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Spirocycles as stable alternative of networks—polycondensations of oligoether diols with metal tetraalkoxides[☆]

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Abstract

Germanium, tin, titanium and zirconium tetraalkoxides were polycondensed with poly(ethylene glycol)s (PEGs) and poly(tetrahydrofuran) (PTHF) diols at temperatures between 100 and 200 °C. The lengths of the diols were varied from PEG-300 over PEG-400, PEG-600 and PEG-1000 to PEG-2000. In the case of PTHF diols number average molecular weights (M_ns) of 650, 1000 and 2000 were used. When $Ge(OEt)_4$ was polycondensed, all reaction products were soluble. In the case of $Sn(OtBu)_4$, all products obtained from diols with M_ns ≥ 600 Da were soluble, whereas a stiff gel was obtained from PEG-400. From $Ti(OnBu)_4$ and $Zr(OEt)_4$ soluble spirocycles were only obtained for diols with M_ns ≥ 1000, whereas the shorter diols yielded stiff networks. In the case of $Ti(OnBu)_4$ and PEG-1000, it was observed that at temperatures ≤ 120 °C initially a stiff gel was formed obviously by a kinetically controlled polycondensation. Upon heating to 140 °C this gel underwent an irreversible transformation into syrupy, soluble spirocycles due to equilibration of Ti–O–R bonds. The thermodynamic stability of the spirocycles is explained by strain-free rings and a gain in entropy. Preliminary experiments with the spirocycles of zirconium proved their usefulness as initiators for the ring-expansion polymerization of ε-caprolactone.

Keywords: Spirocycles; Poly(ethylene glycol)s; Polycondensation

1. Introduction

Step-growth polymerizations in general and polycondensations in particular may take two different courses: either a kinetically controlled one (KCP) or a thermodynamically controlled one (TCP). These different courses may result in different polymer structures (e.g. sequences, branching), different molecular weights and molecular weight distributions, but the classical theory of polycondensations as developed by Carothers [1] and Flory [2,3] did not differentiate between both scenarios. In 1950, Stockmayer and co-workers [4,5] modified this theory, demonstrating that in TCPs cycles may be formed by 'back-biting degradation'. Stockmayer did not want to jeopardize the principles of the Carothers–Flory theory; and calculated that for polycondensations in bulk around 97 wt% of the product obtained at 100% conversion will form one single giant chain (Fig. 2 in Ref. [4]). For a polycondensation performed in bulk with a monomer having a molecular weight of 100 Da the weight fraction of cycles was calculated by Flory to amount to 2.6% [p. 328 in chapter VIII, Ref. [3]]. Therefore, it is still accepted in all textbooks that according to the Carothers Eq. (1) a clean TCP (and KCP) running up to 100% conversion will yield one giant polymer chain with a few weight% of cyclic oligomers as byproducts of the 'back-biting equilibration'.

$$\overline{DP} = \frac{1}{1-p} \tag{1}$$

DP = degree of polymerization, p = conversion of functional groups.

Meanwhile the recent mathematical and experimental treatment of KCPs [6–12] has shown that cyclization can compete with propagation at any concentration and at any stage of the polycondensation process. In a clean KCP, cycles will be the only reaction products at 100% conversion, and the completion of cyclization limits the chain growth in contrast to the Carothers–Flory theory. This new concept of KCPs has also consequences for the proper understanding of TCPs. The formation of cycles by

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'back-biting' does not exclude the formation of cycles via intramolecular reaction of endgroups. The probability of cyclization will decrease with increasing chain lengths as calculated by Stockmayer [4] and others [6,7] but any step growth polymerization is a self-diluting system, and the concentration of active linear chains will decrease with the conversion (Eq. (2)), thereby favoring cyclizations. Furthermore, the molar ratio of cycles vs. linear chains (C/Lc ratio) will increase with higher conversions, because longer chains can form large cycles in addition to the smaller ones. Hence, it has recently been postulated [13] by the first author that also a clean TCP will exclusively yield cycles at 100% conversion, but in contrast to a KCP, all cycles are components of an equilibrium and their frequency distribution is different from that of cycles in a KCP.

$$[\mathrm{La}]_\mathrm{p} = [\mathrm{La}]_\mathrm{o}(1 - p) \tag{2}$$

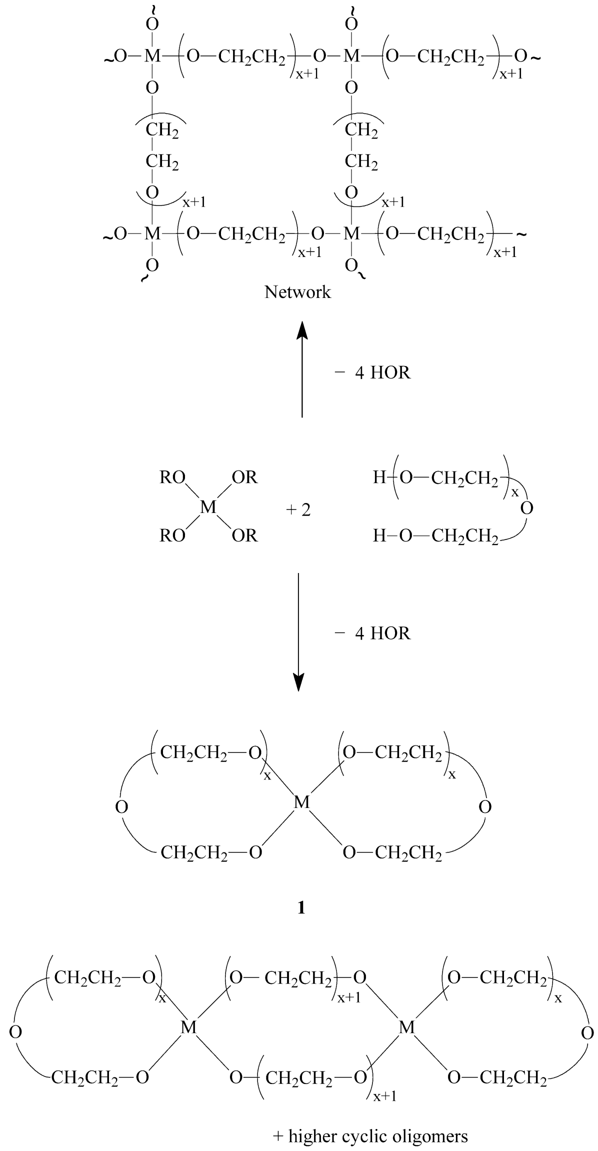
$[\mathrm{La}]_\mathrm{o}$, $[\mathrm{La}]_\mathrm{p}$: molar concentration of active linear chains and monomers at the beginning of the polycondensation and after a certain conversion *p*.

