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Synthesis and characterization of LC side chain AB blockcopolymers

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SUMMARY: The synthesis of liquid crystalline side chain A-B blockcopolymers, prepared by living anionic polymerization in combination with a polymeranalogous reaction is reported. Thereby the A-block was formed from a non mesogenic monomer (styrene, butadiene and n-butylmethacrylate) and the B-block from a monomer with a lateral active group (2-(trimethylsiloxy)-ethylmethacrylate), used for introduction of the side chain mesogens (cholesterylformyl- and 2-(4-[5-hexylpyrimidin-2-yl]-benzoyloxy)-groups). The obtained copolymers show mostly phase separation phenomenons. In dependence of the content of LC side groups a mesomorphic behaviour was observed.

INTRODUCTION

Liquid crystalline side chain polymers are known as substances with an ordered structure due to the effect of self orientation of the mesogenes (1,2). Ordered structures are also observable in the case of blockcopolymers if the single blocks are incompatible with respect to each other (3). A combination of both structures should lead to the presence of both states of ordered matter. Concerning to this topic there are only a few papers existent. ADAMS and GRONSKI referred first time about the synthesis of such liquid crystalline side chain blockcopolymers using a two step polymeranalogous reaction (4). The synthetic route was partially proposed by CHUNG (5). A synthesis of LC side chain diblockcopolymers using a group transfer polymerization reaction was described by HEFFT and SPRINGER (6).

It should be on interest in our investigation to use different types of non mesogenic A-blocks and to study the different effects on the liquid crystalline phases due to the different properties of the A-blocks.

The question is: Is there an influence of the non-LC A-block of the copolymers on the phase structure or phase stability of the liquid crystalline part.

METHODS OF SYNTHESIS

The anionic blockcopolymerization of LC monomers is limited by a bunch of side reactions (7). That is due to the fact, that nearly all typical functional groups of the most

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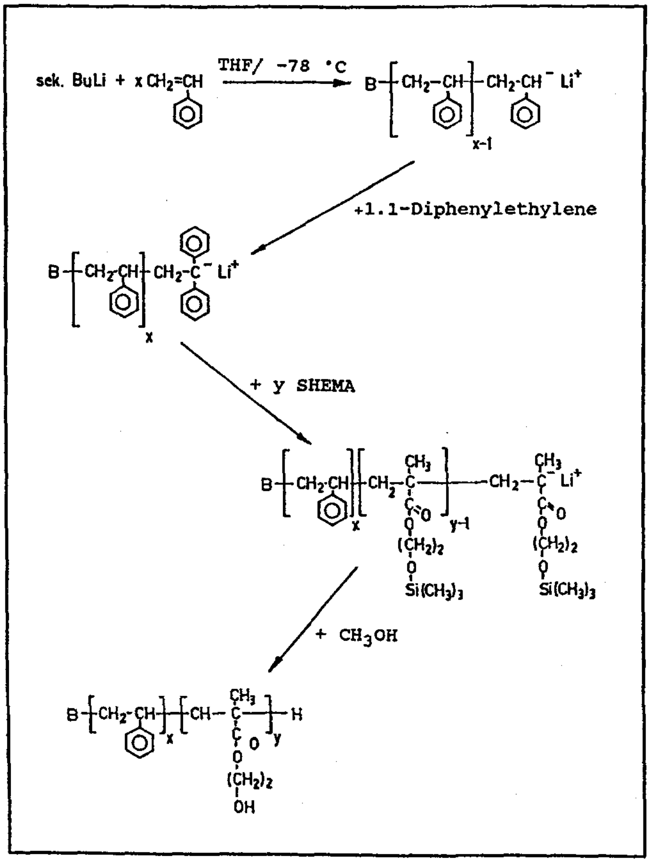
*To whom offprint requests should be sent common mesogens react with the strong anionic center. We have therefore used a synthetic route following scheme 1. The blockcopolymer was synthesized with an anioinic copolymerization using the different A-monomers styrene, butadiene and n-butylmethacrylate and the protected B-monomer 2-(trimethylsiloxy)ethylmethacrylate (SHEMA) (corresponding to the A-blocks: PS, PB, PBMA and the B-block PSHEMA). The polymerization of that monomer was described by HIRAO et.al. (8).



