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Discotic liquid crystalline crosslinkers and anisotropic networks

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Discotic hexa-acrylates based on the triphenylene hexabenzoate group and a triacrylate based on the phenyl benzenetricarboxylate group were synthesized. The first class of compounds is suitable to form anisotropic networks by photopolymerization in the nematic discotic phase. The latter compound shows only a monotropic liquid crystalline phase at low temperatures and is therefore not suitable for formation of these anisotropic networks. Phase separation was observed upon photopolymerization of homogeneous mixtures of one of these reactive compounds and non-reactive discotic compounds.

1. Introduction

Photocrosslinking polymerization is particularly attractive for freezing-in liquid crystalline phases as it makes the polymerization process independent of temperature. The liquid crystal monomer can be heated to the desired mesophase and, once it has been macroscopically oriented, it can be polymerized under UV radiation [1].

Previous work on the photoinitiated polymerization of oriented rod-like liquid crystal (LC) diacrylates led to permanently stable anisotropic networks [1, 2], and a variety of applications [3–5]. These results induced us to apply the technique to discotic liquid crystals [6] to freeze-in discotic LC phases. We synthesized triphenylene hexabenzoate derivatives with acrylate end groups, aligned them in the discotic nematic (N_D) phase and polymerized them [7] (figure 1). The resulting films exhibit a thermally stable negative birefringence [7, 8] and can be used as compensation foils to enlarge the viewing angle of twisted-nematic liquid crystal displays [9].

While we focused mainly on discotics exhibiting the fluid N_D phase because of the ease of alignment, other groups have explored the possibilities of freezing-in discotic columnar phases of triphenylene [10], porphyrin [11], metallomesogen [12], and self-assembling amphiphilic [13] derivatives.

By studying the influence of the number of acrylate groups (1 to 6) on triphenylene benzoate derivatives we showed that the polymerization yield and the degree of ordering of the discotic molecules in an aligned monomer film were both higher when the monomer had fewer reactive groups [14, 15]. However, isolating mono-, di- and tri-acrylate monomers from the reaction products proved a rather tedious and lengthy operation [7]. On the other hand, hexa-acrylate derivatives appeared to be much easier to obtain and purify as the synthesis involves one type of side group only. The question was whether the presence of six polar acrylate groups at the end of the aliphatic spacers would still allow the formation of LC phases with sufficient breadth, at suitable temperatures.

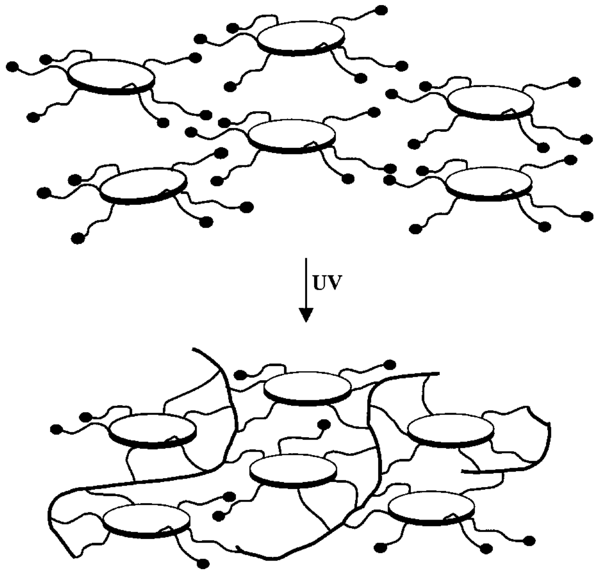

Figure 1. Schematic representation of the crosslinking polymerization in the N_D phase of a discotic liquid crystal with six reactive end groups.

In this article, we describe the synthesis and liquid crystalline properties of discotic hexa-acrylate derivatives of triphenylene hexabenzoate. We discuss the influence of the spacer length on the liquid crystalline properties,

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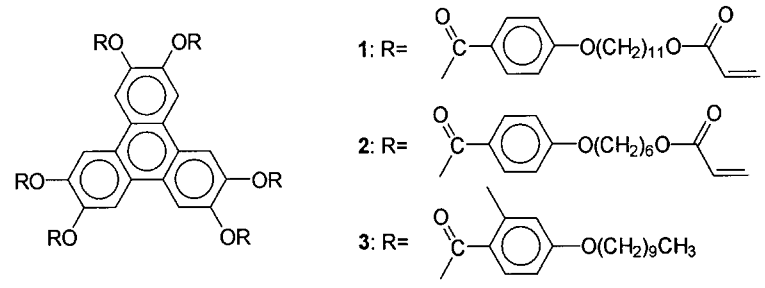


