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Modification of Side-Chain Liquid-Crystalline Poly(maleic anhydride-*alt*-1-alkene)s with Mesogen-Containing Alcohols

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ABSTRACT: Side-chain liquid-crystalline copolymers from maleic anhydride and 1-alkenes carrying biphenyl mesogens have been modified by reaction of the anhydride moieties with different mesogenic alcohols to give maleic acid monoesters. FTIR and ^{1}H NMR showed high degrees of modification. Grafting methoxybiphenyl-containing alcohols having different spacer lengths onto methoxybiphenyl-containing polymers yielded polymers exhibiting smectic A mesophases with a variable degree of interdigitation. The glass transition temperature decreased with spacer length, whereas the isotropization temperature remained almost constant. Grafting azobenzene-containing alcohols onto methoxybiphenyl-containing copolymers yielded side-chain liquid-crystalline polymers exhibiting nematic mesophases. The effect of the 4′-azobenzene terminal group on the temperature window of the mesophase was CN > OMe > F > H. Grafting a cyanostilbene-containing alcohol onto a methoxybiphenyl-containing copolymer resulted in a polymer that exhibited a smectic E mesophase with complete interdigitation of side chains. Introducing methoxybiphenyl mesogens into cyanobiphenyl-containing copolymers or vice versa resulted in polymers with smectic A mesophases. Furthermore, an increase in isotropization temperatures was observed in comparison with polymers carrying only one type of mesogen. This indicates specific favorable interactions between unlike mesogens.

1. Introduction

In a previous study, the synthesis and phase behavior of side-chain liquid-crystalline polymers (SCLCP) from maleic anhydride (MA) and 1-alkenes have been reported.[1,2] The backbone of these SCLCPs has a well-defined structure because of the alternating sequence of 1-alkene and MA moieties. The polymers show high glass transition temperatures and highly ordered smectic mesophases. Because of its reactivity toward amines and alcohols, the anhydride moiety constitutes a nice handle to modify the polymers. These modifications may for example alter the liquid-crystalline properties or enhance the aqueous solubility of the polymers.[3]

Modification may also be used to increase the mesogen density of the polymers in order to tune the liquid-crystalline properties. So far, two approaches have been described that increase mesogen density: (i) coupling compounds with paired mesogens to a preformed polymer[4,5] and (ii) polymerization of monomers carrying two mesogens.[6−8] In comparison to polymers carrying only one mesogen per repeating unit, these polymers show more stable smectic phases with high degrees of order. In this paper we describe a new method to increase mesogen density by grafting a mesogen-containing alcohol onto an MA-containing SCLC copolymer. This approach enables us to combine different spacer lengths and different mesogenic units in an almost alternating sequence in one polymer, which may lead to interesting properties.

The effect of different spacer lengths in one polymer on the phase behavior of SCLCPs has been studied before for poly(vinyl ether)s with cyanobiphenyl mesogens[9−11] and poly(styrene)s with methoxyazobenzene[12] or nitroazobenzene[13] mesogens. Depending on spacer length, poly(vinyl ether)s with cyanobiphenyl mesogens give homopolymers that exhibit nematic (N), smectic A, or no liquid-crystalline phases. When two monomers with different spacer lengths are used of which the corresponding homopolymers give no liquid-crystalline and smectic A phases, respectively, the resulting copolymers display a nematic mesophase over a quite broad range of copolymer compositions.[9−11] In addition, if one of the monomers yields homopolymers that exhibit nematic mesophases, the temperature range of this nematic mesophase can be increased considerably by copolymerization with a monomer of which the corresponding homopolymer exhibits an S_A mesophase. The combination of ethyl and undecyl spacers results in polymers with isotropization temperatures that are significantly lower than the weighted averages of the isotropization temperatures of the corresponding homopolymers. If the disparity in spacer length is smaller than eight carbon atoms, the isotropization temperatures of the copolymers deviate only slightly from ideal behavior. A small deviation from ideal behavior was also observed for poly(styrene)s with methoxyazobenzene[12] or nitroazobenzene mesogens and small disparities in spacer length.[13]

Liquid-crystalline behavior can also be influenced by combining mesogens with electron-withdrawing and electron-donating substituents in the same polymer. The combination of electron-poor and electron-rich mesogens gives rise to specific interactions.[14−21] The precise nature of these interactions is unclear, although it is generally assumed that charge-transfer complexes are involved.[22] In general, the transition temperatures of polymers with different mesogens are higher than those of either polymers with one type of mesogen.

In this study we describe polymers prepared by grafting mesogen-containing alcohols onto SCLC poly(MA-*alt*-1-alkenes), described in a previous paper.[1] The effect of different spacer lengths and different mesogens

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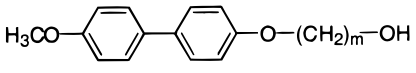
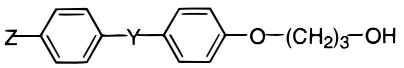
Scheme 1. Structure of Alcohols 2−5



2-*m* m = 2,3,6,8,11



alcohol	Y	Z
2-3OBu	-	OC_4H_9
3	-	CN
4-OMe	N=N	OCH_3
4-CN	N=N	CN
4-H	N=N	H
4-F	N=N	F
5	C=C	CN

in these almost perfectly alternating copolymers on the liquid-crystalline properties are investigated and compared with the properties of the unmodified parent polymers. Three different series will be described: a series in which methoxybiphenyl-containing alcohols with variable spacer lengths are grafted to investigate the disparity in spacer length, another series in which azobenzene-containing alcohols with different terminal substituents or cyanostilbene mesogens are grafted, and finally a series in which electron-rich methoxybiphenyl mesogens are combined with electron-poor cyanobiphenyl mesogens in different ways in the same copolymer. The SCLCPs have been characterized by gel permeation chromatography, ^{1}H NMR, polarizing optical microscopy, differential scanning calorimetry, FTIR, and wide-angle X-ray diffraction.

