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Stable Anisotropic Films Obtained by In-Situ Photopolymerization of Discotic Liquid Crystalline Acrylates

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ABSTRACT: New discotic liquid crystals with one, two, or three reactive acrylate end groups were synthesized. They exhibit a wide discotic nematic phase and show spontaneous homeotropic alignment between substrates. The photoinitiated polymerization of these materials was studied. "In-situ photopolymerization" of these disklike acrylates leads to transparent and thermally stable films with a negative birefringence.

Introduction

Stable anisotropic networks have been obtained from reactive rodlike liquid crystals through in-situ photopolymerization[1] in the nematic,[1,2] cholesteric,[3] or smectic[4,5] phases. In this process, monomers with reactive end groups such as acrylates provided with a photoinitiator are aligned macroscopically and polymerized under UV radiation. In order to improve the stability of optical components based on discotic liquid crystals, we investigated the in-situ photopolymerization of discotic liquid crystalline acrylates. The resulting films can for example be used to make stable optical compensation layers to enlarge the viewing angle of twisted nematic liquid crystal displays.[6]

Photoinitiated polymerization has already been applied to reactive porphyrins and phthalocyanines in the discotic columnar phase.[7,8] To facilitate the alignment step, we chose to focus on discotic liquid crystals exhibiting the less viscous discotic nematic phase (N_D).

The first liquid crystals found to exhibit the N_D phase are the hexaalkoxybenzoates of triphenylene.[9] The N_D phase of these compounds is very broad but is observed at high temperatures.[9] To prevent thermal polymerization while heating for alignment, lower temperatures are more suitable. By adding one or two methyl groups to the peripheral phenyl groups of the hexaalkoxybenzoates of triphenylene, much lower transition temperatures to the N_D phase (T_N) were obtained.[10,11] In particular, 1,2,7,8,13,14-hexakis((2-methyl-4-(decyloxy)benzoyl)oxy)triphenylene (C_{10}MBTP) combines a relatively low T_N with a broad nematic phase (Table 1).[11] In addition, this compound is colorless.

In this article, we describe the synthesis of new discotic liquid crystals with reactive acrylate end groups, derivatives of C_{10}MBTP. We study their polymerization behavior and the optical properties of the resulting polymeric films, in order to determine if "in-situ photopolymerization" can effectively freeze in oriented discotic materials.

Experimental Section

Synthesis of Monomers. All the solvents and inorganic compounds were obtained from Merck. The other chemicals were purchased from Acros Chimica except for *N*-bromosuccinimide and 11-bromo-1-undecanol, which were obtained from Aldrich.

The NMR spectra were obtained with a Bruker DPX-300 (300 MHz) spectrometer.

Table 1. Transition Temperatures of 1, 2, 3, and C_{10}MBTP with the Corresponding Enthalpies ΔH^a

	T_N (°C)	ΔH_N (J·g^{-1})	T_I (°C)	ΔH_I (J·g^{-1})
C_{10}MBTP	109 [51]	21.82	162 [159]	0.15
monoacrylate **1**	101 [37]	18.09	153 [150]	0.12
diacrylate **2**	89 [11]	16.14	141 [139]	0.15
triacrylate **3**	80 [−]	14.14	125 [123]	0.1

[a] T_N = transition temperature to the nematic phase, T_I = transition temperature to the isotropic phase, ΔH_N = enthalpy of the transition to the nematic phae, and ΔH_I = enthalpy of the transition to the isotropic phase. The transition temperatures obtained on cooling are indicated in square brackets.

All the final compounds were purified by means of column chromatography until we could observe no impurities in their NMR spectra, one spot on thin-layer plates (TLC) after elution with an appropriate solvent, and constant melting temperatures (or constant T_N) within a range of 3 °C (measured by DSC).

1,2,7,8,13,14-Hexamethoxytriphenylene (HMTP) was synthesized according to a method described in the literature[12] and was further purified by means of column chromatography (silica gel, $CHCl_3$) until a white powder was obtained. We cleaved HMTP with BBr_3 to obtain 1,2,7,8,13,14-hexahydroxytriphenylene (HHTP) and recrystallized it from water/methanol (5:1) to obtain light gray needles. Before use, we dried it for 1 h under a vacuum of 200 mbar at 120 °C.

For the synthesis of C_{10}MBTP, the side chains (2-methyl-4-(decyloxy)benzoic acid) were synthesized as described below (steps a, b, and c). The final esterification, involving the coupling of the side chains to HHTP, was performed as described in the literature.[10]

(a) 3-(Decyloxy)toluene (4). A mixture of 54 g of *m*-cresol (0.5 mol), 99.5 g of *n*-bromodecane (0.45 mol), and 20 g of ground NaOH (0.5 mol) in 350 mL of 2-butanone was boiled for 24 h. After evaporation of the 2-butanone, 350 mL of water and 300 mL of diethyl ether were added. The two layers were separated and the ethereal layer was extracted twice using 100 mL of a 10% aqueous solution of NaOH and 100 mL of a saturated aqueous solution of NaCl, after which it was dried over magnesium sulfate and evaporated. The resulting oil was distilled under reduced pressure. Yield: 85 g (76%) of a colorless oil (bp 142 °C at 0.3 mmHg).