Scheme 1. Triphenylene hexabenzoate hexa-acrylates **1** and **2**, and non-reactive discotic **3** [26].

polymerization behaviour, and birefringence of both monomers and resulting networks. We also investigate the photoinitiated polymerization of mixtures of those hexa-acrylates with non-reactive discotic LC. Finally, we examine the LC properties and polymerization behaviour of a trifunctional discotic crosslinker with phenyl tribenzoate as a central core. Our general goal is to find simpler discotic crosslinkers and mixtures that can lead to stable, birefringent films, and to study the effect of spacer and central core sizes on the whole process.

2. Experimental part

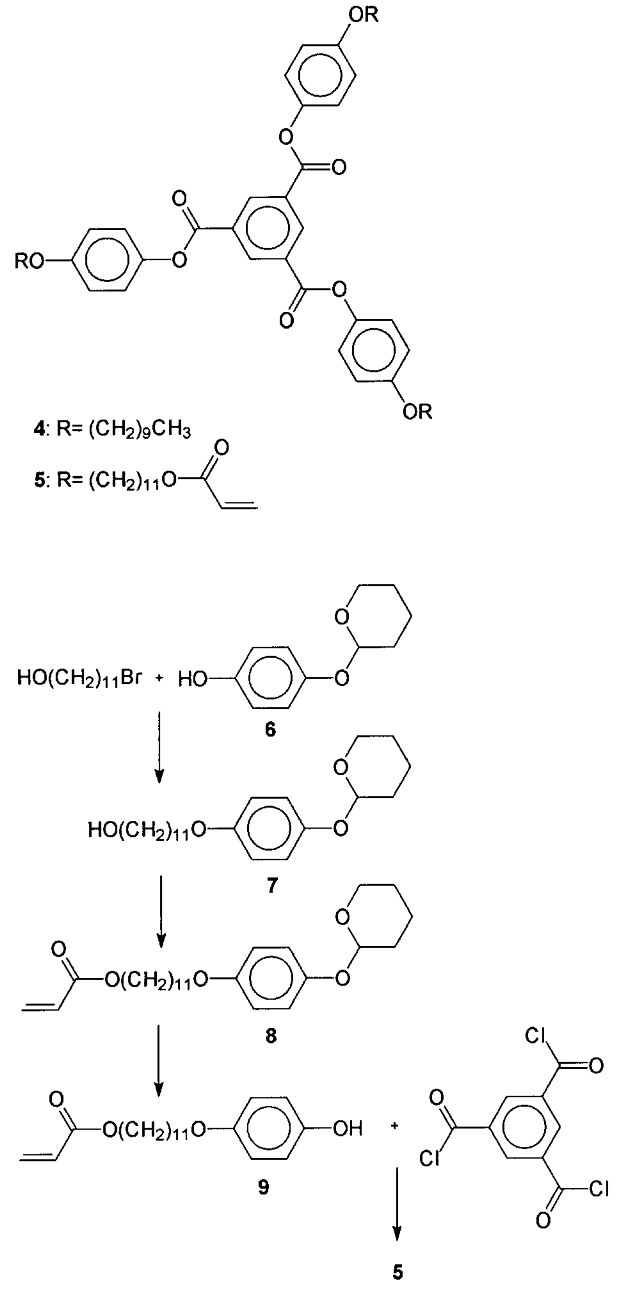
2.1. *Syntheses of the monomers*

The structures of compounds **1** and **2** are outlined in scheme 1. The central core precursor, 2,3,6,7,10,11-hexahydroxytriphenylene, was provided by Dr P. Schumacher (BASF, Ludwigshafen, Germany). The synthesis of the side group precursor 4-(6-acryloyloxyhexyloxy)benzoic acid is described elsewhere [1]. Side group precursor 4-(11-acryloyloxyundecanoxy)benzoic acid was prepared following the same scheme as for the hexyloxy homologue. We performed all the syntheses in a UV-free room.