2. Experimental Part

Materials. The benzene used for polymer modifications was dried over sodium. 4-Hydroxy-4′-methoxyazobenzene, 4-cyano-4′-hydroxyazobenzene, 4-hydroxyazobenzene, and 4-fluoro-4′-hydroxyazobenzene were prepared by reaction of the diazonium salt of 4-methoxyaniline, 4-cyanoaniline, aniline, and 4-fluoroaniline, respectively, with phenol.[23] 4-Hydroxy-4′-methoxybiphenyl,[24] mesogenic alcohols[25] **2-*m***, **2-3OBu**, **3**, **4**, and **5** (Scheme 1), and copolymers **6**, **7**, and **8**[1,2] (Scheme 2) were synthesized as described before. Other reagents used for syntheses were commercially available and used without further purification.

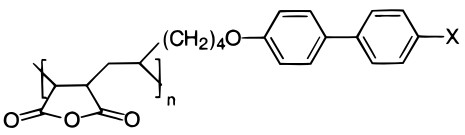
Equipment. Gel permeation chromatography (GPC) measurements were carried out using a series of four microstyragel columns with pore sizes of 10^5, 10^4, 10^3, and 10^6 Å (Waters), with THF containing 5 wt % acetic acid as eluent.[26] A dual detection system consisting of a differential refractometer (Waters model 410) and a differential viscometer (Viscotek model H502) was used. A calibration line was made with this setup, using narrow polystyrene reference standards in THF, and the molar mass (g/mol) of the synthesized polymers was determined referring to this calibration line. Thermal transitions were monitored with a Perkin-Elmer DSC-7. Scan rates of 10 K/min were used in the differential scanning calorimetry (DSC) experiments with sample masses of 5−10 mg. Transition temperatures were taken from the second heating cycle. Polarizing optical microscopy (POM) was performed on an Olympus BH-2 microscope equipped with a Mettler FP82HT hot stage and an FP80HT temperature controller. X-ray diffraction measurements were performed on a Siemens D5000 reflection diffractometer with a HTK oven and Cu Kα radiation. ^{1}H NMR spectra were recorded on a Bruker AC200 spectrometer at 200 MHz. FTIR spectra were recorded on a BioRad FTS-7 spectrometer.

The degree of modification of SCLCPs was determined from FTIR absorption spectra of modified SCLCPs in THF referring to a calibration line. This calibration line was obtained by determining the peak intensities at 1730 and 1780 cm^{-1} of mixtures of succinic anhydride and the monomethyl ester of succinic acid in different ratios in THF. The peaks at 1730 and 1780 cm^{-1} correspond to the C═O stretching band of the carbonyl and the antisymmetric C═O stretching band of the anhydride, respectively.

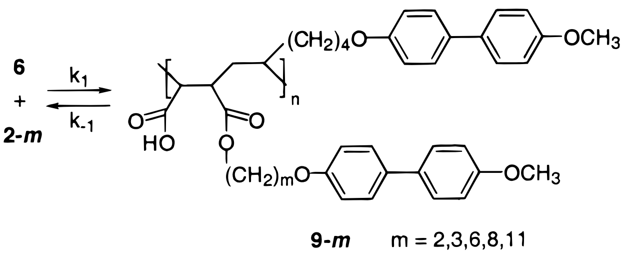
Synthesis. Modification of SCLCPs. All compounds were synthesized according to a modified literature procedure,[27] as an example is given for polymer **9-3**:

6 (0.45 g, 1.19 mmol MA units) was dissolved in benzene (7 mL) at 80 °C under nitrogen atmosphere. The solution was cooled to 60 °C, and **2-3** (0.57 g, 2.20 mmol) and 4-(dimethylamino)pyridine (0.023 g, 0.19 mmol) were added. The reaction mixture was stirred for 8 h under a nitrogen atmosphere at 60 °C, cooled to 50 °C, and stirred for another 2 h. The mixture was added to hexane (10 volumes) to precipitate the polymer and the mesogenic alcohol. The precipitate was collected and repeatedly precipitated from THF into 2-propanol (10 volumes) until TLC showed complete removal of any unreacted mesogenic alcohol. A white powder (0.38 g) was obtained after filtration.

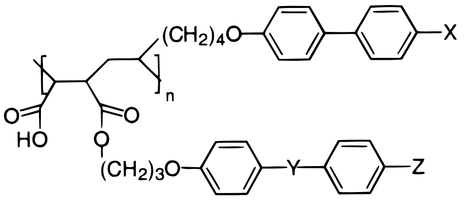
Scheme 2. Synthesis and Structures of Polymers 6−12



polymer	X
6	OCH_3
7	CN
8	CN/OCH_3 (1:1)



9-*m* m = 2,3,6,8,11



polymer	X	Y	Z
9-3OBu	OCH_3	-	OC_4H_9
10-OMe	OCH_3	N=N	OCH_3
10-CN	OCH_3	N=N	CN
10-H	OCH_3	N=N	H
10-F	OCH_3	N=N	F
11	OCH_3	C=C	CN
12-OMe*alt*CN	OCH_3	-	CN
12-OMe*ran*CN	CN/OCH_3 (1:1)	-	CN/OCH_3 (1:1)
12-CN*alt*OMe	CN	-	OCH_3
12-CN*alt*CN	CN	-	CN

Table 1. Yields (%) and Phase Transition Temperatures (°C) of Compounds 2−5[a]

mesogenic alcohol	yield	transition temp
2-2	40	K 174 I
2-3	55	K 170 I
2-6	65	K 149 I
2-8	67	K 145 I
2-11	62	K 143 I
2-3OBu	81	K 166 I
3	64	K 144 I
4-OMe	56	K 145 I
4-CN	70	K (N 161) 170 I
4-H	63	K 97 I
4-F	63	K 116 I
5	75	K 144 N 176 I

[a] K = crystalline, N = nematic, I = isotropic phase.