At high conversions (the exact conversion depends on the individual system), the number of cycles will exceed those of linear chains, and the thermodynamics of the entire process will then be dominated by the ring–ring equilibrium as schematically outlined in Eq. (3). The linear species with its active endgroups plays here the role of the catalyst. The equilibrium constant of these ring–ring equilibria will be decisive for the entire chain growth (in reality K_c of Eq. (4) is a sum of numerous slightly different constants). The formation of large cycles (and long chains) will be favored by ring-strain in the smaller cycles. This means K_c in Eq. (4) is high due to a negative reaction enthalpy for the formation of large cycles. However, when strain-free cycles can be formed, K_c may be small (e.g. <1) because the formation of many small cycles at the expense of a large one is favored by a gain in entropy.

$$C_\mathrm{x} + C_\mathrm{y} \overset{\mathrm{Cat}}{\rightleftharpoons} C_\mathrm{z} \tag{3}$$

$$K_\mathrm{c} = \frac{[\mathrm{C_z}]}{[\mathrm{C_x}][\mathrm{C_y}]} \tag{4}$$

The present work had the purpose to elucidate the consequences of the above consideration for the thermodynamically controlled polycondensation of tetrafunctional monomers. To the best of our knowledge, all previous theories of network formation [3,7,14–21] concern kinetically controlled polymerization and crosslinking processes. The role of ring–ring equilibria for the thermodynamical stability of networks has not been studied so far. In the present work, polycondensations of group IV metal alkoxides with oligoether diols should be studied (Eqs. (5) and (6)) to elucidate if reaction conditions favoring the formation of spirocycles (**1**) at the expense of networks can be found. At least from tin alkoxides it is known [22] that they can easily exchange alkoxide groups via donor–acceptor interactions (Eq. (7)). Therefore, a rapid equilibration between networks and spirocycles was expected for the polycondensations of tin alkoxides. Polyether diols were selected as reaction partners for two reasons. Firstly, numerous PEG and PTHF diols with broad variation of the molecular weights are commercial. Secondly, aliphatic ether groups favor *gauche* conformation in contrast to alkane chains, because the *n*-electrons of the O-atom interfere with the C–H bonds in the all-*trans* conformation, which is the energetically most favorable conformation of alkanes. Therefore, the formation of strain-free loops and cycles is far more likely for aliphatic ether chains than for alkane chains (the easy formation of crown ethers presents the direct experimental evidence). The chance to obtain thermodynamically stable spirocycles was thus higher in the case of polyether diols.



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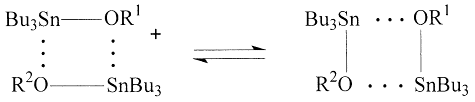
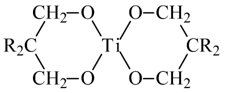
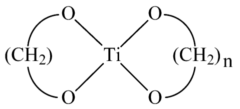


(7)

In this context it is interesting that Takekoshi and Pierce [23] obtained soluble spirocyclic titanates of structure **2** when 2,2-bis-alkyl 1,3-propane diols were used as reaction partners of $Ti(OR)_4$. However, soluble spirocycles of unsubstituted α,ω-alkane diols (**3**) were not described. Since geminal alkyl groups are known to stabilize cycles and cyclic conformations the afore-mentioned results [23] agree well with our hypothesis.



2, R = Alkyl



3, n = 2,3,4

2. Experimental

2.1. Materials

Poly(ethylene glycol)s, such as tetra(ethylene glycol), tetra EG, PEG-300, PEG-400, PEG-600, PEG-1000 or PEG-2000 and poly(tetrahydrofuran)diols, such as PTHF-650, PTHF-1000 and PTHF-2000 were purchased from Aldrich Co. (Milwaukee, WI, USA). All the oligoether diols (the figures indicate the number average molecular weights M_n) were dried azeotropically by addition and distillation of toluene. The rest of the toluene was removed at 50–60 °C in a vacuum of $< 10^{-1}$ mbar. Ge(OEt), $Sn(OtBu)_4$, $Ti(OnBu)_4$ and $Zr(OEt)_4$ were purchased from ABCR Chemicals and used as received. ε-Caprolactone was also purchased from Aldrich Co. and distilled over freshly powdered CaH_2 prior to use. Chlorobenzene, CH_2Cl_2, $CHCl_3$ and $CDCl_3$ were distilled over CaH_2, and toluene was distilled over sodium.

