New Polymer Syntheses. 100. Multiblock Copolyesters by Combined Macrocyclic Polymerization and Silicon-Mediated Polycondensation

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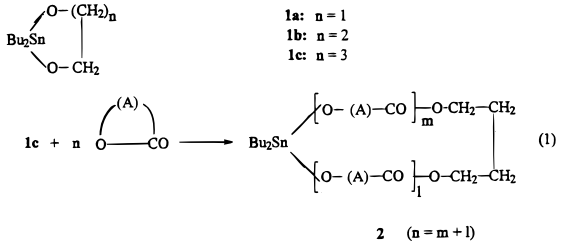
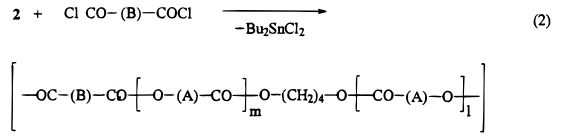
ABSTRACT: Using 2,2-dibutyl-2-stanna-1,3-dioxepane (DSDOP) as cyclic initiator the macrocyclic polymerizations of ϵ-caprolactone were conducted in bulk at 80 °C at monomer/initiator ratios of 20/1. The resulting tin-containing supermacrocycles were reacted in situ with an excess of isophthaloyl chloride, and this reaction mixture was polycondensed with silylated Bisphenol A at temperatures between 150 and 300 °C. The characterization of the isolated copolyesters by DSC measurements and ^{1}H NMR and ^{13}C NMR spectroscopy proved that they possess a perfect multiblock structure up to a reaction temperature of 240 °C. At higher temperatures transesterification causes a more or less perfect randomization of the sequence. In a second series of combined ring-opening polymerizations and ring-opening polycondensations (ROPPOC) silylated methylhydroquinone and 1,10-bis(4-chlorophenoxy)decane were used as comonomers of the macrocyclic poly(ϵ-caprolactone). The isolated multiblock copolyesters showed a two phasic melt with an isotropic phase containing the polylactone blocks and a nematic phase consisting of the aromatic blocks. The relationship between block lengths and phase separation is discussed.

Introduction

It has been demonstrated in several recent publications [1−5] that cyclic tin compounds of structure **1** allow a ring-opening polymerization of lactones with insertion into both Sn−O bonds (eq 1). These so-called macrocyclic



polymerizations were conducted in bulk at temperatures ≥50 °C and allow the preparation of macrocyclic polylactones with conversions close to 100%. When a monomeric cyclic initiator such as **1c** is used, these macrocyclic polymerizations obey largely the "living pattern", so that the number-average molecular weights (M_n's) can be controlled by the monomer/initiator (M/I) ratio.[5] Furthermore, it was demonstrated that the tin-containing macrocycles (**2**) can be used as difunctional macromers in step growth polymerizations using dicarboxylic acid dichlorides as reaction partners (eq 2).[6]



On the other hand we have shown over the past two decades[7] that silylated difunctional compounds as aliphatic diols, diphenols, hydroxy acids, etc. are useful monomers for the syntheses of polyesters, polyethers, and polyanhydrides. These polycondensation reactions proceed in the presence of a suitable catalyst such as chloride or fluoride ions with elimination of chloro- or fluorotrimethylsilane (e.g., eq 3). It is a particular

advantage of these polycondensations that no strong acid or base is liberated or needed as catalyst, and all byproducts are highly volatile and easy to remove. In this connection it was the purpose of the present work to find out, if the tin-initiated macrocyclic polymerizations and the silicon-promoted polycondensations can be combined in an "one-pot procedure" yielding multiblock copolyesters.

Experimental Section

Materials. Bisphenol A, Bisphenol P, and 4-hydroxybenzoic acid were gifts of Bayer AG (Leverkusen, Federal Republic of Germany) and used as received. 1,10-Dibromodecane, ϵ-caprolactone, dibutyltin dimethoxide, and isophthaloyl chloride were purchased from Aldrich Co. (Milwaukee, WI). Hexamethyldisilazane was a gift of Dynamite Nobel AG (Troisdorf, Federal Republic of Germany). The diphenols were silylated with an excess of hexamethyldisilazane in refluxing toluene and isolated by distillation in vacuo.[8,9] 2,2-Dibutyl-2-stanna-1,3-dioxepane (DSDOP) was prepared from dibutyltin dimethoxide and dry 1,4-butanediol as described previously.[5] Also 1,10-bis(4-(chloroformyl)phenoxy)decane (mp 84−86 °C) was prepared from 4-hydroxybenzoic acid and 1,10-dibromodecane as reported previously.[10,11] The ϵ-caprolactone was distilled (in vacuo) over freshly powdered calcium hydride prior to use.