Table 2. Number-Average Molecular Weights (M_n), Weight-Average Molecular Weights (M_w), Polydispersity Indices (PDI), Degrees of Polymerization (DP) As Determined by GPC, and Yields (%) of Polymers 6−8

polymer	$10^{-3}M_n$	$10^{-3}M_w$	PDI	DP	yield
6	3.99	6.54	1.64	21	90
7	2.46	3.70	1.50	13	45
8	2.89	4.04	1.39	15	39

3. Results and Discussion

3.1. Synthesis. An overview of the employed mesogenic alcohols **2-*m***, **2-3OBu**, **3**, **4**, and **5** is given in Scheme 1. These monomers were obtained via etherification of bromo or chloro alcohols and phenols.[25] All monomers were obtained in satisfactory yields and high purity. The observed ^{1}H NMR signals agree well with the chemical structure.

The yields and transition temperatures, which were determined from polarizing optical microscopy (POM), are summarized in Table 1. Only compounds **4-CN** and **5** exhibit liquid-crystalline behavior. For both compounds Schlieren textures were observed with POM indicating a nematic mesophase. The transition temperatures observed with POM agree well with those found with DSC.

Polymers **6**, **7**, and **8** (see Scheme 2) were synthesized by copolymerization of the mesogenic 1-alkenes with MA.[1] Before further characterization or modification reactions were performed, the polymers were dried in vacuo over P_2O_5 at 100 °C until FTIR showed that all carboxylic acid groups were ring closed to anhydride moieties.[1] The molecular weights of the unmodified polymers were determined by GPC and are listed in Table 2.

Scheme 2 displays the modification reaction of the SCLCPs and gives an overview of the synthesized polymers. Normally, the reaction of anhydride moieties with alcohols results in monoesterification that proceeds very slowly without an efficient catalyst. Classical catalysts such as 2-(dimethylamino)pyridine, tributylamine, and pyridine showed a low activity.[27] However, 4-(dimethylamino)pyridine is an efficient catatyst[27] and was therefore used to obtain polymers with a high degree of modification. For this catalyst it was found that the reaction is reversible and that the equilibrium constant of the reaction decreases significantly with increasing temperature.[27] Therefore, the reaction was started at 60 °C, followed by further reaction at 50 °C. According to FTIR measurements using a calibration line, modification degrees between 94% and 98% were obtained with an experimental error of 5%. An example is given for polymer **9-3** in Figure 1. This figure shows that the absorptions at 1780 and 1858 cm^{-1} from the anhydride moiety are almost completely converted into the absorption at 1730 cm^{-1}, which is representative for the acid/ester moiety. ^{1}H NMR signals of the modified polymers correspond to the expected chemical structures, and the peak integrals for polymers with different mesogens also confirmed the high degrees of modification. For example, integration of the cyanobiphenyl and methoxybiphenyl signals of polymers **12-OMe*alt*CN**, **12-OMe*ran*CN**, and **12-CN*alt*OMe** confirm that these polymers contain about equal amounts of methoxybiphenyl and cyanobiphenyl mesogens.

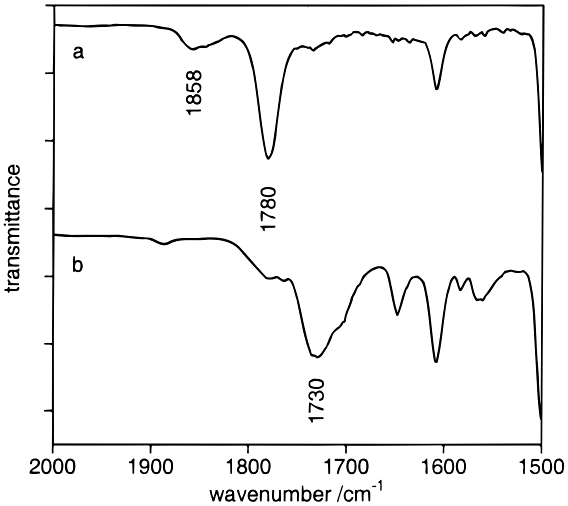


Figure 1. FTIR absorption spectra of polymer **6** (a) and polymer **9-3** (b).

Due to the similar degrees of polymerization of the unmodified polymers and the high degrees of modification, comparison of transition temperatures of different polymers is justified.

3.2. Transition Temperatures and Mesophases of SCLCPs. Table 3 summarizes the mesophases of the polymers, their phase transition temperatures, and the corresponding entropy changes. The mesophases in Table 3 were assigned on the basis of X-ray diffraction patterns of the mesoglass and textures observed with POM. The assignment of mesophases will be discussed later.

Table 4 represents the X-ray diffraction data, comprising experimental *d* spacings and calculated *d* spacings. The *d* spacings were determined in the glassy state at room temperature, after the polymer was cooled from the isotropic state to the glassy state at a cooling rate of 5 °C/s.

Unmodified SCLCPs. Figure 2 shows the DSC thermograms of the parent polymers **6**, **7**, and **8**. Polymer **7**, containing cyanobiphenyl mesogens, shows a T_g and does not exhibit any liquid-crystalline behavior. Polymer **6**, containing methoxybiphenyl mesogens, exhibits both a hexatic smectic B (S_{Bhex}) and an interdigitated smectic A (S_{Ad}) mesophase.[1] Because the T_g is almost immediately followed by the S_{Bhex}−S_{Ad} transition, determination of T_g was difficult. For polymer **8**, which has a random distribution of equimolar amounts of methoxy- and cyanobiphenyl mesogens along the polymer backbone, a higher isotropization temperature (T_i) is found than can be expected from the mesomorphic behavior of polymers **6** and **7**. This behavior has been observed before and has been ascribed to specific favorable interactions between electron-rich and electron-poor groups.[19−21]

