Macromolecules **2004,** *37,* 7955−7959

Spirocycles versus Networks: Polycondensations of $Ge(OEt)_4$ with Various Aliphatic α,ω-Diols[†]

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Received January 5, 2004; Revised Manuscript Received August 3, 2004

ABSTRACT: $Ge(OEt)_4$ was heated with various α,ω-alkanediols beginning with 1,2-ethanediol up to 1,16-hexadecanediol, whereby a nearly quantitative polycondensation with elimination of EtOH took place. All polycondensation products proved to be insoluble and infusible gels with the exception of the six-numbered spirocycle derived from 1,3-propanediol. A soluble spirocycle was also obtained from *cis*-1,4-butenediol, whereas an insoluble, infusible gel was formed by *trans*-1,4-butanediol. When $Ge(OEt)_4$ was polycondensed with monodisperse oligo(ethylene glycol)s soluble syrupy mixtures of spirocycles were obtained in all cases. These results were explained on the basis of different conformational properties of alkane or ethylene oxide chains and on the basis of our theory of thermodynamically controlled polycondensations featuring a decisive role of ring−ring equilibria. The soluble spirocyclic Ge−oligoethylene oxides proved to be useful initiators for the ring-opening polymerization of ϵ-caprolactone.

Introduction

The principles of polycondensations involving difunctional monomers (“a_2”) and tri- or multifunctional monomers (“b_n”), so-called three-dimensional polycondensations, were already studied and discussed by Flory.[1,2] Flory calculated that a mixture of “a_2” and “b_n” monomers with perfect stoichiometry of the functional groups will yield a network, when the conversion goes beyond 75%, even when a few cyclization reactions take place. Experimental studies of polycondensations based on glycerol and various dicarboxyclic acids (or cyclic anhydrides) confirmed these calculations.[1−4] On the basis of these results, Flory and later other authors[5−8] developed theories of network formation. However, to the best of our knowledge all those theories miss a differentiation between kinetically controlled polycondensations (KCPs) and thermodynamically controlled ones (TCPs). We have recently presented a revised theory of TCPs[9] which considers a reaction mixture as a combination of chain−chain, ring−chain, and ring−ring equilibria. The molar ratio cycles/linear chains increases with higher conversion so that the ring−ring equilibria finally dominate the thermodynamic situation. At high conversions (≥99.9%) a TCP may be described as a ring−ring equilibrium (eq 1)

$$\mathrm{c(M)}_x + \mathrm{c(M)}_y \overset{K}{\rightleftharpoons} \mathrm{c(M)}_{xy} \tag{1}$$

and the equilibrium constant becomes decisive for the maximum degree of polymerization ($\overline{\mathrm{DP}}$) which can be achieved at 100% conversion (eq 2)

$$\overline{\mathrm{DP}} = \frac{1}{1 - p(1 - X^{-}K)} \tag{2}$$

where $\overline{\mathrm{DP}}$ is the average degree of polymerization, p is the conversion, X is a factor >1.0, and K is the equilibrium constant of eq 1 (one K-value is a simplification for the sake of a straightforward qualitative discussion). When this theory of “linear polycondensation” is applied to “three-dimensional polycondensations”, the following analogies and consequences will result. Provided that a clean polycondensation with perfect stoichiometry is performed, a high equilibrium constant (K) will result in the formation of networks (in equilibrium with a small amount of oligomeric spirocycles) and a low K value will result in spirocycles as the main reaction product. Low K values will be favored by strain-free spirocycles and by their gain of translational mobility relative to the immobile networks. Ring-strain and unfavorable conformations in the hypothetical spirocycles will favor high K values and thus the formation of networks at the expense of spirocycles. As a probe of this new hypothesis the present work had the purpose to study polycondensations of $Ge(OEt)_4$ with various α,ω-alkanediols or oligo(ethylene glycol)s. Taking into account the results of two previous publications,[10,11] clean and nearly quantitative polycondensations were expected at temperatures below 150 °C. Depending on ring size and conformational properties of the diols, either spirocycles or networks were expected as main reaction products.

