

# Stereocomplexes of A–B–A Triblock Copolymers Based on Poly(L-Lactide) and Poly(D-Lactide) A Blocks

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**ABSTRACT:** A series of A–B–A triblock copolymers was prepared by a Sn(II) 2-ethylhexanoate catalyzed chain extension of various telechelic soft segments, with L,L-lactide (LLA). Poly( $\epsilon$ -caprolactone)s, P $\epsilon$ CL, poly(ethylene glycol)s, PEG, and a poly(dimethyl siloxane), PDMS, served as soft segments. The lengths of both soft and hard segments (poly-LLA, PLLA, or poly-D,L-lactide, PDLA) were varied. For the lactide blocks, average lengths of 25, 50, and 100 lactic acid units were selected. An analogous series of A–B–A triblock copolymers was prepared with DLA. Compositions and block lengths of these triblock copolymers were characterized by <sup>1</sup>H NMR spectroscopy. Furthermore, stereocomplexes (racemates) of PLLA- and PDLA-based triblock copolymers were prepared to find out if the attractive forces between PLLA and PDLA blocks or the repulsive forces between incompatible soft segments dominate the morphology. Both neat triblock copolymers and stereocomplexes were characterized by differential scanning calorimetry measurements by wide-angle X-ray diffraction. The influence of block lengths on glass transition ( $T_g$ ) and melting temperatures ( $T_m$ ) of soft and hard segments was studied in detail. Stereocomplexes of all triblock combinations were obtained, even when the soft segments were incompatible.

## Introduction

Poly(L-lactide), PLLA, and poly(D-lactide), PDLA, like other chiral polymers can form a racemate, the physical properties of which are different from those of the individual enantiomers. Characteristic for most racemates, regardless of low molar mass or polymeric, is a denser crystal packing with the consequence of a higher melting enthalpy. Since the melting entropy is usually the same for both racemate and individual enantiomers, the more stable crystal lattice also means a higher melting temperature  $T_m$ . In the case of cyclic lactides, the  $T_m$  of the racemate (125–126 °C) is about 30 °C higher than that of the enantiomers, and for the racemate of PLLA and PDLA, the  $T_m$  rises 55–60 °C above that of the enantiomers (around 175 °C). Racemates of chiral polymers were called stereocomplexes although the formation of a racemate has nothing to do with complexation in its original sense.

The “stereocomplexes” of PLLA and PDLA was at first described by Ikada et al.<sup>1–7</sup> Later, these studies were expanded by several research groups to di- or triblock copolymers containing PLLA or PDLA as “hard” segments.<sup>8–11</sup> The second “soft” block consisted of poly( $\epsilon$ -caprolactone), P $\epsilon$ CL, or poly(ethylene oxide)s, PEG. Furthermore, “stereocomplexes” of PLLA or PDLA with various polymers or low molar mass enantiomers were reported<sup>12–15</sup> (so-called “heterostereocomplexes”). In this context, the present work served the following purpose. Various A–B–A triblock copolymers based on PLLA or PDLA A blocks should be synthesized. Three different kinds of B-blocks should be incorporated, namely, P $\epsilon$ CL, PEG, and a poly(dimethyl siloxane), PDMS. Furthermore, the average lengths of the polylactide (PLA)

blocks should be varied from 25 to 50 and 100 lactic acid units, because it is known from the work of Ikada and Tsuji that the length of the PLA chains plays an important role for the kinetics and thermodynamics of the stereocomplex formation. Finally, PLLA and PDLA triblock copolymers containing incompatible B blocks should be mixed in solution and crystallized to find out if the crystallization is dominated by the formation of the stereocomplex or by the phase separation of the B blocks. In the latter case, two crystalline phases should be formed, one consisting of PLLA and the other one of PDLA blocks. Differential scanning calorimetry (DSC) and wide-angle X-ray scattering (WAXS) measurements were expected to allow for a differentiation between both scenarios.

## Experimental Section

**Materials.**  $\epsilon$ -Caprolactone ( $\epsilon$ CL) was purchased from Aldrich Co. (Milwaukee, WI) and distilled over freshly powdered calcium hydride in vacuo. L-Lactide (LLA) was kindly supplied by Boehringer-Rhein, Germany). It was recrystallized from ethyl acetate/ligroin and dried in a desiccator over P<sub>4</sub>O<sub>10</sub> in vacuo. D-Lactide (DLA) was kindly supplied by PURAC (Gorinchen, The Netherlands) and purified like LLA. The poly(ethylene glycol)s were also purchased from Aldrich Co. and azeotropically dried with toluene. An  $\alpha,\omega$ -bis(3-hydroxypropyl) PDMS with a number average molecular weight of 4000 Da was kindly supplied by Wacker AG (München, Germany) and used as received. Sn(II) 2-ethylhexanoate (SnOct<sub>2</sub>) was purchased from Aldrich Co. and purified as described previously.<sup>16</sup>

**Syntheses of A–B–A Triblock Copolymers.** All reaction mixtures were prepared under an atmosphere of dry nitrogen.

**A. With PEG.** (Table 2.) DLA or LLA (50 mmol) and PEG-2000 (10 mmol) were weighed into a 50-mL Erlenmeyer flask having silanized glass walls. The reaction vessel was closed with a glass stopper and steel spring and immersed into an oil bath preheated to 100 °C. After homogenization (by shaking), 0.1 mL of a 1 M solution of SnOct<sub>2</sub> in dry chlorobenzene were injected. After 4 h, when the <sup>1</sup>H NMR indicated complete conversion, the product was cooled, dissolved in

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**Table 1. A–B–A Triblock Copolymers and Their Stereocomplexes Having Short SS and Short Poly lactide A Blocks**

product no.	structure	LLA or DLA (co-initiator) <sup>a</sup>	composition ( <sup>1</sup> H NMR)	$\eta_{inh}^b$ (dL/g)	$T_g$ of SS <sup>c</sup> (°C)	$T_m$ of SS <sup>c</sup> (°C)	$T_g$ of PLA <sup>c</sup> (°C)	$T_m$ of PLA <sup>c</sup> (°C)	LP <sup>d</sup> (nm)
1	PLLA–PEG2000–PLLA	25/1	23/1	0.135	–38	39		124	14 w
2	PDLA–PEG2000–PDLA	25/1	23/1	0.135	–39	39		124	14 w
3	PLLA–P $\epsilon$ CL(20)–PLLA	25/20/1 <sup>b</sup>	26/22/1	0.165	–51	56		135	15 w
4	PDLA–P $\epsilon$ CL(20)–PDLA	25/20/1 <sup>b</sup>	26/22/1	0.165	–54	48		136	15 w
5	PLLA–PEG2000–PLLA PDLA–PEG2000–PDLA			0.135	–45	15		183	10 w
6	PLLA–P $\epsilon$ CL(20)–PLLA PDLA–P $\epsilon$ CL(20)–PDLA			0.150	–44			182	12 w
7	PLLA–P $\epsilon$ CL(20)–PLLA PDLA–PEG2000–PDLA			0.163	–51	13		198	

<sup>a</sup> Molar feed ratios, co-initiator = SS. <sup>b</sup> Measured at 20 °C with  $c = 2$  g/L in CH<sub>2</sub>Cl<sub>2</sub>. <sup>c</sup> DSC data of the soft segment recorded with a heating rate of 20 °C/min. <sup>d</sup> LP as determined by SAXS: w = weak, m = middle, s = strong.