Table 3. Phase Transition Temperatures (°C), Corresponding Heat Capacity or Entropy Changes (J/(mol K)) in Parentheses As Determined by DSC, and Phase Types[a] of the Polymers

polymer	phase behavior
6	G_{Bhex} 120 (−) S_{Bhex} 128 (7.1) S_{Ad} 136 (10) I
7	G 114 (103) I
8	G 137 (137) S_{Ad} 177 (5.3) I
9-2	G_{Bcryst} 132 (178) S_{Bcryst} 138 (15.8) $S_{A1,inc}$ 147 (7.3) I
9-3	G_E 134(−) S_E 144 (24.9) S_{A1} 150 (9.0) I
9-6	G_{Bcryst} − S_{Bcryst} 136 (19.9) S_{A1} 148 (13.4) I
9-8	G_{Bcryst} 98 (137) S_{Bcryst} 108 (7.9) S_{A1} 145 (5.3) S_{A2} 147 (4.9) I
9-11	G 93 (74) S_{Ad} 141 (13.9) I
9-3OBu	G_E − S_E 139 (8.9) S_{A1+A2} 147 (3.1) S_{A2} 159 (4.9) I
10-OMe	G 96 (101) N 148 (5.0) I
10-CN	G 108 (99) N 164 (7.5) I
10-H	G 95 (58) N 123 (7.8) I
10-F	G 97 (83) N 143 (4.8) I
11	G − S_E 154 (15.0) I
12-OMe*alt*CN	G_{Bcryst} − S_{Bcryst} 154 (6.6) S_{A1} 170 (9.0) I
12-OMe*ran*CN	G_{Bhex} − S_{Bhex} 129 (3.7) S_{Ad} 157 (8.1) I
12-CN*alt*OMe	G 109 (115) S_{Ad} 150 (7.0) I
12-CN*alt*CN	G − S_{Ad} 134 S_{AX} 137 I

[a] I = isotropic phase; S_{Ad}, S_{A1}, S_{A2} = different smectic A phases; S_{AX} = unidentified smectic A phase; S_{Bhex} = hexatic smectic B; S_{Bcryst} = crystal smectic B; S_E = smectic E; G_X = glass phase, in which X is the frozen in hexagonally or orthorhombically ordered mesophase.

Table 4. Experimental *d* Spacings (Å) at Different Temperatures Obtained from Wide-Angle X-ray Diffraction Experiments and Calculated *d* Spacings (Å) of the Polymers

			calcd *d* spacings	
polymer	*T*, °C	*d* spacings	S_{A1}	S_{Ad}
6	25	23.9; 11.9	20.9	26.6
7	25			
8	25	23.3; 11.5	20.9	26.6
9-2	25	26.3; 22.3; 11.0; 4.48	20.6	26.1
9-3	25	21.8; 10.7; 7.25; 4.47; 3.94; 3.21	21.8	28.5
9-6	25	22.9; 11.5; 4.45	25.4	36.3
9-8	25	23.7; 11.9; 4.46	26.9	39.3
9-11	25	32.1; 16.3; 10.8	30.7	46.7
9-3OBu	25	39.6; 21.8; 19.6; 13.2; 11.0; 4.49; 3.99; 3.22	25.8	28.5
	142	40.1; 21.8; 20.3; 13.5; 11.0		
	155	39.2; 20.1; 13.3		
10-OMe	25	21.5; 10.8	24.2	30.3
10-CN	25	21.6; 10.8	23.4	30.3
10-H	25	22.1; 10.9	21.9	30.3
10-F	25	21.3; 10.7	22.3	30.3
11	25	11.2; 7.5 4.39; 3.99; 3.17	23.7	30.7
10-OMe*alt*CN	25	21.5; 10.8; 7.22; 4.47	21.3	26.6
10-OMe*ran*CN	25	23.5; 11.7; 4.44	21.8	28.5
10-CN*alt*OMe	25	24.1; 12.0; 4.38	21.8	28.5
10-CN*alt*CN	25	27.2	21.8	28.5

If 50% of the methoxybiphenyl mesogens in polymer **6** are replaced by cyanobiphenyl mesogens, like in polymer **8**, the S_{Bhex} mesophase disappears (Figure 2 and Table 3). Introduction of cyanobiphenyl mesogens in a methoxybiphenyl matrix disturbs the efficient packing of mesogens, and only an S_{Ad} mesophase is found. Consequently, a distinct T_g is found.

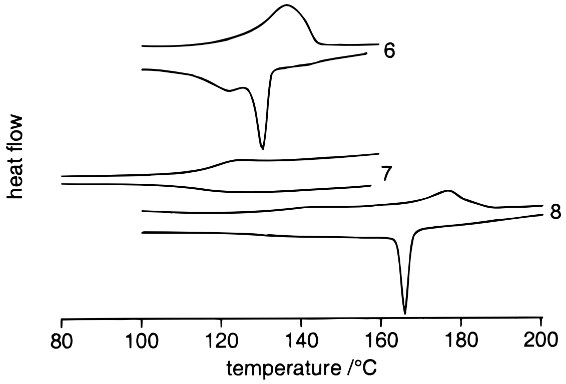


Figure 2. DSC thermograms of polymers **6**, **7**, and **8**. For all compounds the second heating and cooling traces are given.

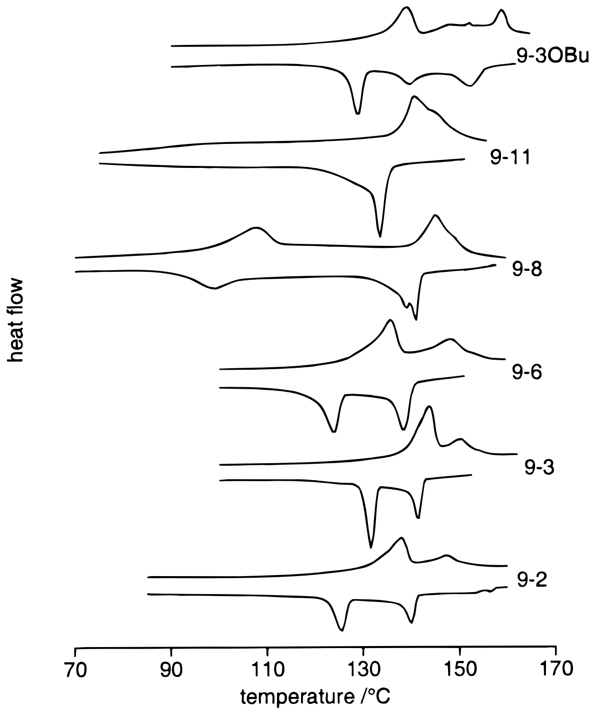


Figure 3. DSC thermograms of polymers **9-*m*** and **9-3OBu**. For all compounds the second heating and cooling traces are given.