2.2. Polycondensations of $Ge(OEt)_4$

2.2.1. With PEG-600

PEG-600 (10 mmol) and $Ge(OEt)_4$ (5 mmol) were weighed under an atmosphere of dry nitrogen into a 100 ml round-bottom flask equipped with a gas-inlet tube. Dry chlorobenzene (2 ml) was added, the reaction vessel was closed with glass-stopper and steel-spring and thermostated in an oil-bath preheated to 120 °C. After 16 h the glass-stopper was replaced by a gas-outlet tube, and the temperature was raised to 140 °C for 7 h, whereby a slow stream of dry nitrogen was passed over the reaction mixture. Vacuum (10^{-2} mbar) was then applied for an additional 4 h, and finally a small sample was taken from the reaction mixture to test the solubility in $CHCl_3$ and chlorobenzene. After cooling, a ^1H NMR spectrum was recorded, displaying a strong singlet signal at 3.65 ppm.

Analogous polycondensations were performed with other PEGs, see Table 1.

Table 1
Polycondensations of $Ge(OEt)_4$ with various polyether diols

Exp. No.	Polyether diol	Further treatment and results	η_{inh}[a] (dl/g)
1	Tetra EG	Syrup at 140 °C	
2	PEG-300	Syrup at 140 °C	–
3	PEG-400	Syrup at 140 °C	–
4	PEG-600	Syrup at 140 °C	–
5	PEG-1000	Syrup at 140 °C	–
6	PEG-2000	Syrup at 140 °C	0.09
7	PTHF-650	Syrup at 140 °C	–
8	PTHF-1000	Syrup at 140 °C	–
9	PTHF-2000	Syrup at 140 °C	–

Standard procedure: 120 °C/16 h, 140 °C/3 h and 140 °C/4 h in vacuo.
[a] Measured at 20 °C with $c = 2$ g/l in CH_2Cl_2.

2.2.2. With PTHF-650

PTHF-650 (10 mmol) and $Ge(OEt)_4$ (5 mmol) were polycondensed as described above for PEG-600. The ^1H NMR spectrum recorded after cooling displayed two multiplets of equal intensity at 3.42 and 1.62 ppm.

The C- and H-elemental analyses of all soluble Ge-compounds agreed with the calculated values within the limits of ± 0.4%, mostly within the limits of ±0.3%.

2.3. Polycondensations of $Sn(OtBu)_4$

2.3.1. With PEG-1000

PEG-1000 (10 mmol) was dissolved in dry chlorobenzene (20 ml) in a 100 ml round-bottom flask containing a magnetic bar and equipped with a gas-inlet tube. This solution was cooled to 4–5 °C in a refrigerator. $Sn(OtBu)_4$ (5 mmol) was dissolved in dry chlorobenzene (10 ml) and again cooled to 4 °C and then rapidly added at once (with stirring under dry nitrogen) to the PEG-1000 solution. A gel formed within a few seconds. The reaction vessel was closed with a gas-outlet tube and placed in an oil-bath preheated to 120 °C. The chlorobenzene and the liberated *t*-butanol were removed with a slow stream of dry nitrogen over a period of 16 h. The temperature was then raised to 140 °C, and after 3 h vacuum (10^{-2} mbar) was applied for 4 h. Afterwards, a sample was removed from the hot reaction mixture to test the solubility. When the product proved to be insoluble, the temperature was raised to 160 °C for 16 h and the solubility was tested again. When still insoluble, the product was heated to 180 °C for 16 h and finally to 200 °C for 16 h. In the case of PEG-300 and PEG-400, the reaction mixture remained a stiff, insoluble gel even after heating to 200 °C (see Table 2).

2.3.2. With PTHF-1000

PTHF-1000 (10 mmol) and $Sn(OtBu)_4$ (5 mmol) were reacted in dry chlorobenzene as described for PEG-1000. After heating to 140 °C, most of the reaction product (approx. 90%) was soluble in $CHCl_3$ or chlorobenzene, but small gel particles were present which did not disappear

Table 2
Polycondensations of $Sn(OtBu)_4$ with various polyether diols

Exp. No.	Polyether diol	Further treatment and results	η_{inh}[a] (dl/g)
1	PEG-300	Stiff gel up to 200 °C	–
2	PEG-400	Stiff gel up to 200 °C	–
3	PEG-600	Gel up to 160 °C, syrup at 180 °C	0.06
4	PEG-1000	Gel up to 140 °C, syrup at 160 °C	0.07
5	PEG-2000	Syrup at 140 °C	0.13
6	PTHF-650	Gel up to 160 °C, syrup at 180 °C	–
7	PTHF-1000	Syrup at 140 °C	–
8	PTHF-2000	Syrup at 140 °C	–

Standard procedure: 120 °C/16 h, 140 °C/3 h and 140 °C/4 h in vacuo.

[a] Measured at 20 °C with $c = 2$ g/l in CH_2Cl_2.

even after heating to 160 °C for 16 h. A ^1H NMR spectrum proved the completeness of the conversion.

The C- and H-elemental analyses of all soluble Sn-compounds agreed with the calculated values within the limits of ±0.4%.

2.4. Polycondensation of Ti(OnBu)$_4$

2.4.1. With PEG-1000

PEG-1000 (10 mmol) and $Ti(OnBu)_4$ (5 mmol) were weighed under dry nitrogen into a 100 ml round-bottom flask containing a magnetic bar and equipped with a gas-inlet tube. Dry chlorobenzene (5 ml) was added, the reaction vessel was closed with a gas-outlet tube and placed into an oil bath preheated to 120 °C. The chlorobenzene and the liberated *n*-butanol were removed with a slow stream of nitrogen. After 16 h the resulting stiff gel was heated to 140 °C for 3 h. A vacuum of 10^{-2} mbar was then applied for 4 h. A small sample was taken which proved that the product was still insoluble. However, after 16 h at 160 °C the product had turned into a syrup which was completely soluble in $CHCl_3$ and warm chlorobenzene. The inherent viscosity measured at 20 °C with $c = 2$ g/l in CH_2Cl_2 was 0.06 dl/g.

