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Synthesis and characterization of graft copolymers containing polystyrene and liquid-crystalline segments

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The synthesis and characterization of novel graft copolymers containing side-chain liquid-crystalline backbones and polystyrene grafts are described. The liquid-crystalline behaviour and the phase separation are examined with respect to the molecular weight of the grafts and the composition of the graft copolymers.

1. Introduction

Block and graft copolymers with non-compatible segments have the tendency to form microphase-separated structures at a supramolecular level. A continuous phase and a disperse phase can be formed with dimensions in the nanometer range of the phase-separated regions [1, 2]. The incorporation of liquid-crystalline (LC) segments into block or graft copolymers opens the possibility of investigating polymers combining two different order phenomena: the liquid-crystalline order at a molecular level and the morphological order of the phase-separated regions at a supramolecular level.

From the variety of possibilities combining liquid-crystalline segments with non-liquid-crystalline segments in block or graft copolymers, only a few examples have been described in the literature. Semiflexible main-chain LC segments have been combined in (AB)*n*-type block copolymers with amorphous poly[oxy(2,6-dimethyl-1,4-phenylene)] segments and aromatic polyethersulphone segments [3, 4]. The first examples of graft copolymers containing side-chain liquid-crystalline segments consisted of LC-backbones with poly[oxy(2,6-dimethyl-1,4-phenylene)] grafts [5]. Recently microphase separation has also been discussed in side-chain liquid-crystalline copolysiloxanes with dimethyl siloxane segments [6–9].

This paper reports on the synthesis and characterization of graft copolymers containing amorphous polystyrene grafts attached to a side-chain liquid-crystalline backbone. This type of graft copolymer is represented by the schematic structure in figure 1. The graft copolymers were synthesized by copolymerization of methacrylate-terminated polystyrene macromonomers with mesogenic methacrylate monomers. The liquid-crystalline behaviour of the graft copolymers was investigated with respect to the copolymer composition and to the molecular weight of the grafts.

2. Results and discussion

2.1. *Polystyrene macromonomers*

Polystyrene macromonomers with methacrylate end groups were synthesized according to a procedure described by Rempp [10] and Milkovich [11], which was slightly modified. Styrene was anionically polymerized in a toluene/tetrahydrofuran mixture with *s*-butyl lithium at − 78°C. The living anion was endcapped at 0°C with

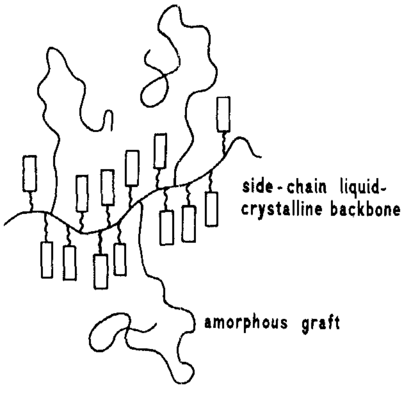
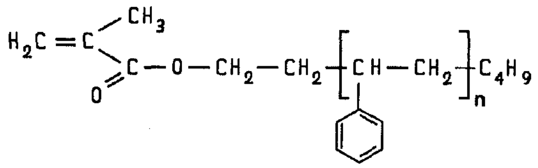


Figure 1. Schematic structure of graft copolymers containing non-liquid-crystalline grafts attached to a side-chain liquid-crystalline backbone.

ethylene oxide and the resulting lithium alcoholate reacted with an excess of methacryloyl chloride. Macromonomers with molecular weights of 1700 g mol^{-1} **1a** and 6400 g mol^{-1} **1b** having a narrow molecular-weight distribution (M_w/M_n) of 1·07 were synthesized (table 1) by varying the monomer/initiator ratio.



1a (n = 16), **1b** (n = 60)

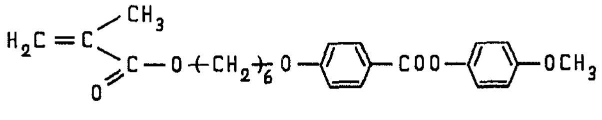
Table 1. Molecular weights (g mol^{-1}) and polydispersities of the polystyrene macromonomers **1a** and **1b**.

