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Synthesis and characterization of polystyrene-polyester liquid crystalline block copolymers

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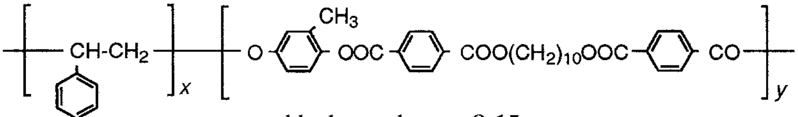
Summary

Liquid crystalline (LC) block copolymers comprising polystyrene and LC polyester blocks were obtained by a three-step procedure. In a first step, hydroxyl-terminated oligoesters were obtained by polycondensation reaction of methylhydroquinone and 4,4'-dicarboxy-1,10-dibenzoyloxydecane in pyridine solution in the presence of tosyl chloride and dimethylformamide. Hydroxyl-terminated oligoesters were then further polymerized with 4,4'-azo-bis(4-cyanopentanoyl chloride) to form azo-macroinitiators which, in a third step, were employed in the free-radical polymerization of styrene to form block copolymers. The thermal and LC properties of the copolymers are presented and discussed in terms of the dependence upon the molecular weight of the polystyrene block.

Introduction

Liquid crystalline (LC) polyesters have shown increased importance in polymer blending because of their ability to form fibrillar structures under shearing, contributing to improved mechanical properties of the polymer matrix. In addition, because of the orientation of the rod-like segments during processing they are able to reduce the viscosity of the polymer matrix, even when they are added in relatively small amounts. However, better mechanical properties of polymer blends are dependent on a good dispersion forming a continuous and uniform polymer matrix. Recently, the use of block copolymers in compatibilization is gaining increased understanding and has proved to be efficient in the control of microphase dimension of pairs of immiscible polymers [1]. Enhancement of the interfacial adhesion by block copolymer is achieved when one block can selectively mix with one component of the polymer matrix and is excluded by the other component, which instead dissolves preferentially the other block.

We have previously described a synthetic route that gives rise to a class of hybrid thermotropic block copolymers with separated microphases [2]. In this paper we present the preparation of block copolymers consisting of amorphous polystyrene and semiflexible LC polyester blocks of different lengths:



block copolymers **8-15**

Block length was shown to play an important role in driving the thermodynamic equilibrium in the blending of immiscible polymers [3] and on the melting behavior of semicrystalline copolyesters [4,5].

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The structurally analogous homopolyester is semicrystalline and forms a nematic mesophase [6]. These features are maintained in the investigated copolymers that can therefore be classified as amorphous-LC block copolymers.

Experimental Part

Materials.

Methylhydroquinone (**1**) was purified by crystallization from toluene.

4,4'-azo-bis(4-cyanopentanoyl chloride) (**5**) was prepared by reacting [7] 4,4'-azo-bis(4-cyanopentanoic acid) (25 g, 89.3 mmol) under nitrogen atmosphere with an excess of thionyl chloride (75ml) at reflux for 30 min. The reaction mixture was then cooled down and poured into cold anhydrous *n*-hexane. The acid chloride that precipitated as a fine and pale yellow powder was filtered and dried under vacuum. Yield: 75 %.

Hydroxyl-terminated oligoesters **3** and **4** were prepared according to [6] using a molar excess of methylhydroquinone in order to adjust the molecular weight of the polycondensation products. For the preparation of **3**, tosyl chloride (5.68 g, 29.8 mmol), pyridine (35 ml) and dimethylformamide (15 drops) were stirred under nitrogen atmosphere at room temperature for 30 min. Then 1,10-decamethylene bis(terephthalic acid) (**2**) (4.0 g, 8.51 mmol) was added and the reaction mixture was kept for an additional 20 min at room temperature and at 120 °C for 30 min. Finally, a solution of **1** (1.48 g, 11.93 mmol) in pyridine (10 ml) was added dropwise. After reacting at 120 °C for 3 h, the mixture was cooled down and precipitated into a large excess of methanol (300 ml). The product was filtered, washed with diluted hydrochloric acid, dried and precipitated from chloroform solution into methanol. Yield: 92 %.

