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MACROCYCLES. 9. SMECTIC MULTIBLOCK COPOLYESTERS VIA MACROCYCLIC POLYMERIZATION OF δ-VALEROLACTONE AND ε-CAPROLACTONE

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Key Words: Macrocyclic Polymerization , ε-Caprolactone, δ-Valerolactone, Ring-Opening Polymerization, Multiblock Copolyesters, Smectic Mesophases

ABSTRACT

Using 2,2-dibutyl-2-stanna-1,3-dioxepane (DSDOP) as cyclic initiator 1:1 copolymerizations of ε-caprolactone (ε-CL) and δ-valerolactone (δ-VC) were conducted in bulk at 80°C. A nearly equimolar incorporation and a random sequence were found by NMR spectroscopy and crystallization below 20°C was detected by DSC measurements. In a second series of experiments, the *in situ* formed macrocyclic copolyesters were reacted with an excess of sebacoyl chloride and after addition of silylated 4,4,′-dihydroxybiphenyl copolycondensations were performed in bulk at 230°C. These copolycondensations proceeded satisfactorily without significant transesterification and despite a biphasic character of the melt. This biphasic character resulted from the formation of a smectic LC-phase by the 4,4′-dioxybiphenyl sebacate blocks. For comparison a homopolyester was prepared from sebacoyl chloride and silylated 4,4′-dihydroxybiphenyl. The

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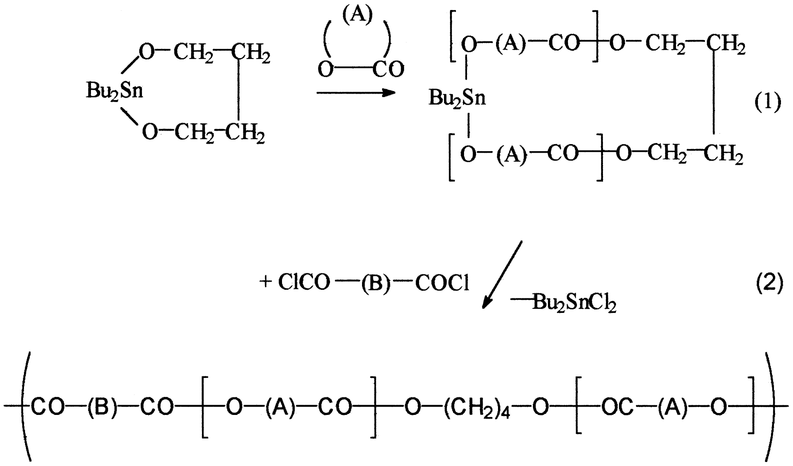
thermal properties of this homopolyester and of the LC-blocks in the copolyester were nearly identical indicating the absence of transesterification during the synthesis at 230°C. However, the properties of the LC-phase above 200-210°C did not completely agree with the data reported for the homopolyester in the literature (which are themselves inconsistent).

INTRODUCTION

This work is part of a broader study of the usefulness of tin containing macrocycles and supermacrocycles (more than 50 ring atoms) in (co)polycondensation processes. The basis of this novel synthetic strategy is the "macrocyclic polymerization" of lactones (or other heterocycles) by means of cyclic tin-initiators (Equation 1) [1-4]. Under optimized conditions, these macrocyclic polymerizations follow the "living pattern" so that the number average molecular weights (M_n's) can be controlled by the monomer/initiator (M/I) ratio [4]. Furthermore, it was found that the living endgroups (i.e., the Sn-O bonds) react easily with acid chlorides, so that the tin-containing supermacrocycles can be used as difunctional monomer for polycondenations (Equation 2) [5]. In this connection, it was also found that tin-containing supermacrocycles allow the copolycondensation with silylated diphenols at temperatures up to 240°C [6].



The purpose of the present work was to study copolycondensation of tin-containing macrocyclic polylactones with 4,4′-bistrimethylsiloxybiphenyl and sebacoyl-chloride. These comonomers were selected because it was known from the corresponding homopolyester [7-11] that it forms a smectic LC-phase above 208-210°C (depending on the molecular weight). The question should be answered whether a satisfactory copolycondensation is feasible in a biphasic system involving a relatively viscous smectic phase. Furthermore, the properties of the resulting multiblock copolyester were of interest. By copolymerization of two different lactones, amorphous soft segments should be prepared so that the final multiblock copolyester would possess the properties of a thermoplastic elastomer.

EXPERIMENTAL

Materials

δ-Valerolactone (δ-VL) and ε-caprolactone (ε-CL) were purchased from Aldrich Co., Milwaukee, Wisc. They were distilled over freshly powdered calcium hydride *in vacuo*. Sebacoyl chloride and 4,4-dihydroxybiphenyl were also purchased from Aldrich Co. and used as received. 4,4′-Bistrimethylsiloxybiphenyl (m.p. 64°C) [12] was prepared by silylation of 4,4′-dihydroxybiphenyl with an excess of hexamethyldisilazane in refluxing toluene and isolated by distillation *in vacuo*.

2,2-Dibutyl-2-stanna-1,3-dioxepane (DSDOP) was prepared from dibutyl tin dimethoxide (purchased from Aldrich Co.) and dry 1,4-dihydroxybutane as described previously [3, 4].