**Table 2. A–B–A Triblock Copolymers and Their Stereocomplexes Having Short SS and Medium Poly lactide A Blocks**

product no.	structure	LLA or DLA co-initiator <sup>a</sup>	composition ( <sup>1</sup> H NMR)	$\eta_{inh}^b$ (dL/g)	$T_g$ of SS <sup>c</sup> (°C)	$T_m$ of SS <sup>c</sup> (°C)	$T_g$ of PLA <sup>c</sup> (°C)	$T_m$ of PLA <sup>c</sup> (°C)	LP <sup>d</sup> (nm)
1	PLLA–PEG2000–PLLA	50/1	48/1	0.185	–29			147	15 m
2	PDLA–PEG2000–PDLA	50/1	49/1	0.185	–30			149	15 m
3	PLLA–P $\epsilon$ CL(20)–PLLA	50/20/1	49/20/1 <sup>b</sup>	0.200	–48		18	149	14 s
4	PDLA–P $\epsilon$ CL(20)–PDLA	50/20/1	47/20/1 <sup>b</sup>	0.200	–46		23	151	14 s
5	PLLA–PDMS4000–PLLA	50/1	49/1	0.225			38	157	17 s
6	PDLA–PDMS4000–PDLA	50/1	48/1	0.220			40	157	17 s
7	PLLA–PEG2000–PLLA PDLA–PEG2000–PDLA			0.185			50	212	13 w
8	PLLA–P $\epsilon$ CL(20)–PLLA PDLA–P $\epsilon$ CL(20)–PDLA			0.200			62	212	13 w
9	PLLA–PDMS4000–PLLA PDLA–PDMS4000–PDLA			0.225			49	223	15 s
10	PLLA–P $\epsilon$ CL(20)–PLLA PDLA–PEG2000–PDLA			0.195			49	212	
11	PLLA–P $\epsilon$ CL(20)–PLLA PDLA–PDMS4000–PDLA			0.200	–43		51	213	
12	PLLA–PEG2000–PLLA PDLA–PDMS4000–PDLA			0.200			58	216	
13	PLLA–PDMS4000–PLLA PDLA–PEG2000–PDLA			0.210			57	216	

<sup>a</sup> Molar feed ratios, co-initiator = SS. <sup>b</sup> Measured at 20 °C with  $c = 2$  g/L in CH<sub>2</sub>Cl<sub>2</sub>. <sup>c</sup> DSC data of the SS recorded with a heating rate of 20 °C/min. <sup>d</sup> LP as determined by SAXS: w = weak, m = middle, s = strong.

**Table 3. A–B–A Triblock Copolymers and Their Stereocomplexes Having Short SS and Long Poly lactide A Blocks**

product no.	structure	LLA or DLA co-initiator <sup>a</sup>	composition ( <sup>1</sup> H NMR)	$\eta_{inh}^b$ (dL/g)	$T_g$ of SS <sup>c</sup> (°C)	$T_m$ of SS <sup>c</sup> (°C)	$T_g$ of PLA <sup>c</sup> (°C)	$T_m$ of PLA <sup>c</sup> (°C)	LP <sup>d</sup> (nm)
1	PLLA–PEG2000–PLLA	100/1	90/1	0.24			33	159	14 w
2	PDLA–PEG2000–PDLA	100/1	90/1	0.26			27	160	14 w
3	PLLA–P $\epsilon$ CL(20)–PLLA	100/20/1	103/22/1 <sup>b</sup>	0.30	–45		36	162	15 s
4	PDLA–P $\epsilon$ CL(20)–PDLA	100/20/1	95/20/1 <sup>b</sup>	0.29	–44		33	161	
5	PLLA–PDMS4000–PLLA	100/1	120/1	0.33			55	167	20 s
6	PDLA–PDMS4000–PDLA	100/1	113/1	0.28			52	165	16 s (2nd order)
7	PLLA–PEG2000–PLLA PDLA–PEG2000–PDLA			0.24			60	230	13 w
8	PLLA–P $\epsilon$ CL(20)–PLLA PDLA–P $\epsilon$ CL(20)–PDLA			0.30			58	231	13 w
9	PLLA–PDMS4000–PLLA PDLA–PDMS4000–PDLA			0.30			55	230	15 s
10	PLLA–P $\epsilon$ CL(20)–PLLA PDLA–PEG2000–PDLA			0.28			50	226	
11	PLLA–P $\epsilon$ CL(20)–PLLA PDLA–PDMS4000–PDLA			0.28			51	228	
12	PLLA–PDMS4000–PLLA PDLA–PEG2000–PDLA			0.29			54	231	

<sup>a</sup> Molar feed ratios, co-initiator = SS. <sup>b</sup> Measured at 20 °C with  $c = 2$  g/L in CH<sub>2</sub>Cl<sub>2</sub>. <sup>c</sup> DSC data of the SS recorded with a heating rate of 20 °C/min. <sup>d</sup> LP as determined by SAXS: w = weak, m = middle, s = strong.

dichloromethane, and poured into diethyl ether. The precipitated polymer was isolated by filtration and dried at 25 °C in vacuo.

Analogous experiments were conducted with 25 mmol of LLA (Table 1) or 100 mmol (Table 3). Furthermore, analogous syntheses were performed with PEG 4600 (Tables 4–6).