Macrocyclic Polymerizations. ϵ-Caprolactone (30 mmol) and DSDOP (1,5 mmol) were weighed into a cylindrical glass reactor having silanized glass walls and equipped with a mechanical stirrer and gas inlet and outlet tubes. The reaction vessel was placed in an oil bath thermostated at 80 °C. After 1 h ^{1}H NMR spectra indicated an almost complete conversion of the ϵ-caprolactone. The inherent viscosity (measured in CH_2Cl_2 at 25 °C) of the crude reaction product was 0.14−0.15 dL/g. Analogous polymerizations were conducted with M/I ratios of 10 or 50 (see Table 2).

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Table 1. Reaction Conditions and Results of Combined Macrocyclic Polymerizations of ϵ-CL (M/I = 20) and Copolycondensations with Isophthaloyl Chloride and Silylated Bisphenol A

polym no.	η_{inh}[a] (dL/g)	M_w/M_n[b]	T[c] (°C)	yield (%)	η_{inh}[d] (dL/g)	T_{m1}[e] (°C)	T_{m2}[e] (°C)	elem form. (form. wt)	elem anal.	C	H
3a	0.15	1.50	150	72	0.35	50	276	$C_{247}H_{302}O_{64}$ (4295)	calcd	69.07	7.09
									found	69.38	7.15
3b	0.14	1.50	180	92	0.45	48	275	$C_{247}H_{302}O_{64}$ (4295)	calcd	69.07	7.09
									found	69.21	7.19
3c	0.14	1.53	210	90	0.46	47	275	$C_{247}H_{302}O_{64}$ (4295)	calcd	69.07	7.09
									found	69.12	7.18
3d	0.15	1.50	240	86	0.50	40	272	$C_{247}H_{302}O_{64}$ (4295)	calcd	69.07	7.09
									found	69.53	7.22
3e	0.15	1.45	270	87	0.53	43	267	$C_{247}H_{302}O_{64}$ (4295)	calcd	69.07	7.09
									found	69.64	7.20

[a] Determined for the poly(ϵ-CL) of DP = 20 at 25 °C with $c = 2$ g/L in CH_2Cl_2. [b] Polydispersities of the poly(ϵ-CL) measured by SEC in tetrahydrofuran and calibrated with $[\eta] = 1.395 \times 10^{-4} M^{0.786}$.[14] [c] Temperature of the polycondensation maintained for a period of 4 h. [d] Determined for the multiblock copolyester at 25 °C with $c = 2$ g/L in CH_2Cl_2/trifluroacetic acid (volume ratio 4:1). [e] Melting endotherm in the DSC heating curves recorded with 20 °C/min.

Table 2. Reaction Conditions and Results of Combined Polymerizations of ϵ-CL[a] and by Copolycondensations[b] with Silylated Methylhydroquinone and 1,10-(4-(Chloroformyl)phenyl)decane

polym no.	Mon/Init[c]	η_{inh}[d] (dL/g)	M_n[e] (theor)	M_w/M_n[f]	feed ratio[g] A:B:C	yield (%)	η_{inh}[h] (dL/g)	elem form. (form. wt)	elem anal.	C	H
5a	10/1	0.11	1500	1.50	1:5:6	98	0.50	$C_{243}H_{356}O_{56}$ (4123)	calcd	70.79	8.70
									found	70.98	8.81
5b	10/1	0.11	1500	1.55	1:10:11	95	0.62	$C_{398}H_{476}O_{86}$ (6636)	calcd	72.04	7.23
									found	71.97	7.21
5c	20/1	0.14	2600	1.50	1:5:6	98	0.60	$C_{303}H_{406}H_{76}$ (5264)	calcd	69.13	7.77
									found	69.63	7.92
5d	20/1	0.15	2600	1.55	1:10:11	93	0.67	$C_{458}H_{576}O_{106}$ (7777)	calcd	70.73	7.46
									found	70.61	7.41
5e	50/1	0.25	6000	1.55	1:5:6	92	0.58	$C_{483}H_{706}O_{136}$ (8689)	calcd	66.77	8.19
									found	66.95	8.27
5f	50/1	0.24	6000	1.50	1:10:11	92	0.60	$C_{638}H_{876}O_{166}$ (11202)	calcd	68.41	7.88
									found	68.44	8.05

[a] Performed at 80 °C/2 h. [b] Conducted at 230 °C/4 h. [c] Molar feed ratio of ϵ-CL and DSDOP. [d] Determined for the macrocyclic poly(ϵ-CL) at 25 °C with $c = 2$ g/L in CH2Cl2. [e] Number average molecular weights of the macrocyclic poly(ϵ-CL) calculated from the M/I ratio with 100% conversion (including the initiator fragments). [f] Polydispersities of the macrocyclic poly(ϵ-CL) measured by GPC in tetrahydrofuran and calibrated with $[\eta] = 1.395 \times 10^{-4} M^{0.786}$.[14] [g] Molar feed ratios used for the copolycondensations: A = macrocyclic poly(ϵCL), B = silylated methylhydroquinone, C = dicarboxylic acid dichloride. [h] Determined for the multiblock copolyester at 25 °C with $c = 2$ g/L in CH_2Cl_2/trifluoroacetic acid (volume ratio 4:1).