Copolymerizations

ε-Caprolactone (10 mmol) and δ-valerolactone (10 mmol) were weighed (under dry nitrogen) into a cylindrical glass reactor (equipped with stirrer, gas-inlet and -outlet tubes), and DSDOP (1 mmol) was added. The reaction vessel was placed into an oil bath preheated to 80°C. After 2 hours, the resulting copolyester was either dissolved in CH_2Cl_2 and precipitated into cold methanol (Table 1) or it was mixed with sebacoyl chloride (see below). The copolyester isolated from methanol was dried at 40°C *in vacuo*.

Polycondensations

Sebacoyl chloride (11 mmol as 2 M solution in toluene), 4,4′-bistrimethylsiloxy biphenyl (10 mmol) and benzyltriethylammonium chloride (10 mg) were added to the copolyester described above and mixed with stirring in an

TABLE 1: DSDOP-Initiated Copolymerization of ε-Caprolactone (ε-CL) and δ-Valerolactone (δ-VL) in Bulk at 80°C/2 hours

Polym. No.	Feed ratio δ-VL/ε-CL/Init.	$\eta_{inh.}$ [a] (dl/g)	M_n [b] (theor.)	M_n [c] (GPC)	M_w/M_n
1	5/5/1	0.07	1400	--- d)	--- d)
2	5/5/1	0.07	1400	--- d)	--- d)
3	10/10/1	0.12	2500	3900	1,55
4	10/10/1	0.11	2500	3800	1,55
5	25/25/1	0.24	5800	7800	1,60
6	25/25/1	0.24	5800	7800	1,60

measured at 25°C with c = 2g/l in CH_2Cl_2

b) calculated from the M/I ratio with 100% conversion including the mass of the initiator

c) GPC measurements in THF calibrated with Equation 3

d) turbide solution, presumably due to Bu_2SnO

atmosphere of dry nitrogen. After 1 hour, the reaction vessel was placed into an oil bath preheated to 150°C, and the temperature was then raised to 230°C within 0.5 hours. After 3.5 hours at 230°C, vacuum was applied for 0.5 hours. The cold polyester was dissolved in a mixture of CH_2Cl_2 and trifluoroacetic acid (TFA, volume ratio 4:1), precipitated into cold methanol and dried at 40°C *in vacuo*.

Measurements

The inherent viscosities were measured with an automated Ubbelohde viscometer thermostated at 25°C.

The DSC measurements were conducted with a Perkin Elmer DSC-4 in aluminum pans under nitrogen.

The 100 MHz ^{1}H NMR spectra were recorded with a Bruker AC-100 FT NMR spectrometer in 5 mm o.d. sample tubes. The 400 MHz ^{1}H NMR spectra and the 100.5 MHz ^{13}C NMR spectra were recorded with a Bruker AM 400 FT NMR spectrometer also in 5 mm o.d. sample tubes. Internal TMS served for shift referencing in all cases.

The WAXD powder patterns were recorded with synchrotron radiation (λ = 0.154 nm) at HASYLAB (DESY) Hamburg. The temperature was varied between 30 and 300°C with a heating rate of 10°C/min. A one-dimensional position sensitive detector was used for these measurements.

RESULTS AND DISCUSSION

Macrocyclic Copolymerizations

In the previous study [6], the synthetic approach described for the first time, was also used in the present work, and the macrocyclic polylactone, and thus, the “soft segment”, was neat poly(ε-CL). Both poly(ε-CL) and poly(δ-VL) are semicrystalline polyesters having melting temperatures ≥ 60°C. In the present work, amorphous soft segments should be used, and for this purpose random 1:1 copolyesters should be prepared. Since no information was available about the copolymerization of δ-VL and ε-CL initiated by tin alkoxides, a first series of experiments was designed to study the DSDOP-initiated copolymerizations of both lactones. The M/I ratios were kept low according to the needs for the later copolycondensations.

The reaction conditions and the results were summarized in Table 1. The 400 MHz ^{1}H NMR spectra of the copolylactones revealed a 55/45 ratio for ε-CL/δ-VL, and thus, a slight deviation from the feed ratio. The ^{13}C NMR spectra (Figure 1) displayed two CO-signals with a 1:1 splitting in agreement with a random sequence. The viscosities and the molecular weights derived from GPC measurements follow the M/I ratios in agreement with the living polymerization described for neat ε-CL [4]. The GPC measurements were calibrated with the “a” and “K” values of Equation 3, which were published for poly(ε-CL) dissolved in tetrahydrofuran [15]. The M_n value obtained in this way slightly overestimate the true M_n′s as discussed previously [4], but the calibration with polystyrene is even worse. The polydispersities agree with those found for poly(ε-CL) under identical polymerization conditions [4].