(b) 2-Bromo-5-(decyloxy)toluene (5). To a cooled (−5 °C) mixture of 85 g of **4** (0.34 mol) in 400 mL of CH_2Cl_2 was added 61 g of *N*-bromosuccinimide (0.34 mol). The solution was stirred for 2 h at room temperature, exposed to natural UV light. After filtration and evaporation of the dichloromethane, the remaining *N*-bromosuccinimide and succinimide were removed by flash column chromatography (silica gel, CH_2Cl_2). Pure product (95 g, yield 85.4%) was obtained as a colorless oil.

(c) 2-Methyl-4-(decyloxy)benzoic Acid (6). Magnesium turnings (3.2 g, 0.13 mol), 20 mL of dry tetrahydrofuran (THF), a few crystals of iodine, and 1 mL of **5** were mixed under nitrogen. Once the reaction had started, the remaining

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2-bromo-5-(decyloxy)toluene (total 40 g, 0.12 mol) in 400 mL of dry THF was added to the mixture drop by drop. The solution was stirred for 4 h. Solid carbon dioxide was then added little by little: the mixture first became warm and then cooled down. After the addition of 200 mL of diethyl ether, the solution was filtered to remove the unreacted magnesium. HCl (150 mL, 2.5 M) was added. The ethereal layer was washed with 150 mL of water and 100 mL of a saturated solution of NaCl. It was dried over magnesium sulfate and the solvent was evaporated. The resulting white solid was recrystallized from petroleum benzine (bp 60−80 °C) to obtain 27 g of pure product (yield 77%).

(d) 2-Bromo-5-methoxytoluene (7). To a cooled mixture (−5 °C) of 35.7 mL of 3-methylanisole (0.28 mol) in 400 mL of CH_2Cl_2 was added 49.8 g of *N*-bromosuccinimide (0.28 mol). The solution was stirred for 2 h at room temperature under sunlight. It was washed twice with 100 mL of a 10% NaOH aqueous solution and 100 mL of a saturated aqueous solution of NaCl, after which it was dried on magnesium sulfate and evaporated. The product was distilled under reduced pressure to give 42.1 g (yield 74%) of a colorless oil (bp 58 °C at 0.4 mbar).

(e) 2-Methyl-4-methoxybenzoic Acid (8). The same starting procedure as described above in (c) for the Grignard reaction was followed with 5.6 g of magnesium turnings (0.23 mol), a few crystals of iodine, 42.1 g of **7** (0.21 mol), and 250 mL of THF. After 2 h of stirring and the addition of solid carbon dioxide, 150 mL of diethyl ether was poured into the mixture, which was then filtered. The magnesium salt of the product was extracted using 400 mL of water: it was washed twice with 150 mL of diethyl ether. The aqueous solution was acidified with 37% HCl: the resulting white precipitate was filtered off and was stirred into 800 mL of water for 20 min to remove the remaining magnesium salts. The white solid was filtered off and dried overnight under a vacuum of 200 mbar at 80 °C. Yield: 76% (26.5 g).

(f) 4-Hydroxy-2-methylbenzoic Acid (9). Boron tribromide (20 mL, 0.21 mol) in 50 mL of CH_2Cl_2 was added drop by drop, under nitrogen, to a suspension of 11.8 g of **8** (0.071 mol) in cooled dichloromethane (−78 °C). The solution was stirred for 20 h at room temperature and was then poured into a well-stirred mixture of ice (100 g) and water (200 mL). The precipitate was filtered off, solubilized in 100 mL of 10% NaOH, and washed twice with 50 mL of diethyl ether. The solution was acidified with 20% HCl, after which the white precipitate was filtered off and washed with water. The solid was dried overnight at 80 °C under 200 mbar. Yield: 78% (8.4 g).

(g) Ethyl 4-Hydroxy-2-methylbenzoate (10). **9** (2 g, 0.013 mol) and 0.2 mL of 97% H_2SO_4 in 10 mL of ethanol were refluxed for 15 h. Twenty milliliters of a $NaHCO_3$ saturated solution containing 10 g of ice was poured into the solution. The precipitate obtained was filtered off, briefly washed with 10 mL of H_2O, and dried overnight in a desiccator over silica. Yield: 82% (1.95 g).

(h) 4-(11-Hydroxyundecanoxy)-2-methylbenzoic Acid (11). Sodium methoxide (2.7 g, 0.05 mol) was dissolved in 40 mL of ethanol under nitrogen. **10** (7.9 g, 0.044 mol) was added, followed by 11 g of 11-bromo-1-undecanol (0.044 mol). The mixture was refluxed for 3 h. The ethanol was evaporated. Water (100 mL) and 150 mL of diethyl ether were added. The two layers were separated: the ethereal layer was washed twice using 50 mL of a 10% NaOH aqueous solution and 50 mL of a saturated aqueous solution of NaCl. The diethyl ether was evaporated. The product obtained was refluxed for 15 h with 3.7 g of KOH (0.066 mol) in 75 mL of water and 25 mL of ethanol. Five milliliters of 37% HCl was added drop by drop, after which the mixture was cooled in an ice bath and the precipitate was filtered off and washed with water. The solid was recrystallized in ethanol and dried overnight in a desiccator, and 6.8 g of white product was obtained (yield 48%).

(i) 4-(11-Acryloyloxy)undecanoxy)-2-methylbenzoic Acid (12). **11** (6 g, 0.019 mL), 2.83 mL of *N,N*-dimethylaniline (0.022 mol), and 0.2 g of 2,6-di-*tert*-butyl-4-methylphenol (0.0009 mol) in 50 mL of 1,4-dioxane were heated to 50 °C. Acryloyl chloride (1.8 mL, 0.022 mol) was then added. After 2 h at 50 °C, the mixture was poured into water (100 mL) containing ice (100 g) and 35% HCl (1 mL). The white precipitate was filtered off and washed with water (100 mL). The product was recrystallized in 20 mL of 2-propanol and dried overnight at 60 °C under 200 mbar, and 5.2 g of **9** was obtained (yield 74%).