When PEG-300, PEG-400 or PEG-600 were reacted in the same way, the reaction products remained insoluble stiff gels even after heating to 180 °C for 16 h and to 200 °C for 16 h. In the case of PEG-2000, the product was a soluble syrup after heating to 140 °C.

2.4.2. With PTHF-2000

PTHF-2000 (5 mmol and $Ti(OnBu)_4$ (2.5 mmol) and chlorobenzene (2.5 ml) were weighed under dry nitrogen into a 100 ml round-bottom flask and heated as described above for PEG. The syrupy reaction mixture was completely soluble after heating to 140 °C (7 h). $\eta_{inh} = 0.16$ dl/g in CH_2Cl_2 at 20 °C. The ^1H NMR spectrum ($CDCl_3$/TMS) displayed two multiplets at 3.42 and 1.62 ppm.

With PTHF-1000, most of the reaction product was soluble after heating to 140 °C, but a few gel particles were present. With PTHF-650, most of the product remained an insoluble gel even after heating to 160, 180 and 200 °C.

The C- and H-elemental analyses of all soluble Ti-compounds agreed with the calculated values within the limits of ±0.4%, mostly within the limits of ±0.3%.

2.5. Polycondensations of Zr(OEt)$_4$

2.5.1. With PEG-1000

PEG-1000 (10 mmol), $Zr(OEt)_4$ (5 mmol) and dry chlorobenzene (5 ml) were weighed into a 50 ml glass reactor equipped with flat-blade stirrer and with gas-outlet tube. The polycondensation was conducted at 120 °C (16 h) and 140 °C (7 h) as described for $Ge(OEt)_4$. The product was syrup which was completely soluble in CH_2Cl_2 and $CDCl_3$. The ^1H NMR spectrum proved a complete conversion. The inherent viscosity measured at 20 °C in CH_2Cl_2 was 0.08 dl/g. The product obtained from PEG-600 or PEG-300 remained insoluble stiff gels even after heating to 160, 180 and 200 °C.

2.5.2. With PTHF-1000

PTHF-1000 (10 mmol), $Zr(OEt)_4$ (5 mmol) and chlorobenzene (5 ml) were polycondensed as described above. After heating to 120 °C (16 h) and 140 °C (7 h), the product was a syrup completely soluble in CH_2Cl_2, $CHCl_3$, chlorobenzene and tetrahydrofuran. The product obtained with PTHF-650 was a stiff gel which remained insoluble after heating to 160, 180 and 200 °C.

The C- and H-elemental analyses of all soluble Zr-compounds agreed with the calculated values within the limits of ±0.4%, mostly within the limits of ±0.3%.

2.6. Measurements

The inherent viscosities were measured at a concentration of 2 g/l in CH_2Cl_2 using an automated Ubbelohde viscometer thermostated at 20 °C. The viscometer and the capillary were silanized with a solution of Me_2SiCl_2 in dry diethyl ether. The 400 MHz ^1H NMR spectra were recorded on a Bruker 'Avance 400' FT spectrometer. $CDCl_3$ dried over P_4O_{10} was used as solvent with TMS as internal shift reference. The SEC measurements were conducted on a home-made SEC apparatus at 25 °C with tetrahydrofuran as eluent. A combination of three PSS-SDV mixed-bed columns was used along with a RT detector. For the calibration see footnote 'd' of Table 6.

3. Results and discussion

3.1. Polycondensations of Ge(OEt)$_4$

From reactions of $Ge(OEt)_4$ with α-ω-dihydroxyalkanes it was known [24,25] that this exchange reaction is sluggish and requires temperatures above 120 °C. Depending on the structure of the diol, temperatures ≥150 °C and long reaction times are needed to achieve an almost complete conversion. In this work $Ge(OEt)_4$ was mixed with Tetra EG or poly(ethylene glycol)s and with a small amount of chlorobenzene at 20 °C and heated to 120 °C for 16 h. ^1H NMR spectra recorded at this time displayed the signals of ethanol (3.65 and 1.20 ppm) and GeOEt groups (3.98 and 1.28 ppm) in addition to the strong signal of the PEGs (3.65 ppm). The temperature was then raised to 140 °C and most of the volatile products were removed with a slow stream of dry nitrogen. After 3 h, vacuum was applied for 4 h. All products obtained from the PEGs listed in Table 1 had a syrupy character and were completely soluble in CH_2Cl_2, $CHCl_3$ and in warm chlorobenzene. When ^1H NMR spectra of these products were recorded, no signals of ethanol or GeOEt groups were detectable anymore. Although the viscometer was silanized with Me_2SiCl_2 and the solutions of reaction products were handled under dry nitrogen, only one successful viscosity measurement was obtained (Table 1). In all other cases, a turbidity (most likely GeO_2) appeared during the measurements. With PTHF-650, PTHF-1000 and PTHF-2000 again completely soluble reaction products were obtained. The C- and H-elemental analyses agreed with the calculated values within the limits of ±0.4%. In the case of $Ge(Tetra\ EG)_2$ a ^1H NMR spectrum with rather sharp signals was obtained which displays characteristic changes relative to the spectrum of neat Tetra EG proving the binding to Ge (Fig. 1).

