

Synthesis and characterization of ABA-triblock copolymers with poly(ethylene glycol) segments and LC-segments

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Summary

This paper describes the synthesis of ABA-triblock copolymers with poly(ethylene glycol) A-blocks and a liquid crystalline polyester B-block. Three block copolymer series are presented with different block length of A- and B-blocks. The block copolymers show thermotropic liquid crystalline behavior up to a content of poly(ethylene glycol) segments of 50 wt%. Depending on their composition and chain length, the block copolymers are microphase separated or non-microphase separated. In the microphase separated block copolymers the poly(ethylene glycol) segments are able to crystallize. The degree of crystallinity and the spherulite diameter is strongly influenced by the length of the poly(ethylene glycol) segment itself as well as by the length of the incorporated polyester segment.

Introduction

Block copolymers with incompatible segments are well known for their ability to form microphase separated structures. The phases possess long range order with spherical, cylindrical or lamellar morphologies (1). The combination of liquid crystalline segments with amorphous segments in block copolymers was first reported in 1985 (2). Since this time a constantly increasing number of studies have been devoted to the field of liquid crystalline block copolymers.

In this paper we will concentrate on block copolymers with main chain LC-segments. A large number of examples for this kind of block copolymers has been summarized by Fischer in a review article (3). In a previous paper we described ABA-triblock copolymers consisting of a liquid crystalline polyester B-block and amorphous polystyrene A-blocks (4). Here we investigate the liquid crystalline behavior and the phase behavior of ABA-triblock copolymers with semi-crystalline, polar poly(ethylene glycol) as A-segments. The LC-polyester segment was combined with two poly(ethylene glycol) segments resulting in poly(ethylene glycol)-*block*-poly(2,2'-dimethyl-4,4'-biphenylene-phenylterephthalate)-*block*-poly(ethylene glycol) ABA-triblock copolymers. Various examples of block copolymers composed of flexible blocks and poly(ethylene glycol) blocks are already described in the literature (5-8).

Experimental

Materials: 4,4'-Dihydroxy-2,2'-dimethylbiphenyl was synthesized from 4-chloro-3-methylphenol according to Percec et al. (9). Phenylterephthalic acid was prepared by the procedure of Land et al. (10). Phenylterephthaloyl chloride was synthesized from phenylterephthalic acid and thionyl chloride and distilled in vacuum (b.p. 145°C at 0.05 mm. Hg). Poly(ethylene glycol) monomethyl ether (Aldrich) was dried in vacuum at 120°C for four hours and stored under argon. Chloronaphthalene was distilled in vacuum and stored under argon.

Optimization of coupling reaction: 1.00 g (0.50 mmol) Poly(ethylene glycol) monomethyl ether **1d** ($M_n = 2000$ g/mol) and 51.0 mg (0.25 mmol) terephthaloyl chloride were dissolved in 10 ml chloronaphthalene and reacted for 6 h at 160°C under a continuous argon flow. At the end of reaction the product was precipitated in 80 ml ether and dried in vacuum at 40°C yielding 806 mg (78 %) of dipoly(ethylene glycol) terephthalate **2**.

Synthesis of poly(2,2'-dimethyl-4,4'-biphenylene-phenylterephthalate) 3a ($M_{n,calc.} = 2800$ g/mol): 698 mg (2.500 mmol) Phenylterephthaloyl chloride and 459 mg (2.143 mmol) 4,4'-dihydroxy-2,2'-dimethylbiphenyl were dissolved in 12 ml chloronaphthalene and reacted for 24 h at 180°C under a continuous argon flow. At the end of reaction the product was precipitated in 100 ml ethanol and dried in vacuum at 60°C. The crude product was dissolved in 10 ml chloroform, precipitated in 100 ml ethanol and finally dried in vacuum at 60°C for 12 h yielding 780 mg (80 %) of polyester **3a**. The LC-polyesters **3b** and **3c** were synthesized analogous to this procedure.