Scheme 2 shows the synthetic route to 4-(11-acryloyloxyundecyloxy)phenyl 1,3,5-benzenetricarboxylate **5**. The synthesis of **4** has been reported elsewhere [16, 15]. 4-(Tetrahydropyran-2-yloxyl)phenol **6** was prepared according to the literature [17, 18].

2.1.1. *2,3,6,7,10,11-Hexakis-[4-(11-acryloyloxyundecanoxy)benzoyloxy]triphenylene,* **1**

Thionyl chloride (1.5 ml, 0.02 mol) was added to a stirred mixture of 4-(11-acryloyloxyundecanoxy)benzoic acid (3.7 g, 0.01 mol), *N*,*N*-dimethylformamide (10 drops), and a few crystals of the inhibitor 2,6-di-*tert*-butyl-4-methylphenol in 30 ml of dichloromethane. Nitrogen was bubbled through the solution during the addition of the $SOCl_2$. The solution was stirred overnight with a calcium chloride guard. The solvent and the remaining SO_2 were evaporated, first at 35°C at 10 mbar and then in a high vacuum (0.4 mbar) at room temperature for 1 h. The resulting acid chloride was dissolved in



Scheme 2. Substituted phenyl 1,3,5-benzenetricarboxylate **4** [17], **5** and their precursors.

60 ml of dichloromethane. 2,3,6,7,10,11-Hexahydroxytriphenylene (0.5 g, 0.0015 mol) was dried for 1 h in a vacuum of 200 mbar at 120°C, cooled, and added to the solution under nitrogen. The mixture was cooled in a water + ice bath and triethylamine (2.2 ml, 0.015 mol) was added dropwise. The solution was stirred for 3 days at room temperature. Dichloromethane (50 ml) was added and the mixture was washed 3 times with 60 ml of 2.5M HCl and 100 ml of a saturated solution of NaCl. The organic layer was dried over anhydrous magnesium sulphate and the solvent was evaporated. The resulting solid product was shaken 3 times with 20 ml of ethanol to remove the unreacted side group materials. It was further purified by flash column chromatography (eluent: CH_2Cl_2/5% ethyl acetate) until a white product was obtained. It was recrystallized from ethanol/benzene 10/1 in the presence of 2,6-di-*tert*-butyl-4-methylphenol to avoid thermal polymerization. Yield: 59% (2.17 g). ^1H NMR (300 Mhz, $CDCl_3$), in ppm: δ 8.42 (ArH, s 6H), 7.95 (ArH, d, 12H), 6.73 (ArH, d, 12H), 6.39 (acryl.H, d, 6H), 6.11 (acryl.H, dd, 6H), 5.80 (acryl.H, d, 6H), 4.15 (acryl.OCH_2, t, 12H), 3.93 ($ArOCH_2$, t, 12H), 1.77 ($ArOCH_2C\underline{H}_2$, quint., 12H), 1.67 (acryl.$OCH_2C\underline{H}_2$, quint., 12H), 1.5–1.2 ($-CH_2-$, m, 84H). Elemental analysis: calc. C 72.34, H 7.59; found C 73.0, H 7.6%.

2.1.2. *2,3,6,7,10,11-Hexakis-[4-(6-acryloyloxyhexyloxy)benzoyloxy]triphenylene,* **2**

Compound **2** was prepared similarly to **1**, using 4-(6-acryloyloxyhexyloxy)benzoic acid as side group precursor. Yield: 57% (1.73 g). ^1H NMR (300 Mhz, $CDCl_3$), in ppm: δ 8.47 (ArH, s, 6H), 8.01 (ArH, d, 12H), 6.80 (ArH, d, 12H), 6.40 (acryl.H, d, 6H), 6.12 (acryl.H, dd, 6H), 5.82 (acryl.H, d, 6H), 4.18 (acryl.OCH_2, t, 12H), 3.96 (ArOCH2, t, 12H), 1.80 (ArOCH2C$\underline{H}$2, quint., 12H), 1.71 (acryl.$OCH_2C\underline{H}_2$, quint., 12H), 1.46 ($-CH_2-$, m, 24H). Elemental analysis: calc. C 69.50, H 6.14; found C 70.0, H 6.2%.

