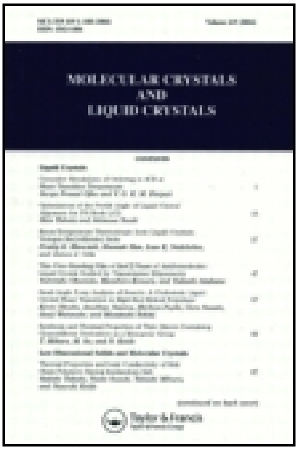

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A Series of Novel Liquid Crystalline Polymers Showing a Nematic Discotic and/or a Nematic Columnar Phase

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A series of novel liquid crystalline side chain polyacrylates was prepared, bearing a disk-shaped pentakis(4-methylphenylethynyl)benzene mesogen *via* an undecanoxy spacer. By using the concept of the polymer analogous reaction, a variety of copolymers with different alkyl acrylate "co-monomers" and increasing mesogen contents were synthesized.

The thermal properties of the polymers were investigated by optical polarization microscopy and differential scanning calorimetry. The results indicated that the liquid crystalline characteristics of the polymers are not determined by nature of the co-monomers, but mainly by the weight fraction of rigid mesogen present in the material. All polymers exhibit a nematic columnar phase at lower temperatures. Polymers with a high mesogen content (>61 %-wt) exhibit an additional nematic discotic phase at high temperatures, which is unique for polymeric materials.

Keywords: Synthesis; Characterization; Polymers; Nematic discotic; Nematic columnar

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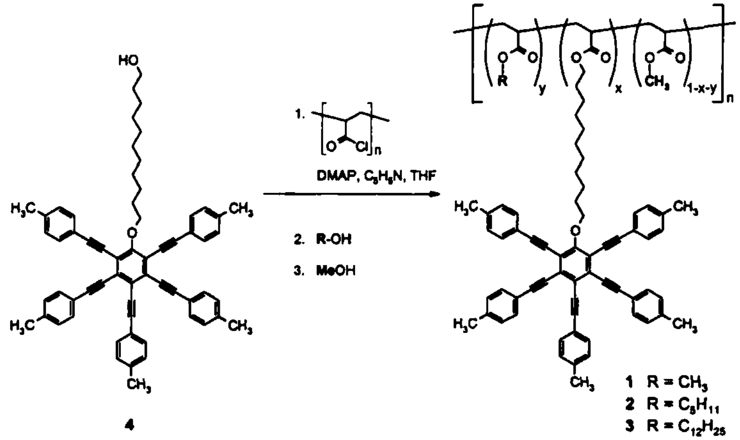
INTRODUCTION

Since their discovery in the late seventies [1], discotic liquid crystals have received growing attention. A wide range of flat and rigid molecules, usually substituted by multiple flexible tails have been synthesized [2]. In order to obtain desired properties, the mesogens were functionalized and incorporated into main chain [3a-e] and side chain polymers [3d-h] as well as in polymer networks [3i,j]. So far, research on discotic liquid crystalline polymers was mainly focussed on substituted triphenylenes. These polymers exhibited highly ordered columnar (D_x and N_{Col}) mesophases (figure 1b,c) in which the molecules are arranged in stacks [3].

FIGURE 1: Commonly observed discotic mesophases: (a) nematic discotic N_D; (b) nematic columnar N_{Col} and (c) discotic hexagonally ordered D_{ho}.

In our group, the five-fold phenylethynyl substituted phenol derivatives serve as the basic element for discotic liquid crystalline research. This mesogen, introduced in the late eighties [4], offers distinct advantages, the most important being the presence of the single hydroxy group. This group provides an easy anchoring site, necessary for side chain polymer synthesis. Previously, we have reported the preparation and characterization of **1a** (x=0.9), a liquid crystalline polymer, exhibiting the low-ordered nematic discotic (N_D) phase (figure 1c) and also the higher ordered nematic columnar (N_{Col}) phase [5].

In this paper, we present a series of discotic side chain liquid crystalline copolymers **1-3**. The polymers were synthesized by a polymer analogous reaction of poly(acryloyl chloride) with the hydroxy functionalized mesogen. With a subsequent quenching of the reaction mixture with an excess of another alcohol, an additional group was introduced on the polymer backbone. This straightforward procedure was used to prepare a range of copolymers with different aliphatic substituents to the polymer backbone and a systematic variation in the degree of mesogen substitution. The polymers were investigated by differential scanning calorimetry and optical polarizing microscopy.