3.2. Polycondensation of $Sn(OtBu)_4$

When neat $Sn(OtBu)_4$ or its solution in chlorobenzene was mixed with PEG solutions in chlorobenzene or CH_2Cl_2. At 20 °C or higher temperatures, a gel was formed immediately, so that no homogeneous reaction mixture could be achieved. Therefore, the solutions of both reactants were precooled to 4 °C and mixed at once, whereby a homogeneous solution was obtained although a gel formed within a few seconds. This mixture was heated to 120 °C for 16 h under a slow stream of nitrogen which removed most of the chlorobenzene and of the liberated tert. butanol. After heating to 140 °C (3 h without and 4 h with vacuum), syrupy products completely soluble in CH_2Cl_2, $CHCl_3$ and chlorobenzene were obtained when PEG-600, PEG-1000 and PEG-2000 were used as starting materials. In contrast, PEG-300 and PEG-400 yielded stiff gels which remained insoluble after stepwise heating to 160, 180 and 200 °C.

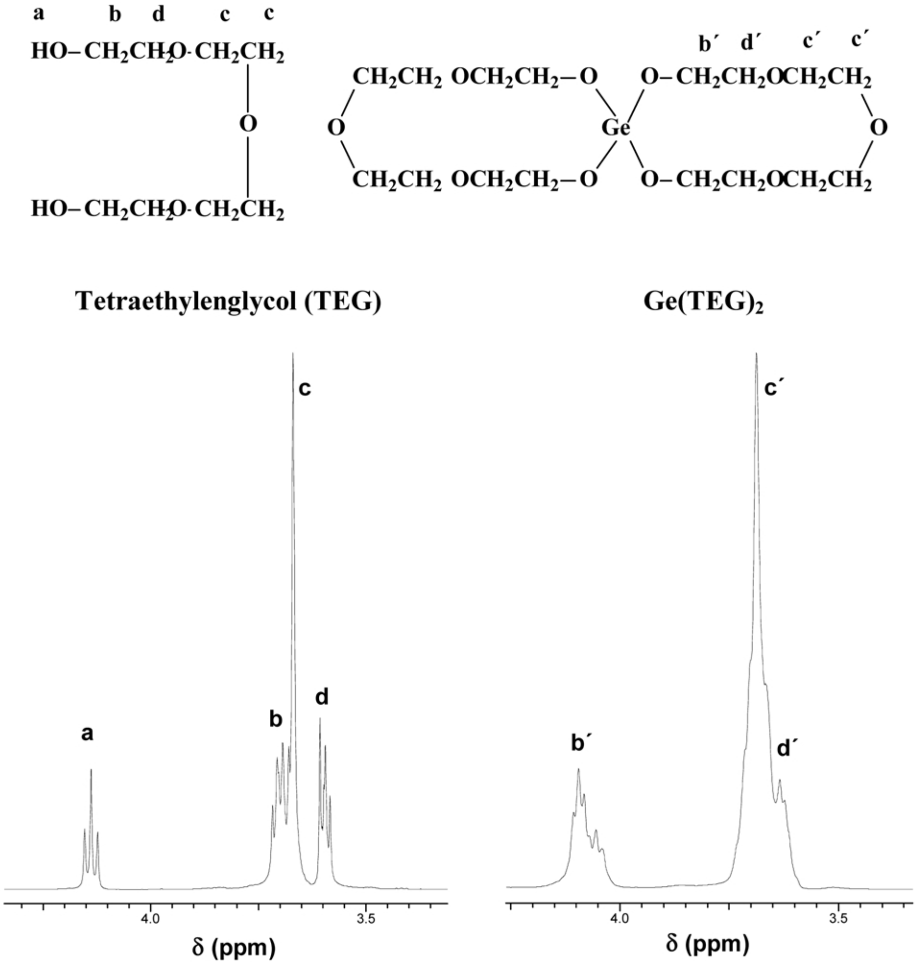


Fig. 1. 400 MHz ^1H NMR spectra recorded in $CDCl_3$: (A) neat tetra(ethylene glycol), (B) spirocyclic $Ge(tetra\ EG)_2$.

Table 3
Polycondensations of $Ti(OnBu)_4$ with various polyether diols

Exp. No.	Polyether diol	Further treatment and results	$\eta_{inh}{}^{a}$ (dl/g)
1	Tetraethylene glycol	Stiff gel stable up to 200 °C	–
2	PEG-300	Stiff gel stable up to 200 °C	–
3	PEG-600	Stiff gel stable up to 200 °C	–
4	PEG-1000	Gel up to 140 °C, syrup at 160 °C	0.06
5	PEG-2000	Gel up to 140 °C, syrup at 160 °C	0.10
6	PTHF-650	Stiff gel stable up to 200 °C	–
7	PTHF-1000	Syrup at 140 °C	–
8	PTHF-2000	Syrup at 140 °C	0.16
9	Polysiloxane diol-1000	Syrup at 140 °C	0.17

Standard reaction conditions: 120 °C/16 h, 140 °C/3 h + 140 °C/4 h in vacuo.

[a] Measured at 20 °C with $c = 2$ g/l in CH_2Cl_2.

However, syrupy soluble products were again obtained from all three PTHF samples (Table 2). These results demonstrate that in the case of tin the formation of meltable and soluble spirocycles requires polyetherdiols with M_ns > 400 Da. The viscosity measurements clearly indicate that the molecular weights of the condensation products were only slightly higher than those of the acetylated polyether diols (Table 5). Therefore, these measurements support the assumption that cyclic reaction products were formed.