No.	M_n (Th)†	M_n (V.P.O.)‡	M_n (G.P.C.)§	M_w (G.P.C.)§	M_w/M_n
1a	1730	1900	1700	1800	1·07
1b	6410	6700	6400	6900	1·07

† Determined by monomer-to-initiator molar ratio.
‡ V.P.O. in $CHCl_3$ at 30°C.
§ Determined by G.P.C. in THF using polystyrene standards.

2.2. *Mesogenic monomer*

The mesogenic monomer 4-[6-(2-methylpropenoyloxy)hexyloxy]benzoic acid-4′-methoxyphenylester **2** was synthesized in three steps similar to a procedure described in the literature [12].



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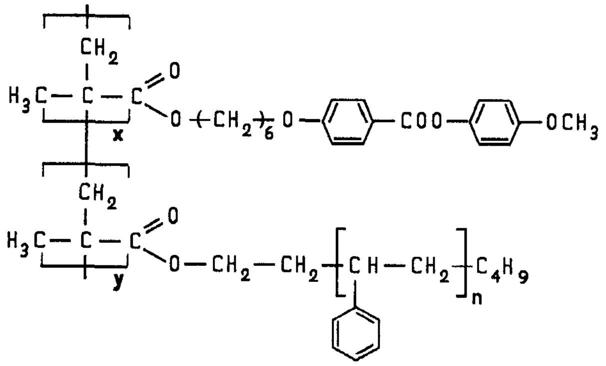
2.3. *Graft copolymers*

The graft copolymers were synthesized by free-radical solution copolymerization of the polystyrene macromonomers **1a**, **1b** and the mesogenic methacrylate monomer **2** in toluene at 60°C with AIBN as radical initiator. No precipitation of the copolymers was observed during copolymerization. Two copolymer series were prepared in order to investigate the influence of the molecular weight of the grafts. The graft copolymer series **3a**–**3e** was synthesized from the macromonomer **1a** (1700 g mol^{-1}) and the mesogenic monomer **2**. In the series **4a**–**4f** the macromonomer **1b** (6400 g mol^{-1}) was used.



3a–**3e** (n = 16), **4a**–**4f** (n = 60)

The unreacted macromonomers and mesogenic monomer were separated from the graft copolymers by preparative gel-permeation chromatography (G.P.C.). The fractionated graft copolymers have a narrow molecular-weight distribution (table 4). Figure 2 shows the analytical GPC curves of the macromonomer **1a** and the purified graft copolymer **4c**. The graft-copolymer composition was determined by elemental analysis.

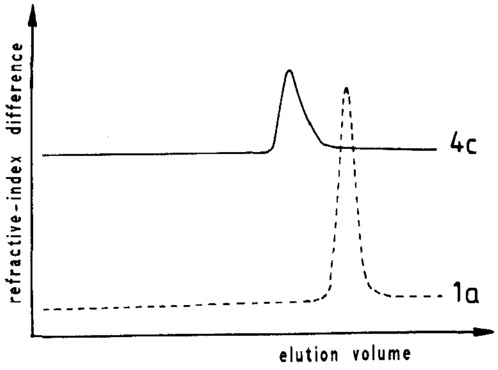


Figure 2. G.P.C. chromatograms of the polystyrene macromonomer **1a** and the purified graft copolymer **4c**.

The mesogenic monomer **2** and the macromonomers **1a** and **1b** were polymerized and purified under the same conditions to give the liquid-crystalline homopolymer **5** and the comb-shaped graft polymers **6a** and **6b** with polystyrene grafts. The homopolymer **5** was first reported with a nematic phase [12], but a reproducible weak endotherm at 70°C (D.S.C. curve 5, figure 3) indicates the existence of an additional smectic mesophase [13, 14]. The comb-shaped graft copolymer **6a** has a glass transition temperature of 57°C whereas **6b**, with longer grafts, has a T_g of 89°C.

2.4. *Phase behaviour of the graft copolymers*

The liquid-crystalline behaviour of the graft-copolymer series was investigated with respect to the molecular weights of the grafts. The results for the thermal transitions, measured by D.S.C., and the copolymer composition, determined by elemental analysis, of the graft copolymer series **3a**–**3e** (macromonomer **1a**, M_n = 1700 g mol^{-1})

Table 2. Thermal data and composition of the graft copolymers **3a**–**3e** (macromonomer **1a**, M_n = 1700 g mol^{-1}), the corresponding homopolymer **5** and the comb-shaped polymer with polystyrene grafts **6a**.