SCHEME 1: Synthesis of polymer series 1-3.

RESULTS

Synthesis

The syntheses of polymers **1**-**3** are outlined in scheme 1. Mesogen **4** was prepared by a five-fold palladium mediated cross-coupling [6] between a terminal acetylene and a pentabromophenol derivative [5,7]. Poly(acryloyl chloride) (PAC) was prepared according to literature procedures [5,8]. To determine the molecular weight, a sample of PAC was converted to polymethylactrylate and subsequently analyzed by gel-permeation chromatography, resulting in a M_n = 8000 gmol^{-1} and a PDI = 2.9.

TABLE 1: Prepared materials

Polymer	R	Degree of substitution [mol-%]			Yield[a] [%]
		Mesogen	Alcohol R	Methanol	
1 a	-	90	-	10	46
1 b	-	64	-	36	70
1 c	-	48	-	52	35
1 d	-	31	-	69	43
2 a	n-C_5H_{11}	69	31	-	33
2 b	n-C_5H_{11}	41	43	16	43
2 c	n-C_5H_{11}	42	50	8	30
3 a	n-$C_{12}H_{25}$	61	11	28	37
3 b	n-$C_{12}H_{25}$	45	45	10	36
3 c	n-$C_{12}H_{25}$	33	42	25	65

[a] Based on mesogen conversion.

TABLE 2: Overview of phase transition temperatures obtained from DSC and OPM of 1-3. The changes in enthalpy are given between brackets.

polymer	transition temperatures [°C] and (enthalpies changes [kJmol^{-1}])[a]						
	G_{Ncol}		N_{Col}		N_D		I
1 a	•	n.d.[b]	•	164 (9.6)	•	235 (0.3)	•
1 b	•	n.d.[b]	•	165 (12)	•	233 (0.2)	•
1 c	•	92	•	158 (9.1)	•	204 (0.1)	•
1 d	•	62	•	149 (8.5)	[•[c]	148 (0.1)]	•
2 a	•	77	•	157 (8.7)	•	209 (0.1)	•
2 b	•	70	•	169 (8.6)			•
2 c	•	51	•	157 (8.3)			•
3 a	•	86	•	155 (8.2)	•	210 (0.1)	•
3 b	•	50	•	154 (8.1)			•
3 c	•	49	•	136 (8.3)			•

Heating rate for DSC and OPM was 10°Cmin^{-1}. [a] G_{Ncol} = Glassy (N_{Col} phase frozen in); N_{Col} = nematic columnar; N_D = nematic discotic; I = Isotropic. [b] Not determined. [c] Monotropic phase transition.

The polymer analogous reaction [9], coupling the mesogen to the polymer backbone was carried out under absolute moist-free conditions to avoid formation of carboxylic acid groups [10]. The crude PAC solution was added to a dilute solution of the mesogen, a catalyst and a base. For polymer series **2** and **3** an excess of alcohol (*n*-pentyl or *n*-dodecyl) was added to the reaction mixture after stirring for 24 hours at ambient temperatures. In the final stages of the reaction, an excess of methanol was added to convert any remained acyl chloride groups to methylesters. The polymers were isolated by precipitation in methanol and reprecipitation from CH_2Cl_2 into aceton to remove low molecular weight oligomers as well as non-reacted mesogen. An overview of the prepared polymers **1-3** is shown in table 1.

The substitution raection of **4** and the other long tail alcohols onto the reactive polymer was often incomplete, resulting in lower mesogen contents and considerable methanol substitution. In addition, the low yields, as reported in table 1, were obtained due to a crude precipitation procedure, that is nessecary to separate the nonreacted mesogen from the polymer. Recently, we demonstrated that by increasing the reaction time and raising the reaction temperature, nearly quantitative substitution can be achieved.

Phase behavior

The liquid crystalline properties were investigated with differential scanning calorimetry (DSC) and optical polarizing microscopy (OPM). The transition data are summarized in table 2.

The results show that all polymers exhibit a N_{Col} mesophase at low ($T \leq 150°C$) temperatures. On cooling from this phase, a weak transition into a glass was found for most polymers and the optical texture was frozen in. As expected, the glass transition temperature increases with increasing degree of mesogen substitution. On heating from the N_{Col} phase, a second nematic phase was found for a limited number of polymers (**1a-c**,**2a**,**3a**), while the others turn isotropic. Strikingly, these transitions took place at a fairly constant temperature (~150°C) and with constant enthalpy changes. The weak transition from N_D to isotropic was strongly dependent on the degree of mesogen substitution. For **1d**, a monotropic N_D phase was found.