Alkoxybiphenyl Mesogens. Figure 3 shows the DSC thermograms of polymers that were obtained by modifying polymer **6** with methoxybiphenyl-containing alcohols having different spacer lengths. In addition, an alkoxybiphenyl mesogen with a butoxy terminal group and a propyl spacer has been grafted onto polymer **6**. From Figure 3, it is clear that these polymers undergo two or even three first-order phase transitions. Polymers **9-2**, **9-3**, and **9-11** exhibit distinct glass transitions in the second heating and cooling scans. Due to the presence of a highly ordered mesophase, polymer **9-8** only exhibits a distinct glass transition in the first heating scan. This can be attributed to the absence of hexagonal order in the freshly precipitated polymer. For polymers **9-6** and **9-3OBu** no glass transition was found with DSC.

On cooling from the isotropic melt, polymers **9** show textures with POM that were similar to those of polymer **6**,[1] although they seem to develop faster during annealing and the domains were slightly larger. When polymer **9-8** is cooled from the isotropic melt, a different texture developed with small bandlike domains that are surrounded by homeotropic regions. After additional cooling, this texture transformed into a more sandlike texture (Figure 4) similar to that observed for the other polymers that exhibit an S_{A1} mesophase. These observations agree well with DSC results that showed two

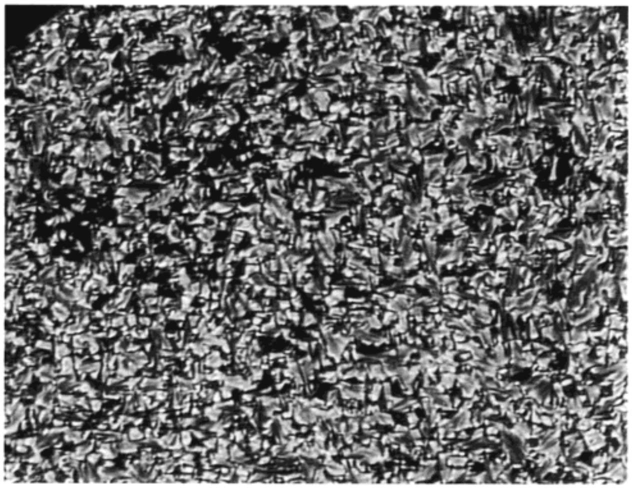


Figure 4. Polarizing optical micrograph of polymer **9-8** in the S_{A1} mesophase.

peaks in a narrow temperature interval. DSC also showed an additional transition for polymer **9-3OBu**. However, no change in texture was observed with POM at the transition temperature of 147 °C.

The X-ray diffraction pattern of polymer **9-2** shows peaks from two first-order reflections that correspond to a mesophase with partially interdigitated side chains (S_{Ad}) and one with fully interdigitated side chains (S_{A1}) (Table 4). This combination of mesophases is also known as $S_{A1,inc}$. The experimental *d* spacing of the S_{A1} periodicity is slightly higher than the calculated *d* spacing, which can be attributed to the presence of an S_{Ad} mesophase that partially disturbs the S_{A1} periodicity. The sharpened reflection in the wide-angle region results from a regular lateral distance between mesogens of 4.48 Å. From the width at half-height of this peak the correlation length of the lateral order was calculated. The magnitude of both the correlation length (14.0 Å) and the entropy change associated with the S_B–$S_{A1,inc}$ transition (see Table 3) are indicative of an S_{Bcryst} mesophase; i.e., besides long-range bond-orientational order there is also long-range positional order.

Polymer **9-3** (Table 4) exhibits an S_{A1} mesophase between 144 and 150 °C. For the mesoglass, the (110), (200), and (210) reflections emerged in the wide-angle region. These reflections result from deviations from hexagonal symmetry which means that polymer **9-3** exhibits a smectic E (S_E) mesophase. In this S_E mesophase the mesogens are densely packed in an orthorhombic cell with the following dimensions: $a = 7.89$ Å, $b = 5.43$ Å, and $c = 21.8$ Å. The surface area ($a \times b$) of the orthorhombic cell has a value of 42.8 Å^2, which is considerably smaller than the 43.7 Å^2 of unmodified polymers with an S_E mesophase and S_{Ad} periodicity.[1] The difference can be attributed to a denser packing of mesogens in the S_{E1} mesophase than in the S_{Ed} mesophase.

The *d* spacing of polymer **9-6** is 22.9 Å, which is 1.1 Å longer than the *d* spacing of **9-3**. However, on going from a propyl to a hexyl spacer an all-trans conformation of the hexyl spacer would lead to an increase of 3.9 Å. This difference is found because this system strives for a maximum of mesogenic interactions and a minimum of free volume. Therefore, the longest spacer (i.e., hexyl spacer) has to adjust its conformation; i.e., the longest spacer has an increased number of gauche conformations. The result is a kind of distorted layer with S_{A1} periodicity (Figure 5a). In addition, polymer **9-6** exhibits an S_{Bcryst} mesophase with a correlation length of 13.3 Å. The disparity in spacer lengths prevents the mesogens from attaining the better ordered S_E phase as found for polymer **9-3**.

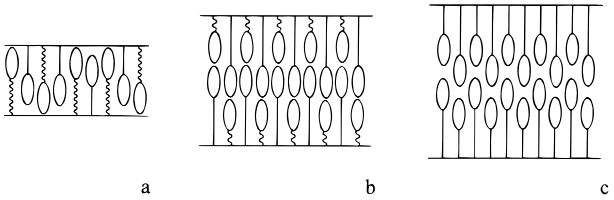


Figure 5. Schematic representation of different smectic mesophases for polymers with different spacer lengths: (a) S_{A1} mesophase, (b) S_{Ad} mesophase, and (c) S_{A2} mesophase.