Synthesis of poly(ethylene glycol)-block-poly(2,2'-dimethyl-4,4'-biphenylene-phenylterephthalate)-block-poly(ethylene glycol) 4a: 698 mg (2.500 mmol) Phenylterephthaloyl chloride and 459 mg (2.143 mmol) 4,4'-dihydroxy-2,2'-dimethylbiphenyl were dissolved in 12 ml chloronaphthalene and reacted for 24 h at 180°C under a continuous argon flow. After this first reaction step the temperature was reduced to 160°C and 250 mg (0.714 mmol) poly(ethylene glycol) monomethyl ether ($M_n = 350$ g/mol) and 3 ml chloronaphthalene were added. The reaction was continued for another 24 h under a continuous argon flow. At the end of reaction the polymer was precipitated in 100 ml ethanol and dried in vacuum at 60°C. The crude product was dissolved in 10 ml chloroform, precipitated in 100 ml ethanol and finally dried in vacuum at 60°C for 12 h. The ABA-triblock copolymers **4b-e**, **5a-e** and **6a-e** were synthesized analogous to this procedure (scheme 1).

Characterization methods: Molecular weight determination was performed on a Knauer vapor pressure osmometer (chloroform, 40°C) and on a Waters GPC system equipped with a W 510 pump (THF, 0.5 ml/min), two PL columns (500 Å and 1000 Å), a RI detector (W 410) and an UV detector (W 440, 254 nm). The GPC was calibrated with polystyrene standards (PSS). ¹H-NMR spectra were recorded on a Bruker AC 250 (250 MHz) spectrometer. Thermal measurements were performed on a Perkin Elmer DSC 7 and on a PL DMTA Mk III. Optical microscopy was carried out on a Leitz Laborlux 12-Pol equipped with crossed polarizers and a Mettler FP 82 hot stage. The morphology of the polymers was observed using a Zeiss CEM 902 transmission electron microscope.

polyester **3a** corresponds to the LC-segment of the block copolymer series **4a-e**, polyester **3b** to the LC-segment of **5a-e** and polyester **3c** to the LC-segment of **6a-e**. At the end of reaction the polymers were precipitated in ethanol resulting in ethylester endgroups of the isolated polyesters. Table 1 summarizes the experimental data of the liquid crystalline polyesters **3a-c**. The molecular weights determined by VPO are in good agreement with the values calculated for a conversion of 99.9 %. The number average molecular weights determined by GPC are higher than the calculated values due to the higher chain stiffness of the LC-polyester compared to polystyrene.

Table 1. Data of liquid crystalline polyesters **3a-c**

Polyester	r_0	X_n	$M_n^{a)}$ [g/mol]	$M_n^{b)}$ [g/mol]	$M_n^{c)}$ [g/mol]	$T_g^{d)}$ [°C]
3a	0.857	13	2800	2650	4200	110
3b	0.923	25	5300	5500	8600	126
3c	0.962	51	10800	10100	14500	129

a) calculated number average molecular weight

b) number average molecular weight by VPO analysis (chloroform, 40°C)

c) number average molecular weight by GPC analysis (polystyrene standards)

d) glass transition temperature (DSC, 2nd heating, heating rate: 10 K/min)

ABA-triblock copolymers:

The three telechelic LC-polyesters with acid chloride endgroups were coupled with five poly(ethylene glycol) monomethyl ethers **1a** ($M_n = 350$ g/mol, $T_m = -5^\circ\text{C}$), **1b** ($M_n = 550$ g/mol, $T_m = 18^\circ\text{C}$), **1c** ($M_n = 750$ g/mol, $T_m = 32^\circ\text{C}$), **1d** ($M_n = 2000$ g/mol, $T_m = 56^\circ\text{C}$) and **1e** ($M_n = 5000$ g/mol, $T_m = 65^\circ\text{C}$) with narrow molecular weight distributions ($M_w/M_n \approx 1.1$) resulting in fifteen ABA-triblock copolymers **4a-e**, **5a-e** and **6a-e** of different compositions (scheme 1). The coupling reaction conditions were checked by a model experiment. In this experiment poly(ethylene glycol) monomethyl ether **1d** was reacted with terephthaloyl dichloride to give dipoly(ethylene glycol) terephthalate **2**. GPC measurements of the coupling product **2** showed a monomodal curve and a doubling in molecular weight compared to the poly(ethylene glycol) monomethyl ether **1d**. The synthesized ABA-triblock copolymers **4a-e**, **5a-e** and **6a-e** showed monomodal molecular weight distributions and polydispersities ranging from 1.5 to 3.2 (GPC, PS calibration). The amount of liquid crystalline polyester in the block copolymers was determined by $^1\text{H-NMR}$ spectroscopy (integration of isolated signals corresponding to the A- and the B-blocks). The data are summarized in table 2.