The only surprising finding was the crystallinity of all copolylactones. The DSC measurements of the samples Nos. 5 and 6, Table 1, revealed a melting endotherm around 15˚C. For a copoly(δ-Val/ε-CL) of higher molecular weight a T_m of 17°C has recently been reported [16], but the ^{13}C NMR evidence of a random sequence was lacking in that case. The results of the present work confirm that the random copolyester of δ-VL and ε-CL is semicrystalline. However, due to the fact that its T_m is below 20˚C multiblock copolyesters containing copoly(ε-CL/δ-Val) soft segments may show the properties of a thermoplastic elastomer above 25°C.

$$[\eta] = 1.395 \times 10^{-4} \times M^{0.786} \qquad (3)$$

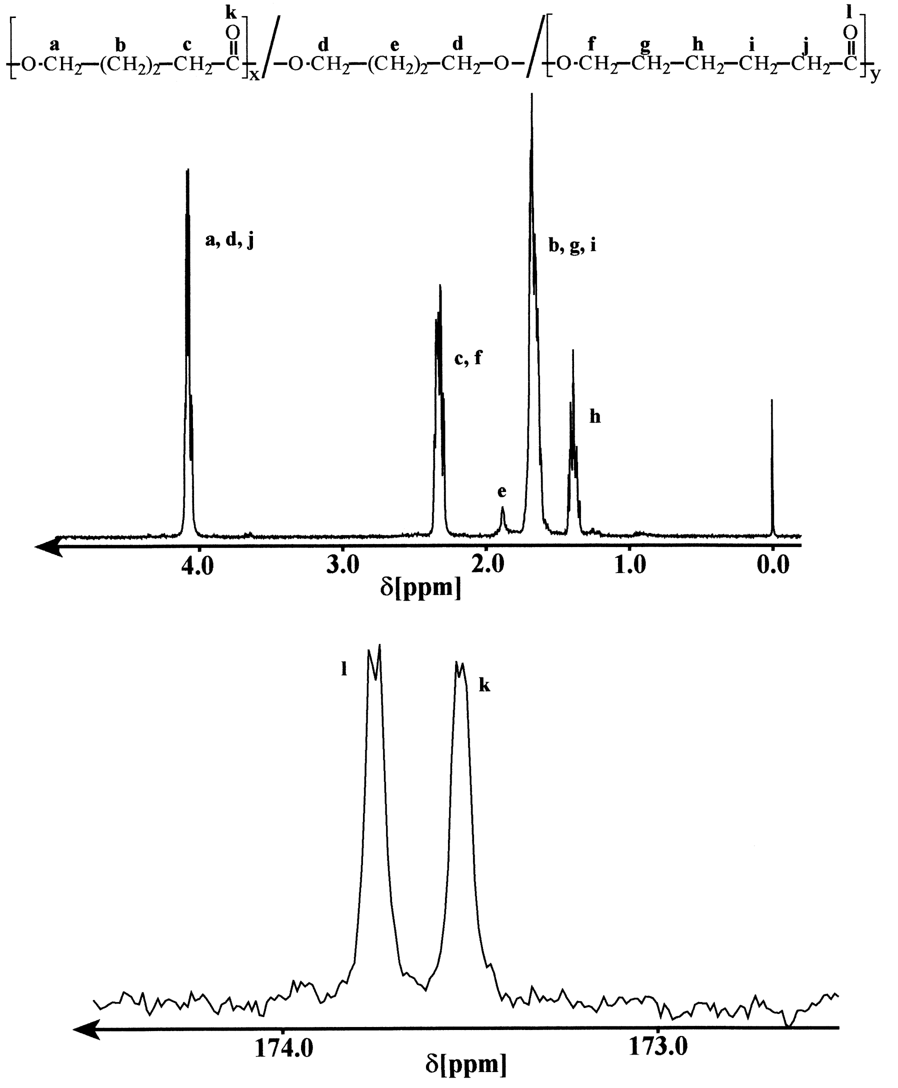


Figure 1. NMR spectra of copoly (ε-CL/δ-VL) No. 5, Table 1; A) 400 MHz ^{1}H NMR spectrum, B) 100,5 Mhz spectrum (CO-signals).

Polycondensations

The polycondensations were conducted in such a way that a 6- or 11-fold molar excess of sebacoyl chloride was added to the molten copolylactone at 80°C. Furthermore, a 5- or 10-fold excess of 4,4-bistrimethylsiloxy biphenyl and a catalytic amount of benzyltriethylammonium chloride were added and mixed by stirring. Under these conditions, the sebacoyl chloride reacts exclusively with the Sn-O bonds of the macrocyclic copolylactones and due to the excess acid chloride functionalized telechelic copolylactones (2) should be formed [6]. However, previous studies [6] also suggest that a chain extension occurs by the reaction of one molecule of sebocoyl chloride with two supermacrocycles, so that longer soft segments of the structure 3 are formed. This suggestion was confirmed by the following model experiment. A macrocyclic copolylactone (1) was prepared as usual with a M/I ratio of 20 (Nos. 3 and 4, Table 1) and a 6- fold molar excess of sebacoyl chloride was added after stirring for 1 hour at 80°C, the reaction product was precipitated into methanol. The inherent viscosity of this copolylactone was of the order of 0.36 dL/g in contrast to the 0.12 dL/g of the parent copolylactone Nos. 3 and 4, Table 1.

The copolycondensation of all comonomers was performed at 230°C over a period of 4 hours. This temperature was selected, because it was found in a previous study of this procedure (using other monomers) [6] that reaction temperatures $\geq$ 240°C favor transesterification. In contrast to the multiblock copolyesters studied previously [6] the multiblock copolyesters of this work (4) have the analytical disadvantage that neither ^{1}H nor ^{13}C NMR spectroscopy allow the detection of beginning transesterification. A reaction temperature of 230°C was expected to avoid any problems with transesterification and the thermal properties of the copolyesters 4 discussed below indeed agree with a perfectly blocky sequence.

