethane **9** (35.7 °C) (Table 3). Figure 12 shows that T_g is only slightly affected by the terpolymer composition. The same observation was made by Duda et al. in the copolymerization reaction of γBL with ϵ-caprolactone.[4] The variation of the glass transition

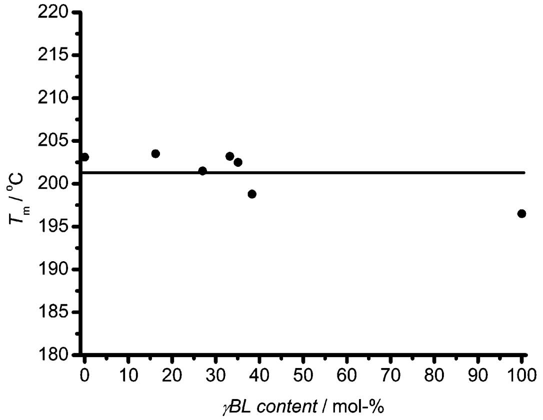


Figure 11. T_m as a function of γBL content for polymers **8**−**14**.

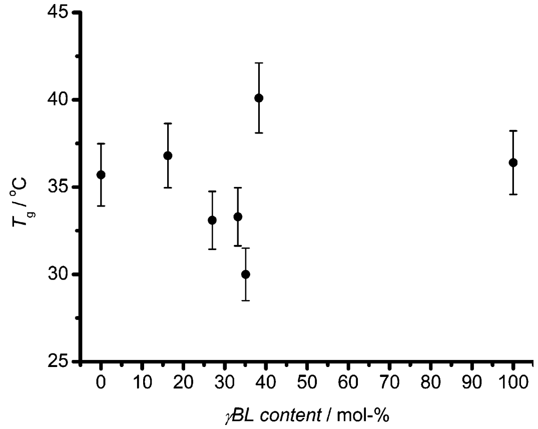


Figure 12. T_g as a function of γBL content for polymers **8**−**14**.

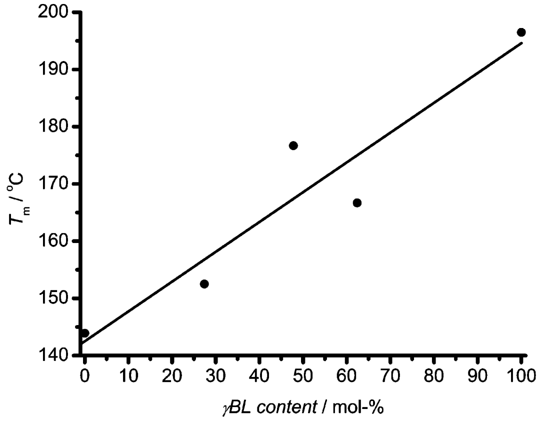


Figure 13. T_m as a function of γBL content for polymers **8** and **16**−**19**.

temperature is explained by the fact that poly[(TeU−γBL)-*stat*-(TeU−EC)] show different microstructures (i.e., sequence of TeU−EC and TeU−γBL diads). Because of the different reactivity of γBL and EC, the ratio of γBL/EC in the feed will influence the statistics of the distribution of repeating units. This very probably is also the origin of the scatter of the T_g the values observed in Figure 12.

Polyurethane **16** (100 mol % PC) exerts a T_m of 143.9 °C (Table 3). Its degree of crystallinity is lower than that of polyurethane **9** because of the atacticity of the polymer. Furthermore, Table 3 shows that the degree of crystallinity of poly[(TeU−γBL)-*stat*-(TeU−PC)] **17**−**19** is lower than that of poly[(TeU−γBL)-*stat*-

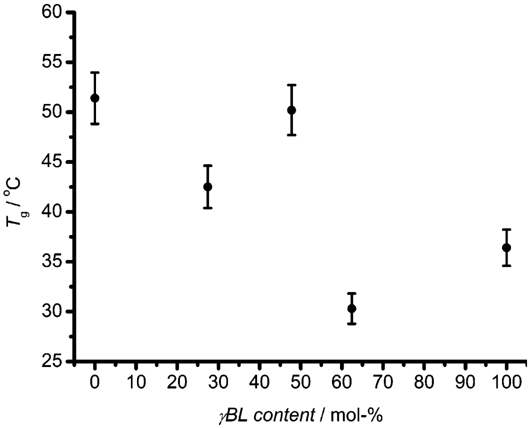


Figure 14. T_g as a function of γBL content for polymers **8** and **16**−**19**.

(TeU−EC)] **10**−**14** because of the atacticity of the terpolymers.

Figure 13 shows that T_m increases from 143.9 to 196.5 °C for polymers **16**−**19** and **8** in which the γBL content increases from 0 to 62.4 mol %, indicating a random structure of the terpolymer. This observation was also made for poly[(TeU−EC)-*stat*-(TeU−PC)] with different terpolymer compositions where T_m decreases continuously with increasing PC content.[1] All values are within a 5% limit from the straight line.

The glass transition temperature of polyurethane **16** is estimated to be 51.4 °C (Table 3). Figure 14 shows that T_g decreases with increasing γBL content.

Conclusions

An almost strictly alternating semicrystalline poly(amide urethane) ($\bar{M}_n = 12\,600$) was prepared from TeU and γBL via an isocyanate-free route. The small defect in the microstructure is unavoidable because of the formation of TeU−TeU diads. Furthermore, terpolymers ($8100 < \bar{M}_n < 19\,300$) with up to 62.4 mol % γBL repeating units were prepared from TeU, EC, or PC and γBL. The thermal properties of poly[(TeU−γBL)-*stat*-(TeU−EC)] are only slightly affected as those of poly[(TeU−γBL)-*stat*-(TeU−PC)] can be controlled by the ratio of PC and γBL in the feed. It is shown that the reactivity of the three five-membered cyclic monomers follows the order EC $\gg$ PC $\approx$ γBL.

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