2.1.3. *1-(11-Hydroxyundecanoxy)-4-(tetrahydropyran-2-yloxyl)benzene,* **7**

18.6 g of compound **6** (0.0956 mol) was dissolved in 100 ml of 2-butanone. Sodium methoxide (5.16 g, 0.0956 mol) was added and after obtaining a clear solution, 11-bromoundecanol (21.62 g, 0.086 mol) was added under nitrogen. The mixture was boiled for 16 h. The solvent was evaporated and 200 ml of ether added. The solution was washed with 100 ml of water, 100 ml of 10% NaOH solution and 100 ml of a saturated NaCl solution. It was dried over anhydrous $MgSO_4$ and the ether evaporated. The product was recrystallized from petroleum ether and dried overnight in a desiccator. Yield: 64%.

2.1.4. *4-(11-Acryloyloxyundecanoxy)phenol,* **9**

20.28 g of compound **7** (0.056 mol), triethylamine (8.44 g, 0.083 mol), and a few crystals of 2,6-di-*tert*-butyl-4-methylphenol were mixed with 100 ml of dichloromethane; 5.42 ml of acryloyl chloride in 10 ml of dichloromethane were added dropwise. The mixture was stirred for 16 h and then washed with 2 × 50 ml of 10% HCl and 100 ml of a saturated NaCl solution. The organic layer was dried over $MgSO_4$ and evaporated. The intermediate product **8** and pyridinium *p*-toluenesulphonate (3.11 g, 0.012 mol) were dissolved in 80 ml of ethanol and heated to 60°C (to remove the THP protection). Once the reaction was finished (controlled by TLC and NMR), the mixture was added dropwise to a mixture of water (200 ml) and ice (200 ml). The precipitate was washed twice with 75 ml of petroleum ether and dried in a desiccator. Yield: 75%.

2.1.5. *4-(11-Acryloyloxyundecyloxy)phenyl 1,3,5-benzenetricarboxylate,* **5**

1,3,5-Benzenetricarboxylic acid chloride (1.75 g, 1 mmol) and compound **9** (1 g, 3 mmol) were added to 15 ml of dichloromethane. Under nitrogen, triethylamine (0.5 ml, 3.6 mmol) was added dropwise. The mixture was stirred overnight, then 2 ml of concentrated HCl in 10 ml of water and 80 ml of dichloromethane were added. The aqueous layer was removed and the organic layer was washed with 2 × 50 ml of water. The organic layer was dried over magnesium sulphate and the solvent evaporated. The product was purified by column chromatography (silica gel, CH_2Cl_2). Yield: 53%. ^1H NMR (300 MHz, $CDCl_3$) in ppm: 9.20 (ArH, 3H, s), 7.16 (ArH, 6H, d), 6.95 (ArH, 6H, d), 6.40 (AcH, 3H, d), 6.10 (AcH, 3H, d), 5.80 (AcH, 3H, d), 4.15 ($AcOCH_2$, 6H, t), 3.96 ($ArOCH_2$, 6H, t), 1.80 ($ArOCH_2C\underline{H}_2$, 6H, quint.), 1.66 ($AcOCH_2C\underline{H}_2$, 6H, m), 1.5–1.2 (42H, m).

2.2. *Polymer network synthesis: photo-initiated polymerization*

Each monomer sample was mixed with 1 wt% photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (Irgacure 651, Ciba-Geigy), and 200 ppm of inhibitor, *p*-methoxyphenol, in 1 ml of dichloromethane. The solvent was evaporated overnight at atmospheric pressure. Just before polymerization, these samples were left for a $\frac{1}{2}$ hour in a vacuum (200 mbar) to remove remaining traces of solvent.

The polymerization kinetics were monitored by a Perkin-Elmer DSC-7 apparatus modified to allow UV irradiation of the samples [19]. A 10 W Philips fluorescent lamp emitting at 370 nm was used to crosslink the monomers.

To prepare thin films, monomers in the N_D phase were sandwiched between two glass plates coated with polyimide, on which we had dispersed 9 μm thick spacers to obtain samples of uniform thickness. The optical measurements of the films were performed as described in a previous publication [7].

3. Results and discussion

3.1. *Liquid crystalline properties of compounds **1** and **2***

Hexa-acrylates **1** and **2** were characterized by differential scanning calorimetry (DSC); the table summarizes our DSC results. The phases were characterized by means of polarized light microscopy.