For the preparation of oligoester **4**, the same procedure was followed, but the amounts of reactants were 4.97 g (26.09 mmol) of tosyl chloride, 3.45 g (7.34 mmol) of **2** and 1.09 g (8.81 mmol) of **1**. Yield: 98 %.

Macroinitiator **6** was prepared by chain extension of **3** with **5** in the presence of triethylamine in chloroform solution. Oligoester **3** (2.00 g, 3.58 mmol r.u.) was dissolved in chloroform (20 ml) and triethylamine (3.5 ml) under nitrogen atmosphere. The solution was then cooled down to 0 °C, and **5** (2.50 g, 7.89 mmol) in chloroform (20 ml) was added in 20 h. The reaction was let to proceed for an additional 10 h at room temperature. The precipitate formed was then filtered and the solution was precipitated into methanol. Yield: 92 %.

The same procedure was followed for preparation of macroinitiator **7**, except that 0.93 g (1.67 mmol r.u.) of oligoester **4** were used to react with 1.16 g (3.66 mmol) of **5**. Yield: 94 %.

Block copolymers **8-11** and **12-15** were prepared [2] by dissolving macroinitiators **6** and **7**, respectively, in THF together with styrene. For the preparation of copolymer **8**, macroinitiator **6** (2 g) was introduced into a glass ampoule with styrene (3.64 g, 35 mmol) and the total volume was adjusted to 70ml with THF ($c = 0.5$ M). After repeated freeze-thaw pump cycles the reaction vessel was sealed after nitrogen purge. The polymerization reaction was carried out at 70 °C for 20 h. The polymeric product was precipitaed into methanol, filtered and purified by extraction with boiling cyclohexane and cyclohexane/toluene (5/2 vol/vol) in the order. Yield 15 %.

Other copolymerizations were carried out from **6** and styrene at 1.0 M (**9**), 1.5 M (**10**), and 3.0 M (**11**) styrene concentrations .

The same procedure was followed by starting from macroinitiator **7** and styrene with 1.0 M (**12**), 1.5 M (**13**), 2.0 M (**14**), and 3.0 M (**15**) styrene concentrations in the feed mixture.

Block copolymers **8-11** and **12-15** were hydrolyzed to yield polstyrene homopolymers **16-19** and **20-23**, respectively, by dispersing the copolymer (0.5 g) in methanol (70 ml) together with sodium hydroxide (7.0 g). The mixture was heated to reflux and the progress of the reaction was monitored by IR spectroscopy up to complete hydrolysis after 3-4 h. The polystyrene residue was filtered, washed with methanol, and dried.

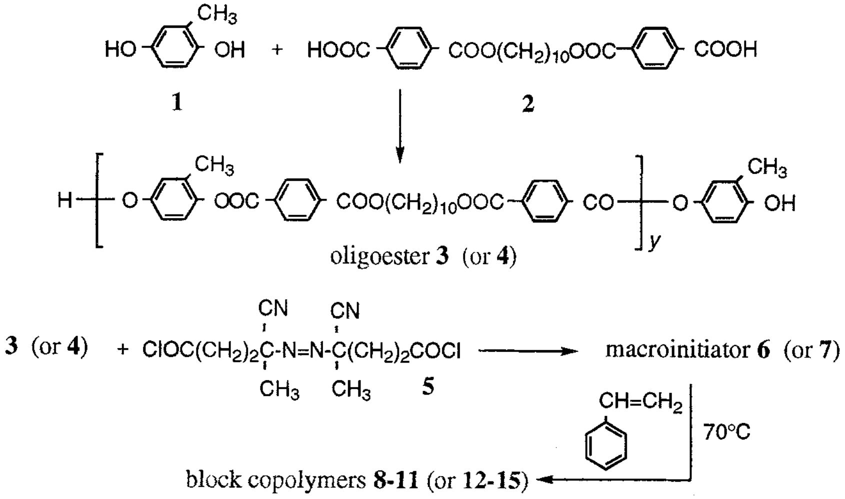
Characterization

Molecular weights were determined by SEC in THF, using an LC10 Perkin-Elmer liquid chromatograph equipped with a Jasco 830-RI refractive index detector and 10^3 Å and 10^4 Å Waters ultrastyragel columns. 3D chromatograms were obtained by using Waters 510 liquid chromatograph pump, a set of 10^3 Å, 10^4 Å, and 10^5 Å Waters ultrastyragel columns and a Waters 996 photodiode array detector. Monodisperse polystyrene standards were used for calibration. Copolymer composition was determined by ^{1}H NMR. Thermal properties and mesophase behaviour were studied with a Mettler DSC-30 calorimeter and a Reichert polarising optical microscope equipped with a Mettler hot stage.