(j) 1-((4-(11-(Acryloyloxy)undecanoxy)-2-methylbenzoyl)oxy)-2,7,8,13,14-pentakis((4-(decyloxy)-2-methylbenzoyl)oxy)triphenylene (Monoacrylate 1), Bis((4-(11-(acryloyloxy)undecanoxy)-2-methylbenzoyl)oxy)tetrakis((4-(decyloxy)-2-methylbenzoyl)oxy)triphenylene (Diacrylate Isomers 2), and Tris((4-(11-(acryloyloxy)undecanoxy)-2-methylbenzoyl)oxy)*tris*((4-(decyloxy)-2-methylbenzoyl)oxy)triphenylene (Triacrylate Isomers 3). To a stirred mixture of 2.3 g of **12** (0.006 mol), 3.6 g of **6** (0.012 mol), 5 drops of *N,N*-dimethylformamide, and 0.02 g of 2,6-di-*tert*-butyl-4-methylphenol in 50 mL of dichloromethane was added 2.6 mL of thionyl chloride (0.036 mol), under nitrogen. The solution was stirred overnight with a calcium chloride guard. SO_2 and the solvent were evaporated, first at 35 °C under 10 mbar and then under high vacuum (0.4 mbar) at room temperature for 1 h. The resulting solid was dissolved in 40 mL of dichloromethane to which 0.9 g (0.0028 mol) of 1,2,7,8,13,14-hexahydroxytriphenylene was added under nitrogen. Triethylamine (3.8 mL, 0.027 mol) was added, drop by drop, to this mixture cooled in an ice bath. This solution was stirred for 3 days at room temperature. Another 100 mL of dichloromethane was added before the solution was washed 3 times with 50 mL of 2.5 N HCl and 80 mL of a saturated aqueous solution of NaCl. It was then dried over magnesium sulfate, and the dichloromethane was evaporated. The final products, mono-, di-, and triacrylate, were isolated by flash column chromatography (CH_2Cl_2 for mono- and diacrylate; silica gel, column length 45 cm, CH_2Cl_2/2.5% ethyl acetate for triacrylate) and were individually purified by column chromatography (same eluents). TLC (CH_2Cl_2): $R_{f,\mathrm{C_{10}MBTP}} = 0.33$; $R_{f,\mathrm{mono}} = 0.11$; $R_{f,\mathrm{di}} = 0.04$; $R_{f,\mathrm{tri}} = 0$. We obtained 1.2 g of monoacrylate **1**, 0.8 g of diacrylate **2** (four isomers), and 0.2 g of triacrylate **3** (four isomers).

^{1}H NMR (300 MHz, $CDCl_3$) of the monoacrylate (in ppm): aromatic, 8.4 (6H, s), 8 (6H, d), 6.6 (6H, d), 6.5 (6H, dd); acrylate, 6.4 (1H, dd), 6.1 (1H, dd), 5.8 (1H, dd), 4.15 (2H, t); $ArOCH_2$, 3.9 (12H, t); $ArCH_3$, 2.5 (18H, s); $ArOCH_2CH_2$, 1.8 (12H, quint); acryl-OCH_2CH_2, 1.9 (2H, quint); 1.2−1.5 (84H, m); 0.9 (15H, t). The diacrylate and triacrylate NMR spectra differ from the monoacrylate spectrum in terms of the integration values only.

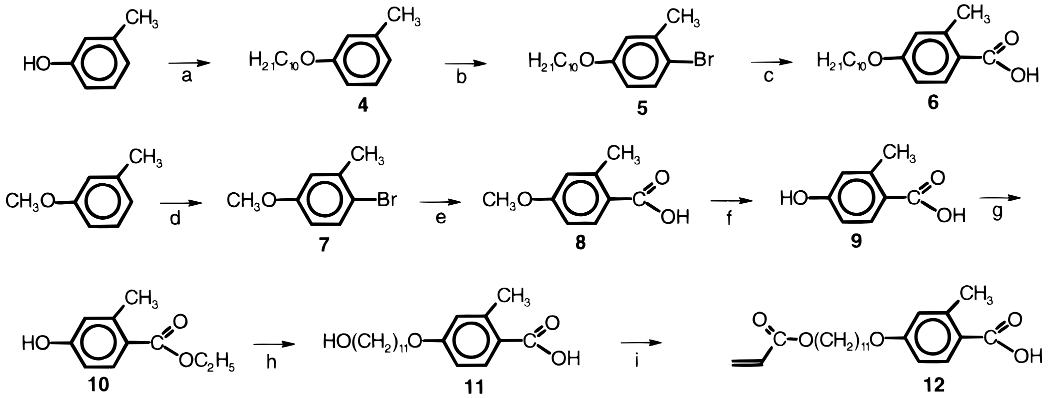
DSC and Photoinitiated Polymerization. We determined the transition temperatures with a Perkin-Elmer differential scanning calorimeter (DSC-7) using heating and cooling rates of 10 °C/min and samples of about 10 mg. We took the maxima of the DSC enthalpic peaks during the second heating as values for the transition temperatures.