Scheme 1: Synthesis of Poly-[styrene-b-(2-hydroxyethyl)-methacrylate]

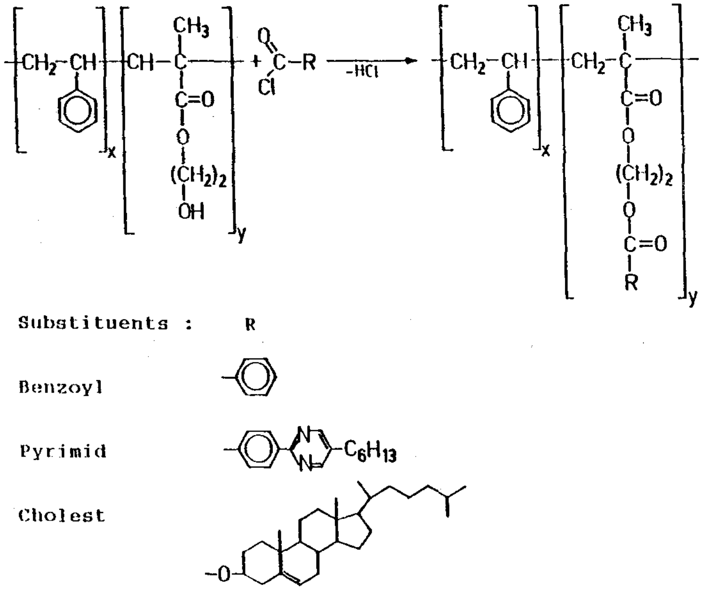
After the synthesis of the blockcoplymer an incorporation of the different side groups was performed by esterification of the free OH-groups of the poly-hydroxyethylmethacrylate parts (see scheme 2). Table 1 shows analytical data of the blockcopolymers. A key for the description of the different samples is demonstrated in the following example:

PB/Cholest/THF

polymerblock A (Table 1)

substituent of the polymerblock B (scheme 2)

solvent of esterification



Scheme 2: Incorporation of substituents into the block-copolymer by esterification of the free OH-groups

Table 1: Characteristics of the synthesized homo and block copolymers

Labelling of the polymers	PHEMA	PS	PB^a)	PBMA
1st block, M_n (g/mol)	-	20500	46200	22900
M_w/M_n	-	1.32	1.3	1.2
M1+M2, M_n (g/mol) b)	14600	31600	78400	33800
M_w/M_n	1.2	1.28	1.3	1.2
molar ratio M1/M2				
weighing in	0:100	82:18	90:10	77:23
GPC	0:100	81:19	86:14	75:25
^{1}H-NMR	0:100	82:18	90:10	-

a) = microstructure detected by ^{1}H-NMR and ^{13}C-NMR: 1,2-PB: 30 %, 1,4 cis-PB: 27 %, 1,4 trans-PB: 43 %

b) = SEC measurements of the whole polymer (M1+M2) have been carried out on samples, esterified with benzoyl chloride

RESULTS AND DISCUSSION

As expected, phase separation and liquid crystalline behaviour could be observed for cholesteryl-substituted block copolymers. The occurrence of LC phase, however, required a sufficiently high concentration of mesogenic units in the LC-block; this could only be achieved for polymers esterified in pyridine (Py), (Table 2).

In contrary to the behaviour of the homopolymer PHEMA/Cholest/Py and to the copolymer PB/Cholest/Py, which exhibit a smectic A phase, was in the case of the copolymer PS/Cholest/Py only a nematic phase observable. The layer distances of the smectic A phase of the homopolymer PHEMA/Cholest/Py and of the copolymer PB/Cholest/Py have also different values (Table 3). This behaviour is only understandable, if there is an influence of the nonmesogenic coblock on the block with the mesophase through the phase boundary. In the case of the 2-(4-[5-hexyl-pyrimidin-2-yl]-benzoyloxy)-substituted blockcopolymers was an existence of any mesophase never detectable with DSC-measurements. Polarization microscopical investigations and first x-ray measurements at room temperature hint the existence of monotropic nematic mesophases.

