Synthesis and Characterization of a Novel Liquid Crystalline Polymer Showing a Nematic Columnar to Nematic Discotic Phase Transition

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ABSTRACT: A novel liquid crystalline polyacrylate, exhibiting a nematic columnar and a nematic discotic phase, the latter not found in any polymer previously, has been synthesized using a polymer analogous reaction, substituting the discotic mesogens on a reactive polymer. The highly flexible concept of the polymer analogous reaction enables us to introduce structural variations and to create and control molecular architectures. The mesophases of polymer **1**, bearing the pentakis(methylphenylethynyl)benzene mesogen via a flexible undecanoxy spacer, as well as its low molar weight homologue **2**, were fully characterized by optical polarizing microscopy, differential scanning calorimetry and powder X-ray diffraction. The thermal behavior of both compounds is qualitatively similar. Both materials exhibit a nematic discotic phase (N_D) at higher temperatures, which is unique for the polymer, as this phase has only been observed in low molar mass materials so far. At lower temperatures **2** crystallizes, whereas **1** undergoes a transition into the nematic columnar phase (N_{col}).

Introduction

Liquid crystalline materials have been known for a long time.[1] In most cases the mesogens, the units that assemble in liquid crystalline phases,[2] are rod-shaped although rigid molecules exhibiting other shapes are shown to be mesogenics as well. Since the late 1970s,[3] the development of liquid crystalline materials in which disk-shaped molecules form discotic or columnar mesophases has received growing attention.[4] To obtain desired properties, rigid molecules have been engineered from a molecular point of view, resulting in a wide range of disk-shaped mesogens, e.g. multisubstituted benzenes,[3,5,6] and hexa(alkoxy)triphenylenes.[7] The properties of discotic liquid crystals (DLC's) are influenced by the architecture of the molecules to which disk-shaped mesogenics are attached. Dimers[8,9c] that contain two disks connected by a flexible spacer, as well as polymers with discotic mesogens incorporated either in the main chain[9a−e] or in the side chain[9a,b,f−h] have been prepared in view of future applications.[10] In addition, specific intermolecular interactions, such as H-bond interactions[11] or donor−acceptor interactions,[12] induce dramatic changes in the mesomorphic properties of discotic liquid crystalline materials.

Because of their shape, discotic liquid crystals order in a (limited) number of phases, of which the most common are depicted in Figure 1. In the nematic discotic (N_D) phase (Figure 1a), the molecules possess some orientational order, but no positional order. A wide range of columnar phases, in which the molecules are stacked on top of each other, are known. In the nematic columnar (N_{col}) phase (Figure 1b) the short columns lack transitional order, whereas in the discotic (D_x) phases, the columnar structure exhibits long range order, for example the discotic hexagonal (D_h) phase shown in Figure 1c. Previously reported polymeric discotic liquid crystals exhibited columnar phases only; their columnar phases were either the highly ordered D_x phases or the less ordered N_{col} phases.[9]

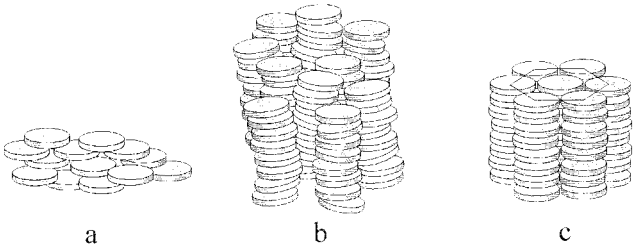

Figure 1. Commonly observed discotic mesophases: (a) nematic discotic N_D; (b) nematic columnar N_{col}; (c) discotic hexagonally ordered D_{ho}.

In our group, the 5-fold phenylethynyl substituted phenol derivatives (see Scheme 1), introduced in the late 1980s,[6a] serve as the basic element for discotic liquid crystals. Some representatives of this class of compounds were reported to exhibit discotic liquid crystalline properties.[13] Their mesomorphic behavior can be tailored by choosing the appropriate combination of lateral substituents at the disk, the length of the flexible spacer, and the nature of the moiety attached to the spacer, i.e., the architecture of the molecules.[13,14]

Here, we report the synthesis and characterization of the polyacrylate based copolymer **1** and its low molecular weight homologue **2**. In polymer **1**, which was synthesized from poly(acryloyl chloride), 90% of the acrylate moieties bear a pentakis(phenylethynyl)phenoxy moiety attached to the main chain by a C_{11} spacer, while the remaining positions are occupied by methyl esters. The mesomorphic behavior of the materials was characterized with differential scanning calorimetry, optical polarizing microscopy and X-ray diffraction measurements. The similarities and the differences between **1** and **2**, caused by the attachment of the mesogens to the polyacrylate backbone are discussed.