3.3. Polycondensation of $Ti(OnBu)_4$

The polycondensation of $Ti(OnBu)_4$ with various PEGs and PTHF diols (Table 3) were conducted like those of $Ge(OEt)_4$. However, from PEG-300, PEG-600 and PTHF-650 stiff gels were obtained at 140 °C which remained stiff and insoluble after stepwise heating to 160, 180 and 200 °C. The products resulting from PEG-2000 and PTHF-1000 or 2000 were syrupy and soluble after heating to 140 °C. An interesting observation was made when PEG-1000 was polycondensed at 120 and 140 °C. The product was an insoluble gel, but upon heating to 160 °C for 16 h, it turned into a syrupy soluble product, and this change was irreversible. Upon standing at room temperature for 4 weeks, this product was still completely soluble in CH_2Cl_2 or $CHCl_3$. The inherent viscosities confirmed that the molecular weights of the condensation products were not much higher than those of the starting materials (Table 3).

3.4. Polycondensation of $Zr(OEt)_4$

The polycondensations of $Zr(OEt)_4$ with various PEGs and PTHF diols (Table 4) were performed like those of $Ge(OEt)_4$. The results were somewhat different, because with PEG-300 and PEG-600, stiff gels were obtained at 140 °C which after stepwise heating to 160, 180 and 200 °C remained stable. A stiff gel stable up to 200 °C was also obtained from PTHF-650. With the longer PEGs and PTHF diols initially gels were formed up to 120 °C which turned into soluble syrups after heating at 140 °C. The viscosity measurements confirmed again the low molecular character of the soluble reaction products. Therefore, these results largely agree with those resulting from polycondensations of $Ti(OnBu)_4$.

3.5. Polymerizations of ε-caprolactone (ε-CL)

It is difficult to identify metal–oxygen bonds formed in the above discussed condensations directly, because their sensitivity to hydrolysis and alcoholysis prevents a successful application of mass spectroscopic methods,

Table 4
Polycondensations of $Zr(OEt)_4$ with various polyether diols

Exp. No.	Polyether diol	Further treatment and results	$\eta_{inh}{}^{a}$ (dl/g)
1	Tetra EG	Stiff gel up to 200 °C	–
2	PEG-300	Stiff gel up to 200 °C	–
3	PEG-600	Stiff gel up to 200 °C	–
4	PEG-1000	Gel up to 120 °C, syrup at 140 °C	0.07
5	PEG-2000	Gel up to 120 °C, syrup at 140 °C	0.10
6	PTHF-650	Stiff gel up to 200 °C	–
7	PTHF-1000	Syrup at 140 °C	–
8	PTHF-2000	Syrup at 140 °C	0.16
9	Polysiloxane diol-1000	Syrup at 140 °C	0.10

Standard procedure: 120 °C/16 h, 140 °C/3 h and 140 °C/4 h in vacuo.

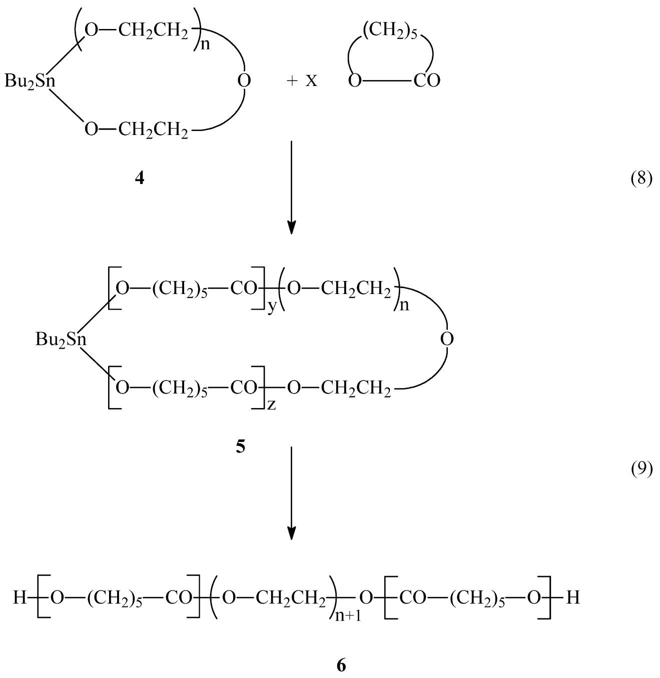
[a] Measured at 20 °C with $c = 2$ g/l in CH_2Cl_2.

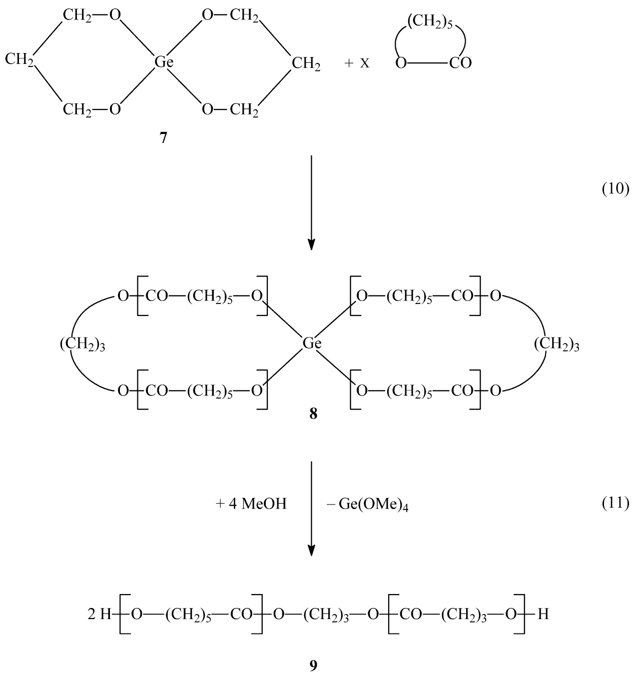
Table 5
Viscosities of the acetylated diols