Table 2: Phase behaviour of LC blockcopolymers

Labelling of the polymers	degree of conversion	phase behaviour temp. in °C	ΔH(clear. point, J/g)
PHEMA/Cholest/Py	100 %	g 95 s_A 167 i	2.3
PS/Cholest/THF	78 %	g 102 i	
PS/Cholest/Py	88 %	g 99 n 190 i	0.9
PB/Cholest/THF	65 %	g -63 i	
PB/Cholest/Py	71 %	g -63 g 99 s_A 202 i	0.9
PBMA/Cholest/Py	70 %	g 44 M 164 i	
PS/Pyrimid/THF	82 %	g 98 i	
PB/Pyrimid/THF	50 %	g -62 g 70 i (monotrop nem.)	

Table 3: Phase type and X-ray diffraction data of the LC copolymers

Labelling of the polymers	liquid crystalline phase		
	type	lateral distance (Å)	layer distance (Å)
PHEMA/Cholest/Py	s_A	5.75 ± 0.1	44 ± 1.5
PS/Cholest/Py	n	5.60 ± 0.1	-
PB/Cholest/Py	s_A	5.70 ± 0.15	50 ± 2.0
PB/Pyrimid/THF	n	4.60 ± 0.1	-

A first characterization of phase separation of the differently substituted derivatives of the basic polymer with PB as the A-block (Table 1) was carried out with electron microscopy and small angle x-ray diffraction (SAXS) examinations (Table 4).

Table 4 : Structure parameter of LC copolymers (long period)

Labelling of the polymers	SAXS (Å)	electron microscopy (Å)
PB/Pyrimid/THF	480 ± 20	570 ± 30
PB/Cholest/Py	420 ± 20	390 ± 30

All blockcopolymers show a lamellar morphology (see Figure 1). The formation of the phase separated structure was in the case of the blockcopolymer PB/Cholest/Py less perfect than at the other samples. Probably that is due to the influence of the cholesteryl group and therefore the dominating liquid crystalline phase (clearing point 202 °C !). During the preparation of the polymer films the formation of the mesophase occour before a phase separation process will take place. That's why a phase separation might be hindered. For the samples with pyrimidin substituents a inverse behaviour could be possible, e.g. phase separation before the formation of the LC-phase.

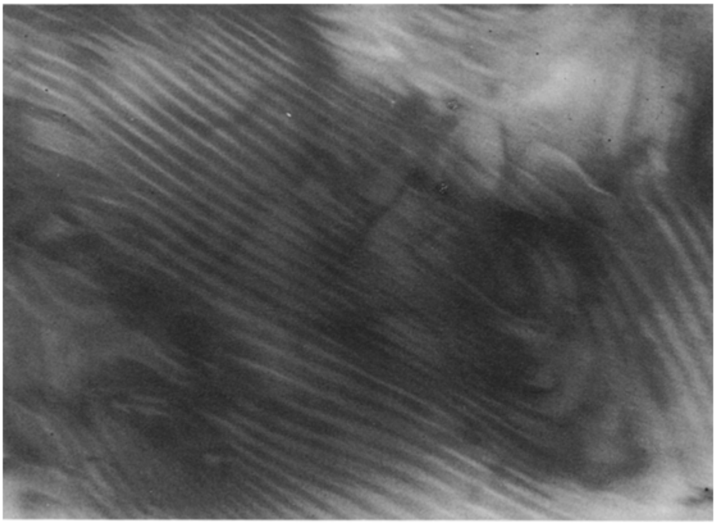


Figure 1: Electron microscopy of the phase separated copolymer PB/Pyrimid/THF (magnification 30000 *)

Fig. 2 shows a proposed structure for the polybutadiene-containing block copolymer PB/Cholest/Py. It is assumed that in the LC phase the main chain of the polymer is relatively stretched in a plane between the smectic layers. The length of the mesogenic unit was determined to be 24 Å using molecular modelling. Thus, a double layer packing structure of the mesogens within the smectic layers is assumed.