In the case of hexa-acrylate **1**, Col is a Col_{rd} phase according to polarized light microscopy. Its texture, observed at 65°C on cooling from the N_D phase, is similar to that of 2,3,6,7,10,11-hexaoctanoyloxytriphenylene in the Col_{rd} $P2_1/a$ phase [20]. In the case of **2**, no clear texture was observed below 118°C, so we cannot draw any conclusion regarding the nature of the Col phase.

Both **1** and **2** display a typical schlieren texture and a high fluidity characteristic of the N_D phase above 69 and 118°C, respectively. Compound **2** polymerizes above 150°C before reaching the isotropic phase.

The presence of 6 acrylate groups significantly shifts the N_D phase boundaries of **1** and **2** towards lower temperatures in comparison with their non-reactive counterparts, hexa-alkoxybenzoates of triphenylene [20]. The polar acrylate end groups interfere with the molecular arrangement in the crystalline, columnar and N_D phases, resulting in the observed decreases in transition temperatures.

In the case of **1**, the Col to N_D phase transition is observed at a lower temperature than that of **2**. The longer side groups in **1** destabilize the columnar arrangement as they weaken the core–core and intercolumnar interactions by steric hindrance and a higher mobility of the acrylate groups relative to the central core. The increasing perturbation of the columnar stacking due to longer chain lengths has already been observed with hexa-alkoxy benzoates of triphenylene when 10 or more carbon atoms are present in the alkoxy chain [20]. Longer spacers in discotic side group polymers were also found to destabilize columnar phases [21].

Thermal polymerization of samples before the alignment is reached can be a problem when the phase to freeze-in occurs at too high temperatures, typically above 130°C with discotic acrylates. The transition temperature to the N_D phase of **2**, is still low enough to allow alignment in the N_D phase without thermal polymerization.

3.2. *Photo-initiated polymerization of compounds **1** and **2***

Monitoring of the photoinitiated polymerization of **1** and **2** by DSC, results in isothermal DSC curves that indicate the heat flow (exothermic reaction) as a function of the exposure time of the samples to UV light. The heat flow is a measure of the reaction rate.

By (partially) integrating these curves, knowing that the heat of polymerization of acrylate groups is $78\,\mathrm{kJ\,mol^{-1}}$ [22], one can calculate the percentage of reacted acrylate groups at any time during the reaction. Figure 2 gives the heat flow during the curing of **1** and **2** at 120°C as a function of the calculated % of reacted acrylate groups (also called % conversion).

Upon illumination with UV light both compounds readily polymerize in the N_D phase. The reaction immediately autoaccelerates, which points to a low termination rate at the onset of polymerization. Autoacceleration is a feature common to most acrylates [23]. Below 10% conversion, the reaction rate of **2** is higher.

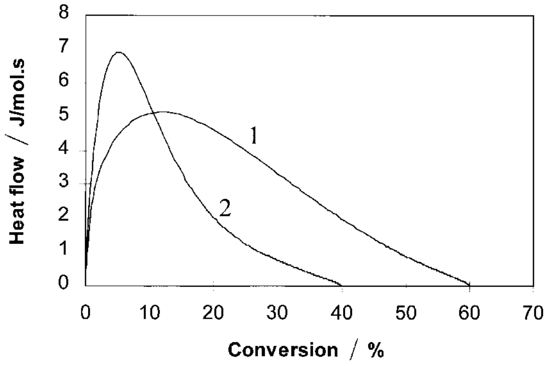


Figure 2. Heat flow as a function of the monomer conversion during the photoinitiated polymerization of **1** and **2** at 120°C, as observed by DSC.

Table. Transition temperatures (°C) and enthalpies (in brackets, $\mathrm{J\,g^{-1}}$) of **1** and **2**. Cr stands for crystal, X for crystal or discotic columnar (undetermined), Col for discotic columnar, N_D for discotic nematic, and I for isotropic. The values between square brackets are the transition temperatures during the cooling run.

Compound	Cr		X		Col		N_D		I
1	•	55 [-] (22.95)	•	61 [32] (20.25)	•	69 [54] (0.95)	•	154 [153] (0.14)	•
2			•	99 [-] (0.22)	•	118 [59] (11.34)	•	> 150 (polym)	

The shorter C_6-spacers in **2** induce a lower mobility of the reactive groups and a tighter network both of which decrease the termination rate.