Experimental Section

Materials. $Ge(OEt)_4$ was purchased from Gelest Inc. (Tullytown, PA) and used as received. The α,ω-alkanediols and the oligo(ethylene glycol)s were purchased from Aldrich Co. (Milwaukee, WI) and dried by azeotropic distillation of toluene. The residual toluene was removed at 140 °C in a vacuum of 10^{-2} mbar.

Polycondensations. $Ge(OEt)_4$ (10 mmol) and a dry diol (20 mmol) were weighed under dry nitrogen in a 100 mL round-bottom flask having silanized glass walls and containing a magnetic bar. Dry chlorobenzene (2 mL) was injected, and the closed reaction vessel was immersed into an oil bath preheated to 120 °C. The reaction mixture was stirred for 16 h at 120 °C. The glass stopper was then replaced by a head having gas-inlet and -outlet tubes. The temperature was raised to 140 °C, and the liberated ethanol and the chlorobenzene were removed with a low stream of nitrogen. After 7 h vacuum was applied for 5 h.

After cooling the solubility of the reaction product was tested in dry dichloromethane, chloroform, and chlorobenzene. If the product proved insoluble, it was heated to 160 °C for 16 h. If again insoluble, heating was continued at 180 °C for 16 h and finally at 200 °C for 16 h.

When $Ge(OEt)_4$ (10 mmol) polycondensed with *cis*-1,4-butenediol (20 mmol) at 140 °C again a syrup was obtained

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[†] Part 39 of the series “Macrocycles”.

10.1021/ma040002u CCC: \$27.50

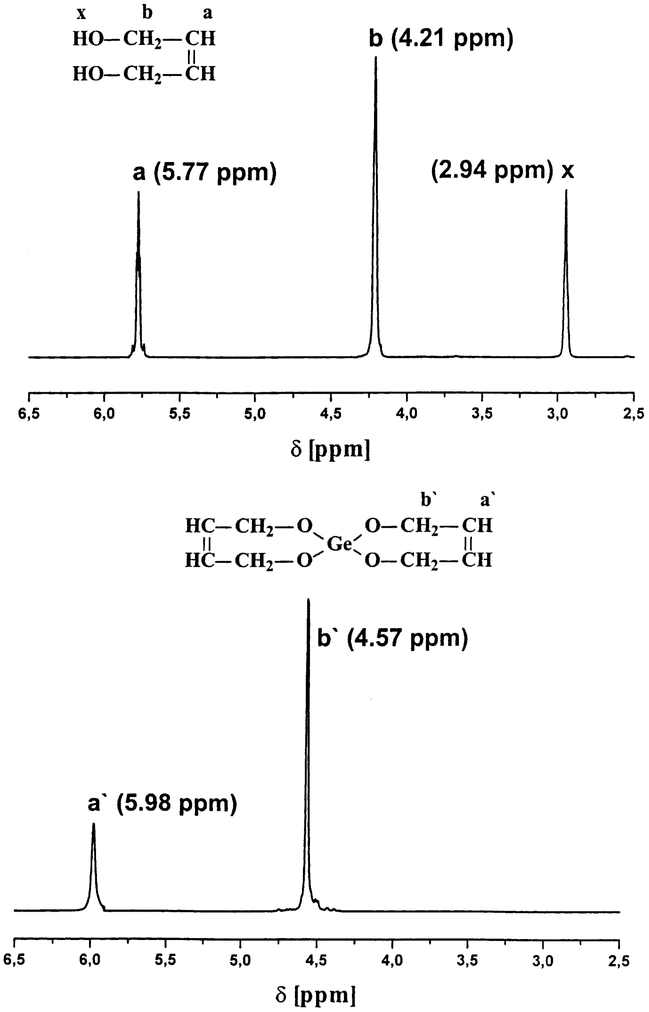


Figure 1. 400 MHz ^{1}H NMR spectra of *cis*-1,4-butenediol and its spirocyclic Ge derivative (in $CDCl_3$).

which had a much higher solubility in chloroform (and other solvents) than the parent *cis*-1,4-butenediol. The ^{1}H NMR spectrum is displayed in Figure 1. The following ^{13}C NMR shift data were recorded in $CDCl_3$/TMS: $\delta = 62.8$ and 132.4 ppm. For the diol the following values were measured: $\delta = 58.2$ and 131.0 ppm.