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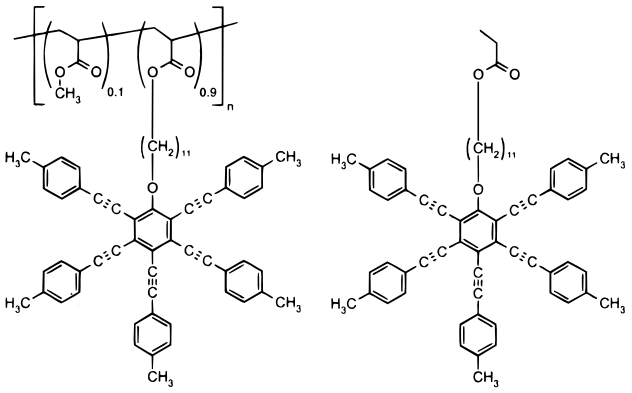
Scheme 1



1 **2**

Experimental Section

Materials. All materials were used as purchased and used without further purification unless mentioned otherwise. Tetrahydrofuran (THF) was distilled from $LiAlH_4$, dichloromethane from P_2O_5, and dioxane from sodium. Petroleum ether and *n*-hexane were distilled prior to use, and pyridine was dried on molecular sieves. The pentabromophenol ether **4** was prepared according to a literature procedure.[14]

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. Infrared spectra were recorded between NaCl plates on a Mattson Polaris infrared Fourier transform spectrometer. Molecular weights were determined by gel-permeation chromotography (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 of **1** for optical polarizing microscopy (OPM) were either spin cast from chloroform solution or obtained by strongly shearing the material at elevated temperatures between two glass plates. The mesophases were identified by X-ray diffraction measurements, using a Siemens Kristalloflex 710D X-ray generator equipped with a Siemens P4 HI−STAR area detector. The samples were oriented in a magnetic field using a Supper SmCo parmanent magnet with a field of about 1.5 T and a custom build capillary heating element.

Synthesis. 4-Ethynyltoluene (3). 4-Methylacetophenone (25 g, 187 mmol) was added to phosphorus pentachloride (42.8 g, 205 mmol) over 15 min. The clear solution was stirred overnight at room temperature. Phosphorus oxychloride was removed under reduced pressure, and carefully 150 mL of DMSO was added to the mixture, which was cooled in a water bath. Potassium *tert*-butoxide (41.9 g, 374 mmol) was added in small portions over 60 min. After the addition was completed, the water bath was removed and the mixture was heated at 70 °C for 1 h. The reaction mixture was poured into water and extracted three times with ether. The combined organic layers were washed with water and brine successively and dried over $MgSO_4$, and the solvent was removed in vacuo. Distillation under reduced pressure, T_b = 99−100 °C, 80 mmHg, lit. 168−170 °C,[15] yielded 11.35 g (55%) of **3**, a colorless oil.