Polycondensations. (A) With Silylated Bisphenol A. Isophthaloyl chloride (9 mmol) was added to the macrocyclic poly(ϵ-caprolactone) prepared with M/I = 20 (as described above), and this mixture was stirred for 1 h at 80 °C. Bis-(trimethylsilyl)bisphenol A (7.5 mmol) and 10 mg of benzyltriethylammonium chloride were then added, and the reaction vessel was placed in an oil bath preheated to 150 °C. Then the reaction temperature was constantly raised to the desired value (see Table 1). The reaction mixture was stirred until solidification occurred and was kept at 150 °C for 4 h. The liberated chlorotrimethylsilane was removed with a slow stream of nitrogen. Finally, vacuum was applied for 0.5 h. After cooling, the reaction product was dissolved in CH_2Cl_2/trifluoroacetic acid (TFA volume ratio 4:1), precipitated into cold methanol and dried at 60 °C in vacuo.

(B) With Silylated Bisphenol P. One polycondensation was conducted using bis(trimethylsilyl)bisphenol P at 240 °C and stopped after 4 h. The resulting copolyester (structure **4**) was isolated in a yield of 97% having an inherent viscosity 0.33 dL/g in CH_2Cl_2/TFA (4:1 by volume). A second analogous polycondensation was stopped after 8 h, and a yield of 93% and a inherent viscosity of 0.50 dL/g were obtained. The ^{1}H NMR and ^{13}C NMR spectra were quite similar to those displayed in Figures 1 and 2 for the multiblock copolyesters of Bisphenol A (no transesterification after 4 h).

(C) With Silylated Methylhydroquinone. ϵ-CL (20 mmol) was polymerized with DSDOP (1 mmol) as described above, and 1,10-bis(4-(chloroformyl)phenoxy)decane (6 or 11 mmol) was added. After stirring for 1 h at 80 °C bis-(trimethylsilyl)methylhydroquinone (5 or 10 mmol) was added together with benzyltrimethylammonium chloride (10 mg). The polycondensation was then continued for 4 h at 230 °C (+0.5 h with vacuum).

All other copolycondensations listed in Table 2 were conducted analogously.

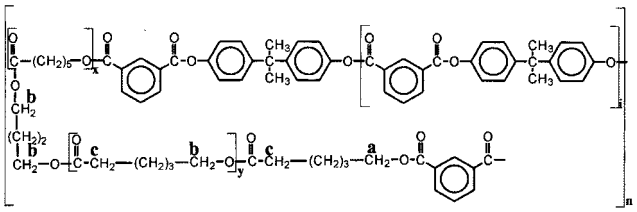
Measurements. The inherent viscosities were measured in an Ubbelohde viscosimeter thermostated at 25 °C. Neat CH_2Cl_2 was used for poly(ϵ-CL) and CH_2Cl_2/TFA mixtures (volume ratio 4:1) for the multiblock copolymers.

The DSC measurements were conducted with a Perkin-Elmer DSC-7 in aluminum pans under nitrogen using a heating rate of 20 °C/min.

The 100 MHz ^{1}H NMR spectra were recorded with a Bruker AC-100 FT NMR spetrometer in 5 mm o.d. sample tubes. The 25.2 MHz ^{13}C NMR spectra were recorded with the same instrument using 10 mm o.d. sample tubes. TMS served as the internal standard for all measurements. All NMR spectra of block copolyesters were recorded in $CDCl_3$/TFA (volume ratio 4:1) containing TMS for shift referencing.

Results and Discussion

Isotropic Copolyesters. The first series of combined macrocyclic polymerizations and polycondensations was designed to serve two purposes. First, it should be determined if a satisfactory copolycondensation of tin-containing poly(ϵ-caprolactone)s (poly(ϵ-CL) and silylated diphenols is possible at all. Second, the maximum reaction temperature should be determined, which allows the synthesis of multiblock copolyesters without a significant influence of transesterification