Polymerizations of ϵ-Caprolactone. ϵ-Caprolactone (50 mmol) was weighed under dry nitrogen into a 50 mL Erlenmeyer flask having silanized glass walls, and 10 mL of a 0.05 M solution of germanium bis(triethylene glycol)oxide, Ge(TriEG)$_2$, in 1,1,2,2-tetrachloroethane was injected. The reaction vessel was closed with a glass stopper and steel spring and immersed into an oil bath preheated to 120 °C (or 100 °C). After periods of 4 h the conversion was checked by ^{1}H NMR spectroscopy. After 24 h at 120 °C (or after 48 h at 100 °C) the reaction product was dissolved in dichloromethane (50 mL) and precipitated into diethyl ether (500 mL), and the isolated polylactone was dried at 25 °C in vacuo.

The polylactone prepared at 100 °C gave a yield of 88% with an inherent viscosity of 0.21 dL/g in CH_2Cl_2 at 20 °C, and the 120 °C product gave a yield of 90% with an inherent viscosity of 0.20 dL/g.

Measurements. The inherent viscosities were measured with an automated Ubbelohde viscometer thermostated at 20 °C. The 400 MHz ^{1}H NMR spectra were recorded on a Bruker Avance 400 FT NMR spectrometer in 5 mm o.d. sample tubes. $CDCl_3$ containing TMS served as solvent and shift reference. The 100.4 MHz ^{13}C NMR spectra were recorded with the same NMR spectrometer.

The MALDI–TOF mass spectra were recorded with a Bruker Biflex III spectrometer equipped with a nitrogen laser ($\lambda = 337$ nm). Both mass spectra were measured in the reflection mode using an acceleration voltage of 20 kV. The irradiation targets were prepared from tetrahydrofuran solutions of poly(ϵ-caprolactone) with dithranol as matrix and K-trifluoroacetate as dopant. Since the spirocycles of germanium were highly sensitive to hydrolysis, alcoholysis, or phenolysis, they were not suited for FAB or MALDI–TOF spectrometry.

Results and Discussion

Polycondensations of α,ω-Alkanediols. Polycondensations of $Ge(OEt)_4$ with 1,2-ethanediol, 1,3-propanediol, 1,4-butanediol, and 1,6-hexanediol wre previously described by Mehrotra and Chandra.[9] Those authors found that the reaction products of the even-numbered diols were insoluble in all inert solvents and infusible. In contrast, the product derived from 1,3-propanediol[1] proved to be a syrup soluble in chloroform and other chlorinated solvents. Quite recently, we have repeated the synthesis of **1**[11] and confirmed that this compound is a soluble syrup useful as an initiator for the ring-opening polymerization of lactones.

In the present work polycondensations of $Ge(OEt)_4$ with 10 α,ω-alkanediols were studied, beginning with 1,2-ethanediol (Table 1). With exception of **1** all reaction products were infusible and insoluble solids. It is particularly important to note that **1** is an exception, and the products of other odd-numbered diols are insoluble materials. The lacking meltability and solubility of the solid reaction products prevented, of course, a detailed characterization of the solid polycondensates. However, four arguments clearly suggest that thermodynamically stable networks were formed. First, the solid Ge–bis(alkylene oxide)s were heated to 160, 180, and 200°C for 48 h in total, but their properties did not change. Heating to higher temperatures (tested up to 240 °C in two cases) resulted in discoloration and decomposition. Therefore, the solidification during the preparation cannot be explained by rapid, kinetically controlled network formation followed by slow equilibration (yielding spirocycles). Second, the solidification and the stability of the solid state up to 200 °C (and higher) cannot be explained by association via dipole–dipole or donor–acceptor interactions because **1** is a liquid and soluble. It is absurd to assume that intermolecular electronic interactions are absent for **1** (and for $Ge(OEt)_4$) but very strong for Ge derivatives of all other alkanediols. The third argument originates from polycondensations of $Ge(OEt)_4$ with *cis*-1,4-butenediol and *trans*-1,4-butenediol. Whereas the "trans product" was an insoluble solid infusible up to 200 °C, the "cis product" was a colorless syrup soluble in chloroform. It is obvious that the cis configuration favors cyclization for thermodynamic (and kinetic) reasons in contrast to the trans isomer, so that spirocycles of structure **2** should be the thermodynamically most stable reaction products. The ^{1}H NMR (Figure 1) and ^{13}C NMR spectra proved that the *cis*-1,4-diol had quantitatively reacted with $Ge(OEt)_4$. The fourth argument results from the polycondensations of $Ge(OEt)_4$ with various oligo(ethylene glycol)s as discussed below.