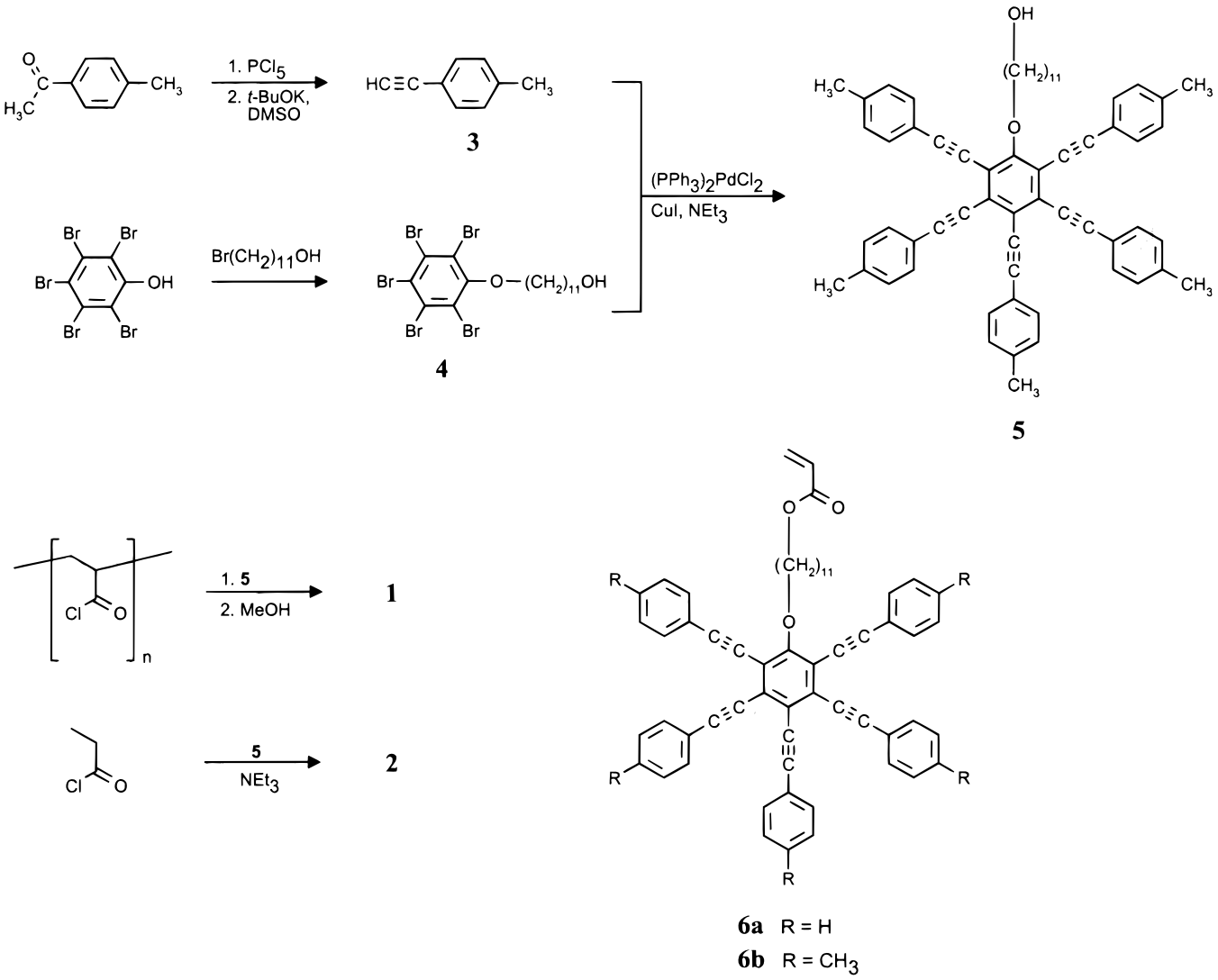
11-[Pentakis(4-methylphenylethynyl)phenoxy]undecan-1-ol (5). A mixture of **3** (9.8 g, 84.5 mmol), **4** (11.0 g, 7.25 mmol), $Pd(II)Cl_2(PPh_3)_2$ (580 mg, 0.83 mmol), and PPh_3 (228 mg, 0.87 mmol) in 70 mL of distilled triethylamine was degassed and stirred in inert atmosphere until the alcohol was dissolved. Copper(I)iodide (220 mg, 1.15 mmol) was dissolved in 5 mL of THF with anhydrous LiBr (1.2 g) and added to the reaction mixture. After 5 h of stirring at 90 °C, the mixture was poured into a 200 mL 2 N HCl solution, and the product was extracted with CH_2Cl_2. The reaction product was purified by flash chromatography (silica gel, eluent: CH_2Cl_2: petroleum ether 4:1) and repeated crystallization from methanol. Yield: 4.4 g, 73% of a pale yellow, highly fluorescent powder. Transition temperatures (°C) and changes in enthalpy (kJ/mol): K 174 N_D 223 I, lit.[16] K 172 (43.9) N_D 226 (0.5) I. ^{1}H NMR ($CDCl_3$): δ 1.20−1.98 (m, 18H, aliphatic spacer); 2.38 (s, 15H, lateral methyl); 3.62 (t, 2H, CH_2OH); 4.37 (t, 2H, CH_2-OPh); 7.14−7.19, 7.48−7.54 (m, 20H, aromatic). ^{13}C NMR ($CDCl_3$): δ 21.58 (lateral CH_3); 25.79, 26.42, 29.49, 29.68, 30.63, 32.82 (CH_2, spacer); 63.00 (CH_2OH); 74.72 (CH_2OPh); 84.11, 86.66, 87.12 (outer ethynyl); 97.27, 99.33, 99.49 (inner ethynyl); 120.07, 124.02, 128.73 (inner phenyl); 120.26, 120.32, 120.49 (outer phenyls, attached to ethynyl); 129.17 (outer phenyls, CH); 131.53, 131.59, 131.71 (outer phenyls, CH); 138.66, 138.83, 138.97 (outer phenyls, attached to CH_3); 160.26 (inner phenyl, C−O).

11-[Pentakis(4-methylphenylethynyl)phenoxy]undecanyl Propionate (2). A mixture of **5** (650 mg, 0.78 mmol) and dry pyridine (370 mg, 4 mmol) was dissolved in 25 mL anhydrous THF. Freshly distilled propionyl chloride (320 mg, 4 mmol) was added through a syringe. The mixture was stirred overnight and the solvent was evaporated in vacuo. The mixture was poured into water and extracted with CH_2Cl_2. The combined organic layers were washed with water, dried over $MgSO_4$ and the solvent was evaporated in vacuo. The pure product was obtained by flash chromatography (silica gel, eluent: CH_2Cl_2: hexane 3:2) Yield: 555 mg, 80% of a pale yellow, highly fluorescent powder. ^{1}H NMR ($CDCl_3$): δ 1.13 (t, 3H, CH_3 propionate); 1.20−1.96 (m, 18H, aliphatic spacer); 2.33 (q, 2H, CH_2 propionate); 2.38 (s, 15H, lateral methyl); 4.05 (t, 2H, CH_2OPropionate); 4.36 (t, 2H, CH_2OPh); 7.18−7.26, 7.47−7.53 (m, 20H, aromatic). ^{13}C NMR ($CDCl_3$): δ 9.18 (CH_3 propionate); 21.58 (lateral CH_3); 25.7−32.82 (CH_2, spacer and propionate); 64.51(CH_2OProp); 74.78 (CH_2OPh); 84.07, 86.55, 87.04 (outer ethynyl); 97.25, 99.32, 99.48 (inner ethynyl); 120.09, 124.04, 128.75 (inner phenyl); 120.27, 120.34, 120.39 (outer phenyls, attached to ethynyl); 129.20 (outer phenyls, CH); 131.57, 131.59, 131.73 (outer phenyls, CH); 138.66, 138.83, 138.97 (outer phenyls, attached to CH_3); 160.26 (inner phenyl, CO); 174.63 (carbonyl).