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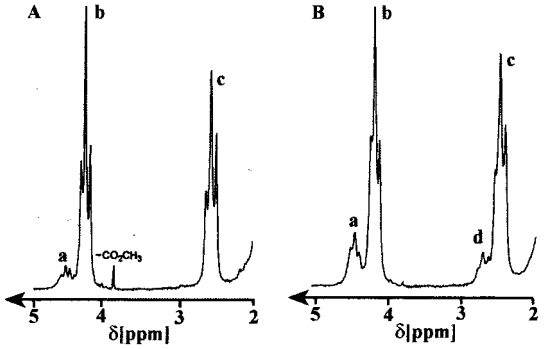
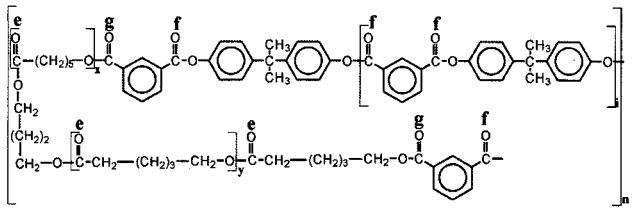


Figure 1. 100 MHz ^{1}H NMR spectra (recorded in $CDCl_3$/TFA, 4:1 by volume) of (A) copolyester **3c** (Table 1) and (B) copolyester **3e** (Table 1).



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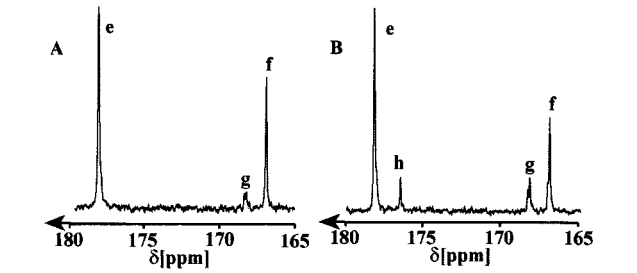
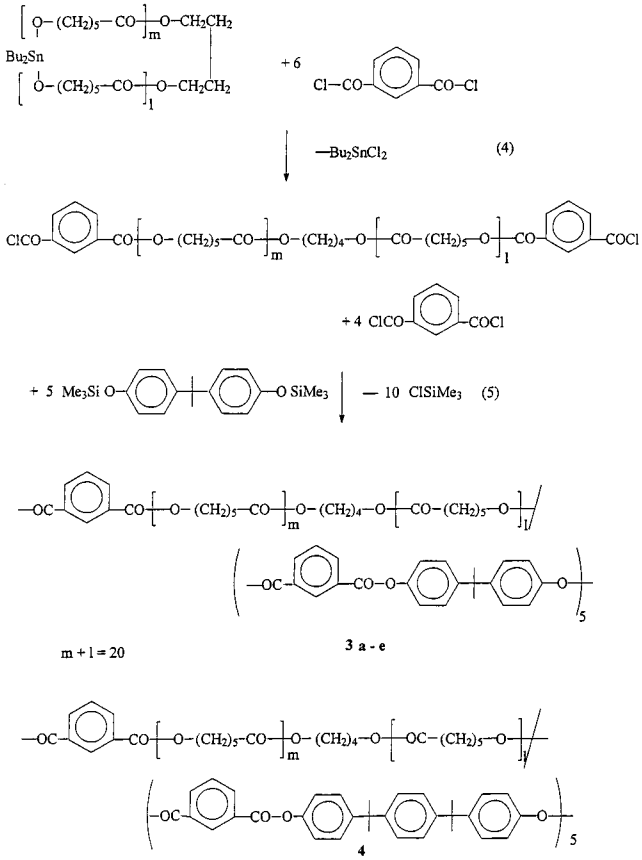


Figure 2. 25.2 MHz ^{13}C NMR spectrum (CO signals) recorded in $CDCl_3$/TFA 4:1 by volume of (A) copolyester **3c** (Table 1) and (B) copolyester **3e** (Table 1).

reactions. The macrocyclic polymerizations were conducted in such a way that the ϵ-CL and DSDOP (**1c**) were heated to 80 °C in bulk, whereby a complete conversion was found after 1 h.[5] As reported previously,[5,12] the resulting average degrees of polymerization (DP) agree with the monomer/initiator ratios. This agreement is not only a theoretical conseqence of the nearly 100% conversion, it has also been experimentally confirmed by end group analyses.[12] Hence the number average molecular weights (M_n's) of the poly(ϵ-CL) prepared for the polycondensations listed in Table 1 is of the order of 2400 Da (calculated without the Bu_2Sn group). It has also been demonstrated and discussed[5,12] that SEC measurements regardless of the calibration method overestimate the M_n's, and thus, neither M_n nor M_w values have been listed in Table 1. The inherent viscosities and polydispersities were given as basic characterization and to demonstrate that the poly(ϵ-CL) samples of almost identical properties were used for all polycondensations.

After complete conversion of the ϵ-CL, an excess of isophthaloyl chloride (relative to Bu_2Sn) was then added, hoping that mainly ring-opening and functionalization of the polycaprolactone according to eq 4 will



take place. After 1 h at 80 °C silylated Bisphenol A and a catalytic amount of benzyltriethylammonium chloride (needed as catalyst) were added and the reaction vessel was placed in an oil bath of higher temperature to promote the polycondensation according to eq 5.