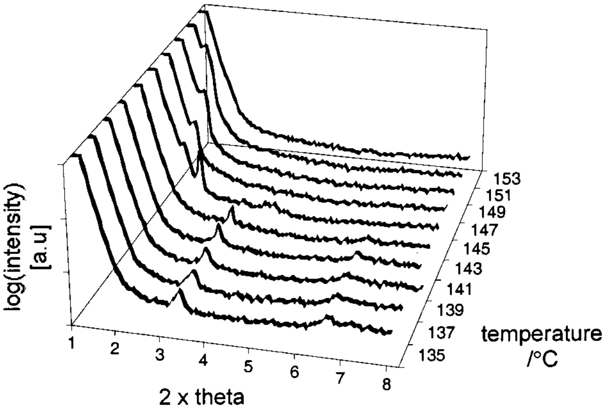


Figure 6. Temperature-dependent wide-angle X-ray diffraction patterns of polymer **9-8**.

Below 145 °C polymer **9-8** exhibits an S_{A1} mesophase with a *d* spacing of 23.7 Å (Table 4, Figure 6). As found for polymer **9-6**, the *d* spacing is smaller than expected for a S_{A1} mesophase with an all-trans conformation of the octyl spacer. Due to steric hindrance in the smectic layers, the S_{A1} mesophase transforms into an S_{A2} mesophase with a *d* spacing of 49.0 Å at 145 °C (Figure 5c). In the S_{A2} mesophase there is no overlap of side chains. In addition, a reflection corresponding to a *d* spacing of 39.2 Å can be observed at 145 °C, which corresponds to an S_{Ad} mesophase with overlap of biphenyl mesogens with octyl spacers (Figure 5b). However, this mesophase is constrained because of the low disparity in spacer length, and it transforms almost immediately in the S_{A2} mesophase (Figure 5c). Below 108 °C, polymer **9-8** exhibits an S_{Bcryst} mesophase with a correlation length of 15.4 Å.

The *d* spacing of 32.1 Å of polymer **9-11** (Table 4) indicates that the side chains interdigitate partially. If the experimental *d* spacing is compared with the calculated *d* spacings of the interdigitated mesophases (Figure 7), then it is most likely that the interdigitation is as depicted in Figure 7b. The strong disparity in spacer length prevents the mesogens from ordering hexagonally.

In the X-ray diffraction pattern of polymer **9-3OBu**, five weak reflections can be seen that arise from a smectic structure with *d* spacings of 21.8 and 39.6 Å. These *d* spacings correspond to S_{A1} and an S_{A2} periodicity, respectively. Up to 147 °C these two periodicities coexist, but between 147 and 159 °C only the S_{A2} periodicity remains. Besides the S_A mesophases, polymer **9-3OBu** also exhibits an S_E mesophase of which the orthorhombic cell dimensions are $a = 7.98$ Å and

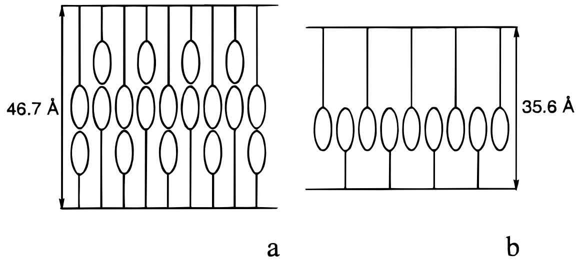


Figure 7. Schematic representation of different interdigitated smectic mesophases including the calculated *d* spacings for polymer **9-11**: (a) S_{Ad} mesophase with overlap of mesogens with equal (i.e., the longest) spacer length and (b) S_{Ad} mesophase with overlap of mesogens with different spacer lengths.

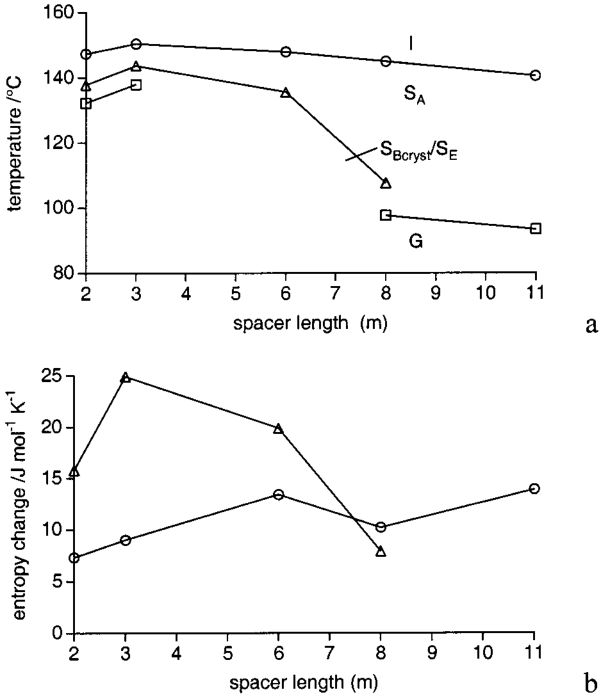


Figure 8. (a) Dependence of the transition temperatures as found with DSC on spacer length *m* for polymers **9-*m***: (□) glass transitions; (△) $S_B/S_E{-}S_A$ transitions; (○) isotropic transitions. (b) Dependence of the entropy change as found with DSC on spacer length *m* for polymers **9-*m***: (△) $S_B/S_E{-}S_A$ transitions; (○) isotropic transitions.

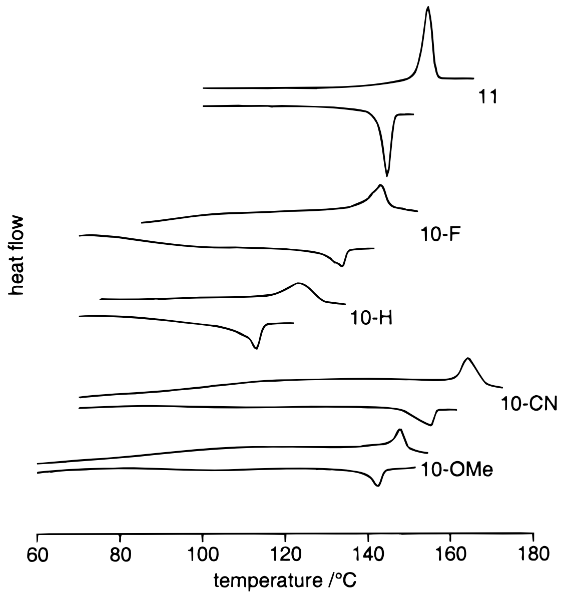


Figure 9. DSC thermograms of polymers **10** and **11**. For all compounds the second heating and cooling traces are given.