**B. With  $\epsilon$ CL.** (Tables 4–6.)  $\epsilon$ CL (44 or 20 mmol) and 1,4-butanediol (1 mmol) were weighed into a 50-mL Erlenmeyer flask having silanized glass walls. The reaction vessel was closed with glass stopper and steel spring. When, after a few minutes (with short shaking), a homogeneous liquid was obtained, a 1 M solution of SnOct<sub>2</sub> in dry chlorobenzene

**Table 4. A–B–A Triblock Copolymers and Their Stereocomplexes Having Long SS and Short Poly lactide A Blocks**

product no.	structure	LLA or DLA co-initiator <sup>a</sup>	composition ( <sup>1</sup> H NMR)	$\eta_{inh}^b$ (dL/g)	$T_g$ of SS <sup>c</sup> (°C)	$T_m$ of SS <sup>c</sup> (°C)	$T_g$ of PLA <sup>c</sup> (°C)	$T_m$ of PLA <sup>c</sup> (°C)	LP <sup>d</sup> (nm)
1	PLLA–PEG4600–PLLA	25	21	0.20		55		132	12.5 m
2	PDLA–PEG4600–PDLA	25	21	0.19		58		122	12.5 m
3	PLLA–PεCL(44)–PLLA	25/44/1 <sup>b</sup>	25/50/1	0.23	-44	62		137	14 w
4	PDLA–PεCL(44)–PDLA	25/44/1 <sup>b</sup>	25/50/1	0.23	-43	64		134	14 w
5	PLLA–PEG4600–PLLA PDLA–PEG4600–PDLA			0.20		57		185	12 w
6	PLLA–PεCL(44)–PLLA PDLA–PεCL(44)–PεCL			0.23		60		193	14 w
7	PLLA–PEG4600–PLLA PDLA–PεCL(44)–PDLA			0.22	-53	48		193	

<sup>a</sup> Molar feed ratios, co-initiator = SS. <sup>b</sup> Measured at 20 °C with  $c = 2$  g/L in CH<sub>2</sub>Cl<sub>2</sub>. <sup>c</sup> DSC data of the SS recorded with a heating rate of 20 °C/min. <sup>d</sup> LP as determined by SAXS: w = weak, m = middle, s = strong.

**Table 5. A–B–A Triblock Copolymers and Their Stereocomplexes Having Long SS and Medium Poly lactide A Blocks**

product no.	structure	LLA or DLA co-initiator <sup>a</sup>	composition ( <sup>1</sup> H NMR)	$\eta_{inh}^b$ (dL/g)	$T_g$ of SS <sup>c</sup> (°C)	$T_m$ of SS <sup>c</sup> (°C)	$T_g$ of PLA <sup>c</sup> (°C)	$T_m$ of PLA <sup>c</sup> (°C)	LP <sup>d</sup> (nm)
1	PLLA–PEG4600–PLLA	50/1	42/1	0.23	-43	51		155	
2	PDLA–PEG4600–PDLA	50/1	43/1	0.22	-46	50		145	
3	PLLA–PεCL(44)–PLLA	50/44/1 <sup>b</sup>	47/47/1	0.27	-54	62		156	
4	PDLA–PεCL(44)–PDLA	50/44/1 <sup>b</sup>	46/46/1	0.26	-51	64		158	
5	PLLA–PEG4600–PLLA PDLA–PEG4600–PDLA			0.23		34		209	
6	PLLA–PεCL(44)–PLLA PDLA–PεCL(44)–PDLA			0.27	-50	40		211	
7	PLLA–PEG4600–PLLA PDLA–PεCL(440)–PDLA			0.25	-50	30		215	

<sup>a</sup> Molar feed ratios, co-initiator = SS. <sup>b</sup> Measured at 20 °C with  $c = 2$  g/L in CH<sub>2</sub>Cl<sub>2</sub>. <sup>c</sup> DSC data of the SS recorded with a heating rate of 20 °C/min. <sup>d</sup> LP as determined by SAXS: w = weak, m = middle, s = strong.

**Table 6. A–B–A Triblock Copolymers and Their Stereocomplexes Having Long SS and Long Poly lactide A Blocks**

product no.	structure	LLA or DLA co-initiator <sup>a</sup>	composition ( <sup>1</sup> H NMR)	$\eta_{inh}^b$ (dL/g)	$T_g$ of SS <sup>c</sup> (°C)	$T_m$ of SS <sup>c</sup> (°C)	$T_g$ of PLA <sup>c</sup> (°C)	$T_m$ of PLA <sup>c</sup> (°C)	LP <sup>d</sup> (nm)
1	PLLA–PEG4600–PLLA	100/1	85	0.31	-48	48		165	16 s
2	PDLA–PEG4600–PDLA	100/1	87	0.29	-44	49		161	14.5 s (2nd order)
3	PLLA–PεCL(44)–PLLA	100/44/1 <sup>b</sup>	95/44/1	0.35		58		165	16 m
4	PDLA–PεCL(44)–PDLA	100/44/1 <sup>b</sup>	97/44/1	0.34		61	30	166	16 m
5	PLLA–PEG4600–PLLA PDLA–PEG4600–PDLA			0.30		26		220	14.5 s
6	PLLA–PεCL(44)–PLLA PDLA–PεCL(44)–PDLA			0.35		30	60	224	14.5 s
7	PLLA–PEG4600–PLLA PDLA–PεCL(440)–PDLA			0.32	-50		60	221	

<sup>a</sup> Molar feed ratios, co-initiator = SS. <sup>b</sup> Measured at 20 °C with  $c = 2$  g/L in CH<sub>2</sub>Cl<sub>2</sub>. <sup>c</sup> DSC data of the SS recorded with a heating rate of 20 °C/min. <sup>d</sup> LP as determined by SAXS: w = weak, m = middle, s = strong.

(0.09 or 0.04 mL) was injected by means of syringe. From time to time a small sample was removed (under dry nitrogen) to monitor the conversion by <sup>1</sup>H NMR spectroscopy. After almost complete conversion the reaction mixture was cooled, and LLA or DLA (25, 50 or 100 mmol) were added together with dry chlorobenzene (30 mL). The reaction vessel was then again thermostated at 100 °C until the conversion of the lactide reached 97 ± 1% (checked by <sup>1</sup>H NMR spectroscopy). The cold reaction mixture was diluted with dichloromethane (20 mL) and precipitated into cold (+5 °C) dry diethyl ether. The polyester was isolated by filtration and dried at 20–25 °C in vacuo.