Six such polycondensations were conducted at temperatures between 150 and 300 °C. The first five experiments of this series are summarized in Table 1. For the brownish glassy polymer obtained at 300 °C the ^{1}H NMR spectrum indicated a significant loss of ϵ-caprolactone due to transesterification and "back-biting degradation". Therefore this product was not included in Table 1. However, the ^{13}C NMR spectra proved (see below) that even at this high temperature the randomization of the sequence was not complete yet. This result is surprising because Sn compounds are known to be excellent transesterification catalysts. However, it is also known that Bu_2SnCl_2 is several orders of magnitude less reactive as $Bu_2Sn(OMe)_2$ and, when the conversion of the macrocycles according to eq 4 is complete at 80 °C prior to the polycondensation step (eq 5), no active Sn−O bonds are present at the higher polycondensation temperatures.

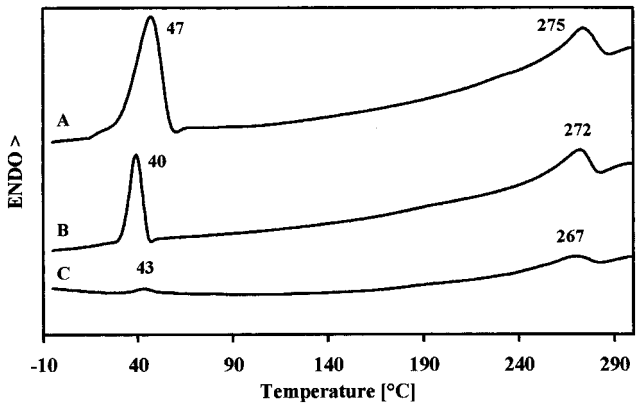


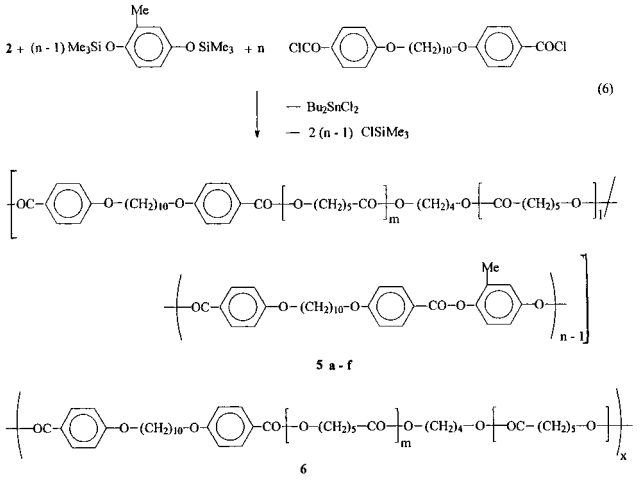
Figure 3. DSC heating curves (first heating) of (A) copolyester **3** (Table 1), (B) copolyester **3d** (Table 1), and (C) copolyester **3e** (Table 1).

For the five copolyesters obtained up to temperatures of 270 °C the elemental analyses (Table 1) and the ^{1}H NMR spectra (Figure 1) confirmed a composition according to the feed ratio. Furthermore, the ^{1}H NMR specra displayed a weak triplet at $\delta = 4.5$ ppm (signal "a"), which represents the O−CH_2 groups of ϵ-CL units acylated by isophthalic acid. In other words, these signals prove the coupling of isophthaloyl units and poly(ϵ-CL) blocks according to eq 4. In the absence of transesterification the intensity ratio of the "a" and "b" signal was 1:9 (Figure 1A) in good agreement with the M/I ratio. Under the influence of transesterification the *a*/*b* ratio increased, as demonstrated by Figure 1B. This interpretation was confirmed by ^{13}C NMR spectroscopy. The signal "g" in Figure 2A represents the crossover from isophthaloyl units to poly(ϵ-CL) blocks. Transesterification at temperatures above 240 °C enhances its intensity and produces a new signal ("h" in Figure 2B) that indicates a crossover from ϵ-CL to Bisphenol A.

The DSC measurements showed a good agreement with the NMR data. Two strong melting endotherms were observable up to a reaction temperature of 240 °C (Figure 3, curves A and B). The endotherms in the range 40−50 °C indicate the melting of the poly(ϵ-CL) blocks. Due to the low block length and the incorporation of isophthaloyl units (see below) these T_m's are approximately 15 °C lower than the T_m of neat poly(ϵ-CL). The second endotherm in the range 265−275 °C (Figure 3) originates from the melting of the aromatic blocks, and thus, these DSC measurements confirm the blocky sequences of those copolyesters. In perfect agreement with this interpretation both endotherms are weak in the DSC curve of the partially transesterified sample prepared at 270 °C (Figure 3C).