The photoinitiated polymerization experiments were carried out with the above-mentioned calorimeter modified for UV irradiation[13] (with a 10 W Philips fluorescent lamp PL 10), under nitrogen, with 15 min exposure to UV, using samples weighing from 1.4 to 1.8 mg. The samples were prepared by adding to the monomer 1 wt % photoinitiator, Irgacure 651 (Ciba-Geigy), and 200 ppm of inhibitor, p-methoxyphenol, to avoid thermal polymerization. The conversion of the acrylates was calculated from the heat of polymerization (integration of the DSC exotherms), knowing the heat of polymerization for acrylate groups (78 kJ/mol[14]). The conversion rates (in percentage of reacted acrylates per second) were determined in the same way using the heat flow values.

To prepare the films, we pressed the above melted mixture between clean glass plates or glass plates coated with polyimide (AL-1051, JSR, Japan) and exposed them to UV radiation (using the same PL 10 lamp) for 15 min after the alignment had been realized.

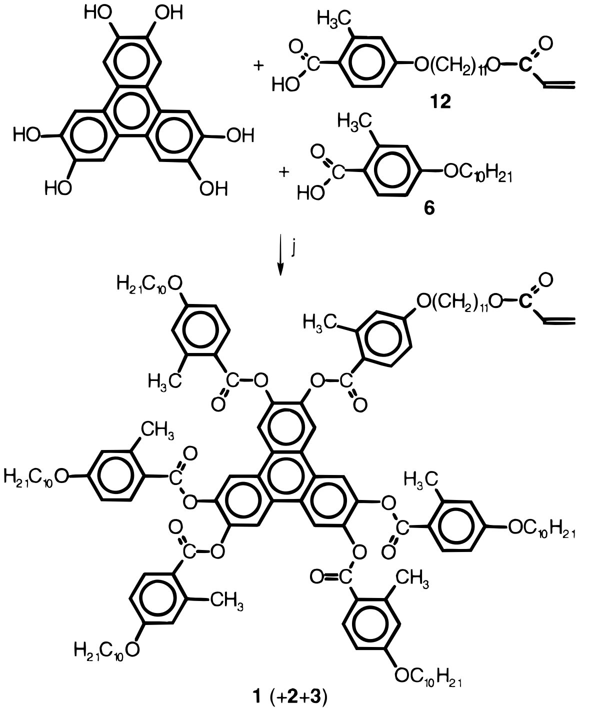
Optical Measurements. The textures of the discotic materials were studied with a Leitz Laborlux 12 Pol polarizing light microscope ($\lambda = 565$ nm) equipped with a Mettler FP82 hot stage (central processor FP80). The same microscope equipped with a tilting compensator (1942 K) was used to

Scheme 1^a



^{a} Reagents: (a) n-$C_{10}H_{21}Br$, NaOH, 2-butanone; (b) NBS, CH_2Cl_2; (c) Mg, THF, followed by CO_2; (d) NBS, CH_2Cl_2; (e) Mg, THF, followed by CO_2; (f) BBr_3, CH_2Cl_2; (g) H_2SO_4, EtOH; (h) $HOC_{11}H_{22}Br$, NaOMe, EtOH, followed by KOH, ethanol−water; (i) DMA, acryloyl chloride, dioxane.

Scheme 2^a



^{a} Reagents: (j) $SOCl_2$, DMF, CH_2Cl_2, followed by TEA, CH_2Cl_2.

measure the optical retardation of the polymerized films as a function of the temperature and θ (θ is the angle between the incident light and the normal of the film). The birefringence was calculated from the phase retardation values, knowing the thickness of the films. The angular dependence of the birefringence was also obtained from the phase retardation measured with a He−Ne laser device[15] (λ = 632 nm).

The thickness of the films was determined by means of interferometry using a UNICAM 8700 UV−vis spectrometer. It was controlled by means of spacers which were purchased from Shinshikyu (Japan).

We measured the refractive indices of the materials with an Abbe refractometer (Carl Zeiss), λ = 589 nm, which could be thermostated up to 140 °C. The films could be removed from their substrates with a razor blade to allow these measurements.

Results and Discussion

Scheme 1 shows the synthetic route for the peripheral moieties (a−i). The final reaction (j), leading to the discotic acrylates, appears in Scheme 2. In the esterification reaction (j), we obtained higher yields using triethylamine/CH_2Cl_2 (the method currently used for esterification in the synthesis of some rodlike molecules[3,4]) instead of using pyridine as is usually reported for the synthesis of nonreactive benzoates of triphenylene.[10,16] A statistical distribution of **1**, **2**, and **3** is obtained at the end of the reaction (j). We performed the reaction with 2 equiv of **12** and 4 equiv of **6** to form in theory 26.3, 32.9, and 21.9% (molar percentages) of **1**, **2**, and **3**, respectively, on the assumption that the acrylated and nonacrylated acid chlorides had the same reactivity. We obtained a greater proportion of monoacrylate mainly because of the purification process (the monoacrylate being most readily eluted). The different isomers of **2** (or **3**) could not be separated. We used the mixture of isomers for the experiments described below.