Although the ^{1}H NMR spectra did not give any sequence information, they confirmed together with the elemental analyses that the molar composition of the isolated copolyesters 4 agrees with the feed ratio (Figure 2). The inherent

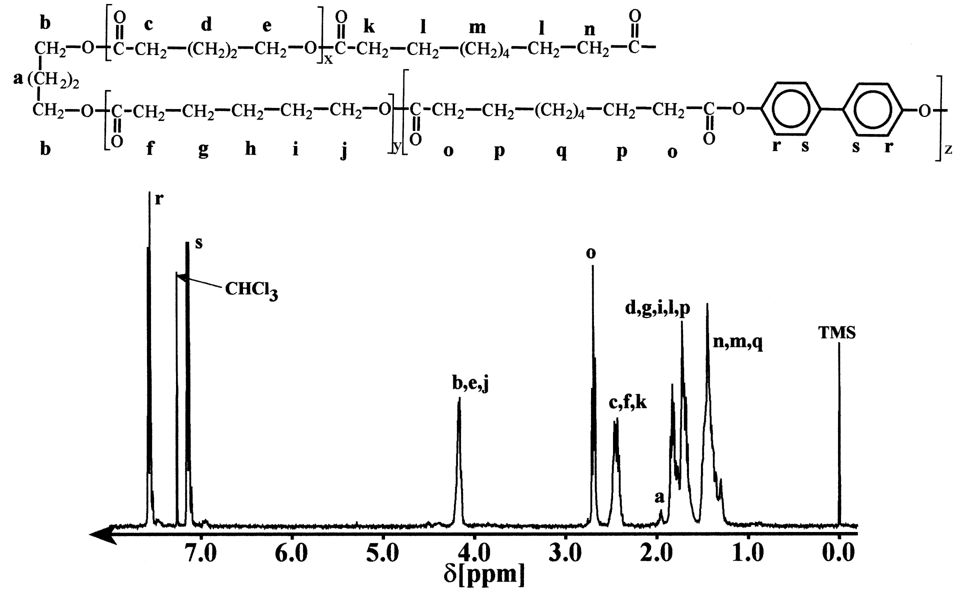
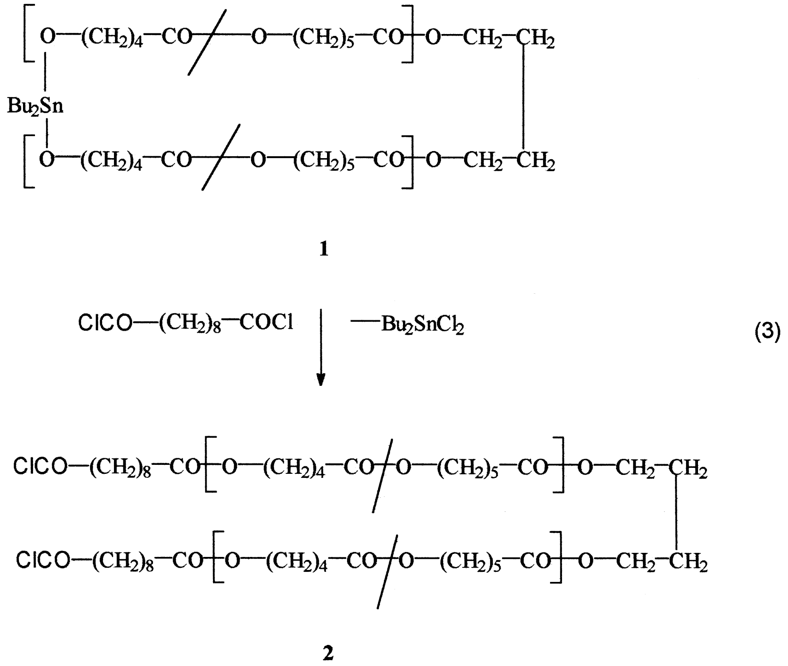


Figure 2. 400 MHz ^{1}H NMR spectrum of the copolyester 4 No. 4, Tables 2 and 3.

viscosities in turn confirm that the polycondensation process has resulted in a chain extension. Unfortunately, the multiblock copolyesters 4 did not dissolve in nonacidic solvents so that GPC measurements were not feasible. However, this poor solubility had also an analytical advantage. Poly(ε-CL), poly(δ-Val) and their copolymers are well soluble in tetrahydrofuran. Therefore, it should be feasible to extract soft segments not attached to aromatic blocks. However, several extraction experiments performed with refluxing tetrahydrofuran failed. The multiblock copolyesters 4 proved to be completely insoluble in this solvent.