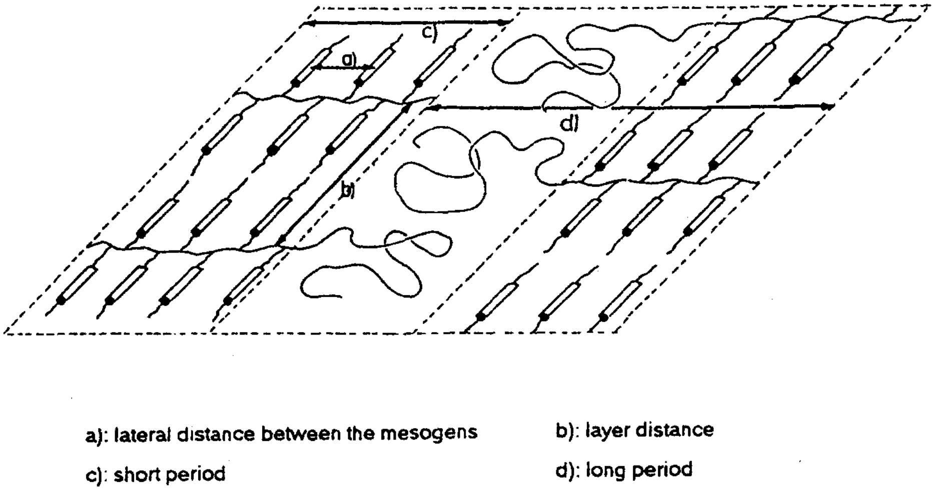


Figure 2: Proposed structure of PB/Cholest/Py

To summarize it can be said that the steps of synthesis described in this paper make it possible to synthesize liquid crystalline side chain block copolymers with a defined block length ratio and a confined molecular weight distribution. Both a liquid crystalline behaviour and phase separation could be established for cholesteryl and pyrimidine-substituted block copolymers, where the results of investigation suggest an influence of the amorphous block component on the LC phase.

EXPERIMENTAL

2-(Trimethylsiloxy)ethylmethacrylate: At a temperature of 0 °C 0.5 mol of 2-hydroxyethylmethacrylate was slowly added to 0.6 mol trimethylchlorsilane in presence of 0.6 mol urea. After stirring for 1 hr. the temperature was increased to room temperature and the solution was stirred for additional 6 hrs. After removing of the solid products, the solution was fractionally distilled. All operations have been carried out using a dry argon blanket. Yield: 89 %, b.p. (1 Torr) 55 °C

Anionic polymerization procedure: The operations have been carried out in an all-glass apparatous using high vacuum technique and/or dry argon as protecting gas. The solvents and the monomers were purified as reported in the literature (9,10). After distillation from potassium/ benzophenone the solvents were condensed from a vessel containing "living" polystyrene into the reactor. Styrene and the methacrylates were polymerized at -78 °C, butadiene was polymerized at 20 °C. All polymerizations were initiated by sec.-butyllithium. Before polymerizing the methacrylates 1,1-diphenylethylene was added to decrease the reactivity of the "living" anions. The polybutadiene block of the basic polymer PB was polymerized in cyclohexane with a trace of THF obtaining a high content of 1,4-polybutadiene. The polymerization of the second block (methacrylate) requires a surplus of THF. By adding some methanol the polymerization was stopped and the protecting groups were split off. Then the solvents were removed by a vacuum evaporator.

Polymeranalogous reaction: The different acid chlorides (cholesterylchlorformiate (Aldrich) or 4-(5-hexyl-pyrimidine-2-yl)-benzioc acid chloride 1)) were slowly added at 0 °C to the polymers with free OH-groups, dissolved either in THF/triethylamine or in pyridine.
Conditions of the reactions: Solvent: 70 ml; polymer: 2.5 g; acid chlorides: 110 %; triethylamine: 300 % (corresponding to the OH-groups of the hydroxyethylmethacrylate blocks). After stirring for one hour at 0 °C, heating to 20 °C and additional stirring for 20 hrs. the polymers were precipitated into methanol. To remove completely the unattached mesogenes it was necessary to reprecipitade the polymers for several times from THF into methanol and afterwards purified by preparative HPLC.

Measurements: The thermal characteristics were examined by means of a Perkin-Elmer DSC-7 and DMA-2. The liquid crystalline behaviour was also investigated using a polarization microscope and X-ray measurements (fibres drawn from the polymer melts and performed on a diffractometer (TUR M62) using CuK$_\alpha$ radiation monochromaized by a graphite monocrystal). The phase separation was investigated by small angle X-ray measurements (Kratky-camera, CuK$_\alpha$ radiation) and electron microscopy (samples were prepared by a cryo-ultramicrotom and exposed to a vapor of a aqueous solution of OsO$_4$). Molecular weights were determined using a KNAUER-HPLC (column: Schodex 80 M/S; solvent: THF; RI-viscosity detection). ^{1}H- and ^{13}C-NMR spectroscopy using a BRUCKER WP 200 spectrometer.

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