The high melting temperature of the poly(bisphenol A isophthalate) had the consequence that these blocks crystallized early in the polycondensation process, and the crystallization protected them against transesterification. Therefore, the polycondensation based on Bisphenol A did not definitely prove that a temperature of 240 °C is low enough to prevent transesterification when blocks are in the molten state. This problem prompted us to conduct two more polycondensations at 240 °C using silylated Bisphenol P as comonomer. The poly(bisphenol P isophthalate) has a T_m around 215 °C, and thus, cannot crystallize during its synthesis at 240 °C. When the resulting multiblock copolyesters of structure **4** were examined by ^{1}H and ^{13}C NMR spectroscopy, no influence of transesterification was found after a reaction time of 4 h, but slight transesterification occurred after 8 h. These results confirm that 240 °C is the threshold temperature for a successful synthesis of perfect multiblock copolyesters.

Thermotropic Multiblock Copolyesters. A second series of combined macrocyclic polymerizations and copolycondensations were performed with silylated methylhydroquinone and 1,10-bis(4-(chloroformyl)phenoxy)decane as aromatic comonomers (eq 6). The purpose of these syntheses was 3-fold. First, the aforementioned results of the first series should be confirmed, and it should be elucidated if a successful copolycondensation can be obtained in a diphasic (isotropic/nematic) melt. Methylhydroquinone and 1,10-bis(4-(chloroformyl)phenoxy)decane were selected as comonomers, because their homopolyester was known to melt below 200 °C and to form a broad nematic phase (up to 285 °C).[10,11,13] Second, the influence of the length of the caprolactone blocks on the stability of the nematic phase should be studied. Third, a crude estimation of the phase separation and its correlation with the block lengths should be made.



The reaction conditions and results of the second series are summarized in Table 2. In this series the length of the poly(ϵ-CL) block was varied by macrocyclic polymerizations with M/I ratios of 10, 20, and 50.

Each type of macrocyclic poly(ϵ-CL) was polycondensed with two different feed ratios of the aromatic comonomers, so that six multiblock copolyesters were obtained. All polycondensations were conducted at 230 °C. Despite the biphasic character of the reaction mixture, higher viscosities were obtained, suggesting that the early crystallization of the Bisphenol A isophthalate blocks hinders the chain growth in the case of the copolyesters **3**. The ^{1}H NMR spectra proved that the composition of the isolated copolyesters were nearly identical with the feed ratios (Table 2). Furthermore, the downfield shift of the O−CH_2 signal (signal "a" in Figure 4) proved that the aromatic dicarboxylic acid was connected with the poly(ϵ-CL) blocks. No indication of transesterification was detectable. This interpretation was confirmed by the ^{13}C NMR spectra (Figure 5), which exhibit a CO signal ("c") representing the connection between aromatic dicarboxylic acid and poly(ϵ-CL) whereas no direct links between ϵ-CL units and methylhydroquinone were detectable.

The thermal properties of the multiblock copolyesters **5a**−**f** were compiled in Table 3. The optical microscopy confirmed the existence of a nematic phase for all six

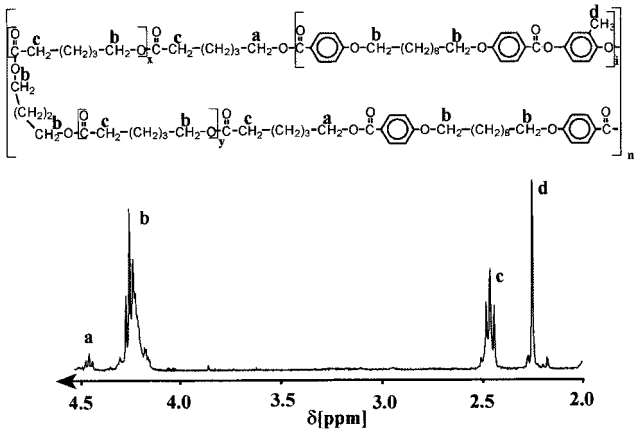


Figure 4. 400 MHz ^{1}H NMR spectrum of the copolyester **5a** (Tables 2 and 3) recorded in $CDCl_3$/TFA 4:1 by volume.

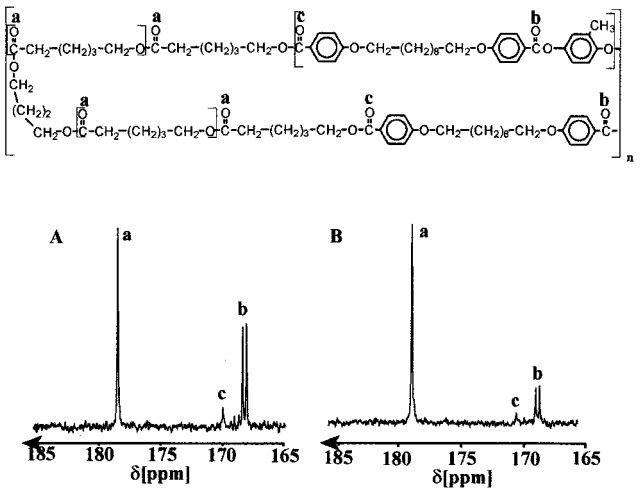


Figure 5. 25.2 MHz ^{13}C NMR spectra (CO signals recorded in $CDCl_3$/TFA 4:1 by volume) of (A) copolyester **5d** (Tables 2 and 3) and (B) copolyester **5f** (Tables 2 and 3).