11-[Pentakis(phenylethynyl)phenoxy]undecanyl Acrylate (6a). A mixture of 11-[pentakis(phenylethynyl)phenoxy]-undecan-1-ol[14,17] (2.0 g, 2.6 mmol), freshly distilled acryloyl chloride (474 mg, 5.2 mmol), and dry triethylamine (529 mg, 5.2 mmol) was stirred in anhydrous CH_2Cl_2 (50 mL) for 2 h. The reaction mixture was poured into water and extracted with CH_2Cl_2. The organic phase was washed with water and brine and dried over $MgSO_4$, and the solvent was evaporated in vacuo. The pure product was obtained by flash chromotography (silica gel; eluent CH_2Cl_2:hexane 2:1). Yield: 1.95 g, 91% of pale yellow highly fluorescent powder. ^{1}H NMR ($CDCl_3$): δ 1.20−1.98 (m, 18H, aliphatic spacer); 4.14 (t, 2H, CH_2OAcr); 4.39 (t, 2H, CH_2OPh); 5.80 (dd, 1H, *trans*-acrylare); 6.12 (dd, 1H, *gem*-acrylate); 6.39 (dd, 1H, *cis*-acrylate); 7.33−7.40, 7.57−7.66 (m, 25H, aromatic). ^{13}C NMR ($CDCl_3$): δ 25.94, 26.35, 28.63, 29.26, 29.52, 29.54, 29.61, 30.60 (CH_2, spacer); 64.73 (CH_2OH); 74.93 (CH_2OPh); 84.51, 86.96, 87.41 (outer ethynyl); 97.24, 99.31, 99.44 (inner ethynyl); 120.23, 124.08, 130.43 (inner phenyl); 123.19, 123.27, 123.42 (outer phenyls, attached to ethynyl); 128.46−128.97, 131.67−131.83 (outer phenyls, CH and acrylate CH and CH_2); 160.58 (inner phenyl, C−O); 166.37 (carbonyl).

11-[Pentakis(4-methylphenylethynyl)phenoxy]undecanyl Acrylate (6b). A mixture of **5** (0.9 g, 1.3 mmol), freshly distilled acryloyl chloride (237 mg, 2.6 mmol), and dry triethylamine (265 mg, 2.6 mmol) was stirred in anhydrous CH_2Cl_2 (20 mL) for 2 h. The reaction mixture was poured into water and extracted with CH_2Cl_2. The organic phase was washed with water and brine and dried over $MgSO_4$, and the solvent was evaporated in vacuo. The pure product was obtained by flash chromotography (silica gel, eluent: CH_2Cl_2: hexane 2:1). Yield: 856 mg, 88% of pale yellow highly fluorescent powder. ^{1}H NMR ($CDCl_3$): δ 1.20−1.98 (m, 18H, aliphatic spacer); 2.38 (s, 15H, CH_3); 4.12 (t, 2H, CH_2OAcr);

Scheme 2



4.37 (t, 2H, CH_2OPh); 5.80 (dd, 1H, *trans*-acrylare); 6.12 (dd, 1H, *gem*-acrylate); 6.39 (dd, 1H, *cis*-acrylate); 7.15−7.18, 7.48−7.53 (dd, 20H, aromatic).

Polymer 1. To 10.0 g of double distilled acryloyl chloride in 10.0 g of distilled 1,4-dioxane was added 0.272 g (1.5%) of AIBN. The reaction mixture was stirred at 58 °C under an argon atmosphere for 66 h. Using FT-IR spectroscopy (25 μm films between NaCl plates), the progress of the reaction was monitored. After 66 h the reaction was completed; the carbonyl absorption was shifted from 1762 to 1785 cm^{-1} and the typical monomer absorptions at 1609, 1369, and 704 cm^{-1} were absent. A specific polymer absorption emerged at 946 cm^{-1}. After reaction, the slightly yellow, highly viscous polymer solution was diluted with 10.0 g of THF, stored at −20 °C, and used without further purification.