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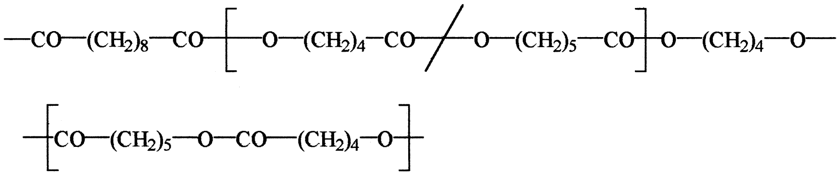

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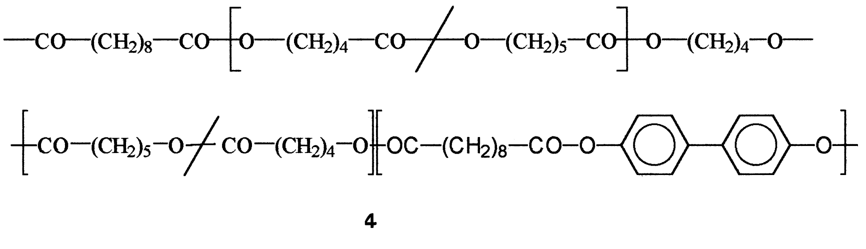

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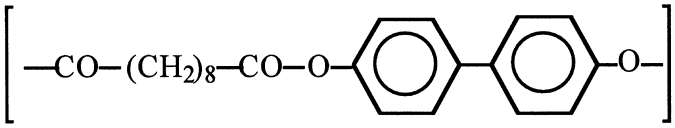
Thermal Properties



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For a better understanding of the thermal properties of the multiblock copolyesters 4, the corresponding homopolyester 5 was prepared by polycondensation of 4,4′-bistrimethylsiloxybiphenyl and sebacoyl chloride in bulk at 230°C. Its properties were listed under the running number 7 in Table 3. With this exception, the numbering of the multiblock copolyesters listed in Table 3 corresponds to that of Table 2.

The WAXD powder patterns revealed that all multiblock copolyesters were semicrystalline materials showing almost identical reflections. These powder patterns also agreed with that of the homopolyester and no additional reflections of the soft segments were detectable. This result agrees with the information provided by the DSC measurements. No melting endotherm of the copolylactone blocks was detectable in the case of samples Nos. 1 and 2 as illustrated by the heating curve A in Figure 3. Weak endotherms around 17 or 18°C were observed for the sample Nos. 3 and 4 and stronger endotherms at 19 or 21°C for the samples Nos. 5 and 6 (curve B). Therefore, the soft segments were in the molten state when the WAXD patterns were recorded at 25°C.

However, the most important aspect of these endotherms si that they indicate the absence of transesterification with the “aromatic blocks”, because a more or less random sequence of all comonomers should lack any crystallinity.

Another interesting result of the DSC measurements is the finding that the appearance and intensity of the T_{m1} endotherm depends on the length of the copolylactone segments as defined by the M/I ratio of the macrocyclic polymerization. Obviously, the later chain extension by sebacoylchloride (Structure 3) does not level off the influence of the M/I ratio. Thus, it is satisfactory to see that the design of the macrocyclic polymerization has a direct and significant influence on the properties of the final multiblock copolyesters.

The DSC heating traces exhibited two more endotherms, T_{m2} and T_i (with exception of No. 1). The weak, broad endotherm T_i which fell into the temperature range of 230-270°C was identified by optical microscopy as the isotropization temperature. The T_i values of the multiblock copolyesters showed a remark

TABLE 2: Syntheses of the Multiblock Copolyesters from Macrocyclic Poly (ε-CL/δ-VL) 4,4'-Dihydroxybiphenyl and Sebazoyl Chloride

Polym. No.	Feed ratio [a)] Lact./Diph./Acid	Yield %	ηinh. [b)] (dl/g)	Elem-Formula (Form weight)	Elemental Analyses	C	H
1	10/5/6	892	0.42	$C_{174}H_{234}O_{44}$ (3089.8)	Calcd.	67.64	7.63
					Found	67.91	7.82
2	10/10/11	92	0.93	$C_{289}H_{354}O_{64}$ (4851.9)	Calc.	70.80	7.35
					Found	71.62	7.47
3	20/5/6	91	0.40	$C_{234}H_{324}O_{64}$ (4161.2)	Calc.	67.54	7.85
					Found	67.29	7.74
4	20/10/11	93	0.70	$C_{344}H_{444}O_{84}$ (5923.3)	Calc.	69.75	7.55
					Found	69.49	7.39
5	50/5/6	92	0.41	$C_{399}H_{594}O_{124}$ (7375.2)	Calc.	64.98	8.12
					Found	65.25	8.25
6	50/10/11	95	0.86	$C_{509}H_{714}O_{144}$ (9137.4)	Calc.	66.91	7.88
					Found	66.26	7.89

a) molar ratios: same of both lactones/silylated diphenol/sebazoylchloride
b) measured at 25 °C with c = 2g/l in CH2Cl2/TFA (volume ratio 2:1)

TABLE 3: Weight Percent of Soft and Hard Segments and Thermal Properties of the Multiblock Copolyesters

Polym. No	Weight percent Soft Seg.	Hard Seg.	T_{m1} a)	T_{m2} a)	T_i a)	T_i b)	T_{ai} b)
1	43	57	---	156	---	~ 170	~ 150
2	27	73	---	197	267	~ 275	~ 250
3	57	42	18	198	255	~ 270	~ 245
4	40	60	17	195	250	~ 275	~ 250
5	76	24	19	200	253	~ 265	~ 240
6	61	39	21	197	253	~ 270	~ 250
7	0	100	---	192 a) 215 c)	278 a,c)	~ 290	~ 250

a) from DSC measurements (1st heating) with a heating/cooling rate of 20 °C/min

b) complete isotropization from optical microscopy with a heating/cooling rate of 10 °C/min (T_{ai} = beginning anisotropization upon cooling)

c) second heating curve

ably good fit with the T_i of the homopolyester 5 with exception of No. 1. This agreement suggests that the "aromatic blocks" were longer than expected from the feed ratio. This is a reasonable interpretation, because the chain extension of the soft segments (Structure 3) has the automatic consequence that also the "aromatic blocks" increase in length.