Table 3. Thermal Properties of the Multiblock Copolyester 5a−f

polym. no.	T_{m1}[a] (°C)	T_{m2}[a] (°C)	T_i[a] (°C)	T_{ai}[b,c] (°C)	T_{cr1}[b,d] (°C)	T_{cr2}[b,d] (°C)	T_i[e] (°C)	T_{ai}[e] (°C)
5a	40	182	270	253	104	−7	∼265	∼250
5b	35	180	282	264	87	−7	∼290	∼270
5c	45	178	274	255	93	−6	∼285	∼260
5d	42	182	283	263	85	−7	∼290	∼270
5e	52	176	273	253	91	12	∼280	∼260
5f	50	181	276	255	92	5	∼285	∼270

[a] From the second heating curve of DSC measurements recorded with a heating rate of 20 °C/min. [b] From the first cooling curve recorded with a cooling rate of −20 °C/min. [c] Anisotropization temperature (beginning formation of the LC phase upon cooling). [d] Crystallization exotherms in the first cooling trace. [e] Determined by optical microscopy at a heating/cooling rate of 10 °C/min.

copolyesters of structure **5**. Figure 6 illustrates exemplarily the DSC measurements. Three endotherms are reproducible in the second (and third) heating trace. The first endotherm (35−52 °C) represents the melting (T_{m1}) of the poly(ϵ-CL) blocks. The second endotherm (176−182 °C) indicates the melting of the aromatic blocks (T_{m2}). The third endotherm is the isotropization process (T_i). The corresponding three exotherms were detectable in the cooling traces (Figure 6, curve B). Thus, the results of the DSC measurements agree completely with our interpretation of the NMR spectra.

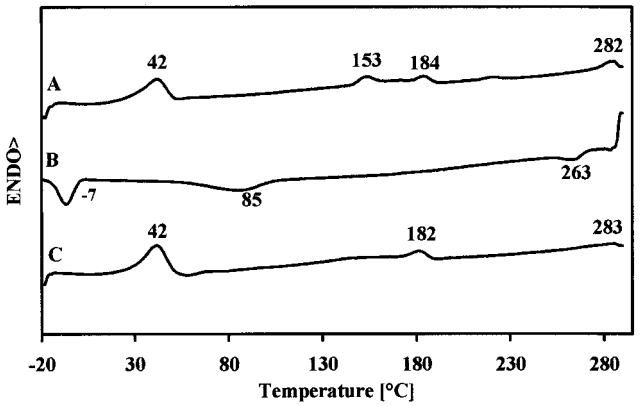


Figure 6. DSC measurements of copolyester **5d** (Tables 2 and 3): (A) first heating; (B) first cooling; (C) second heating (heating and cooling rates: 20 °C/min).

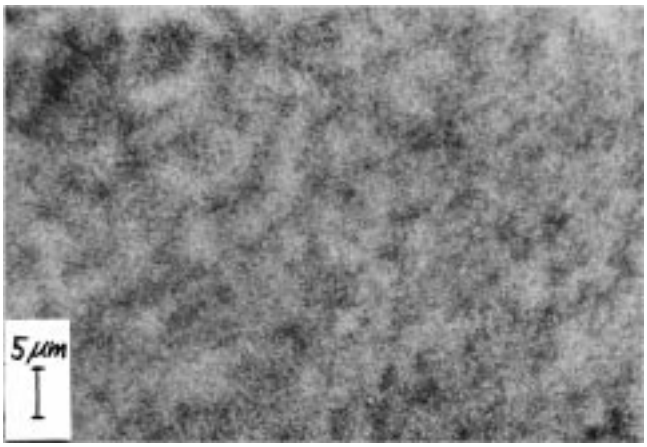


Figure 7. Textures of the copolyester **5d** (Tables 2 and 3) at 245 °C (magnification 300). Figure reduced to 65% for publication.