Results and discussion

The synthetic procedure adopted for the preparation of the LC block copolymers **8-15** is illustrated in Scheme 1. Hydroxyl-terminated oligoesters **3** and **4** of different molecular weights (M_w = 4500 and 10,000, respectively) were first obtained by a direct diphenol/diacid condensation in the presence of tosyl chloride [6] using different molar excesses of the diphenol **1**. They were then chain-extended with diacyl chloride **5** to produce azo-macronitiators **6** and **7** (M_w = 7000 and 13,000, respectively) incorporating thermally labile azo groups. The macroinitiators were finally used to initiate the free-radical polymerization of styrene producing block copolymers **8-15**.

Scheme 1. Synthetic procedure for the preparation of block copolymers **8-15**.



They were purified by extraction with cyclohexane to separate polystyrene homopolymer and extraction with a boiling a cyclohexane/toluene (5/2 vol/vol) mixture to separate unreacted polyester. Yields ranged from 10 to 15%. As the polymerization of styrene preferentially terminates by a combination mechanism [8], ABA triblock and $(AB)_n$ multiblock copolymers can be formed from macroinitiators that consisted of one and more than one azo group per polymer chain respectively, the LC polyester being the A component and polystyrene being the B component. The macromolecular species formed (M_w = 10,000 - 191,000) depended on the concentration of styrene in the monomer feed, when the polystyrene block size ranged from one which is comparable to copolymer size, e.g. **8**, down to almost half of M_w of copolymer, e.g.**10**. Variation of polydispersity of copolymers, M_w/M_n = from 1.25 to 2.22, should be attributed to specific amounts of copolymer types present in the product (Tabs.1 and 2).

Tab.1. Physico-chemical characteristics of macroinitiator **6** and block copolymers **8-11** prepared from oligoester **3**.

Sample	Polyester block (wt. %)	M_na)	M_wa)	Sample	Polystyrene block	
					M_nb)	M_wb)
3	100	3000	4500		-	-
6	100	4000	7000		-	-
8	63	5500	10000	**16**	6000	8000
9	39	9500	21000	**17**	10000	17500
10	29	36000	54500	**18**	16500	28500
11	16	74500	110500	**19**	42500	69500

a)Molecular weights of the block copolymer (or oligoester and macroinitiator), by SEC.
b)Molecular weights of the polystyrene block in the copolymer, by SEC.

Tab.2. Physico-chemical characteristics of macroinitiator **7** and block copolymers **12-15** prepared from oligoester **4**.

Sample	Polyester block (wt. %)	M_na)	M_wa)	Sample	Polystyrene block	
					M_nb)	M_wb)
4	100	5500	10000		-	-
7	100	7000	13000		-	-
12	38	26500	57000	**20**	15000	26500
13	37	61000	86000	**21**	40000	66000
14	36	54500	68000	**22**	38000	69500
15	28	146000	191000	**23**	84000	142500

a)Molecular weights of the block copolymer (or oligoester and macroinitiator), by SEC.
b)Molecular weights of the polystyrene block in the copolymer, by SEC.