$b = 5.43$ Å. Comparison of these values to those of polymer **9-3** shows that the presence of a terminal butoxy tail group slightly affects the mesogen packing.

Figure 8a illustrates the effect of the spacer length *m* of mesogenic alcohols on the transition temperatures of polymers **9-*m***. In comparison to the unmodified polymer **6**, it is clear that for low *m* modification results in (i) higher transition temperatures and (ii) more ordered mesophases. Increasing spacer length *m* hardly affects T_i. The T_g and $S_E{-}S_A$ or $S_B{-}S_A$ transition are strongly affected by spacer length: T_g decreases as a consequence of the increase in free volume.

In Figure 8b the entropy changes at the $S_{Bcryst}{-}S_{A1}$ and isotropization transition are plotted against spacer length *m*. For comparison, the total enthalpy change of the $S_{A1}{-}S_{A2}$ and $S_{A2}{-}I$ transitions for polymer **9-8** is given. It can be seen that the isotropization entropy tends to increase with spacer length. The entropy change at the $S_E{-}S_A$ or $S_B{-}S_A$ transition increases on going from $m = 2$ to $m = 3$ and decreases for longer spacers, which agrees with the X-ray diffraction results that showed the highest degree of order for polymer **9-3**. A large disparity in spacer length prevents the mesogens from attaining a mesophase with order within smectic layers.

Stilbene and Azobenzene Mesogens. The effect of terminal substituent on the liquid-crystalline behavior has been studied by grafting azobenzene-containing alcohols with different terminal substituents onto methoxybiphenyl-containing polymer **6**. In addition, a cyanostilbene-containing alcohol has been grafted onto polymer **6**.

DSC showed that the resulting azobenzene-containing polymers **10** all exhibit a clear glass transition followed by an isotropization transition (Figure 9). In addition, POM revealed Schlieren textures which indicate a nematic mesophase. This was confirmed by X-ray diffraction, although some reflections with a very low intensity were observed in the low-angle region. These reflections result from smectic fluctuations with S_{A1} periodicity (Table 4).

The effect of the terminal group of the azobenzene mesogen on the temperature range of the mesophase is CN > OMe > F > H (Table 3). This is in complete agreement with the behavior of low-molar-mass mesogens[28] and SCLCPs with a poly(styrene) backbone.[29] This trend has been explained by the polarizability of the terminal group and its capability to give different conjugative interactions.[31]

Polymer **11**, which contains cyanostilbene mesogens, exhibits only an S_E mesophase which is obvious from the one transition observed with DSC (Figure 9) and the X-ray diffraction pattern (Table 4). In the small-angle area, the X-ray diffraction pattern only shows the second- and third-order reflections. The absence of a first-order reflection results from an additional maximum in the electron density profile, which induces an apparent *d* spacing (the strongest small angle reflection) that is half the smectic *d* spacing. The *d* spacing of 22.4 Å (Table 4) corresponds to a mesophase with S_{A1} periodicity. The orthorhombic cell dimensions of polymer **11** in the S_E mesophase are $a = 7.98$ Å and $b = 5.25$ Å. The *a*-dimension of the orthorhombic cell is slightly

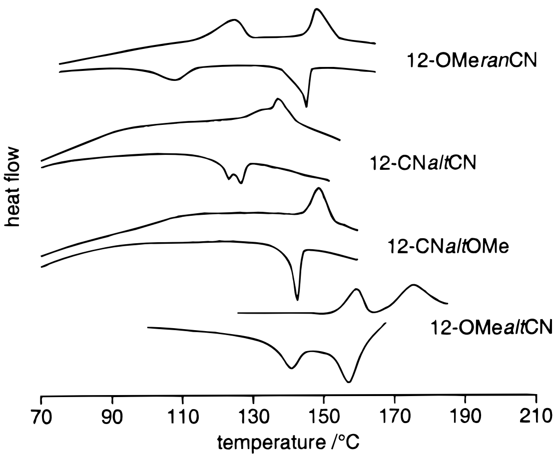


Figure 10. DSC thermograms of polymers **12**. For all compounds the second heating and cooling traces are given.

bigger, and the *b*-dimension is 0.18 Å smaller than the values found for polymer **9-3**. The presence of cyanostilbene mesogens results in a slightly different packing of mesogens than found for biphenyl mesogens. Because of the presence of a highly ordered S_E mesophase, the change in specific heat capacity at T_g was too low to be detected by DSC.[30]

If we compare the mesomorphic behavior of polymers **10** and **11**, it is remarkable that polymers **10** exhibit nematic mesophases, whereas polymer **11** exhibits an S_E mesophase. The only difference between these mesogens is the polarity of the central linkage in the mesogen, which is an azo or a vinyl moiety, respectively. An explanation for this behavior could be that, in the case of the apolar stilbene mesogens, the polar backbone is strictly phase separated from the apolar mesogen layer, whereas in the case of azobenzene mesogens the polar polymer backbone can mix with the polar azobenzene moieties and phase separation is not so strict. This results in less ordered mesophases for polymers **10**.

Specific Interactions. The effect of combining electron-rich and electron-poor mesogens on liquid-crystalline behavior has been studied by grafting cyanobiphenyl mesogens and methoxybiphenyl mesogens onto polymers **6** and **7**, respectively. These reactions yield polymers in which mesogens are attached to the polymer backbone in an almost alternating sequence. A random arrangement of mesogens was obtained by grafting a 1:1 mixture of cyanobiphenyl and methoxybiphenyl mesogens onto polymer **8**. The properties of these polymers will be described below and compared to those of polymers with only one type of mesogen, i.e., polymers **9-3** and **12-CN*alt*CN**.

Polymer **12-OMe*alt*CN** undergoes two phase transitions; however, no glass transition was observed by DSC (Figure 10). This polymer exhibits mesophases with S_{A1} periodicity and a *d* spacing of 21.5 Å. Below 154 °C the mesogens are hexagonally ordered with a lateral distance of 4.47 Å. The correlation length of 13.3 Å indicates that the hexagonally ordered mesophase is of the S_{Bcryst} type.