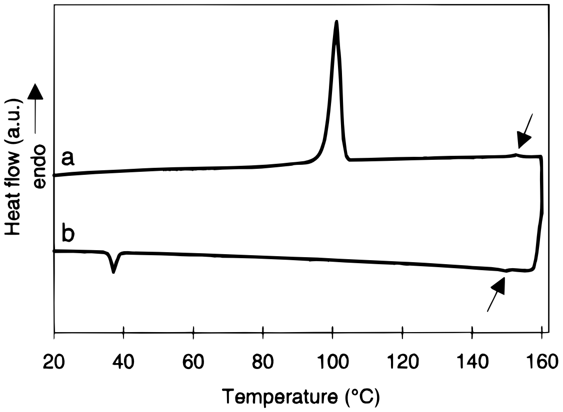


Figure 1. DSC curves of monoacrylate **1** obtained at a rate of 10 °C/min ((a) heating; (b) cooling). The arrows indicate the transitions between the nematic and isotropic phases.

The transition temperatures of **1**, **2**, **3**, and C_{10}MBTP appear in Table 1. Figure 1 shows the DSC runs of **1**. The DSC runs of **2** and **3** are qualitatively similar to those of **1**. All monomers show a sharp endotherm when entering the N_D phase (run a, Figure 1). This phase is identified on the basis of its fluidity and its typical schlieren texture between crossed polarizers. A second endotherm with a much lower enthalpy value corresponds to the transition from the N_D to the isotropic phase (run a, Figure 1). Upon cooling, these transitions appear to be reversible (run b, Figure 1). The N_D phase supercools to a very low temperature. In fact, the monomers gradually become more and more viscous while cooling in the supercooled N_D phase, the schlieren

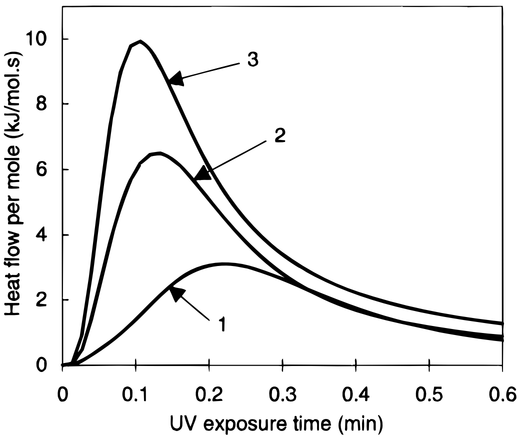


Figure 2. Isothermal DSC curves (heat flow per mole of monomer) of the polymerization of **1**, **2**, and **3** at 100 °C versus the irradiation time.

defect texture being preserved. The viscosity probably delays the transition to a higher ordered phase and is one reason leading to the large supercooled effect observed.

Below the N_D phase, at room temperature for example, the monomers form an extremely viscous gel (C_{10}MBTP is crystalline[11]). They show no fluidity and cannot be sheared easily between substrates, so they are not liquid crystalline. Photoinitiated polymerization experiments show that almost no conversion of the acrylate groups occur in this phase upon irradiation, which also suggests that the side chains are not liquid-like. In fact, the crystallization of these compounds is hindered by the presence of the acrylate groups and the mixture of isomers (for **2** and **3**) which induce disorder in the side chains. As a consequence, only very small crystallites can form, leading to gellike rather than crystallike materials.

Comparison of the transition temperatures in Table 1 shows that the presence of acrylate groups causes T_N and T_I to decrease. The presence of the polar groups at the end of the aliphatic chains slightly disturbs the nematic discotic ordering as well as the crystalline ordering. Terminal chains of different lengths (in one molecule) probably also contribute to the lowering of the transition temperatures, as was found to be the case with the hexaalkoxytriphenylenes.[17] The mixture of isomers in the case of **2** and **3** does not seem to affect markedly the transition temperatures. The nematic phase remains as broad as in the case of C_{10}MBTP for **1** and **2**. It is slightly smaller for **3**. The addition of photoinitiator and inhibitor for the polymerization causes the transition temperatures to decrease by 2−5 deg.

The isothermal DSC curves of the photoinitiated polymerization of **1**, **2**, and **3** in the discotic nematic phase are given in Figure 2. All three monomers polymerize readily. The polymerization reaction first accelerates because of the Trommsdorff effect, the suppression of the chain termination due to the gelation of the materials.[18] The acceleration is instantaneous, as was already observed with rodlike liquid crystalline acrylates.[1,19] The gelation and therefore the acceleration are greater for the multifunctional acrylates **2** and **3** because they lead to densely cross-linked networks (represented in Figure 3). **1** only forms a side-chain polymer upon irradiation (Figure 3). The polymerization of the acrylates **1**, **2**, and **3** in the isotropic phase leads to similar initial accelerations; therefore the liquid crystalline ordering is not likely to contribute to the early gel effect.

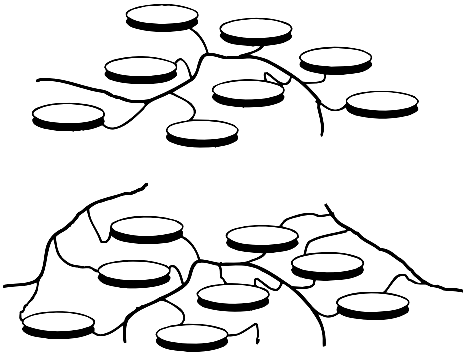


Figure 3. Schematic representation of the side-chain polymer obtained by polymerization of **1** (top) and the densely cross-linked network obtained by polymerization of **2** (below).