Polycondensations of Oligo(ethylene glycol)s. When $Ge(OEt)_4$ polycondensed with the monodisperse oligo(ethylene glycol)s listed in Table 1, soluble transparent syrups were obtained in all cases, although the length of these glycols was comparable to those of α,ω-

Table 1. Diols Used for the Polycondensation of Ge(OEt)$_4$ and Solubility of the Reaction Products

expt no.	α,*ω*-alkanediols	solubility[a]	expt no.	various diols	solubility[a]
1	1,2-ethanediol	−	11	*cis*-1,4-butenediol	+
2	1,3-propanediol	+	12	*trans*-1,4-butenediol	−
3	1,4-butanediol	−	13	di-EG	+
4	1,5-pentanediol	−	14	tri-EG	+
5	1,6-hexanediol	−	15	tetra-EG	+
6	1,7-heptanediol	−	16	penta-EG	+
7	1,9-nonanediol	−	17	hexa-EG	+
8	1,10-decanediol	−	18	PEG-300	+
9	1,12-dodecanediol	−			
10	1,16-hexadecanediol	−			

[a] Tested in CH_2Cl_2, $CHCl_3$, $Cl_2CH-CHCl_2$, and $Cl-C_6H_5$ (hot).

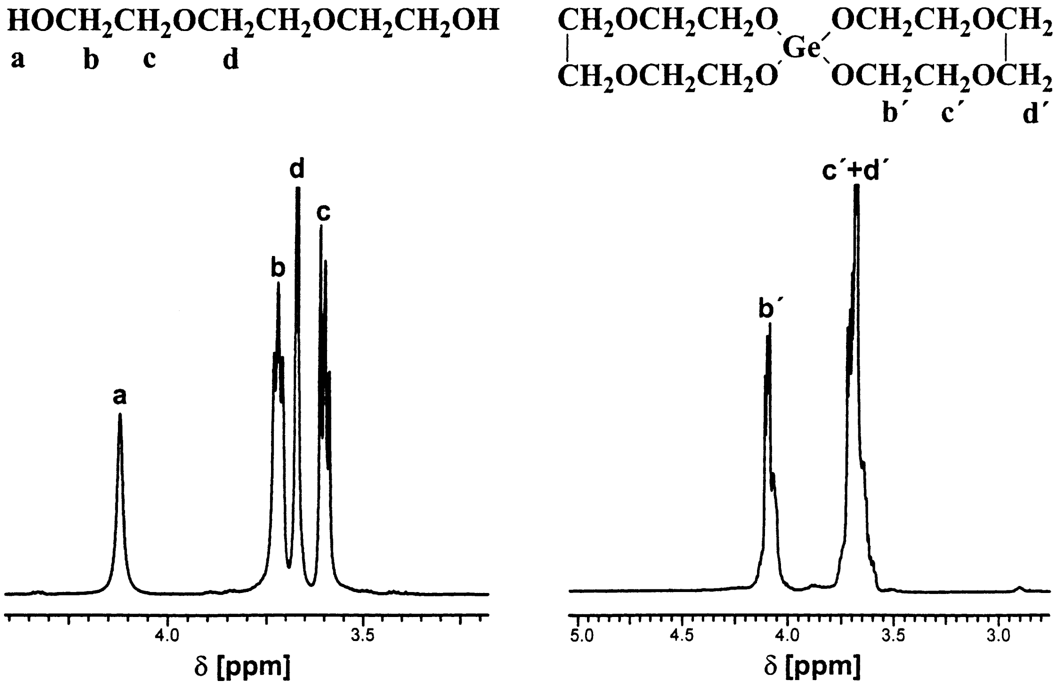


Figure 2. 400 MHz ^1H NMR spectra of triethylene glycol and its spirocyclic Ge derivative (in $CDCl_3$).

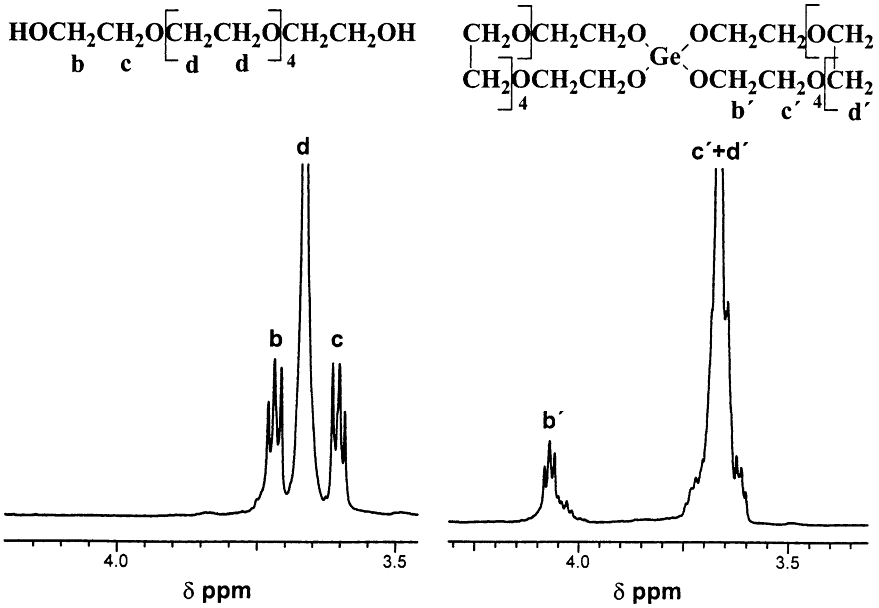


Figure 3. 400 MHz ^1H NMR spectra of hexaethylene glycol and its spirocyclic Ge derivative.

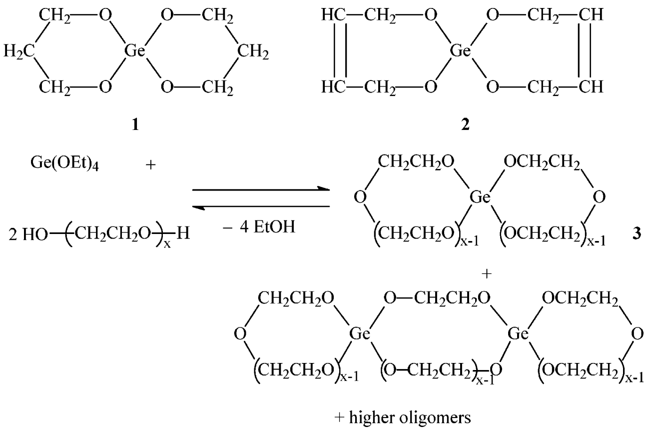
alkanediols used in this work. The ^1H NMR spectra (exemplarily illustrated in Figures 2 and 3) and the ^{13}C NMR shift data compiled in Table 2 clearly indicate that the CH_2OH groups of the oligo(ethylene glycol)s were transformed into $Ge-O-CH_2$ groups. The low solution viscosities ($\lambda_{inh} = 0.03 \pm 0.01$ dL/g in CH_2Cl_2) confirm the formation of low molar mass compounds. Finally, when Ge(OEt)$_4$ polycondensed with a polydisperse poly-