Polymer **12-OMe*ran*CN** undergoes two phase transitions, but no glass transition was observed with DSC (Figure 10). POM and X-ray diffraction showed that this polymer exhibits an S_{Ad} mesophase with a *d* spacing of 23.5 Å, and below 129 °C the mesogens order hexagonally. The magnitude of both the correlation length (8.6 Å) and the entropy change associated with the S_B-S_{Ad} transition are indicative of an S_{Bhex} mesophase; i.e., there is only long-range bond-orientational order but no long-range positional order.

In contrast to polymer **12-OMe*alt*CN**, polymer **12-CN*alt*OMe** exhibits a distinct glass transition and an S_{Ad} mesophase (Figure 10) with a *d* spacing of 24.1 Å. No hexagonal order was found.

Polymer **12-CN*alt*CN** exhibits a distinct glass transition and two other transitions at 134 and 137 °C (Figure 10). However, POM only showed the isotropization transition at 137 °C. Furthermore, temperature-dependent X-ray diffraction did not reveal any change at 134 °C: below and above 134 °C this polymer probably exhibits an S_{Ad} mesophase with a *d* spacing of 27.2 Å. This kind of mesophase is common for cyanobiphenyl mesogens because of the tendency to form antiparallel pairs.[31]

The degree of interdigitation of side chains increases on going from **12-CN*alt*OMe** to **12-OMe*ran*CN** to **12-OMe*alt*CN**. The concentration of methoxybiphenyl mesogens is not exactly equal for these polymers due to the fact that the grafting reaction does not proceed completely. This could mean that the degree of interdigitation of the side chains increases with increasing concentration of methoxybiphenyl mesogens. The observed trend in degree of interdigitation can then be explained by the tendency of cyanobiphenyl mesogens to form antiparallel pairs and the tendency of methoxybiphenyl containing side chains to interdigitate completely.[33]

Since the transition temperatures of both polymers with one type of mesogen (**9-3** and **12-CN*alt*CN**) and polymers with different types of mesogens (**12-OMe*alt*CN**, **12-OMe*ran*CN**, and **12-CN*alt*OMe**) are known (Table 3), the relative magnitude of deviations from ideal behavior can be calculated. Therefore, a scaled deviation temperature, ΔT_{SC}, has been introduced defined as[20]

$$\Delta T_{SC} = \frac{2T_{AB} - (T_A + T_B)}{T_A + T_B}$$

where T_{AB} is the T_i for the copolymer, and T_A and T_B are those of the homopolymers. If the copolymer has a lower T_i than predicted by ideal mixing, ΔT_{SC} will be negative, whereas a positive value of ΔT_{SC} indicates a higher T_i than predicted by ideal mixing. The values of ΔT_{SC} for polymers **12-OMe*alt*CN**, **12-OMe*ran*CN**, and **12-CN*alt*OMe** are 0.18, 0.09, and 0.04, respectively, and runs parallel to the trend observed for the degree of interdigitation. For comparison, for poly(styrene)s with nitroazobenzene and methoxyazobenzene mesogens the maximum value of ΔT_{SC} is 0.08,[19] whereas for poly(methacrylate)s with cyanobiphenyl and butylazobenzene mesogens a value of 0.14 has been found.[20]

The positive values of ΔT_{SC} for polymer **12-OMe*alt*CN**, **12-OMe*ran*CN**, and **12-CN*alt*OMe** mean that the interactions between unlike mesogens are stronger than the interactions between like mesogens; i.e., specific favorable interactions exist between unlike mesogens. In addition, ΔT_{SC} increases with increasing degree of interdigitation, i.e., increasing concentration of methoxybiphenyl mesogens. This can probably be ascribed to the increase in packing density of mesogens with increasing degree of interdigitation.[33]

Because of small variations in polymer composition and the influence of these variations on ΔT_{SC}, it was not possible to determine whether two different mesogens should be attached to the backbone in an alternating or a random sequence in order to obtain SCLCPs with a maximum ΔT_{SC}.

4. Conclusions

This study showed that SCLCPs with high mesogen densities can be obtained by the reaction of mesogen-containing alcohols with maleic anhydride-containing SCLCPs in the presence of 4-(dimethylamino)pyridine as a catalyst. Grafting of methoxybiphenyl-containing alcohols with different spacer lengths onto maleic anhydride-containing SCLCPs induces an increase in the degree of order in the mesophase and broadens the temperature window of the mesophase. The best ordered modified polymers were obtained from alcohols with a spacer length comparable to the spacer length in the parent polymer. In this case, an S_E mesophase is obtained. For slightly smaller or larger spacer lengths S_B mesophases are obtained, and if the disparity in spacer length is high, the tendency to form an S_{Ad} mesophase increases. The isotropization temperature was hardly affected by the spacer length of the grafted mesogenic alcohol. However, for octyl and undecyl spacers the increase in free volume in their S_A mesophases resulted in strongly decreased glass transition temperatures.

In contrast, grafting azobenzene-containing alcohols onto methoxybiphenyl-containing polymer **6** yielded polymers that exhibit only nematic mesophases. This is ascribed to the absence of microphase separation between mesogen and polymer layers, which disturbs the lamellar structure. The effect of the terminal group on the temperature range of the mesophase is CN > OMe > F > H. The coupling of a cyanostilbene mesogen to polymer **6** resulted in a SCLCP with a smectic E mesophase with smectic A1 periodicity.

Combining methoxybiphenyl and cyanobiphenyl mesogens in both unmodified and modified polymers resulted in smectic A mesophases with higher isotropization temperatures than can be expected on the basis of the weighted average of the isotropization temperatures of both polymers with only one type of mesogen. This can be attributed to specific favorable interactions between electron-rich methoxybiphenyl mesogens and electron-poor cyanobiphenyl mesogens.

Summarizing, increasing the mesogen density by grafting mesogen-containing alcohols with spacers and mesogens differing from those of the parent SCLCP is a powerful tool to tune the transition temperatures and to alter the mesophase types.

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