The second endotherm (T_{m2}) in the temperature range of 195-200°C represented the melting of a smectic crystalline phase. Again, a good agreement between all copolyesters 3 and the homopolyester 5 was found suggesting that no significant transesterification had taken place. Futhermore, the temperature range and interpretation of T_{m2} agrees well with the data reported by several research groups [7-13]. In order to confirm the existence of a layer structure in the solid state (below T_{m2}) and in the LC-phase above T_{m2} middle angle and wide angle X-ray measurements (MAXS and WAXS) were conducted with synchrotron radiation at a heating or cooling rate of 10°C/min. As illustrated by Figure 4(A) a middle angle reflection (MAR) is detectable representing a layer distance of 20.3± 0.2 Å. Assuming an equilibrium of gauche and trans-conformation for the aliphatic spacer computer modelling gave a length of 20.2 Å for a linear arrangement of the repeating unit. This means that the mesogens are in upright position (smectic B or E) in the solid state.

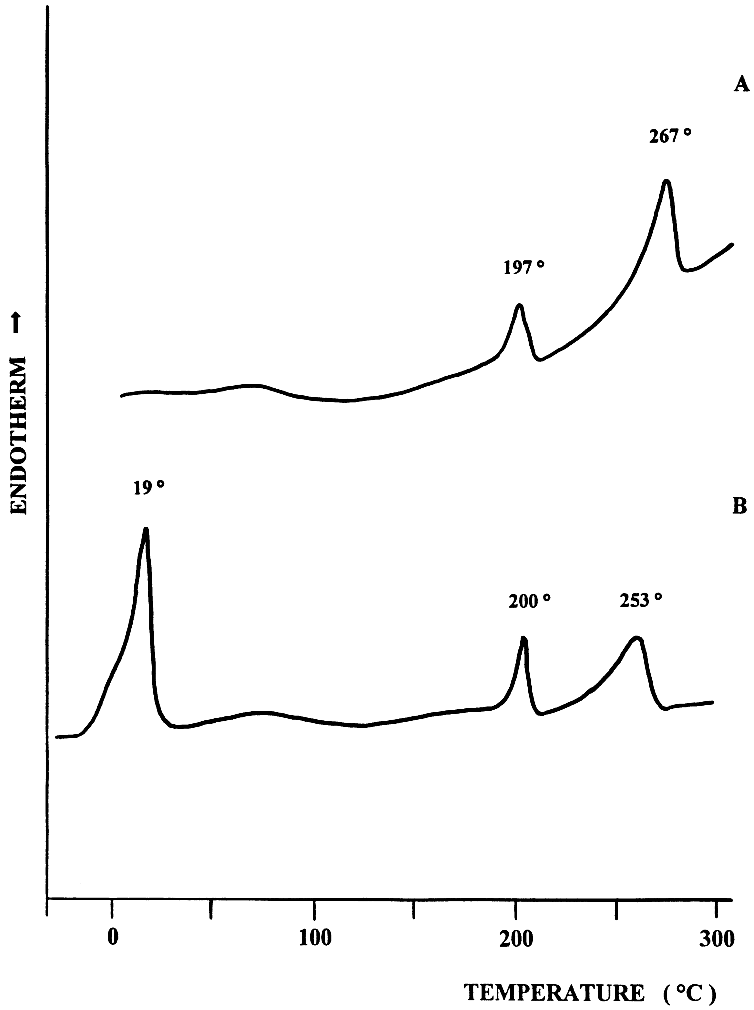

Figure 3. DSC measurements (1st heating, heating rate 20°C/min) of: A) multiblock copolyester No. 2, Tables 2, 3; B) multiblock copolyester No. 5, Tables 2 and 3.

Around 202°C (corresponding to T_{m2} in the DSC curve) the MAR rapidly looses its intensity and shifts immediatly to a value representing a layer distance of 17.7 D. In other words, the smectic LC-phase above T_{m2} must contain a tilted array of repeating units. At 240-250°C the MAR and the main WAR disappear corresponding to the T^i endotherm in the first heating curve. It should be emphasized that the synchrotron radiation measurements of the homopoly-ester 5 gave quite similar results. The optical measurements confirmed that a mobile melt is formed above T_{m2} and that the melt is completely isotropic above T_i.

Again, the multiblock copolyesters and the homopolyester 5 agree in this regards. Hence, absolutely consistent results were obtained from all observations and measurements conducted in this work. The properties of the LC-blocks in the copolyesters agree with each other and with those of the homopolyester 5. Futhermore, the finding of a mobile phase above T_{m2} is in perfect agreement with the successful course of all polycondensations at 230°C (including the observation of a stirrable melt).