No.	Macromonomer content†/per cent by weight	Phase transitions‡ T_g/°C	T_{ni}/°C	H_{ni}/J g^{-1}
5	0 (0)	39	103§	1·80
3a	20 (19)	43	86	1·22
3b	31 (29)	43	—	—
3c	43 (41)	44	—	—
3d	54 (51)	45	—	—
3e	69 (65)	45	—	—
6a	100 (94)	57	—	—

† Macromonomer content calculated from carbon values of elemental analysis. The polystyrene content is given in parentheses.

‡ T_g = glass transition temperature; T_{ni} = nematic-to-isotropic transition.

§ An additional endotherm is observable at 70°C, indicating a smectic-to-nematic transition.

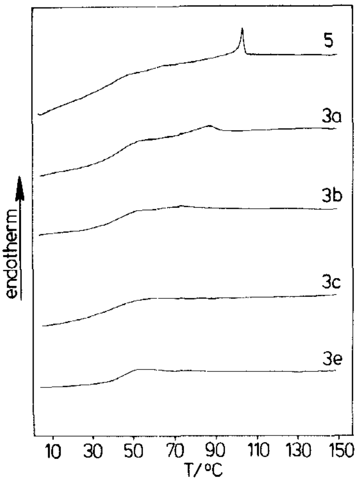


Figure 3. D.S.C. curves (second heating) of the homopolymer **5** and the graft copolymers **3a**, **3b**, **3c** and **3e**. Heating rate 10°C min^{-1}.

are summarized in table 2. The corresponding D.S.C. curves are shown in figure 3. The liquid-crystalline phase is destroyed with increasing polystyrene content, indicating partial miscibility of the polystyrene grafts with the side-chain liquid-crystalline backbone. Only the graft copolymer **3a**, with a polystyrene content of 19 per cent by weight, has a broad nematic-to-isotropic transition at 86°C, which is 17°C lower than the clearing temperature of the homopolymer **5**. The copolymer **3b** is not birefringent, although a weak and broad endotherm is detectable above the glass transition of the liquid-crystalline segment at 43°C. All other copolymers show only one glass transition, which was found to be independent of the polystyrene content (figure 4).

The graft copolymers **4a**–**4f** containing the higher-molecular-weight macromonomer **1b** ($M_n = 6400\,\mathrm{g\,mol^{-1}}$) show microphase separation of the polystyrene grafts and the side-chain liquid-crystalline backbone. The thermal data and the copolymer composition are listed in table 3, and D.S.C. curves are given in figure 5. The phase transitions are plotted versus composition in figure 6. Up to a polystyrene

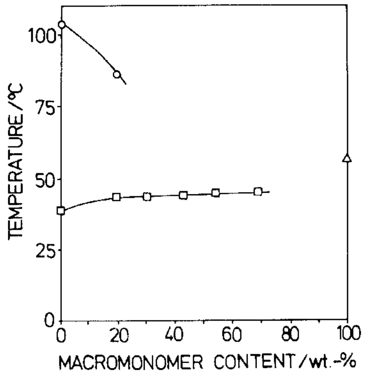


Figure 4. Influence of copolymer composition on the phase behaviour of the graft copolymers **3a**–**3e**. Transition temperatures are plotted versus macromonomer content. □, glass transition temperature of the liquid-crystalline segment; △, glass transition temperature of the comb-shaped polymer **6a**; ○, nematic-to-isotropic transition.

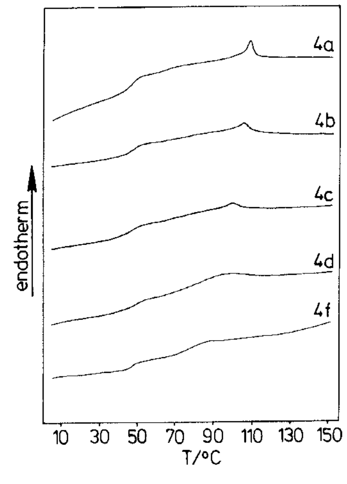


Figure 5. D.S.C. curves (second heating) of the graft copolymers **4a**–**4d** and **4f**. Heating rate $10^{\circ}\mathrm{C\,min^{-1}}$.