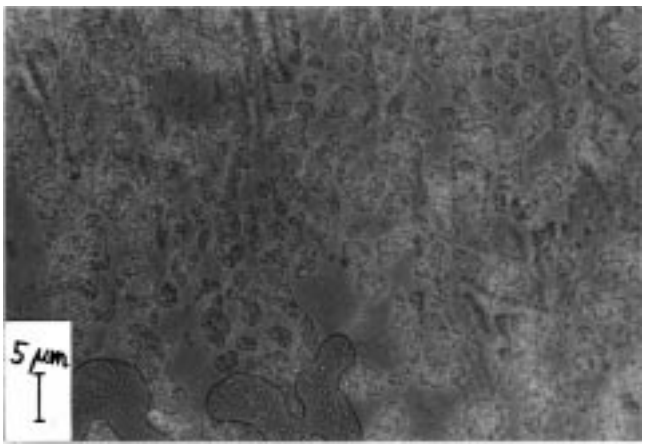


Figure 8. Texture of the copolyester **5f** (Tables 2 and 3) at 245 °C (magnification 300). Figure reduced to 65% for publication.

Problem of Phase Separation. It has been revealed by optical microscopy that the multiblock copolyesters **5a−f** undergo the expected phase separation in the molten state below the isotropization temperature (T_i). As illustrated by the textures of Figures 7 and 8, the extent of this phase separation depends very much on the lengths of the original poly(ϵ-CL) blocks (i.e., on the M/I ratio used for the macrocyclic polymerization). In the case of samples **5a** and **5b** the phase separation is not clearly detectable at a magnification of 300, and

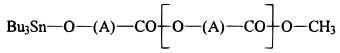
even in the case of **5c** and **5d** it is barely observable at a magnification of 300 (Figure 7). However, in the case of samples **5e** and **5f** (M/I = 50), the diameters of the isotropic and nematic domains are of the order of several micrometers (Figure 8). When the average DP of the poly(ϵ-CL) blocks is 50 (**5e** and **5f**) these samples may contain a sizable fraction of blocks having a DP of 100 and more. An extended poly(ϵ-CL) chain of 110 units has a length of 0.1 μm. Hence the observed dimensions of the phase separation are roughly a factor of 10 larger than expected from a random copolycondensation of the macrocyclic polylactones. Two hypotheses may account for this discrepancy: (I) The coupling between the aromatic dicarboxylic acid dichloride and the macrocycles was far from complete so that the isolated copolyesters contain a considerable fraction of unreacted poly(ϵ-CL) chains. (II) The initial reaction of macrocycles and dicarboxylic dichloride resulted in chain extension, yielding long blocks of the structure **6** prior to the formations of the aromatic blocks.

Two experimental results clearly rule out the validity of hypothesis I. First, the NMR spectra (Figures 4 and 5) unambiguously indicate a nearly quantitative coupling of the poly(ϵ-CL) blocks and aromatic dicarboxylic acid. Second, poly(ϵ-CL) is soluble in tetrahydrofuran, but it was impossible to extract poly(ϵ-CL) from the multiblock copolyesters by refluxing tetrahydrofuran.

Hypothesis II is supported by the following observations. First, the T_m's of the poly(ϵ-CL) blocks are depressed by ca. 20 °C and the T_g's increased by 20 °C, as expected for an incorporation of less mobile comonomers. Second, the T_m's and T_i's of the aromatic blocks are almost identical with those of a high molecular weight homopolyester.[10,13] This agreement suggests that the aromatic blocks are longer than expected from the feed ratio and a random copolycondensation. Third, a model reaction was conducted in such a way that a 6-fold excess of the aromatic dicarboxylic dichloride was added to a macrocylic poly(ϵ-CL) of M/I = 20, and after stirring for 1 h at 80 °C, the reaction mixture was poured into methanol. The isolated poly(ϵ-CL) had an inherent viscosity of 0.30 dL/g, whereas the poly(ϵ-CL) isolated from the unreacted macrocycle had a η_{inh} of 0.16 dL/g. (Furthermore, two different elution times were found by SEC measurements.) This comparison clearly proves that a chain extension of the poly(ϵ-CL) had indeed occurred despite the large excess of the dicarboxylic dichloride.

Conclusion

The results discusssed above allow the conclusion that tin-containing macrocycles can be copolycondensed with silylated diphenols, so that multiblock copolyesters are obtained. Preliminary results of our ongoing research also demonstrate that this approach is not limited to silylated diphenols and other silylated monomers may be included. Therefore, this new approach, macrocyclic polymerization combined with ring-opening polycondensation in an "one-pot procedure", is highly versatile. The chemical structure and the lengths of both blocks can be varied independently. Furthermore, this approach can be extended to "monofunctional" polyesters obtained by tributyltin methoxide-initiated polymerization of lactones (structure **7**) so that A−B diblock and



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A−B−A triblock copolyesters can be prepared. Therefore, this new approach, the combined ring-opening polymerization and ring-opening polycondensation, will be nicknamed the ROPPOC strategy and further examples illustrating the versatility and usefulness of this synthetic strategy will be published soon.

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