Alcohol **5** (1.11 g, 1.32 mmol), pyridine (0.2 mL), and a catalytic amount of (dimethylamino)pyridine (DMAP) were dissolved in 20 mL of anhydrous THF under an argon atmosphere. A solution of poly(acryloyl chloride) (1.20 mmol acyl chloride groups) was added through a syringe. The mixture was stirred overnight and the polymer was precipitated into dry methanol, a procedure by which the remaining acyl chloride groups are converted into methyl esters. The polymer was purified (removing excess of **5**) by repeated precipitation from a chloroform solution into aceton. Yield: 0.56 g (50%) of a yellow solid. ^1H NMR ($CDCl_3$): all peaks have broadened enormously, so that no peak splitting could be detected; δ 1.2−1.9 (aliphatic spacer and backbone CH_2); 2.2−2.5 (lateral disk CH_3 and backbone CH); 3.62 (CH_3 methyl acrylate); 4.0, 4.3 (CH_2O ends of the spacer); 7.1, 7.4 (aromatic). From the relative intensities, a 90% degree of substitution of the mesogen to the polymer is calculated.

Results

Synthesis. The synthesis of **1** and **2** is outlined in Scheme 2. Ethynyltoluene (**3**) was prepared by a modified literature procedure.[18] Using dimethyl sulfoxide as a solvent instead of *tert*-butyl alcohol, the reaction time of the second step was reduced from 36 h to only 1 h. The mesogenic unit was synthesized by a 5-fold palladium(0) mediated cross-coupling[19] between the terminal acetylene **3** and a pentabromophenol derivative **4**, similar as described in the literature.[6,20] Model compound **2** was prepared by an esterification of the alcohol **5**.

The most straightforward manner to synthesize **1** would be the radical polymerization of the acrylate **6b**. In the course of preliminary research we have made several attempts to polymerize the acrylate **6a** under various conditions. No polymer was detected in our reaction mixtures, although some positive results of polymerizations of (meth)acrylate with bulky substituents have been reported.[9a,b,f−h] This result strongly suggests that **6b** cannot be polymerized either. In addition to the inherent low concentration of double bonds, it is likely that the benzylic hydrogens of **6b** act

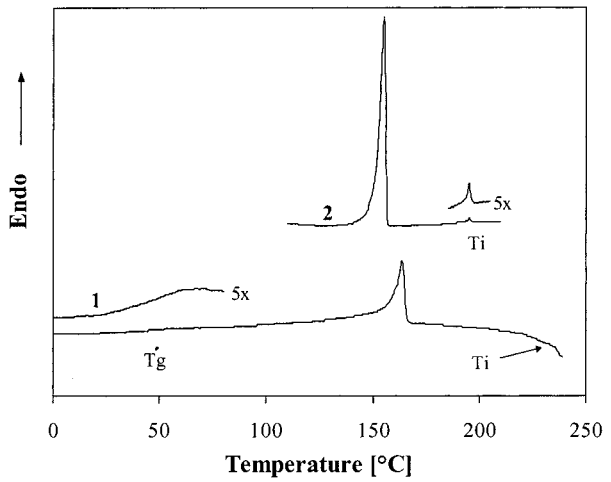


Figure 2. Normalized DSC thermograms for **1** (bottom) and **2** (top). Both second heating scans, recorded with a heating rate of 10 °C/min. For **1**, some decomposition at temperatures above 220 °C is observed.

as an efficient chain transfer reagent, thereby further hampering the polymerization process.

Therefore, we decided to use an alternative approach and prepared the desired polymer by functionalizing a reactive polymer. Poly(acryloyl chloride) was prepared according to literature procedures.[21] After 66 h, a small sample was taken from the reaction mixture and analyzed with FT-IR spectroscopy. From the absence of the specific monomer absorptions at 1609, 1396, and 704 cm^{-1}, it was concluded that no monomer was present, indicating a quantitative conversion. The molecular weight of poly(acryloyl chloride) was determined by gel-permeation chromatography (GPC) of poly(methyl acrylate) formed by a reaction of poly(acryloyl chloride) with methanol.[22] A molecular weight distribution, $M_n = 8000$ and PDI = 2.9, typical for a radical polymerization, was observed. The reaction of poly(acryloyl chloride) with the alcohol **5**, followed by quenching with methanol, yielded polymer **1**, in which 90% of the acryloyl units were substituted by **5**, according to the ^{1}H NMR spectrum.[23]

Mesomorphic Behavior. Differential Scanning Calorimetry (DSC). Both **1** and **2** showed clear and reproducible thermograms, as depicted in Figure 2. For the low molar mass compound **2**, two first-order transitions were observed; a strong melting peak at 155 °C (ΔH = 32.3 kJ mol^{-1}) and a small isotropization peak at 195 °C (ΔH = 0.3 kJ mol^{-1}). Polymer **1** showed a weak glass transition at 43 °C (ΔC_p = 0.1 kJ $mol^{-1}K^{-1}$). Furthermore, two first-order transitions were observed; a fairly strong transition at 164 °C (ΔH = 8.1 kJ mol^{-1}) and a minor transition at 235 °C (ΔH = 0.3 kJ/mol^{-1}). A slow decomposition of the polymer was observed at temperatures above 220 °C.