In addition to the aforementioned reasonable and consistent results, the properties of the copolyesters 4 and of the homopolyester 5 above T_{m2} presented some unsolved problems. Futhermore, these properties do not agree well with the data published for the homopolyester by several research groups, and the litera-

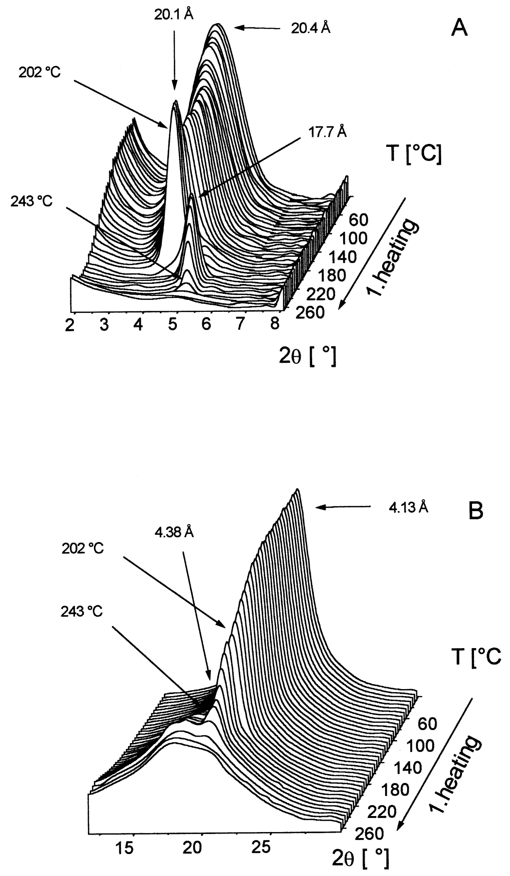

Figure 4. Synchrotron radiation measurements of the multiblock copolyester No. 4, Tables 2 and 3 performed at a heating rate of 10°C/min.; A) middle angle reflection, B) wide angle reflection.

ture data are themselves inconsistent. A detailed investigation of all these problems was beyond the scope of this work, which had the purpose to test the usefullness of a new synthetic approach. Nevertheless, these unsolved problems should be briefly mentioned as a basis for further discussions and investigations. Firstly, when the heating-cooling cycle of the copolyester 4 (No. 4, Tables 2 and 3) was repeated in combination with synchrotron radiation (at a rate of 10°C/min) the MAR disappeared completely, whereas the WAR's persisted. Since the homopolyester 5 showed the same properties the finding cannot attributed to an intensive transesterification of the copolyesters. Secondly, at temperatures above 220-230°C the optical microscope shows a biphasic situation with bâtonet-like paticles dispersed in an isotropic melt (Figure 5). Intensive shearing between thin glass-plates revealed that the isotropic melt is indeed isotropic and not homeotropic. Futhermore, the "bâtonets"did not smear out as it is typical for a smectic A texture, but seemed to be solid or highly viscous. A biphasic melt below T_i is of course, plausible for the multiblock copolyesters 4 , but the same observation was made for the homopolyester 5 with a smaller fraction of the isotropic phase. Whereas, van Luyen *et al*. [7] assumed a nematic LC-phase, other authors [8] mentioned an undefined smectic LC-phase and Krigbaum *et al.* [10] postulated even a smectic H-phase on the basis of X-ray studies. However, this interpretation of the LC-phase is inconsistent with other results of Krigbaum *et al.* [10] and further authors. A smectic H phase is in the case of main chain LCP's an absolutely immobile crystalline phase. Nonetheless, Krigbaum *et al.* [10] and other authors reported on stirring of the LC-phase and drawing of fibers. Futhermore, a smectic H phase represents the highest degree of order a smectic LC-main chain polyester can adopt. For thermodynamical reasons no other smectic phase can exist below smectic H. Yet Krigbaum *et al.* [10] describes another smectic crystalline phase below T_{m2}. Thirdly, repeated heating and cooling of the polyester 5 caused a shift of T_{m2} to 215°C and a shift of T_i to 275°C. this high T_i (also reported as melting of the smectic-H phase in Reference 10) is due to the melting of the solid "bâtonets". Hence, it is not clear if the shift of T_{m2} and T_i to higher temperatures is a consequence of an increasing fraction of a thermodynamically more stable, crystalline phase, or a consequence of increasing molecular weights, (due to postcondensation). Futhermore, side reactions as the Fries-rearrangements (which may also entail crosslinking) should be taken into account, when the samples are heated to temperatures ≥280°C. In this connection, it should be noted, that an increasing fraction of insoluble materials was obtained, when the synthesis of the homopolyester 5 was repeated at 260 or 280°C. In summary, the properties of the homopolyester above T_{m2} are rather