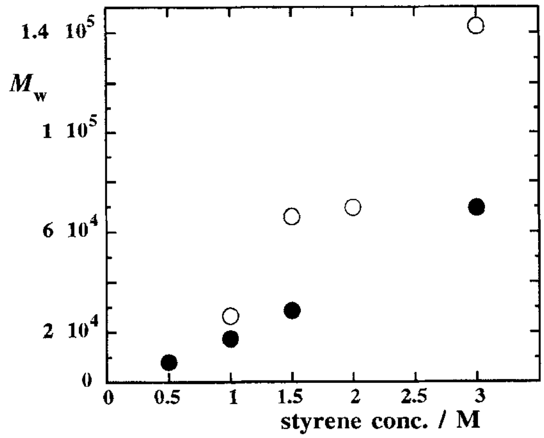


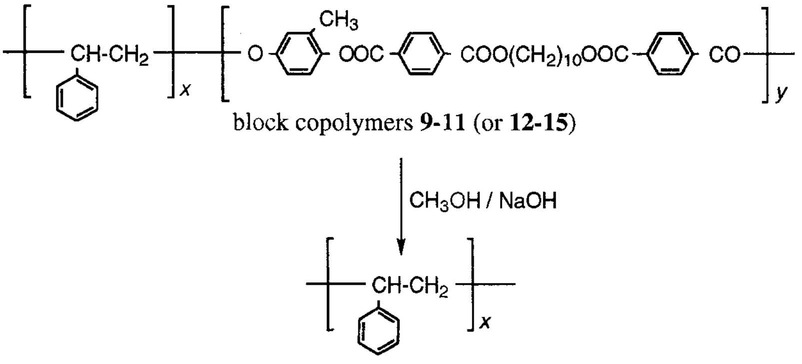
Fig.1. Weight average molecular weight of the polystyrene block for copolymers **8-11** (●) and **12-15** (○) as a function of the molar concentration of styrene in the feed mixture.

3D SEC curves recorded with a photodiode array detector showed that the copolymer samples were not uniform in polyester concentration and the lower molecular weight copolymer fractions contained more polyester segments. Therefore, the M_n and M_w values detected were approximate.

Block copolymers **8-11** were completely hydrolyzed under alkaline conditions thus giving polystyrene homopolymers **16-19**, while block copolymers **12-15** were hydrolyzed under the same conditions thus leading to polystyrene homopolymers **20-23** (Scheme 2). The M_w values of these polystyrenes were in the range 8000-142,5000 (Tabs.1 and 2) and strongly depended on the type of macroinitiator, while they varied almost linearly with the amount of feed monomer (Fig.1). The molecular weight polydispersities determined were similar (M_w/M_n = 1.39 to 1.83) in the two homopolymer series. No clear correlation could be established between the chemical composition of the copolymers and the molecular weight of the polystyrene and polyester blocks, because of the uncertainty on the blocky structure of the copolymers and the limitations inherent in the SEC measurements.

The copolymers presented distinct glass transition temperatures for the polyester block (T_{g1}) and the polystyrene block (T_{g2}) (Tabs.3 and 4), indicating the existence of amorphous phase-separated domains. The glass transition temperatures of the polystyrene blocks in the copolymer were compared to those in the recovered polystyrenes after alkaline hydrolysis (Figs.2 and 3). The T_g values of the polystyrene blocks remained nearly constant for both series of copolymers in the range of 102-105 °C and were significantly higher than those found for the copolymers.

Scheme 2. Hydrolysis of block copolymers **9-12** to polystyrene homopolymers **16-23**.



polystyrenes **16-19** (or **20-23**)

Tab.3. Transition temperatures and enthalpies of block copolymers derived from oligoester **3**.

Sample	T_{g1} a) (°C)	T_{g2} b) (°C)	T_m a) (°C)	$T_{n\text{-}i}$ a) (°C)	$\Delta H_{n\text{-}i}$ a) (J/g)
3	20	-	127	141	9.6
8	40	91	122 c)	122 c)	17.4 c)
9	21	89	134 c)	134 c)	9.3 c)
10	23	95	128	140	2.9
11	24	101	130	141	1.8

a) Glass (g), melting (m), and nematic-isotropic (n-i) transition temperatures of the polyester block. b) Glass transition temperature of the polystyrene block. c) Single and broad peak for melting and nematic-isotropic transitions.

Tab.4. Transition temperatures and enthalpies of block copolymers derived from oligoester **4**.