Optical Polarizing Microscopy (OPM). The low molecular weight compound **2** showed the typical *schlieren* texture of a nematic phase at temperatures between 153 and 191 °C; see Figure 3a. For a sample between two glass plates, the domain size increased upon heating, and just before the clearing temperature at 191 °C, the material had a strong tendency to form a homeotropic texture (single domain sample with the director perpendicular to the glass plates).

Samples of polymer **1** were heated to the isotropic phase prior to measurement. Upon cooling, a moderately viscous nematic phase (Figure 3b) was formed initially.

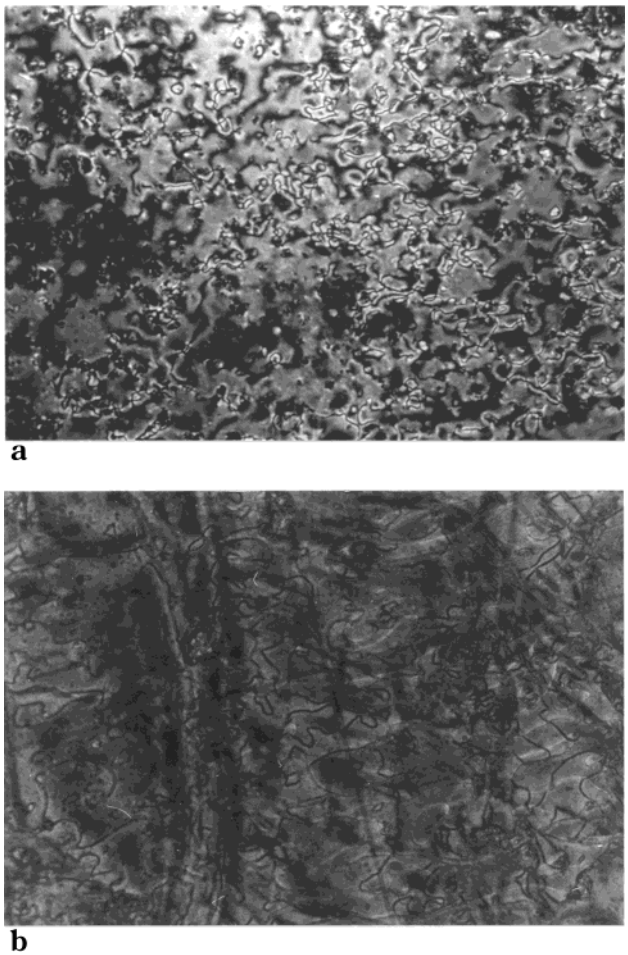


Figure 3. Optical polarized micrographs of nematic textures of (a) **2** at 160 °C and (b) **1** at 181 °C, both on cooling from isotropic melt. Samples are observed between crossed polarizers.

Table 1. Phase Transition Temperatures Obtained from DSC (Heating Rate 10 °C/min) and OPM (Heating Rate 5 °C/min) of 1 and 2 Where the First Transition of 1 Is a Glass Transition (ΔC_p = 0.12 J g^{-1} K^{-1})

sample		transition temperatures (°C) and (enthalpy changes) (kJ/mol)						
1	DSC	g	43	N_{col}	164 (8.1)	N_D	235 (0.3)	I
	OPM			N_{col}	168	N_D	233	I
2	DSC	K			155 (32.3)	N_D	195 (0.3)	I
	OPM	K			153	N_D	191	I

g = glassy; K = crystalline; N_{Col} = nematic columnar; N_D = nematic discotic; I = isotropic.

The optical texture did not change when the sample was cooled below the transition at 164 °C (measured with DSC) nor after annealing for 24 h at 130 °C. At temperatures as high as 140 °C, i.e., just below the transition temperature, the sample "solidified", and rather behaved like a rubber instead of a highly viscous liquid. Passing the glass transition temperature upon further cooling did not alter the optical texture, which was frozen in and remained unchanged for months. Data from OPM and DSC measurements are summarized in Table 1.

Powder X-ray Diffraction. The mesophases of **1** and **2** were studied by X-ray diffraction in the presence of a magnetic field. Their diffractograms are shown in Figures 4 and 5. Because of the negative diamagnetic anisotropy of the nematic discotic materials, the director

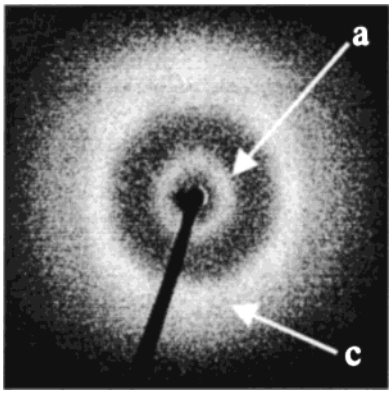


Figure 4. X-ray diffraction patterns of model compound **2** at 160 °C (N_D phase). Maximum diffraction angle: $2\theta = 30°$.

alignment was found to be perpendicular to the magnetic field lines. Although director alignment by a magnetic field is not unusual for calamitic nematic samples, this was the first discotic sample investigated by us that showed this behavior.