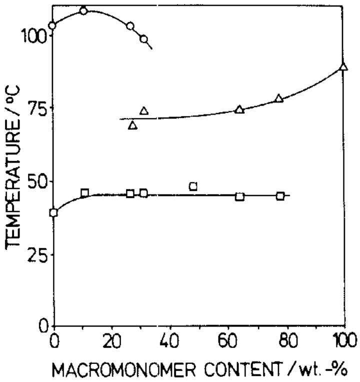


Figure 6. Influence of copolymer composition on the phase behaviour of the graft copolymers **4a**–**4f**. Transition temperatures are plotted versus macromonomer content. □, glass transition temperature of the liquid-crystalline segment; △, glass transition temperature of the polystyrene segment; ○, nematic-to-isotropic transition.

Table 3. Thermal data and composition of the graft copolymers **4a**–**4f** (macromonomer **1b**, M_n = 6400 g mol^{-1}) and the comb-shaped polymer with polystyrene grafts **6b**.

No.	Macromonomer content† / per cent by weight	Phase transitions‡			
		T_g^{LC}/°C	T_g^{PST}/°C	T_{ni}/°C	H_{ni}/J g^{-1}
4a	11 (11)	46	—	108	1·43
4b	27 (26)	46	69§	103	1·22
4c	31 (30)	46	74§	98	0·94
4d	46 (45)	48	—‖	—‖	—
4e	64 (62)	44	74	—	—
4f	76 (74)	44	78	—	—
6b	100 (97)	—	89	—	—

† Macromonomer content calculated from carbon values of elemental analysis. The polystyrene content is given in parentheses.

‡ T_g^{LC} = glass transition temperature of liquid-crystalline segments; T_g^{PST} = glass transition temperature of polystyrene segments; T_{ni} = nematic-to-isotropic transition.

§ Weak glass transition, detectable on magnification of this part of the curve.

‖ Glass transition temperature and nematic-to-isotropic transition cannot be separated.

content of 30 per cent by weight (**4a**, **4b**, **4c**), where the liquid-crystalline segments form the continuous phase, a nematic-to-isotropic transition is observable. The slight variation in the clearing temperature with increasing polystyrene content and the weak glass transition of the polystyrene segment around 74°C in **4c**, in addition to the glass transition temperature of the liquid crystalline segment at 46°C, indicate a two-phase system. Samples of **4a**–**4c** are birefringent in the polarizing microscope, but, even upon annealing, the formation of a uniform nematic texture is not observed. The graft copolymer **4d** with a polystyrene content of 45 per cent by weight has a glass transition temperature of the liquid-crystalline segment at 48°C. At higher temperatures neither the T_g of the polystyrene segments nor the nematic-to-isotropic transition can be clearly defined. In the case of the graft copolymers **4e** and **4f** with polystyrene contents of 62 and 74 per cent by weight only two glass transition temperatures, corresponding to the phase-separated mesogenic side-chain segments and the polystyrene grafts, were found. No nematic-to-isotropic transition can be detected by

D.S.C. Both samples are optically isotropic between crossed polarizers. Additional investigations will have to be conducted on these samples to study the morphology and the molecular order of the mesogenic side groups in the phase-separated regions.

3. Experimental

3.1. *Synthesis of polystyrene macromonomers*

Materials. Styrene was washed with NaOH and water to remove the inhibitor, predried over $CaCl_2$, stirred over CaH_2 at room temperature for three days in the dark and distilled in vacuum. Immediately before use, it was redistilled in an argon atmosphere. Toluene was predried over KOH, refluxed over potassium and directly distilled into the reaction flask. Tetrahydrofuran was predried over KOH, refluxed over potassium/benzophenone and distilled immediately before use. *s*-Butyl lithium (1·4 M in cyclohexane/isopentane, Aldrich), ethylene oxide (Fluka) and methacryloyl chloride (Fluka) were used as received.