Above 6% conversion in the case of **2** and 13% conversion in the case of **1**, the increasing viscosity and crosslink density suppress the monomer mobility, causing the rate of polymerization to decrease. In the case of **1** the reaction continues at a relatively high rate after the maximum rate is passed. The long C_{11}-spacers of **1** decouple the mobility of the reactive groups from that of the central cores and also lead to a less tight network.

When the heat flow reaches zero, the heat the reaction generates is below the detection limit of the DSC. The polymerization reaction is practically over. As a result of the polymerization kinetics the average final degree of conversion in the N_D phase is approximately 60% in the case of **1** and 40% in the case of **2** (figure 2). In the case of **2**, we checked the final conversion by FTIR (Fourier transform infra-red) using the vinyl absorption band at 811 cm^{-1}. Crosslinked films of **2** showed a 50% decrease of the vinyl absorption band compared with the monomer. This indicates a final conversion of about 50%, slightly higher than that found by DSC. When this photopolymerized sample was annealed for 20 min at 200°C under UV radiation, the vinyl band absorption decreased to about 15% of the initial value, pointing to a conversion of 85%.

All the samples which were crosslinked in the N_D phase, showed no transition according to DSC and remained transparent up to at least 200°C. Thus, the networks formed were thermally stable.

3.3. *Birefringence of oriented thin films prepared from compounds **1** and **2** before and after polymerization*

Now that the polymerization behaviour is known, we can determine to what extent the optical properties of aligned monomer films are preserved during the crosslinking process. Figure 3 shows the refractive indices of oriented thin films of monomers **1** and **2** prior to polymerization (with photoinitiator and inhibitor).

The higher refractive indices of **2** are attributed to the closer packing of the aromatic discotic groups as a result of the shorter spacers. Short lateral chains also allow a better ordering and therefore **2** has a higher birefringence than **1**. This result recalls that of the influence of side group lengths on the charge transport properties (very sensitive to ordering) of columnar triphenylene ethers for which shorter spacers led to a higher charge carrier mobility than longer spacers [10, 24].

Oriented thin films of **1** and **2** were crosslinked at various temperatures. Upon curing, the average refractive indices of both **1** and **2** increased by 2 to 3% due to polymerization shrinkage. Figure 4 shows the birefringence of **1** and **2** as a function of temperature, and the birefringence at 25°C of **poly(1)** and **poly(2)** (polymer networks formed by crosslinking of **1** and **2**, respectively) as a function of the curing temperature. **Poly(2)** displays the highest birefringence value of all the discotic networks we have made so far. Only a small decrease in birefringence was observed between **2** and **poly(2)**. The spacer length again appears to be a critical parameter as a much larger decrease in birefringence was found between **1** and **poly(1)**. The columnar phase displayed by monomer **2** occurs at temperatures very close to the curing temperatures. This proximity seems to favour a higher ordering in the resulting network. It is probable that, as the molecular mass increases during the beginning of polymerization, a transition to a columnar order occurs, limited by the boundaries imposed by the newly created network. Such a local columnar ordering would also justify the sharper decrease in the crosslinking rate observed in the case of **2**, in that it would restrict

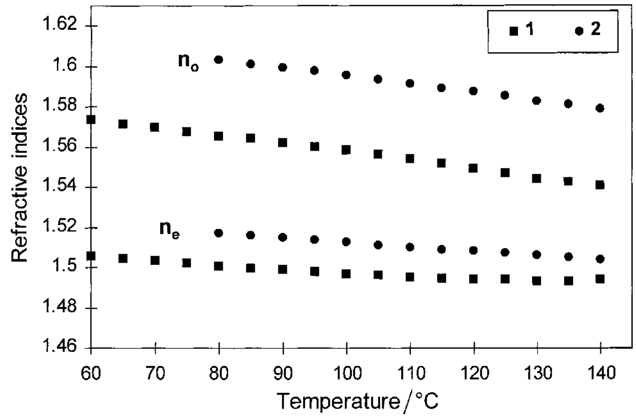


Figure 3. Ordinary (n_o) and extraordinary (n_e) refractive indices of **1** and **2** as a function of temperature.