The X-ray diffractogram of model compound **2**, recorded at 160 °C is shown in Figure 4. Two diffuse reflections correspond to spacings of 4.2−5.5 [c] and 17−18 Å [a]. The reflections are attributed to the planar and the lateral disk−disk distance, respectively.

X-ray investigations of polymer **1** showed a well-oriented sample at 140 °C (Figure 5a). Two sharp reflections were observed, corresponding to spacings of 3.8 [c] and 16.6 Å [a], attributed to the planar and the lateral disk−disk distance, respectively. Besides, a more diffuse reflection at 4.65 Å [b] was observed that, we believe, is due to incomplete sampling of the reciprocal space as caused by the 2-D disordered director alignment in the sample perpendicular to the magnetic field lines. At 170 °C, the sample was less oriented (Figure 5b). The pattern was much more diffuse and showed only two haloes at 3.9 [c] and 16−18 Å [a], analogous to **2**. The results of the X-ray measurements are summarized in Table 2.

It should be stressed that the lateral disk−disk distances in the N_{col} phase (16.6 Å) and in the N_D phase (16−18 Å) are smaller than the distance of two opposite lateral methyl-groups calculated for **1** or **2** (19.5 Å).[6b] This result suggests that the methyl groups are interdigitated to some extent.

Table 2. X-ray Diffraction Data, Where the Spacings Are Calulated by the Bragg Law $n\lambda = 2d \sin \theta$

sample	temp (°C)	structure spacings[a] (Å)
1	140	[**c**] 3.8 (s); [**b**] 6.2 (d); [**a**] 16.6 (s)
1	170	[**c**] 3.9 (d); [**a**]16−18 (d)
2	160	[**c**] 5.5−4.2 (d); [**a**] 17−18 (d)

[a] The [assignments] correspond to the reflections in Figures 4 and 5. Reflections: s = sharp; d = diffuse.

Discussion

By combining the results obtained by DSC, OPM and X-ray measurements a detailed picture of the mesomorphic behavior of **1** and **2** has been constructed. For the low molar mass material **2**, all data obtained by various methodes are consistent with a nematic discotic (N_D) phase asignment. The positions and magnitudes of the phase transitions, the diffuse X-ray diffraction patterns and the optical texture of liquid crystalline phase are similar to those reported for lateral-substituted analogues of **2**.[16]

For polymer **1**, a more complex phase behavior was observed. The X-ray diffraction pattern taken at 170 °C, the small change in enthalpy at the clearing point (0.3 kJ/mol) and the texture observed in optical microscopy strongly indicate that between 165 and 235 °C, **2** exhibits a nematic discotic (N_D) phase. At about 165 °C, a transition into a second mesophase took place. No changes in the optical texture were observed going through the transition, even after annealing for 24 h at 130 °C. Most probably, the physical structure below 165 °C can be identified as a N_{col} phase. A transition between the N_{col} and N_D phases will not alter the director field of the molecules and therefore, no significant changes of the optical texture are anticipated. The proposed nematic columnar phase is in full agreement with the X-ray diffraction data that shows a sharp reflection at 3.8 Å for the periodic disk distances in the nematic columns and a somewhat more diffuse reflection at 16.6 Å for the less ordered lateral columnar distances. Hence, we conclude a N_{col} phase for **1** below 165 °C. It should be noted that the change in enthalpy at the $N_{col} \rightarrow N_D$ transition (8.1 kJ/mol) is rather high compared to literature values. For polymers containing other discotic side groups, enthalpies of $N_{col} \rightarrow$ I transitions on the order of 1−3 kJ/mol are reported,[9f] although enthalpies close to 8 kJ/mol have been reported for $D_h \rightarrow$ I transitions.[9b,d,g,h] The N_{col} phase is preserved on cooling below the T_g of the polymer.

The observed mesomorphic behavior of polymer **1** and "monomer" **2**, give insight in the factors influencing the phase behavior of these liquid crystalline materials. Differences between **1** and **2** emphasize the importance of the molecular architecture of the molecules containing mesogenic groups.