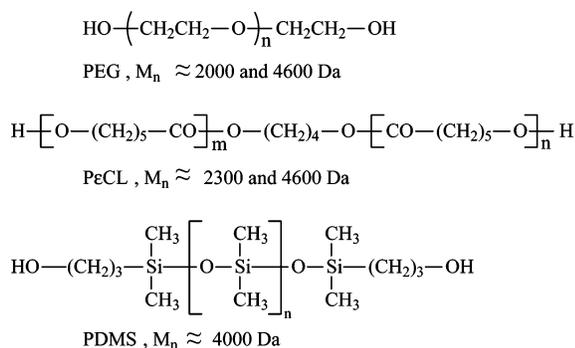
**C. With PDMS in Solution.** DLA or LLA (30 mmol) and PDMS-4000 (0.16 mmol) were weighed into a 50-mL Erlenmeyer flask with silanized glass walls. Dry chlorobenzene (20 mL) was added, and the closed reaction vessel was immersed into an oil bath preheated to 100 °C. After homogenization, 0.06 mL of 1 M solution of SnOct<sub>2</sub> in chlorobenzene were then injected. After 24 h the reaction mixture was cooled and poured into diethyl ether. The precipitated block copolymer was isolated by filtration and dried at 25 °C in vacuo.

**Preparation of Stereocomplexes.** A solution of PLLA-based triblock copolymers (1 g) in dichloromethane (10 mL) and an analogous solution of a PDLA-based triblock copolymer

(1 g/10 mL CH<sub>2</sub>Cl<sub>2</sub>) were prepared and mixed in a 100-mL round-bottom flask and homogenized by stirring for 10 min. A weak stream of dry nitrogen was passed through the reaction vessel to remove the solvent slowly (over a period of approximately 20 h). Finally, the remaining polymer was dried at 25 °C in vacuo for 6 h. The virgin reaction products were characterized.

**Measurements.** The inherent viscosities were measured in CH<sub>2</sub>Cl<sub>2</sub> with an automated Ubbelohde viscometer thermostated at 20 °C. The 400-MHz <sup>1</sup>H NMR spectra were recorded on a Bruker Avance 400 FT NMR spectrometer in 5 mm outside diameter sample tubes. CDCl<sub>3</sub> containing trimethylsilane served as solvent and shift reference. The DSC measurements were conducted with a Mettler-Toledo Md 821 in aluminum pans under nitrogen at a heating rate of 10 °C/min. Only the first heating curve was evaluated to avoid misinterpretation due to transesterification. The DSC curves were calibrated with *n*-heptane, mercury, gallium, indium, and zinc. The  $T_g$  values were defined as the midpoints of the sigmoidal curve and the  $T_m$  values as maxima of the endotherms. The WAXS powder patterns were measured with a X-ray diffractometer Siemens D500 in combination with Simac V using Ni-filtered Cu K $\alpha$  radiation ( $\lambda = 1.54$  Å). The powder patterns

Chart 1

Table 7.  $T_g$  and  $T_m$  values of the SS Used in This Work

SS	$T_g^a$ (°C)	$T_m^a$ (°C)
PEG2000	-95	56.5
PEG4600	-95	67.0
PεCL (DP ≈ 20)	-96	55.0
PεCL (DP ≈ 44)	-96	58.5
PDMS ( $M_n \approx 4000$ Da)	-119	

<sup>a</sup> DSC measurement with a heating rate of 10 °C/min.

were recorded in steps of 0.05° with a radiation time of 60 s pro step.

The SAXS was measured by means of synchrotron radiation at the Hamburger Synchrotron Laboratorium (HASYLAB), FRG, at a wavelength of  $\lambda = 0.15$  nm with a one-dimensional detector and an acquisition time of 4 min. The scattering curves were normalized with respect to the primary beam intensity, the background scattering was subtracted, and the curves were multiplied by  $s^2$  with  $s = (2/\lambda) \sin \theta$  being the scattering vector. The long period  $L$  is the reciprocal of the scattering vector at maximum intensity  $s_{\text{max}}$ .

## Results and Discussion

**Syntheses and Properties of the A-B-A Triblock Copolymers.** The triblock copolymers described in this work are based on three kinds of soft segments (SS, central, or B blocks of the triblock copolymers), the structures of which are outlined in Chart 1. To these SS belonged commercial PEGs having number average molecular weights of 2000 or 4600 Da. Furthermore, telechelic PεCL was prepared by polymerizations of εCL at 120 °C in bulk initiated with 1,4-butane diol in combination with SnOct<sub>2</sub><sup>13</sup> as catalyst (or with bismuth(III)acetate as catalyst).<sup>14</sup> Syntheses and characterization of the telechelic polylactones were described in recent publications,<sup>17,18</sup> and similar polylactones and their LLA-based triblock copolymers were also reported by other research groups.<sup>19,20</sup> The third type of SS was a commercial, 3-hydroxypropyl functionalized poly(dimethyl siloxane) having a  $M_n$  around 4000 Da. The molecular weight of all these SS were selected so that PEG 2000, PεCL prepared with a feed ratio of 20/1, and PDMS 4000 had nearly identical chain lengths. The A-B-A triblock copolymers and stereocomplexes derived from these so-called short SS are summarized in Tables 1–3. The chain length of the PεCL prepared with a feed ratio of 44/1 (relative to 1,4-butane diol) had a chain length comparable to that of PEG 46000. A PDMS having a similar chain length was not available, so that only two long SS were used in this work (see Tables 4–6). The  $T_g$  and  $T_m$  values of the neat SS were compiled in Table 7.

The short SS were used as co-initiators of a SnOct<sub>2</sub>-initiated ring-opening polymerization of LLA or DLA. The chain lengths of the polylactide blocks were varied

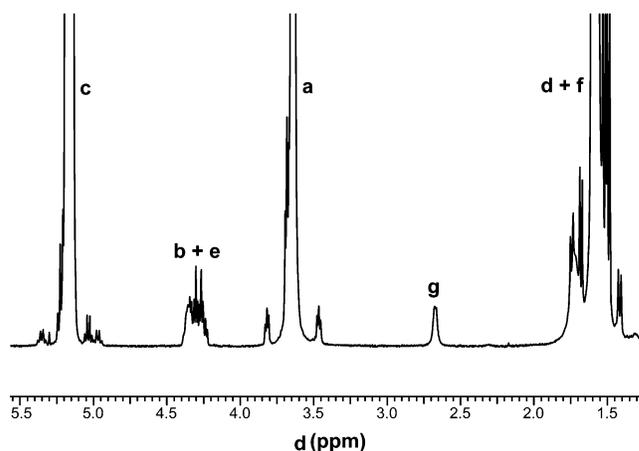
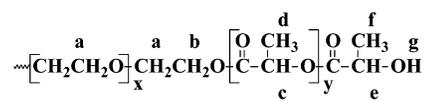


Figure 1. 400-MHz <sup>1</sup>H NMR spectrum of the A-B-A triblock copolymer prepared from PEG-2000 and LLA with M/I = 50 (No. 1, Table 2).