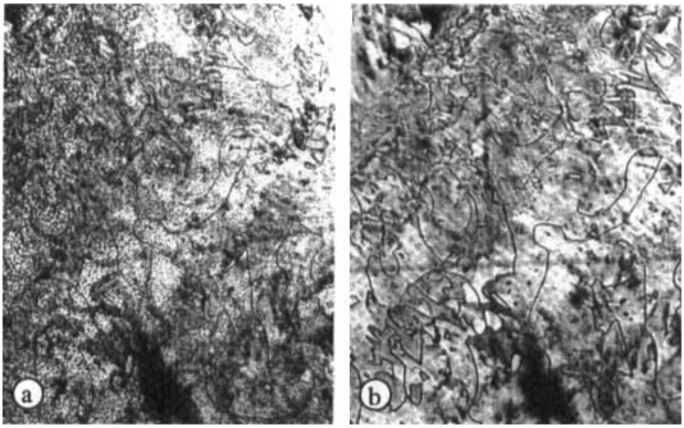


FIGURE 2: Optical polarized micrographs of nematic textures of (a) **1b** at 140°C (N_{Col} phase) and (b) **1b** at 170°C (N_D phase), both obtained on cooling the sample. Samples between crossed polarizers, magnification 125x.

Figure 2 shows optical micrographs of the liquid crystalline textures of **1b**. On cooling from the isotropic phase, a clear nematic texture of the N_D phase was found (figure 2b), easily characterized by its disclination lines. Upon further cooling into the N_{Col} phase, the viscosity rapidly increased and after annealing for 10 hours at 140°C, the optical texture shown in figure 2a was found. The disclination lines are still visible in the background while another smaller texture has developed on top.

DISCUSSION

In order to make a fair comparison between the liquid crystalline polymers **1**-**3**, the different submolecular constituents were expressed in weight fractions. The polymers are divided in three parts: (i) the rigid part of the mesogen (without the flexible spacer); (ii) the flexible backbone together with the spacer and (iii) the dangling ends of the co-substituted alcohols (methyl, pentyl and dodecyl groups). The results are shown in table 3.

TABLE 3: Weight fractions of rigid material (mesogens) and flexible material (spacer, backbone and alkyl groups).

Polymer	R	Mesogen substit. [mol-%]	Weight content [wt-%][a]		
			Rigid Mesogen	Backbone and spacer	Alkyl groups
1 a	-	90	73.8	26.0	0.2
1 b	-	64	70.8	28.3	0.9
1 c	-	48	67.5	30.8	1.7
1 d	-	31	61.5	35.4	3.1
1 e[b]	-	56	64.5	33.1	2.4
2 a	n-C_5H_{11}	69	69.7	27.0	3.3
2 b	n-C_5H_{11}	41	62.0	30.5	7.5
2 c	n-C_5H_{11}	42	61.7	30.1	8.2
3 a	n-$C_{12}H_{25}$	61	68.3	27.9	3.8
3 b	n-$C_{12}H_{25}$	45	57.8	27.2	15.0
3 c	n-$C_{12}H_{25}$	33	52.9	29.3	17.8

[a] The weight fraction of mesogen was calculated as the fraction of pure rigid materials, that is without the flexible spacer. The fraction of alkyl groups was calculated as the fraction dangling side groups of the alkyl acrylate "co-monomers"; [b] This sample was made by mixing polymers 1c and 1d *via* dissolving them in a common solvent and removing the solvent *in vacuo*.

Due to the high molecular weight of the mesogen, compared to that of the backbone, the mesogen weight fraction in polymer series 1 only slightly decreases with decreasing degree of substitution. Upon introduction of longer alkyl groups, the mesogen content was reduced further. However, the lowest mesogen weight fraction obtained, was 53% for 3c. Using the mesogen weight fraction, the liquid crystalline properties of all materials can be collected into a master phase diagram as shown in figure 3.

The figure clearly shows that the thermal properties of the materials are strongly dependent on the mesogen content in the material and much less on the kind of alkylacrylate co-monomer. When a certain amount of mesogen is present in the material (> ~61%) an extra mesophase is observed, the N_D phase. The clearing temperatures of these polymers are again, strongly dependent on the mesogen content.