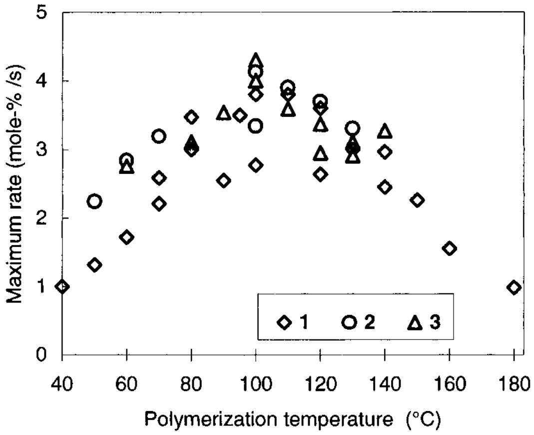


Figure 4. Maximum polymerization rates (expressed in percentage of reacted acrylate groups per second) of **1**, **2**, and **3** as a function of the polymerization temperature.

After the initial acceleration, the polymerization rates reach a maximum (Figure 2). This occurs after an average of 6, 8, and 13 s of irradiation of **3**, **2**, and **1**, respectively. The average degree of conversion (percentage of reacted acrylate groups versus the total number of acrylate groups) at this point is 22.5, 15.4, and 11.7% for **1**, **2**, and **3**. The absence of cross-link in the case of the monoacrylate allows a higher degree of conversion before the rate starts to decrease. The maximum rate of polymerization is proportional to the number of acrylate groups per molecule (Figure 2). The maximum rate versus the temperature is plotted in Figure 4. The rate is expressed, in this case, in degree of conversion per second. For all three monomers, the rate is maximum at about 100 °C. It decreases at higher temperatures because of the increased mobility of the reactive polymer end groups, which favors termination. The Trommsdorff effect is then reduced, leading to lower maximum rates. Besides the increased termination, depropagation might also occur at high temperatures as was previously argued.[1] The decrease of the maximum rate below 100 °C is probably due to the high initial viscosity that limits the diffusional mobility. Further conversion of the acrylate groups (Figure 2) leads to a decrease of the polymerization rate due to the immobilization and the depletion of these groups.

The final degrees of conversion (Figure 5) remain roughly constant for each monomer when polymerizing above T_N. Although the rate of polymerization decreases above 100 °C (Figure 4), there is no decrease in the final degree of conversion up to 160 °C. We did not

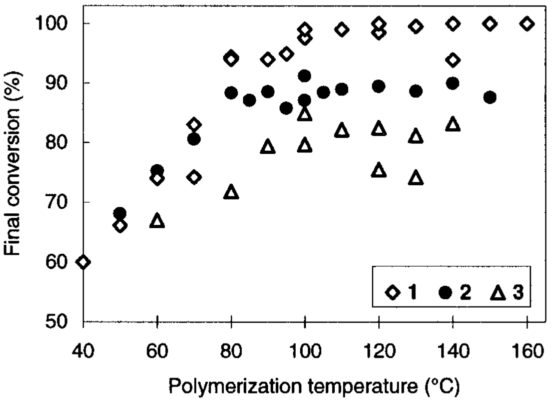


Figure 5. Final degrees of conversion (in percentage of reacted acrylate groups) of **1**, **2**, and **3** as a function of the polymerization temperature.

detect any influence of the transition to the isotropic phase of the final conversions. However, the samples of **1** become turbid when polymerized above the isotropic point, which indicates a phase separation in the material between polymer-rich and monomer-rich areas.[19] This phenomenon probably appears because of the combination of the lower polymerization rates in the isotropic phase (Figure 4) with the higher mobility at higher temperatures.

Monoacrylate **1** shows the highest final degrees of conversion, close to 100% in the N$_D$ phase. The polymerization is almost complete because the monomers remain relatively mobile even at a high degree of conversion due to the absence of cross-links. The average final degrees of conversion in the N$_D$ phase for **2** and **3** are 88 and 78%. These final degrees of conversion are relatively high and suggest a significant mobility of the terminal chains even at an advanced stage of the polymerization reaction. The long spacers make the reactive end groups quasi-independent of the triphenylene core, enabling them to diffuse in the polymer matrix.

For a polymerization temperature (T_p) below T_N, the sample is first heated for 1 min in the stable N$_D$ phase (T_N + 10 °C) and is then cooled to the desired temperature of polymerization (10 °C/min). Below T_N, the final degrees of conversion drop progressively with T_p (Figure 5). Incomplete conversion of acrylates (or methacrylates) is usually assigned to vitrification[1,20,21] or crystallization[19,22] during the polymerization. In our case, this drop can possibly be due to a local crystallization of the monomers in the metastable nematic phase, the nucleation of these crystallites starting at an earlier conversion with a lower T_p. For a T_p below 60 °C, the samples obtained are turbid because of the formation of bigger crystalline domains. Vitrification might also play a role in the case of the polymers made from **2** or **3** (poly(**2**) and poly(**3**)) but their glass transitions could not be detected by means of DSC because of the rigidity of the networks.

All the polymers made from **2** or **3**, T_p above 60 °C, have no transitions between −25 and +200 °C according to DSC. In the case of the polymers made from **1** (poly(**1**)), T_p above T_N, the DSC curves show a small and reversible transition to the isotropic phase at 156 °C (ΔH = 0.01 J/g). Poly(**1**) is a stiff material at room temperature and becomes progressively malleable above 90−100 °C although no transition is observed by DSC.