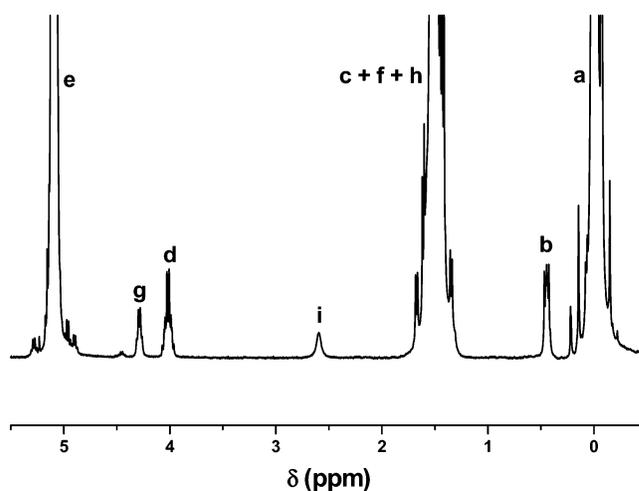
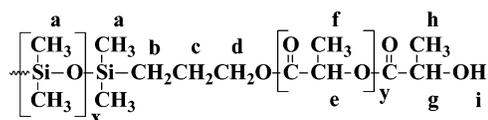
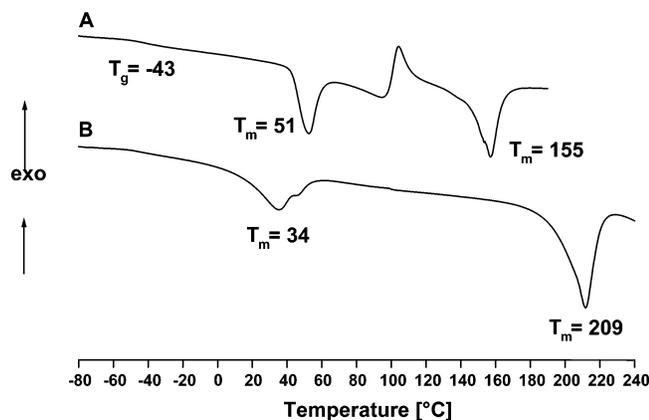


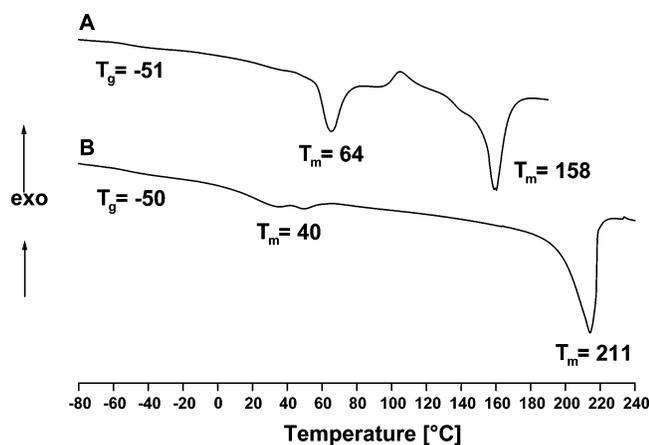
Figure 2. 400-MHz <sup>1</sup>H NMR spectrum of the A-B-A triblock copolymer prepared from PDMS and LLA with M/I = 50 (No. 5, Table 2).

via the feed ratio, and LLA (or DLA)/co-initiator ratios of 25/1 (Table 1), 50/1 (Table 2), and 100/1 (Table 3) were applied. The isolated triblock copolymers were characterized by viscosity measurements and by <sup>1</sup>H NMR spectroscopy as exemplarily illustrated in Figures 1 and 2. The molar compositions determined in this way were in satisfactory agreement with the feed ratios. The long SS were treated in the same way. They were used as co-initiators of LLA or DLA with feed ratios of 25/1 (Table 4), 50/1 (Table 5), or 100/1 (Table 6).

The DSC measurements of the A-B-A triblock copolymers conducted with a heating rate of 20 °C/min revealed the following trends. In the case of short SS full information about glass transition ( $T_g$ ) and melting temperatures ( $T_m$ ) was only available, when the PLA were relatively short (Table 1). When the lengths of the



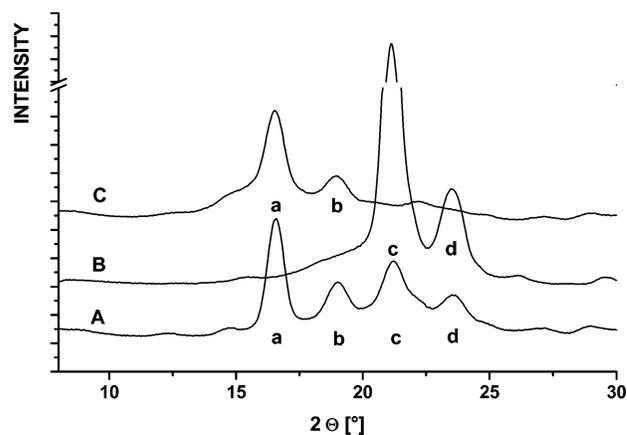
**Figure 3.** DSC measurements (first heating, with a rate of 20 °C/min) of (A) triblock copolymer based on PEG-4600 and PLLA having a DP of 50 (No. 1, Table 5) and (B) stereocomplex based on PEG-4600 and PLLA plus PDLA blocks having DP of 50 lactyl units each (No. 5, Table 5).



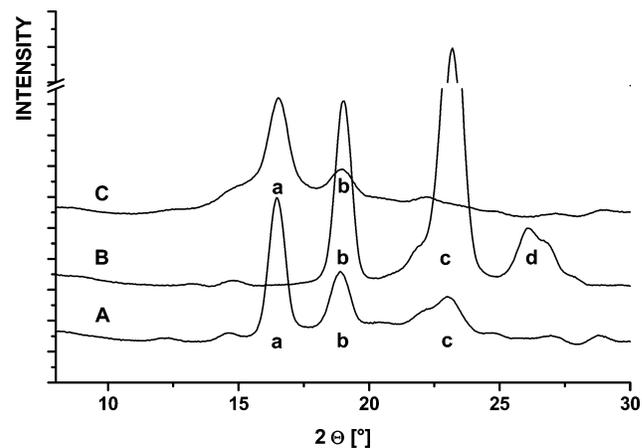
**Figure 4.** DSC measurements (first heating, with a rate of 20 °C/min) of (A) triblock copolymer based on long P $\epsilon$ CL SS and PLLA blocks having a DP of 50 (No. 4, Table 5) and (B) stereocomplex based on P $\epsilon$ CL and PLLA plus PDLA blocks having DP of 50 lactyl units each (No. 6, Table 5).