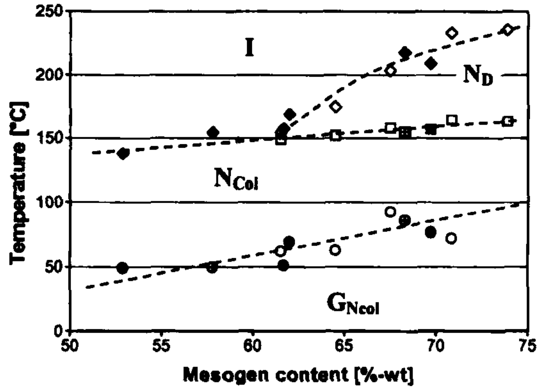


Figure 3: Phase diagram of polymer series 1 (open), 2 (solid) and 3 (with cross). Circles represent T_g, squares $T_{NCol \to ND}$ and diamonds T_i. I = isotropic; N_D = nematic discotic; N_{Col} = nematic columnar; G_{NCol} = Glass with N_{Col} phase frozen in. The dotted lines between the phases are just a guide for the eye.

CONCLUSIONS

We have prepared a series of novel discotic liquid crystalline side chain polymers 1-3, using the polymer analogous reaction. This highly flexible concept allowed us to vary of the degree of substitution and the nature of the "co-monomers" in a systematical way.

Analysis of the liquid crystalline properties by OPM and DSC showed that the thermal properties are mainly dependent on the weight fraction of rigid mesogen in the polymers. Polymers with a high mesogen content (> 61 %-wt) exhibited a N_D phase at high temperatures, which is unique for a polymer, as this phase was only observed in low molar mass materials so far. All polymers enter the N_{Col} phase at approximately 150°C, forming (short) columns of disc-shaped molecules. Remarkably, the $N_{Col} \rightarrow N_D/I$ transition is almost independent of the mesogen content.

Current research focuses on X-ray investigations and dielectric relaxation spectroscopy to gain more insight into the sturcture and mobilities of the polymer mesophases.

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Nico van der Knaap and Ben Norder are gratefully acknowledged for technical assistance.

EXPERIMENTAL SECTION

Materials

All materials were used as purchased without further purification unless mentioned otherwise. Dichloromethane was distilled from P_2O_5 and pyridine from CaH_2. 1-Pentanol and 1-dodecanol were dried on molecular sieves prior to use. The mesogen 4 and poly(acryloyl chloride) were prepared according to literature procedures. The crude polymerization mixture of PAC was stored in a refrigerator and used without further purification.

Measurements

Nuclear magnetic resonance (NMR) spectra were taken on a Varian VXR 300 or VXR 400 MHz spectrometer. Chemical shifts are reported in ppm relative to TMS. Molecular weights were determined by gel-permeation chromatography (GPC) in THF against narrow polystyrene standards. The thermal properties of the materials were investigated by a Perkin Elmer DSC 7 Differential Scanning Calorimeter (in nitrogen atmosphere) and a Jenapol optical polarizing microscope, equipped with a Mettler FP82 HT hot stage and a Mettler FP80 Central Processor. Thin films for optical polarizing microscopy (OPM) were either spin cast from chloroform solution or obtained by shearing the material at elevated temperatures between two glass plates.

Polymer Synthesis

A solution of the mesogen 4 (417 mg, 0.5 mmol), pyridine (1 ml) and 4-(*N,N*-dimethylamino)pyridine (catalytic amount) in 20 ml freshly distilled CH_2Cl_2 was flushed with argon. The crude polymer solution (91 mg, 1.0 mmol acylgroups) was added *via* a syringe. The mixture was stirred for 24 hours at room temperature. An excess of 1-pentanol was added (2 ml) via a syringe and the reaction mixture was stirred for another 24 hours. To convert any remaining acylgroups, dry methanol (2 ml) was added. After 2 hours, the mixture was precipitated in dry methanol, filtered and reprecipitated from CH_2Cl_2 into aceton. After filtration and drying, the polymer was obtained as a pale yellow powder (230 mg, 40% based on mesogen conversion).

The degree of substitution was calculated from peak integrations of the ^1H NMR spectrum. All peaks have broadened enormously, so that no peak splitting could be detected. ^1H-NMR ($CDCl_3$): 1.2-1.9 (aliphatic spacer and backbone CH_2); 2.2-2.5 (lateral disc CH_3 and backbone CH); 3.62 (CH_3 methylacrylate); 4.0, 4.3 (CH_2O ends of the spacer); 7.1, 7.4 (aromatic).

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