We can conclude that the photoinitiated polymerization successfully freezes in the materials, as the disappearance of the monomer melting transition in DSC testifies. The conversion rates in the N$_D$ phase (above 60 °C) are fast enough to prevent phenomena such as polymer/monomer phase separation that lead to turbid films, as observed with **1** polymerized in the isotropic phase. Diacrylate **2** and triacrylate **3** lead to thermally stable discotic films (at least until 200 °C). The optimal polymerization temperatures leading to the highest final degrees of conversion and conversion rates range from 80 to 120 °C.

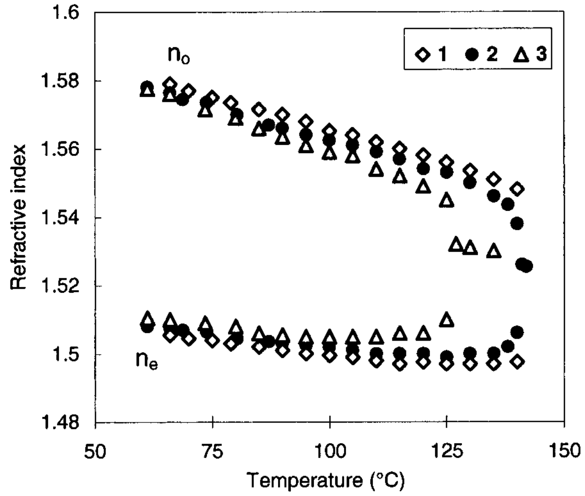


Figure 6. Ordinary (n_o) and extraordinary (n_e) refractive indices of **1**, **2**, and **3** mixed with 400 ppm of inhibitor as a function of the temperature.

It is now important to determine the influence of the polymerization on the orientation of the materials to see if the anisotropic properties of aligned monomers are preserved after polymerization.

The temperature dependence of the refractive indices of **1**, **2**, and **3** provided with 400 ppm of inhibitor to avoid thermal polymerization is shown in Figure 6. The monomers spontaneously align on the refractometer prism in the N$_D$ phase. They have a negative birefringence on the order of −0.07, as was previously established for the hexabenzoates of triphenylene.[23,24] An increase in the number of acrylate groups apparently causes a slight decrease in the order. The mixture of different isomers in the case of **2** and **3** may also be partly responsible for this decrease. Below 60 °C, the materials become turbid: the refractive indices could not be measured on further cooling.

To obtain polymer films, the monomers, provided with initiator and inhibitor, are aligned homeotropically (disks parallel to the substrate) between two glass plates coated with nonrubbed polyimide by heating them for about 10 min at 120−125 °C. Defect-free monomer films of about 2 cm^2 are obtained, as observed by polarizing microscopy. After alignment, the monomers can be cooled (10 °C/min) to 60 °C without any visible modification of the homeotropic alignment.

After exposure to UV irradiation, the films obtained from **1** and **2**, which are between 4 and 15 μm thick, apparently conserve the homeotropic alignment and do not shown any defect when examined with the polarizing microscope. The films are also transparent and colorless.

Figure 7 shows the refractive indices of a film of **1** polymerized at 120 °C, poly(**1**)120, and two films of **2** polymerized at 120 and 80 °C, poly(**2**)120 and poly(**2**)-80. The birefringence of poly(**2**) remains stable from room temperature up to 140 °C. The birefringence of

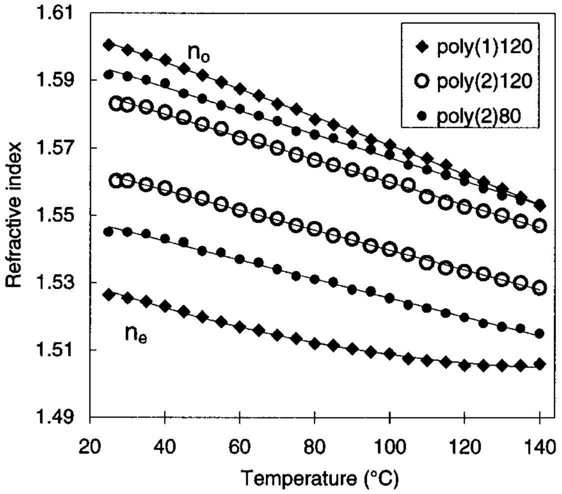


Figure 7. Ordinary (n_o) and extraordinary (n_e) refractive indices of poly(**1**), $T_p = 120$ °C, and poly(**2**), $T_p = 80$ and 120 °C, as a function of the temperature.

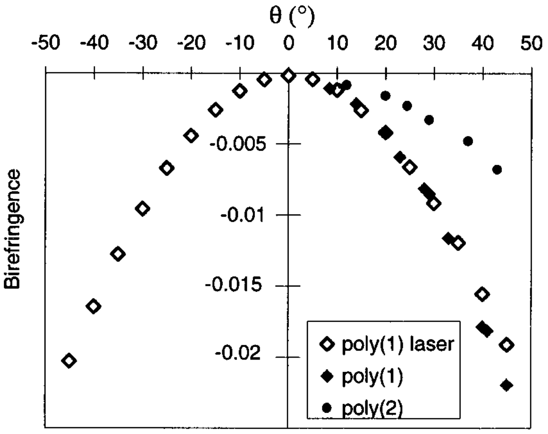


Figure 8. Angular dependence of the birefringence of poly(**1**) and poly(**2**) (polymerized at 120 °C), measured with a polarizing light microscope equipped with a tilting compensator (closed symbols). Angular dependence of the birefringence of the same poly(**1**), measured with a He−Ne laser device[15] (open symbol).