PLA blocks increased, crystallization of the short SS was suppressed at feed ratios of 50/1 (Table 2) or higher (Table 3). However, the long SS crystallized even at a feed ratio of 100/1 (Tables 4–6). Figures 3 and 4 illustrate the existence of melting endotherms of long PEG or P $\epsilon$ CL segments connected to PLA blocks having degrees of polymerization (DPs) around 50 lactyl units. The long SS showed, as expected, lower  $T_g$  values but higher  $T_m$  values than the short SS. Unfortunately, the PDMS blocks did not provide any thermal data, first because they do not crystallize and second because their  $T_g$  values were not detectable although the DSC measurements were started at a temperature of  $-150$  °C.

For the PLA blocks, the following tendencies were found. In combination with short SS the  $T_g$  values were barely detectable when the lactide blocks were short (i.e., 25 lactyl (O–CHMe–CO) units). Obviously, only one amorphous phase existed which was dominated by the mobility of the SS. For the higher block lengths (Tables 2 and 3)  $T_g$  values were observed in almost all cases. Interestingly, the highest  $T_g$  values of the lactide blocks were found for combinations with PDMS segments, indicating a more perfect separation into two amorphous phases (Nos. 5 and 6, Tables 2 and 3). When block lengths of 50 lactyl (O–CHMe–CO) units were



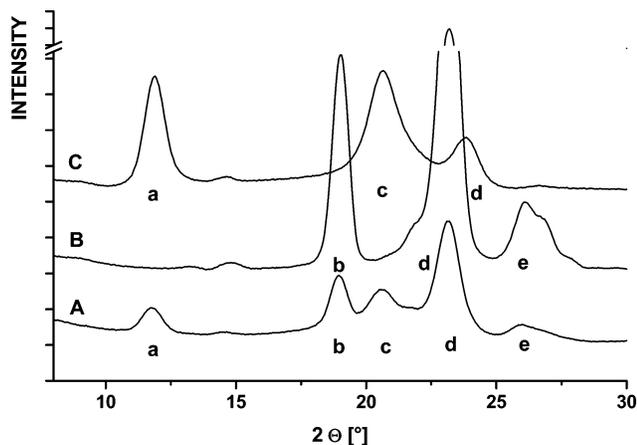
**Figure 5.** WAXS powder patterns of: (A) PLLA–PEG-4600–PLLA (No. 1, Table 5); (B) neat PEG-4600; (C) neat PLLA.



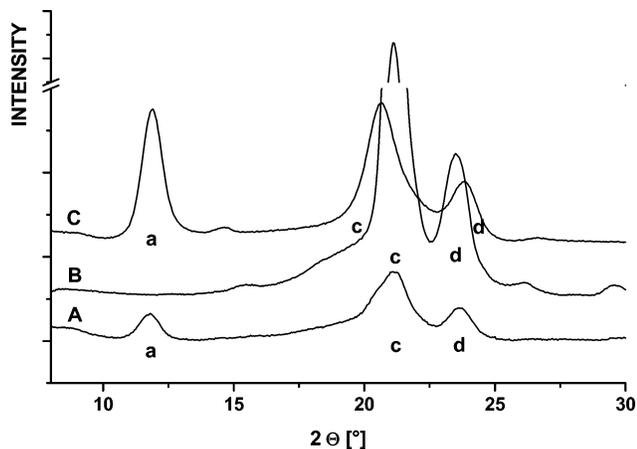
**Figure 6.** WAXS powder patterns of: (A) PLLA–P $\epsilon$ CL(44)–PLLA (No. 3, Table 5); (B) neat P $\epsilon$ CL; (C) neat PLLA.

compared with those of 100 lactyl units (Table 3) two differences were observed. First, the  $T_g$  values of the longer blocks were higher, and in combination with PEG-2000 SS the  $T_g$  values were only detectable for the long PLA blocks (Nos. 1 and 2 in Table 3). These findings suggest that the triblock copolymers containing the longest PLA blocks possess a relatively large amorphous polylactide phase well separated from the amorphous phase of the short SS. The melting temperatures  $T_m$  of the PLA blocks were observable for all triblock copolymers and displayed the expected upward trend with increasing block lengths. In this regard, no difference between triblock copolymers based on short or long SS was found. However, the long SS had a distinct influence on the amorphous phase. A  $T_g$  of a separate polylactide phase was only detected in one case (No. 4, Table 6). In other words, the longer SS hindered the phase separation in the amorphous part of the triblock copolymers.

The WAXS powder patterns of those block copolymers derived from short SS did not give clear-cut evidence for crystallization of the short SS. However, the crystallization of the long SS was clearly detectable as illustrated by Figures 5 and 6. The reflections “c” and “d” characteristic for crystalline PEG and crystalline P $\epsilon$ CL were present in the WAXS powder patterns of all triblock copolymers, but their intensity decreased relative to the “a” and “b” reflections with increasing lengths of the PLA blocks.



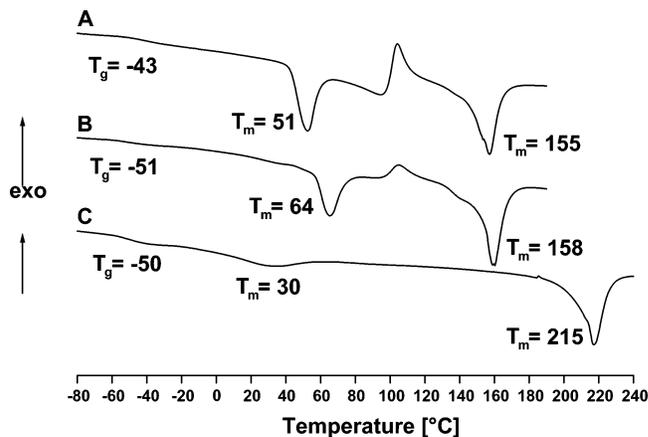
**Figure 7.** WAXS powder patterns of: (A) stereocomplex based on PEG-4600 and PLLA plus PDLA blocks having a  $\overline{DP} = 25$  each (No. 5, Table 4); (B) neat PEG-4600; (C) neat stereocomplex of PLLA and PDLA.