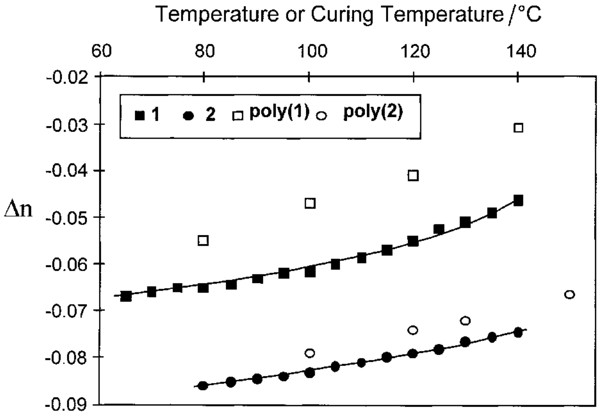


Figure 4. Birefringence of **1** and **2** as a function of temperature (closed symbols), and birefringence at 25°C of **poly(1)** and **poly(2)** as a function of the curing temperature (open symbols).

the growing chain conformations to the one dimensional, intercolumnar channels. X-ray experiments performed on previously studied crosslinked discotic diacrylates revealed the presence of such a local columnar ordering that we attributed to a pretransitional order in the monomer [8]. In the present case, a pretransitional arrangement cannot justify the relatively high birefringence of **poly(2)** formed at 150°C, more than 30°C above the transition between columnar and N_D phase.

As the polymerization temperature increases, the anisotropy of the networks formed decreases progressively, and varying the crosslinking temperature allowed us to obtain birefringence values between − 0.03 and − 0.08 with **poly(1)** and **poly(2)** (figure 4).

Using the approximation method of Haller *et al.* [25] described in an earlier work [14], we evaluated the order parameter of **1** as a function of temperature using the refractive indices (figure 5). The extrapolated value of the polarizability ratio—mean polarizability divided by the polarizability anisotropy [14]—is 4.77 in absolute value. This ratio is slightly lower than the ratios we obtained for mono- and di-acrylate derivatives of compound **3** (scheme 1) for which we obtained 4.80 and 4.90 in absolute values, respectively [14]. If we assume that the acrylate end groups are free to adopt random configurations, additional acrylate groups on a monomer should result in a higher polarizability ratio as they increase the mean polarizability without changing the polarizability anisotropy. So as **1** bears six acrylate groups, its ratio should be higher than that found for the previously studied mono- and di-acrylates. This is not the case, so another effect must take place. A molecular modelling study of non-reactive discotics [26] suggested that triphenylene benzoates with and without methyl groups on the lateral phenyl rings adopt dissimilar molecular conformations. In particular, the difference in angles between the triphenylene core and the peripheral phenyl ring (or ester linkage) is probably the source of a higher polarizability anisotropy in the case of **1** and would justify the smaller ratio found.

The order parameter of **1** increases from 0.5 at 140°C to 0.7 at 60°C (figure 5). Because of the frozen nature of **poly(1)**, the extrapolation method of Haller cannot be applied. Using the same polarizability ratio as for **1**, we estimated the order parameter for **poly(1)** (figure 5). Using the same ratio as for the monomer is not very accurate—the mean polarizability is expected to decrease due to the disappearance of the vinyl bonds during polymerization—but it should nonetheless provide an indicative value. The order parameter of **poly(1)**, between 0.6 and 0.3, is 15 to 20% lower than before crosslinking. Low curing temperatures result in networks with a higher order.

Poly(2) most likely has much higher order parameter values than **poly(1)** but we could not evaluate them as we do not know the clearing temperature of **2**.

3.4. *Mixtures of compounds 1 or 2 with the non-reactive discotic 3*

Non-reactive discotics are much easier to synthesize and purify than their reactive counterparts. To avoid having to prepare large quantities of reactive discotics like **1** and **2**, we examined whether stable discotic polymeric networks could be obtained by curing the mixture of a discotic crosslinker with a non-reactive discotic.

We mixed hexa-(2-methyl-4-decyloxybenzoyloxy)-triphenylene **3** (scheme 1) with hexa-acrylate **1** to check their miscibility and to determine what percentage of **1** is necessary to freeze-in the mixture by photopolymerization. Figure 6 gives the phase diagram of **3** and **1** as observed by DSC and optical microscopy.