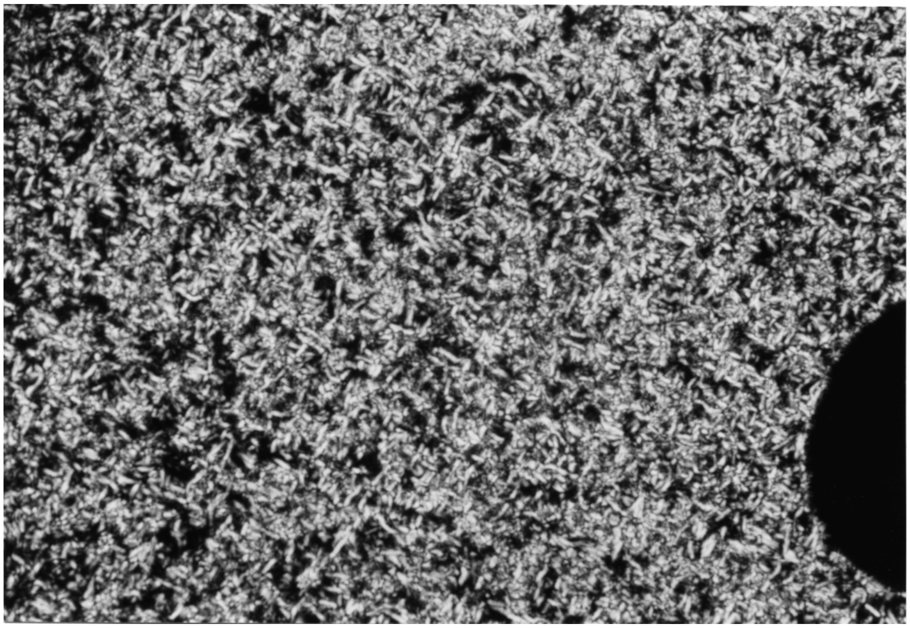

Figure 5. Texture of the multiblock copolyester No. 6, Tables 2 and 3, recorded upon slow cooling at 250°C.

complex and poorly understood. A full elucidation of all problems requires a time consuming, intensive reinvestigation including syntheses with different methods which was not foreseen and intended in this work.

CONCLUSION

The main result of this work is the confirmation that the novel synthetic strategy reported in a previous paper is a useful and versatile approach which also allows the syntheses of smectic multiblock copolyesters. This novel approach consists of the macrocyclic polymerization of lactones combined with direct copolycondensation of the resulting tin-containing macrocycles and silylated comonomers (4,4′-dihydroxybiphenyl in the present work). This is a special case of the ROPPOC strategy: the ring-opening polymerization and ring-opening polycondensation combined in an "one-pot procedure." The thermal properties of the LC-blocks and their goog agreement with the properties of the homopolyester 5 suggest that no significant transesterification has occurred. The successful copolycondensation in the biphasic melt and the synthesis of the homopolyester 5 at 230°C proved that the smectic blocks do not form a smectic-

H phase above their melting temperature (T_{m2}) in contrast to literature data [10]. The ongoing and future syntheses of multiblock copolyesters via this new approach have the purpose to develop fully biodegradable self-reinforcing composites and biodegradable thermoplastic elastomers.

REFERENCES

[1] H. R. Kricheldorf and S.-R. Lee, *Macromolecules, 28*, 6718 (1995).

[2] H. R. Kricheldorf, S.-R. Lee, and S. Bush, *Macromolecules 29*, 1375 (1996).

[3] H. R. Kricheldorf, S.-R. Lee, and N. Schittenhelm, *Macromol. Chem. Phys.*, *199,* 273 (1998).

[4] H. R. Kricheldorf and S. Eggerstedt, *Macromol. Chem. Phys., 199*, 283 (1998).

[5] H. R. Kricheldorf and S. Eggerstedt, *J. Polym. Sci. Part A, Polym. Chem., 36*, 1373 (1998).

[6] H. R. Kricheldorf and S. Eggerstedt, *Macromolecules, 31,* 6403 (1998).

[7] D. van Luyen and I. Strzlecki, *Eur. Polym. J., 16*, 303 (1980).

[8] A. Blumstein, K. N. Sivaramakrishnan, R. B. Blumstein, and S. B. Clough, *Polymer, 23*, 47 (1982).

[9] J. Asrar, H. Toricuni, J. Watanabe, W. R. Krigbaum, and A. Ciferri, *J. Polym. Sci., 21*, 1119 (1983).

[10] W. R. Krigbaum, J. Watanabe, and T. Ishikowa, *Macromolecules, 16*, 1271 (1983).

[11] D. Acierno, F. P. La Mantia, G. Polizotti, A. Liferri, W. R. Krigbaum, and R. Kotek, *J. Polym. Sci., 21*, 2027 (1983).

[12] Y. Maeda and H. Toricemi, *Makromol. Chem., 194*, 3123 (1993).

W. R. Krigbaum, A. Ciferri, and D. Acierno, *J. Appl. Polym. Sci., Appl. Polym. Symp.*, *41*, 293 (1985).

[14] H. Stanley, S. Connel, and J. Wender, *J. Org. Chem., 23*, 50 (1958).

[15] A. Schindler, Y. M. Hibionada, and C. G. Pitt, *J. Polym. Sci., Polym. Chem. Ed., 20*, 319 (1982).

[16] K. Imaska, T. Nagai, M. Yoshida, H. Fukuzaki, M. Asano, and M. Kumakura, *Euro. Polym. J., 26*, 831 (1990).

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