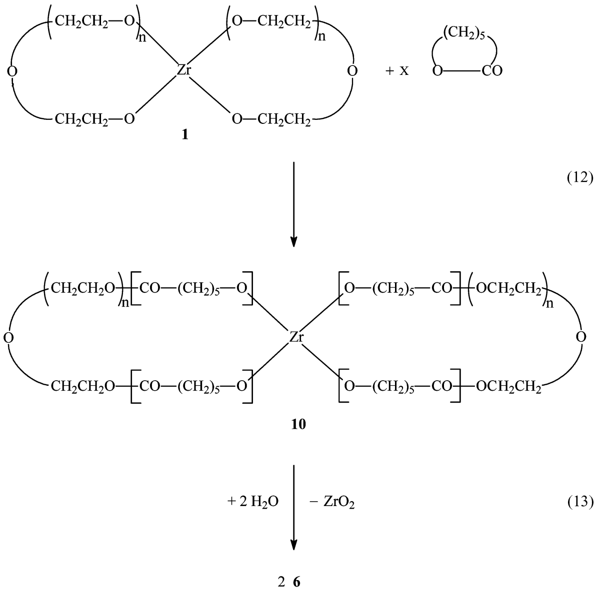
Diol	η_{inh}
PEG-300-Ac	0.03
PEG-400-Ac	0.03
PEG-600-Ac	0.04
PEG-1000-Ac	0.05
PEG-2000-Ac	0.09
PTHF-650-Ac	0.06
PTHF-1000-Ac	0.09
PTHF-2000-Ac	0.15
Polysiloxane-1000-Ac	0.07

Acetic anhydride was used for acetylation.

such as FAB or MALDI-TOF. Therefore, attempts were made to prove their formation indirectly via their reactivity. It was demonstrated in numerous experiments that $Bu_2Sn(OMe)_2$ reacts with PEGs (or other diols) by formation of macrocycles **4** which due to their reactive Sn–O bonds can initiate the ring-expansion polymerization of lactones (Eq. (8)). The reactive cyclic triblock copolymers **5** were transformed into linear A–B–A triblock copolymers **6** (Eq. (9)) or into other architectures. Analogously, the spirocycle **7** was prepared from $Ge(OEt)_4$ and 1,3-propane diol and used as initiator of ε-caprolactone (ε-CL, Eq. (10)). The linear polylactones **9**, isolated after hydrolysis of the Ge–O bonds in **8** (Eq. (11)) were characterized by viscosities, ^1H NMR spectroscopy and MALDI-TOF mass spectrometry [25]. Furthermore, the Ge-PEG-spirocycles of structure **1** (prepared in our laboratory) were successfully used by Albertsson et al. [26] for syntheses of A–B–A triblock copolymers derived from L-lactide. Analogous triblock- and multiblock-copolymers were prepared from Ge-PEG spirocycles and ε-CL in a future publication [27].







In order to complement the numerous results obtained from Ge-PEG spirocycles with polymerizations initiated by another metal the spirocycles derived from $Zr(OEt)_4$ and PEG-2000 were used as initiators in this work. It was found that it initiated the ring-expansion polymerization of ε-CL at 80 °C (yielding the cyclic block-copolymer **10**), so that after 24 h a conversion above 90% was achieved as monitored by ^1H NMR spectroscopy of the reaction mixture (Eq. (12)). The inherent viscosities and SEC measurements of the isolated A–B–A triblock copolymers Eq. (13) and (structure **6**) confirmed the expected chain growth (Table 6).

Table 6
Polymerization of ε-caprolactone initiated with Zr (PEG-2000)$_2$ at 80 °C in bulk

Exp. No.	Mon/In[a]	Calculated average block length	Time (h)	Yield (%)	η_{inh}[b] (dl/g)	M_n[c] (theor.)	M_n[d] (SEC)	M_w/Mn[b]
1	200/1	50	8	65	0.40	13,400	13,000	1.5
2	200/1	50	24	68	0.46	13,400	14,000	1.5
3	200/1	50	48	60	0.45	13,400	14,000	1.5
4	400/1	100	8	89	0.60	24,800	23,000	1.6
5	400/1	100	24	86	0.62	24,800	24,000	1.6
6	400/1	100	48	86	0.62	24,800	24,000	1.6

[a] Molar ε-CL/Zr (PEG-2000)$_2$ ratio.

[b] Measured at 20 °C with $c = 2$ g/l in CH_2Cl_2.

[c] Calculated from the Mon/In-ratio for 100% conversion.

[d] From SEC measurements in THF calibrated with the M.H. equation $[\eta] = 1.395 \times 10^{-4} \times M^{0.786}$ [31].

The ^{1}H NMR spectra also proved the covalent connection between lactone and PEG blocks, as exemplarily shown in Fig. 2 (signals y and z). It is typical for the acylation of the $HO-CH_2$ endgroup of PEGs that acylation causes a downfield shift of 0.6 ppm (from 3.7 to 4.3 ppm). The yields of the precipitated triblock copolymers were relatively low, because the conversions of ε-CL were not quantitative and because fractions of high PEG/ε-CL ratios remained soluble in methanol.