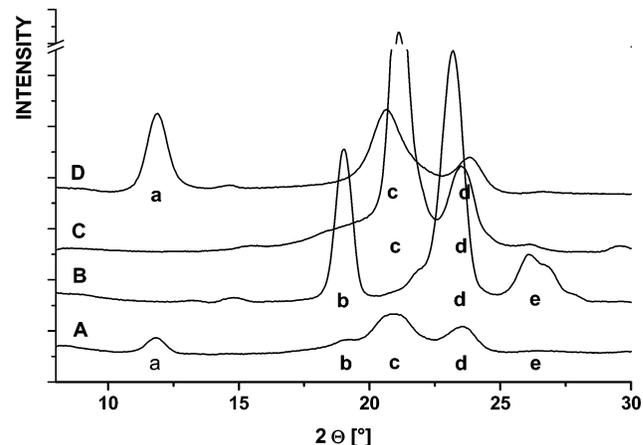
**Figure 8.** WAXS powder patterns of: (A) stereocomplex based on P $\epsilon$ CL(44) and PLLA plus PDLA blocks having a  $\overline{DP} = 25$  each (No. 6, Table 4); (B) neat P $\epsilon$ CL(44); (C) neat stereocomplex of PLLA and PDLA.

For most triblock copolymers and their stereocomplexes having identical SS, SAXS measurements were also conducted to determine the long periods (LPs). The following over-riding tendencies were found. First, the length of the PLA blocks has no influence when the SS are short, but the LP slightly increases with PLA lengths when the SS are long. Second, stereocomplexes have slightly shorter LPs. Third, the intensity of the SAXS reflections increases with the lengths of the PLA blocks and is particularly high for triblock copolymers having polysiloxane SS. In summary, both the LPs and the intensity respond to the extent of phase separation which has an influence on the degree of crystallinity and on the size of the crystallites. But the SAXS measurements are not well suited for a specific characterization of stereocomplexes.

**Stereocomplexes Combining Identical SS.** When A-B-A triblock copolymers of LLA and DLA having identical SS were mixed in solution stereocomplexes were formed upon drying in all cases. For the stereocomplexes based on short SS the DSC measurements revealed the following trends.  $T_g$ s and one  $T_m$  were only observed for stereocomplexes with the shortest PLA blocks (Nos. 5 + 6, Table 1). Longer PLA blocks had the consequence that neither  $T_g$  values nor  $T_m$  values of the SS were detectable (Nos. 7–9, Table 2, and Nos.



**Figure 9.** DSC measurements (first heating, with a rate of 20 °C/min) of: (A) triblock copolymer based on PEG 4600 and PLLA blocks having a  $\overline{DP}$  of 50 (No. 1, Table 5); (B) triblock copolymer based on P $\epsilon$ CL and PDLA having a  $\overline{DP}$  of 50 (No. 4, Table 5); (C) mixed stereocomplex consisting of the triblock copolymer mentioned above (No. 7, Table 5).



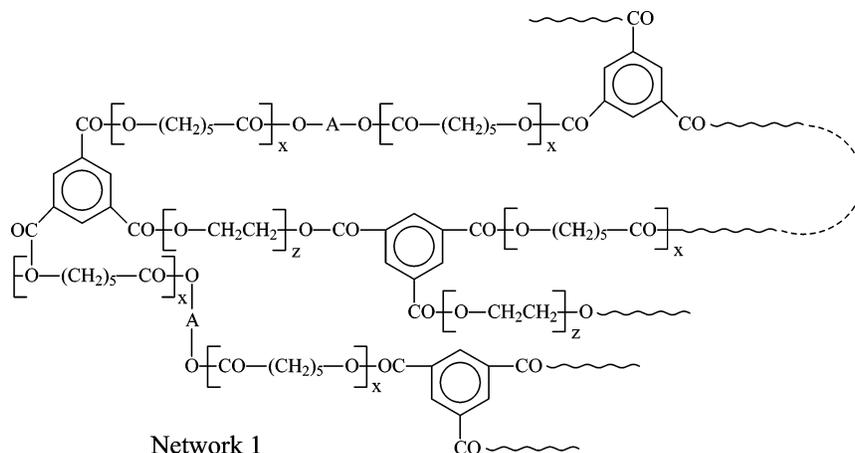
**Figure 10.** WAXS powder patterns of: (A) mixed stereocomplex consisting of the triblock copolymers PEG-4600/PLLA and P $\epsilon$ CL(44)/PDLA having a  $\overline{DP} = 25$  each (No. 7, Table 4); (B) neat PEG-4600; (C) neat P $\epsilon$ CL(44); (D) neat stereocomplex of PLLA and PDLA.

7–9, Table 3). In the case of long SS,  $T_m$  values were observable for all stereocomplexes (Nos. 5 + 6 in Tables 4–6). All these  $T_m$  values were relatively low compared to those of neat PEG or P $\epsilon$ CL.

In this connection, the DSC measurements of A-B-A stereocomplexes of other research groups should be mentioned. PEG-1000,<sup>6</sup> PEG-3400,<sup>6</sup> or PEG-6000<sup>4</sup> were used as central B blocks. In agreement with our results no crystallization of the PEG-1000 blocks were observed. Yet, surprisingly, even the PEG-3400 did not crystallize.<sup>6</sup> Possibly, the longer PLA blocks ( $\overline{DP} \geq 200$ ) were responsible for this effect. As expected, the long PEG-6000 segments crystallized regardless the PLA block lengths.<sup>4</sup> In the case of P $\epsilon$ CL SS,<sup>5,7</sup> the diblock copolymers showed a high tendency of crystallization, whereas in stereocomplexes of A-B-A triblock copolymers the crystallization of the P $\epsilon$ CL block ( $\overline{DP} \approx 35$ ) was suppressed<sup>7</sup> in analogy to the properties of the short P $\epsilon$ CL blocks in our triblock copolymers (Tables 2 and 3).

For the PLA blocks of the stereocomplexes,  $T_m$  values were 55–60 °C higher than those of the individual enantiomer. The  $T_m$  values increased with the lengths of the PLA blocks from values around 180–185 °C (Nos.