Table 2. Comparison of ^{13}C NMR Data of Free Oligoethylene Glycols and Their Spirocyclic Ge Derivatives[a]

diol	^{13}C atom under consideration	δ [ppm] diol	δ [ppm] Ge(diol)$_2$
diethylene glycol	$\mathrm{HO}\mathit{C}\mathrm{H_2CH_2O}-$	61.3	62.7
	$\mathrm{HOCH_2}\mathit{C}\mathrm{H_2O}-$	72.3	71.4
triethylene glycol	$\mathrm{HO}\mathit{C}\mathrm{H_2CH_2OCH_2}-$	60.9	64.7
	$\mathrm{HOCH_2}\mathit{C}\mathrm{H_2OCH_2}-$	72.3	72.5
	$\mathrm{HOCH_2CH_2O}\mathit{C}\mathrm{H_2}-$	69.9	70.6
tetraethylyene glycol	$\mathrm{HO}\mathit{C}\mathrm{H_2CH_2OCH_2CH_2O}-$	60.8	61.6
	$\mathrm{HOCH_2}\mathit{C}\mathrm{H_2OCH_2CH_2O}-$	72.2	73.0
	$\mathrm{HOCH_2CH_2O}\mathit{C}\mathrm{H_2CH_2O}-$	69.9	70.5
	$\mathrm{HOCH_2CH_2OCH_2}\mathit{C}\mathrm{H_2O}-$	69.5	70.0
hexaethylene glycol	$\mathrm{HO}\mathit{C}\mathrm{H_2CH_2[OCH_2CH_2]_2O}-$	60.9	64.8
	$\mathrm{HOCH_2}\mathit{C}\mathrm{H_2[OCH_2CH_2]_2O}-$	72.1	72.6
	$\mathrm{HOCH_2CH_2[O}\mathit{C}\mathrm{H_2CH_2]_2O}-$	69.9	70.8
	$\mathrm{HOCH_2CH_2[OCH_2}\mathit{C}\mathrm{H_2]_2O}-$	69.8	70.6

[a] Measured in CDCl$_3$ containing TMS.

Scheme 1



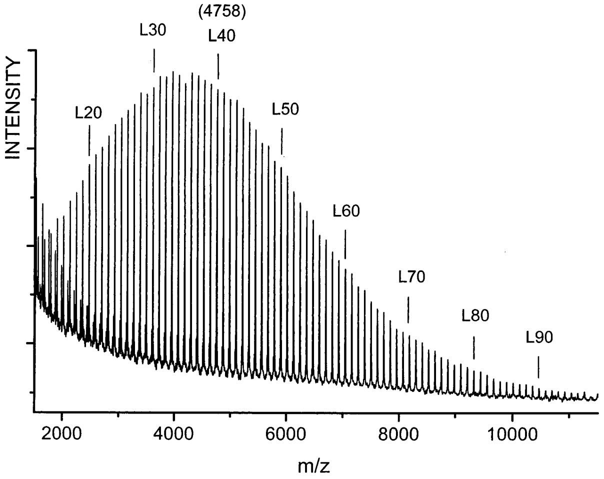
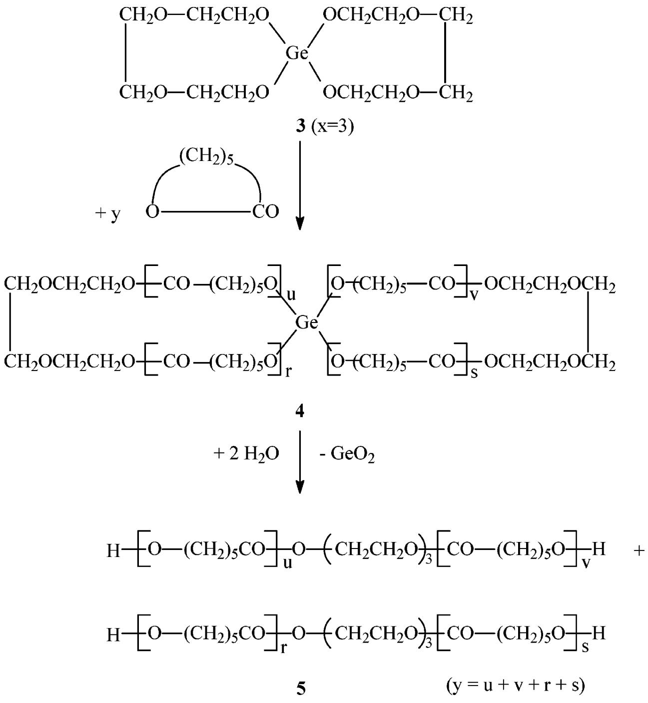