Finally, it is noteworthy that neat PEGs, when heated with ε-CL to 80 °C for 24 or 48 h, did not initiate any polymerization. Therefore, all results obtained with Zr (PEG-2000)$_2$ support the conclusion that spirocycles were formed capable of initiating the polymerization of ε-CL quite analogous to the 'Sn-cycles' and the 'Ge-spirocycle' (**7**).

4. Conclusion

The condensations of tetravalent metal alkoxides with various poly(ethylene glycol)s or poly(tetrahydrofuran) diols suggest the following interpretation. Two types of product were obtained, depending on the metal and on the lengths of the polyether diols: either stiff gels which were stable up to 200 °C or syrupy soluble mixtures of spirocycles. It is not clear at this time why the condensation products of all PEG diols with $Ge(OEt)_4$ are soluble, whereas the condensation products of short PEG diols with Ti, Zr and Sn tetraalkoxides are insoluble. In this connection the following observations indicate that cycles based on Ge do not have the same structure property relationships as analogous cycles of other group IV metals. In the case of cyclic Ge alkylene oxides the six-membered cycles are the thermodynamically most stable [24,32], but the seven-membered rings in the case of tin [33,34]. Furthermore, when gels were obtained by heating of PEG-1000 with Ti $(OBu)_4$ or $Zn(OEt)_4$ up to 120 °C, further heating to 140 °C caused irreversible transformation into soluble syrupy spirocycles. Obviously, the initial formation of gels is a consequence of a kinetically controlled polycondensation process, and the further heating completes the equilibration yielding the thermodynamically more stable spirocycles. Regardless of these differences, the overriding tendency of all these polycondensations is the preferential formation of soluble products from longer polyether diols.

In this context, it should be mentioned that thermodynamically controlled formation of spirocycles at the expense of networks has recently been observed for a completely different reaction pathway [28–30]. When ethoxylated pentaerythritols (**11**, commercial) were condensed with $Bu_2Sn(OMe)_2$ with quantitative elimination of methanol, soluble spirocycles of structure **12** were obtained

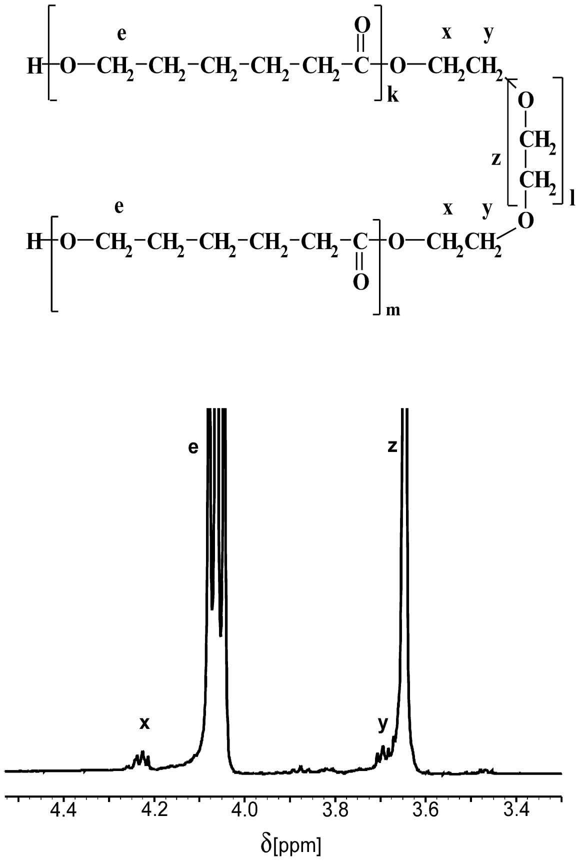
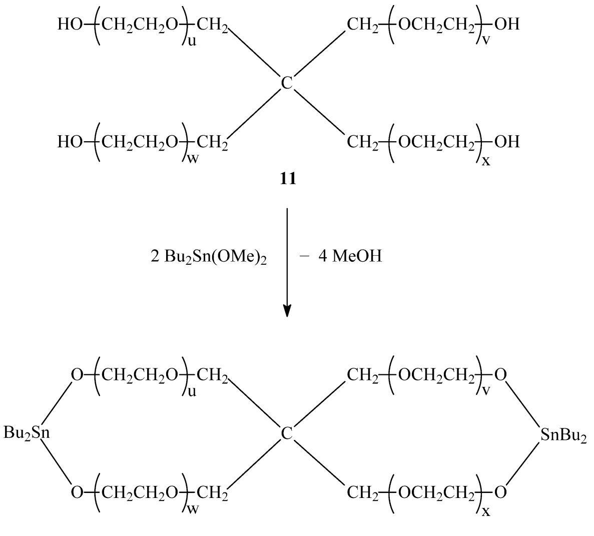


Fig. 2. 400 MHz ^{1}H NMR spectrum of the A–B–A triblock copolymer prepared from Zr(PEG-2000)$_2$ and ε-caprolactone (no. 2, Table 6).

without any appreciable formation of gel particles (Eq. (14)). These spirocycles were isolated in a pure form with correct elemental analyses. Furthermore, polycondensations of either the free pentaerythritols or of the stannylenated species **12** with dicarboxylic acid dichlorides yielded networks via kinetically controlled polycondensations. All these results support the argumentations and interpretations presented in this work.



12

(14)

The thermodynamically controlled formation of spirocycles of structure **1** or **12** is not only of interest for the theory of polycondensation and network synthesis. The resulting soluble spirocycles (both **1** and **12**) are useful initiators of ring-expansion polymerizations of lactones and lactides, whereby A–B–A triblock copolymers, star-shaped polylactones and biodegradable networks can be prepared in a one-pot procedure [26–30].

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