Chart 2



5 + 6, Table 1) to values around 230 °C (Nos. 7–9, Table 3). In the case of long SS,  $T_m$  values of the PLA blocks are somewhat lower than those of triblock copolymers consisting of short SS and long PLA blocks (Nos. 7–9, Table 3). Such trends were also reported by other authors for stereocomplexes of similar triblock copolymers. The DSC measurements also proved that at least the long SS not only crystallized in the triblock copolymers of the neat enantiomers (Nos. 1–4 in Tables 4–6) but also in the corresponding stereocomplexes (Nos. 5 + 6 in Tables 4–6). However, both temperatures and melting enthalpies indicated that crystallization of the SS is more efficiently suppressed in the stereocomplexes. The  $T_m$  values of the long SS decrease with higher lengths of the lactide blocks. This aspect is exemplarily illustrated in Figure 3 (long PEG blocks) and Figure 4 (long P $\epsilon$ CL blocks).

The WAXS powder patterns of the stereocomplexes containing short SS did not provide any information on the crystallization of the SS quite analogous to the WAXS powder patterns of the parent triblock copolymers. Even in the case of long SS, the usefulness of the WAXS measurements was limited to those triblock copolymers containing the shortest PLA blocks (Nos. 5 and 6, Table 4). As demonstrated by the WAXS pattern A in Figure 7, the reflections “b” and “e” typical for PEG are present in the powder pattern of the stereocomplex and the intensity of reflection “d” is higher and its  $2\theta$  value slightly lower than expected for the stereocomplex of the homopolymer (curve C). In the case of P $\epsilon$ CL-based long SS (Figure 8), it is only the higher intensity of reflection “c” (relative to “a”) in the powder pattern of the stereocomplex (curve A) which suggests a partial crystallization of P $\epsilon$ CL segments. None the less, this interpretation is in agreement with the DSC measurements.

**Stereocomplexes Combining Different SS.** Stereocomplexes containing equimolar amounts of two different SS were prepared by dissolution of a triblock copolymer having PLLA blocks and a triblock copolymer consisting of PDLA blocks and another SS. After a slow drying process, stereocomplexes were isolated from all experiments as indicated by the high  $T_m$  values of the PLA blocks (No. 7 in Tables 1, 4, 5, and 6, Nos. 10–13, Table 2, and Nos. 10–12, Table 3). The formation of stereocomplexes was confirmed by the WAXS measurements discussed below. These results demonstrate that the crystallization enthalpy of the stereocomplex dominates over the repulsive forces between the incompatible SS.

The DSC measurements also revealed the following details. From the short SS, a weak melting endotherm of the SS was only detectable when combined with the shortest PLA blocks (No. 7, Table 1). In the case of long SS, a  $T_m$  was observable, when the PLA blocks were relatively short ( $DP \approx 25$  and  $50$ , No. 7 in Tables 4 and 5), whereas the longest PLA blocks ( $DP \approx 100$ ) suppressed the crystallization of the long SS completely. This aspect represents a significant difference between stereocomplexes containing identical SS and mixed SS. Nonetheless, the weak endotherms observed for the SS in three mixed stereocomplexes are particularly interesting, because they indicate a partial phase separation of the incompatible SS (Figure 9).

The  $T_m$  values of the PLA blocks showed the expected trends. They increase with greater block lengths from 193 to 213–216 and finally to 226–231 °C when different short SS were combined (Tables 1–3). In the case of the long SS (No. 7 of Tables 4–6), the  $T_m$  values of the PLA blocks increase again with block lengths. The  $T_g$  values of the long PLA blocks in the mixed stereocomplexes had values between 50 and 60 °C, indicating an almost perfect phase separation from the amorphous phases of the short or long SS.

The WAXS powder patterns of all mixed stereocomplexes confirmed the formation of stereocomplexes. However, information about the crystallization of SS was only available from the stereocomplex combining PEG-4600 with long P $\epsilon$ CL chains and short PLA blocks (No. 7, Table 4). The partial crystallization of both long SS is evident from the following features of the WAXS pattern (curve A in Figure 10). First, a weak reflection “b” is present typical for crystalline PEG. Second, the reflections “c” and “d” are more intensive relative to “a” in contrast to the reflections in the powder pattern of the stereocomplex of the homopolymer (curve D in Figure 9). This interpretation is confirmed by the detection of a  $T_m$  around 48 °C in the heating trace of No. 7, Table 4). This result is particularly interesting, because it indicates that the long SS can undergo partial phase separation in mixed stereocomplexes. Furthermore, such a mixed stereocomplex contains three different crystalline phases, which is an unusual property even for block copolymers.

## Conclusion

The DSC and WAXS powder patterns presented in this work clearly prove that all combinations of triblock copolymers derived from LLA with those derived from

DLA yield stereocomplexes. Neither different chemical structures of the SS nor variation of their lengths affected the formation of stereocomplexes. However, the stability of the stereocomplexes (as indicated by their melting temperatures) increased with the lengths of the polylactide blocks. Even when incompatible SS were combined, the crystallization enthalpy of the stereocomplex dominated over the negative entropic effect of the incompatibility of the SS. However, at least in the case of long SS partial phase separation of incompatible SS takes place, and the concomitant crystallization of both types of SS reduces the negative entropic influence of the incompatibility.

Another interesting aspect of the homogeneous and of the mixed stereocomplexes is the multitude of coexisting phases. For instance, the triblock copolymers Nos. 3 and 4, Table 1, obviously consist of two amorphous phases and two crystalline phases. In the case of the mixed stereocomplex No. 7, Table 4, three crystalline phases coexist and at least one amorphous phase. Studies of the mechanical properties of selected stereocomplexes and studies of their usefulness in drug-release devices are in progress.

Finally, a comparison of the stereocomplexes having incompatible SS with “combi-networks” containing the same incompatible SS should be discussed. Solutions of P $\epsilon$ CL diols and PEGs (having  $M_n$  values around 2000 Da) in CH<sub>2</sub>Cl<sub>2</sub> were cross linked by addition of trimesoyl chloride and pyridine so that networks of structure **1** were obtained (Chart 2). Regardless how the ratio of P $\epsilon$ CL/PEG chains was varied, all “combi-networks” proved to be highly crystalline, indicating a high extent of phase separation. This finding stands in sharp contrast to the almost perfect suppression of crystallinity observed for the stereocomplexes with short SS (Tables 1–3). The chemical cross linking resulting in structure **1** produces chains having a random distribution of compatible and incompatible chains in their neighborhood which favors phase separation relative to

the alternating array of incompatible chains typical for stereocomplexes. The higher mobility of the chemical cross links in **1** relative to the “physical cross-link” of the crystalline stereocomplexes is certainly another factor which contributes to the largely different extent of phase separation.

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