Figure 4. MALDI−TOF mass spectrum of poly(ϵ-caprolactone) polymerized with Ge(TriEG)$_2$ as initiator at 100°C/48 h (after precipitation in diethyl ether).

Scheme 2

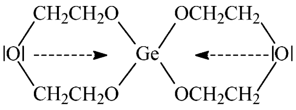


(ethylene glycol) having a number-average molecular weight of 300 (PEG-300, see Table 1), again a soluble syrupy product was obtained.

An indirect confirmation of the spirocyclic structure **3** with a quantitative formation of Ge−OCH$_2$ groups was obtained by the reaction with ϵ-caprolactone. When Ge(TriEG)$_2$ (**3**, $x = 3$) was heated with the 50-fold amount of ϵ-caprolactone, a nearly quantitative ring-expansion polymerization took place as outlined in Scheme 2 (quite analogous to previous experiments with the spirocyclic **1** as initiator[10]). The structure spirocycles **4** and the structure of the linear chains **5** were confirmed by ^{1}H NMR spectroscopy. The structure of the linear chains (**5**) was also confirmed by MALDI−TOF mass spectrometry as demonstrated by Figure 4. Since ϵ-caprolactone does not polymerize with free tri(ethylene glycol) at 100 or 120 °C, these successful polymerization experiments prove the almost quantitative formation of Ge−OCH$_2$ groups according to Scheme 2.

Conclusion

The most important conclusion of this work is the point that our ring−ring equilibration theory of thermodynamically controlled polycondensations allows a satisfactory and consistent interpretation of all experimental results. The formation of cycles with *trans*-1,4-butenediol as a building block is unfavorable, corresponding to a high K value in eqs 1 and 2, so that networks should be formed in polycondensations with Ge(OEt)$_4$. In contrast, *cis*-1,4-butenediol favors the formation of stable cycles with a low K value, so that the spirocycle **2** (and a few higher oligomers) are the most stable reaction products in this case. In the case of alkanediols one has to take into account that the all-trans conformation is thermodynamically most stable, and thus, the formation of cycles is energetically unfavorable with exception of cyclohexane. Hence, the K value is high and networks should be more stable than spirocycles. The spirocycle **1** is an exception which confirms this rule. Its thermodynamical stability is comparable to that of cyclohexane, which is the thermodynamically most stable species of all linear or cyclic alkanes.



3 (x=2)

In the case of oligo(ethylene oxide)s gauche transcombinations are thermodynamically more stable than the all-trans conformation. This characteristic property originates from unfavorable interactions between the lone electron pairs of O atoms and C−H σ-bonds in the β-position. The energy minimum of gauche conformations stabilizes in turn cycles (and entails low K values), so that spirocycles are favored over networks. Furthermore, spirocycles of structure **3** may be stabilized by intramolecular donor−acceptor interactions as indicated by the dotted arrows in formula **3** ($x = 2$). Intermolecular DA interaction networks may compete with the intramolecular ones. Yet, for reasons of entropy the intramolecular DA interactions in spirocycles should be stronger. In summary, the results obtained in this work and the above-presented interpretation perfectly agree with our ring−ring equilibration theory of TCPs and demonstrate that this theory is not only useful for a proper understanding of "linear polycondensations".

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