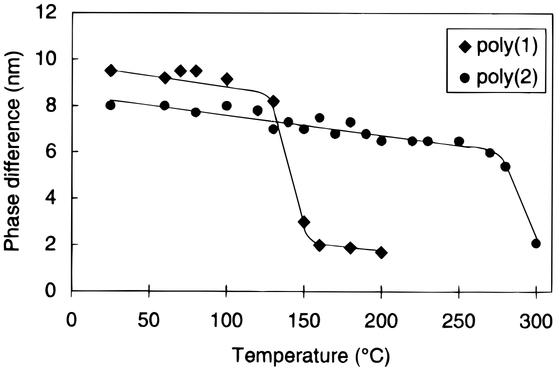


Figure 9. Phase differences (optical retardation) as a function of the temperature for poly(**1**) and poly(**2**) polymerized at 120 °C. They were measured in a Mettler hot stage with a polarizing light microscope equipped with a tilting compensator at angles of 14 and 22°, respectively, between the film normal and the light beam.

poly(**1**) decreases progressively from about 90 °C. The refractive indices decrease slightly as the temperature increases because of the thermal expansion of the materials. They are higher than those of the monomers in the nematic phase because of the shrinkage that occurs during the polymerization.[25] In the case of **2**, this increase is much larger for the extraordinary index n_e (in our case, the lower index) than for the ordinary index n_o. The consequence is that poly(**2**) has a much lower birefringence ($\Delta n = n_e - n_o$) than **2**. The birefringence indeed shows a 65% decrease during the polymerization of **2** at 120 °C. We obtained a higher birefringence by polymerizing **2** at a lower temperature, 80 °C. In this case, only a 30% decrease occurs and a birefringence on the order of −0.045 is obtained. Obviously, the polymerization alters the ordering of the mesogenic disks. This behavior is the opposite of what was found for some rodlike diacrylates, for which the birefringence increased during polymerization, and increased all the more with higher polymerization temperatures.[26] A crucial factor to preserve the orientation during polymerization is the strength of association between molecules.[4] It is very weak in our case because of the bulky methyl groups that prevent a close packing of the disklike molecules. As a consequence, the stress induced by the growing polymer chain is stronger than the intermolecular forces leading to the liquid crystalline order. A higher polymerization temperature leads to a higher disorder in the resulting poly(**2**) because of the thermal agitation. On the contrary, it favors a higher ordering in the final polymer for diacrylates with a high strength of association, because the mesogenic units can more easely accommodate (pack) during the polymerization due to the lower viscosity.[4,26]

The mixture of isomers of **2** possibly contributes to the final disorder by influencing the paths taken by the growing polymer chain during polymerization, although the kinetics shows no difference with that of well-defined rodlike diacrylates. Nevertheless, the birefringence values obtained for poly(**2**) are in a suitable range for applications like compensation layers (film thicknesses of 5−10 μm).[6] In addition, the birefringence can be varied by changing the polymerization temperature. For monomer **1**, the birefringence decreases only slightly during the polymerization (7% decrease at $T_p = 120$ °C). The monofunctionality of **1** implies less stress on the orientation during and after polymerization than in the case of **2**.

To study the behavior of the polymer anisotropy above 140 °C, we measured the birefringence of the materials in a hot stage, at a given angle, with the polarizing microscope. First, we determined the angular dependence of the birefringence, at room temperature, for a 4.4 μm-thick film of poly(**1**) polymerized at 120 °C (Figure 8). To confirm this result, we also performed the measurement with He−Ne laser device[15] ($\lambda = 632$ nm). The values obtained, shown in Figure 8, are lower than those determined with the polarizing microscope ($\lambda = 565$ nm) because of dispersion. The resulting curve is symmetric, centered at $\theta = 0°$ and independent of the orientation of the film around its normal, which confirms the homeotropy of the alignment.[15]

Figure 8 also shows the angular dependence of the birefringence of poly(**2**) polymerized at 120 °C (thickness: 11 μm). Its birefringence is significantly lower than that of the poly(**1**), as already observed with the Abbe refractometer (Figure 7).

Figure 9 illustrates the behavior of the anisotropy of the polymers as a function of the temperature. Poly(**2**), polymerized at 120 °C, remains stable from room temperature up to 270 °C. We expect the results to be the same for different polymerization temperatures, provided that the final degree of conversion is the same.

Poly(**1**), polymerized at 120 °C, loses its order around 140−150 °C (Figure 9) because of the relative freedom of the disklike molecules in the side chains of the polymer (see drawing in Figure 3). This result is consistent with the transition to the isotropic phase observed in DSC.

The residual birefringence (or phase difference) above 150 °C for poly(**1**) (in Figure 9) is due either to the accuracy of the measurement or to a residual order in the material.

Conclusion

The presence of methyl groups on the peripheral phenyl groups as well as acrylates on the triphenylene hexabenzoates leads to nematic phases in temperature ranges suitable for in-situ photopolymerization. The discotic acrylates align easily between (coated) glass substrates. Provided with a photoinitiator, they polymerize readily under UV irradiation. Their polymerization kinetics is very similar to what has already been observed with rodlike acrylates. In-situ photopolymerization of oriented films of monoacrylate **1** and diacrylate **2** results in thermally stable and colorless anisotropic films. The birefringence of the oriented discotic materials decreases during polymerization but remains suitable for applications. This loss of order is attributed to the weakness of intermolecular forces due to the steric hindrance created by the bulky methyl groups. The birefringence of poly(**2**) depends on the polymerization temperature and can probably be tuned via this temperature.

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