Sample	T_{g1}a) (°C)	T_{g2}b) (°C)	T_ma) (°C)	$T_{n\text{-}i}$a) (°C)	$\Delta H_{n\text{-}i}$a) (J/g)
4	20	-	152	172	10.0
12	24	97	127c)	127c)	6.9c)
13	22	96	129c)	129c)	11.1c)
14	25	100	152c)	152c)	8.8c)
15	24	105	153	171	1.2

a)Glass (g), melting (m), and nematic-isotropic (n-i) transition temperatures of the polyester block. b)Glass transition temperature of the polystyrene block. c)Single and broad peak for melting and nematic-isotropic transitions.

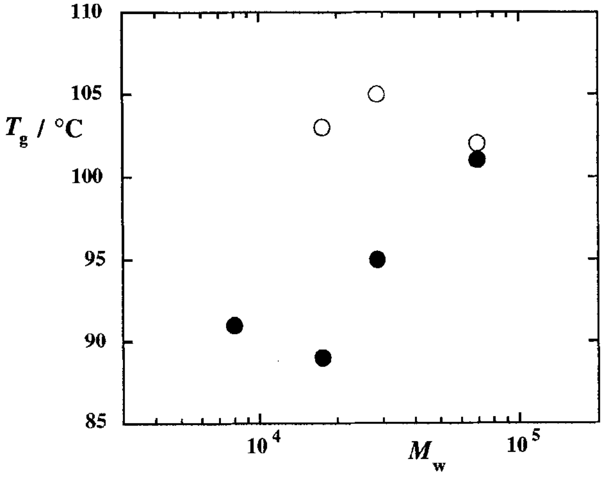


Fig.2. Glass transition temperatures of the polystyrene block in block copolymers **8-11** (●) and polystyrene homopolymers **17-19** (○) as a function of the M_w of polystyrene block.

The glass transition temperature of the polyester phase remained virtually constant, except for sample **8**, whose major constituent was polyester.

The lowering of T_g of the polystyrene phase in the copolymer is a result of an increased solubilization of amorphous polyester blocks rather than an effect of the decreased molecular weight of the polystyrene segments. Copolymers with shorter polyester blocks presented higher compatibility with polystyrene than those with longer polyester blocks, but for both series of copolymers lower glass transition temperatures were detected for the polystyrene phase when its molecular weight decreased. Thus, a partial solubilization of the polyester in the polystyrene phase occurred.

The copolymers exhibited thermotropic LC behaviour forming a nematic mesophase in each case (Tabs.3 and 4). However, in both series of copolymers the transition temperatures and the range of existence of the nematic phase were strongly influenced by the molecular weight of the polystyrene block. The melting temperature (T_m) and the nematic-isotropic temperature ($T_{n\text{-}i}$) shifted from higher to lower values when the molecular weight of copolymer decreased, noticeably in copolymers **12-15**. The depression of T_m may be attributed to an increased solvating effect of crystallites by the amorphous matrix as the molecular weight of the polystyrene block decreased. In a similar way, the strong decrease of $T_{n\text{-}i}$ derived from a disordering effect on the mesophase of the partially miscible polystyrene blocks with lower molecular weight.

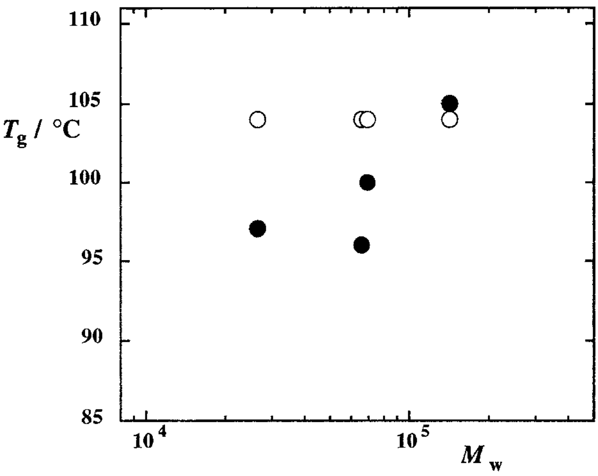


Fig.3. Glass transition temperatures of the polystyrene block in block copolymers **12-15** (●) and polystyrene homopolymers **20-23** (○) as a function of the M_w of polystyrene block.

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