Into a carefully flame-dried 500 ml round-bottomed flask equipped with inert-gas inlet and dropping funnel, and maintained under continuous argon purging, were distilled 240 ml of toluene. The 20 ml of tetrahydrofuran and 20 ml of styrene (0·174 mol) were added via syringe. The flask was cooled to −78°C. Impurities were titrated by adding the *s*-butyl lithium until a slight yellow colour persisted. The calculated amount of *s*-butyl lithium was then added. The polymerization mixture was kept for one hour at −78°C and allowed to warm up to −10–0°C within three hours. A twofold excess (based on initiator) of liquid ethylene oxide was added. The red colour of the polystyryl anion disappeared immediately. A tenfold excess of methacryloyl chloride (based on initiator) was slowly added, and the reaction mixture was stirred overnight at room temperature. The macromonomer was precipitated in methanol, filtered off and freeze-dried from benzene. The yield is almost quantitative. ^{1}H-N.M.R. (300 MHz) analysis of the macromonomers showed the complete incorporation of ethylene oxide (methylene group at 3·85 ppm) and methacryloyl chloride (vinyl group at 5·4–5·9 ppm). In addition F.T.-I.R. analysis showed the carbonyl vibration at 1720 cm^{-1} of the ester group.

3.2. *Synthesis of the graft copolymers*

The graft copolymers were synthesized by free-radical copolymerization of the polystyrene macromonomers **1a** and **1b** with the mesogenic monomer **5** in toluene under an argon atmosphere at 60°C for 72 h. One mole per cent AIBN with respect to the amount of polymerizable groups was used in all cases. The ratio of monomers to solvent was kept constant (0·54 mmol mesogenic monomer and macromonomer in 1 ml of solvent). All polymerization reactions were homogeneous. After the polymerization was finished, toluene was evaporated. The dried reaction mixture was dissolved in THF and purified by preparative G.P.C. The graft copolymers **3a**–**3e** prepared with the polystyrene macromonomer **1a** (M_n = 1700 g mol^{-1}) were isolated by preparative G.P.C., using Merckogel 6000, and the graft copolymers **4a**–**4f** (polystyrene macromonomer **1b**, M_n = 6400 g mol^{-1}) using Merckogel 20000. In both cases freshly distilled THF was used as the eluent. Yields of graft copolymers varied from 60 to 80 per cent after fractionation. The absence of macromonomers and mesogenic monomers was checked by analytical G.P.C. The copolymers were dried in vacuum at 120°C. The copolymer compositions were calculated from the carbon and hydrogen values of elemental analysis. Details are shown in table 4.

Table 4. Monomer feed, copolymer composition (macromonomer content) and molecular weights of graft copolymers **3a**–**3e**, **4a**–**4f**, homopolymer **5** and the comb-shaped polymer **6a**.

	Macromonomer content†				
No.	Monomer feed	Copolymer per cent	M_n‡/g mol^{-1}	M_w‡/g mol^{-1}	M_w/M_n
3a	20	20	66 400	95 400	1·44
3b	40	31	48 600	83 800	1·73
3c	50	43	85 600	107 800	1·26
3d	60	54	67 900	99 200	1·46
3e	80	69	62 700	90 200	1·43
4a	20	11	40 300	66 300	1·64
4b	40	27	51 800	75 100	1·45
4c	50	31	68 200	89 800	1·32
4d	60	46	50 000	62 900	1·28
4e	70	64	65 300	88 700	1·36
4f	80	78	69 000	89 300	1·49
5§	0	0	55 400	82 300	1·49
6a§	100	100	34 900	42 900	1·23

† Macromonomer content calculated from carbon values of elemental analysis.

‡ Samples obtained after fractionation of the preparative G.P.C.; molecular weights determined by analytical G.P.C. in THF using polystyrene standard.

§ Elemental analysis:

5	calc.	C 69·89	H 6·84	**6a**	calc.	C 90·12	H 8·02
	found	C 69·84	H 7·12		found	C 88·09	H 7·92

3.3. *Characterization methods*

The thermal behaviour of the compounds was investigated by a DSC7 differential scanning calorimeter (Perkin Elmer). The scan speed of heating and cooling runs was 10°C min^{-1}. The second heating run was taken for the determination of glass and phase transition temperatures. Optical investigations were carried out with Orthoplan polarizing microscope (Leitz). The samples were prepared between untreated glass slides and heated with a Mettler FP 82 hot stage controlled by a Mettler FP 800 central processor. Molecular weights were determined using polystyrene standards on a Waters GPC chromatograph equipped with an U.V. detector 440 and a refractometer R4. The structures of the compounds described were determined by elemental analysis, ^{1}H-N.M.R. spectroscopy using a Bruker AC300/300 Mz spectrometer and I.R. spectroscopy using a Nicolet 5DX F.T.-I.R. spectrometer.

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