Phase behavior of ABA-triblock copolymers:

The phase behavior of the block copolymers was investigated by DSC, DMTA and polarizing microscopy. The results are summarized in table 3. The block copolymers exhibit thermotropic liquid crystalline behavior up to a content of poly(ethylene glycol) segments of 50 wt%. The DSC curves of the block copolymers **4a-c**, **5a-c** and **6a-c** with the shorter poly(ethylene glycol) segments ($M_n = 350$, 550 and 750 g/mol) show only one glass transition. The glass transition temperature is decreasing with increasing length of the incorporated poly(ethylene glycol) segments (figure 1). Thus, these block

copolymers seem not to be microphase separated and the poly(ethylene glycol)-segments should be regarded more as flexible endgroups of the polyester segment.

Table 2. Molecular weight and composition of ABA-triblock copolymers

Polymer	$M_{n,PEG}^a)$ [g/mol]	$M_n^b)$ [g/mol]	$M_n^c)$ [g/mol]	M_w/M_n	LCP _{calc.} ^{d)} [wt%]	LCP _{NMR} ^{e)} [wt%]
4a	350	3350	4500	2.49	80.0	86.3
4b	550	3750	5300	1.93	71.8	74.4
4c	750	4150	5700	2.20	65.1	73.6
4d	2000	6650	8500	1.51	41.1	44.0
4e	5000	12650	14000	1.50	21.9	20.8
5a	350	6200	5300	2.63	87.3	90.3
5b	550	6600	6100	1.86	81.4	82.0
5c	750	7000	6500	2.52	76.2	82.7
5d	2000	9500	11900	2.14	54.5	55.3
5e	5000	15500	14500	1.59	32.4	30.6
6a	350	10800	10800	3.16	93.4	94.7
6b	550	11200	11800	3.18	90.0	89.0
6c	750	11600	12400	3.13	86.8	89.8
6d	2000	14100	14200	2.43	71.2	82.5
6e	5000	20100	21700	2.23	49.7	55.0

a) number average molecular weight of poly(ethylene glycol) segments

b) calculated number average molecular weight of block copolymer ($=M_{n,CHVPE} + 2M_{n,PEG}$)

c) number average molecular weight of block copolymer (GPC, polystyrene standards)

d) calculated LCP-content of block copolymer (feed)

e) LCP-content of block copolymer determined by ¹H-NMR spectroscopy

The DSC curves of the block copolymers **4d,e**, **5d,e** and **6e** show only a melting peak of the poly(ethylene glycol) segments, but no glass transition of the polyester segment (figure 1). Nevertheless, at least the block copolymers **5d,e** and **6d,e** should exhibit a glass transition due to their increased length of the LC-segment. But, due to the high amount of poly(ethylene glycol) the transition is difficult to detect. From the DMTA measurements a glass transition of the polyester segment of the block copolymers **5e** and **6e** was detected in the range of 100-120°C, indicating a two-phase morphology. In addition, the block copolymers **6d** and **6e** were investigated by transmission electron microscopy. In both cases features of a lamellar morphology were found confirming the predicted microphase separation.

The degree of crystallinity of the poly(ethylene glycol) segments in the block copolymers can be estimated by integration of the melting peaks in the DSC curves (2nd heating, heating and cooling rates: 10 K/min). The crystallinity of the poly(ethylene glycol) monomethyl ethers **1d** and **1e** was calculated by the use of a reference enthalpy value (6). While a crystallinity of 90 % (**1d**) is a reasonable value for poly(ethylene

glycol) in a molecular weight range from 1000-20000 g/mol, a value of 99 % (**1e**) seems rather high (7).

Both the crystallinity and the spherulite diameter decrease with increasing length of the polyester segment. As figure 2 shows, this effect is more significant for the poly(ethylene glycol) segment of 2000 g/mol molecular weight. The block copolymers with the longest poly(ethylene glycol) segment ($M_n = 5000$ g/mol) have the highest degree of microphase separation. Therefore, the crystallinity should be only a little influenced by the length of the polyester segment. The extrapolated line in figure 2 indicates no crystallinity for block copolymers with $M_{n,PEG}$ of 2000 g/mol above a polyester segment length of $X_n = 30$. This is in agreement with the experimental results of block copolymer **6d** ($X_n = 49$) where no melting peak could be detected in the DSC curve and no formation of spherulites was observed in the optical microscope.