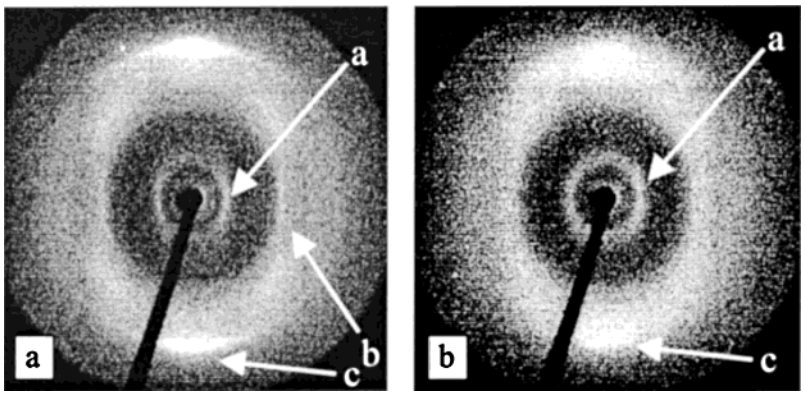
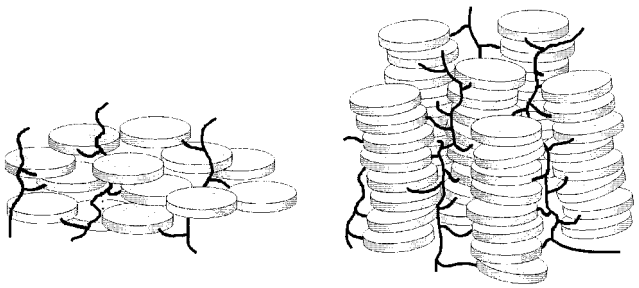


Figure 5. X-ray diffraction patterns of (a) polymer **1** at 140 °C (N_{col} phase) and (b) polymer **1** at 170 °C (N_D phase). Maximum diffraction angle: $2\theta = 30°$.



a b

Figure 6. Schematical representation of polymer **1** in (a) the N_D phase and (b) the N_{col} phase.

Studies by Praefcke and co-workers have elucidated the phase behavior of hexakis(4-alkylphenylethynyl)-benzenes,[6] the 6-fold substituted analogues of **2**. With small alkyl tails, these highly symmetrical materials do not exhibit mesophases.[24] Substitution of one 4-alkylphenylethynyl group by a long, flexible alkyl chain induces liquid crystalline phases (all N_D) for the laterally substituted materials.

Comparing **1** and **2**, their phase behaviors are qualitatively similar. Both form a nematic discotic phase between ~165 and ~195 °C, due to the large anisotropy of the disk-shaped groups and the absence of strong attractive $\pi-\pi$ interactions. To our knowledge, this is the first time that a nematic discotic phase is reported for a polymer (see Figure 6a). The clearing temperature for **1** is higher, 235 vs 195 °C, but the transition to a more ordered, columnar phase occurs at similar tempratures for both compounds. The low molecular weight compound **2** forms a crystalline phase, whereas the polymer **1** forms the less ordered nematic columnar phase. This difference in phase behavior between **1** and **2** cannot be traced back to spatial arguments, since the volume per mesogenic unit in **1** and **2** is virtually identical.[25] It must be due to the fact that owing to covalent attachment to the polymer backbone, the mobility of mesogens is strongly reduced and hence, a regular packing of the columns into highly ordered structures is not possible. Because of the flexibility of polyacrylate main chain and the length and flexibility of the undecanyl spacer, disks attached to one chain are not expected to be ordered in one stack but rather form a three-dimensional network; see Figure 6b.

Conclusions

We have prepared a novel discotic liquid crystalline side chain polymer **1**, exhibiting a nematic columnar phase at lower temperatures *and* a nematic discotic phase at higher temperatures. This is unique since up until now this low ordered phase was found solely in low molecular weight discotic materials. For comparison, the low molar mass homologue **2** was synthesized as well, which exhibited a N_D phase only.

The attachment of the mesogens to the reactive polymer followed by quenching the remaining reactive groups offers a highly flexible route for synthesizing many structurally similar polymers. Hence, this concept enables us to manipulate many molecular parameters, such as the following: (i) the lateral substituents on the rigid core;[6,26] (ii) the nature of the spacer and the spacer length between the mesogen and the polymer backbone;[27] (iii) the degree of substitution of the mesogen on the polymer backbone; (iv) the nature of the alcohol used for quenching the reactive polymer.

These variations are expected to have a large impact on the thermal properties of the materials and can ultimately lead to tailor-made material properties. Another way to manipulate the properties is to use a second component that undergoes specific (noncovalent) interactions with the mesogenic groups. For example, upon complexing **1** or **2** with strong electron acceptors,[9a,12b,28] charge transfer complexes are formed, resulting in supramolecular architectures. Such systems are currently under investigation.

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(22) 0.1 mL of the PAC solution was added to 50 mL of dry methanol. The mixture was stirred for 2 h and the methanol (and traces of methyl acrylate) were evaporated. The molecular weight was determined by GPC. Poly(methyl acrylate): $M_n = 21 \times 10^3$; $D = 2.9$.
(23) Using the same procedure, we were able to attach other mesogens and primary alcohols in different ratios.
(24) Unpublished results show that symmetrical hexakis(alkylphenylethynyl)benzenes with alkyl being methyl, ethyl, or *tert*-butyl are not liquid crystalline in contrast to derivatives with *n*-pentyl of larger tails.
(25) This assumes that the presence of 10% of methyl acrylate groups in the backbone (corresponds with only 1% in total mass) does not play a major role, although its influence may not be discarded a priori since small changes in molecular architecture can have dramatic effects.
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