Table 3. Phase behavior of ABA-triblock copolymers (samples indicated with an asterisk are microphase separated)

Polymer	LCP _{NMR} [wt%]	T _g ^{a)} [°C]	T _{m,PEG} ^{b)} [°C]	T _{g,LCP} ^{c)} [°C]	LC-phase ^{d)}
4a	86.3	66	-	-	+
4b	74.4	48	-	-	+
4c	73.6	41	-	-	+
4d	44.0	-	48	-	-
4e	20.8	-	59	-	-
5a	90.3	86	-	-	+
5b	82.0	69	-	-	+
5c	82.7	65	-	-	+
5d*	55.3	-	44	- ^{e)}	+
5e*	30.6	-	55	100-120 ^{f)}	-
6a	94.7	98	-	-	+
6b	89.0	92	-	-	+
6c	89.8	85	-	-	+
6d*	82.5	-	-	- ^{e)}	+
6e*	55.0	-	55	100-120 ^{f)}	+

a) glass transition temperature of non-microphase separated block copolymer

b) melting temperature of PEG segments (DSC, 2nd heating, 10 K/min)

c) glass transition temperature of polyester segment (DSC, 2nd heating, 10 K/min)

d) determined by optical microscopy (crossed polarizers, 180°C)

+ : homogenous liquid crystalline melt; - : homogenous isotropic melt

e) not detectable by DSC and DMTA

f) features of a glass transition in the range of 100-120°C (DMTA)

In table 4 the results of the block copolymers **4d,e**, **5d,e** and **6d,e** are compared with the corresponding homopolymers **1d,e** and the model compound **2**. In addition, the spherulite diameters determined by optical microscopy (samples cooled from the melt and annealed at 25°C) are presented.

Table 4. Melting temperature, crystallinity and spherulite diameter

Polymer	$M_{n,PEG}^a)$ [g/mol]	$X_{n,LCP}^b)$	$T_m^c)$ [°C]	$X^d)$ [%]	$d_{spherulite}^e)$ [μm]
1d	2000	0	56	90 ^{f)}	800-1000 ^{g)}
2	2000	1	52	70	800-900
4d	2000	13	48	45	80-210
5d	2000	25	44	16	60-100
6d	2000	49	-	-	-
1e	5000	0	65	99 ^{f)}	800-1000 ^{g)}
4e	5000	13	59	70	170-420
5e	5000	25	55	66	150-240
6e	5000	49	55	62	70-180

a) number average molecular weight of poly(ethylene glycol) segment

b) average degree of polycondensation of polyester segment

c) melting temperature of PEG segment (DSC, 2nd heating, 10 K/min)

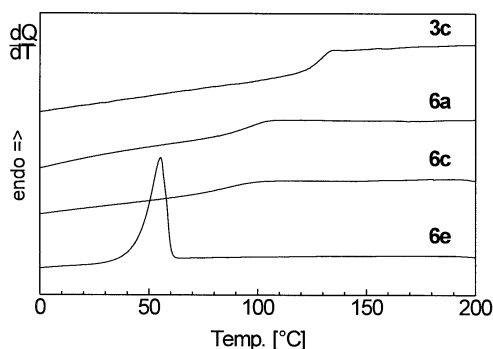
d) crystallinity of poly(ethylene glycol) segments

e) spherulite diameter (optical microscope, 25°C)

f) calculated by the use of a reference enthalpy value (6)

g) from Hardenstine et al. (8)

In conclusion, the presented route enables a systematic synthesis of ABA-triblock copolymers with a liquid crystalline polyester B-block and with poly(ethylene glycol) A-blocks. Depending on the length of the polyester segment and of the poly(ethylene glycol) segments, one can obtain non-microphase separated liquid crystalline block copolymers or microphase separated block copolymers with a liquid crystalline polyester B-block. Besides the interest as thermotropic LC-materials, these poly(ethylene glycol) containing block copolymers represent also a new class of non-ionic surfactants.

**Figure 1:** DSC curves of LC-polyester **3c** and of block copolymers **6a**, **6c** and **6e**

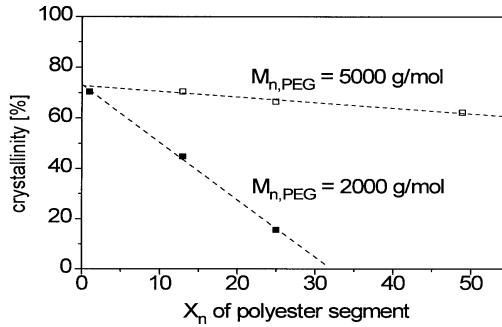


Figure 2: Influence of X_n of the LC-segment on the crystallinity of the poly(ethylene glycol) segments

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