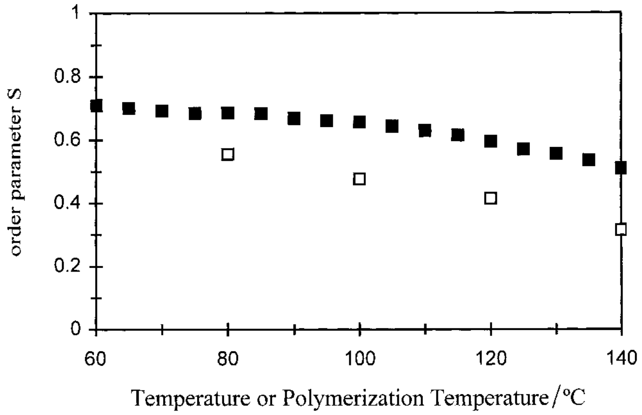


Figure 5. Order parameter of **1** as a function of temperature (closed symbols), and order parameter of **poly(1)** at 25°C as a function of the polymerization temperature (open symbols).

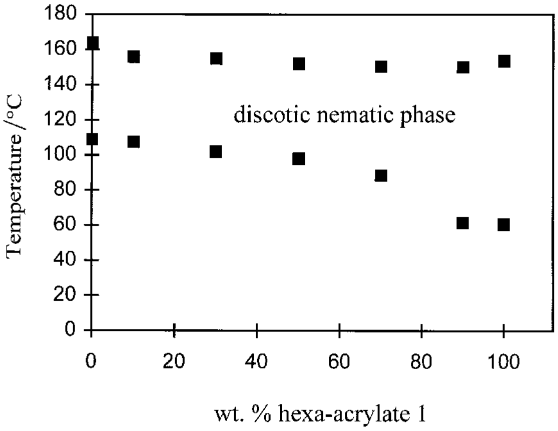


Figure 6. Phase diagram of binary mixtures of **1** and **3**.

As expected, **1** and **3** are miscible in all proportions due to their very similar chemical structures.

We polymerized mixtures with 10, 30, and 70 wt % of **1** in **3**. The final conversions, percentage of reacted acrylates, are 95, 70, and 70%, respectively. The polymerization yields are higher than when pure **1** is used. The samples turned turbid during polymerization, which points to a phase separation. In addition, a DSC temperature scan of the crosslinked materials displayed the melting peak of pure **3** at 109°C. Using the melting enthalpy of pure **3**, integration of this peak showed that 90, 60 and 10%, respectively, of compound **3** was not fixed by the network. These results showed that phase separation indeed occurs leading to a polymer-rich phase and to a phase mainly consisting of non-reactive discotic compound **3**.

3.5. *Synthesis and properties of triacrylate* **5**

As an alternative to crosslink mixtures of reactive discotic compounds and non-reactive compounds, we chose to look at simpler molecules than the hexa-acrylates **1** or **2**. Takenaka *et al.* [16] described a family of non-reactive 1,3,5-tri-substituted benzenes exhibiting a monotropic discotic nematic phase. Of the compounds reported, 4-decyloxyphenyl 1,3,5-benzenetricarboxylate **4** (scheme 2) melts at 57.5°C and displays the monotropic $\mathrm{N}_{(\mathrm{D})}$ phase up to 25.5°C [16]. Shorter side groups lead to lower nematic–isotropic transition temperatures. For that reason, we chose to synthesize a triacrylate **5**, with a structure similar to that of **4** and with long ‘C_{11}’ spacers (scheme 2). The advantage of discotic LCs with three acrylate groups is that they usually show high polymerization yields [14]. Moreover, substituted phenyl 1,3,5-benzenetricarboxylates are relatively easy to synthesize, the central core precursor being commercially available.

The phase transitions of triacrylate **5** measured by DSC are given in figure 7. Compound **5** melted at 63°C during the first heating run. A monotropic nematic phase with a typical schlieren texture appeared on cooling at − 1°C. On reheating, the sample became isotropic at 8°C. Obviously, the addition of acrylate groups causes the nematic phase to appear at lower temperatures compared with compound **4**. Another difference with non-reactive compound **4** is that the presence of the reactive groups hinders the crystallization process and no crystallization occurs on reheating above the nematic phase.

Whether monomer **5** adopts a discotic shape in which side groups form an angle of about 120° with each other, rather than a rod-like shape (1 single side group and 2 paired groups opposite one another along one axis) in the nematic phase, has not been verified. The optical properties (birefringence sign, for example) should be affected by the conformation, but they were difficult to measure due to the instability of the monotropic phase and the fact that it occurs below 0°C.

The study of the photoinitiated polymerization of triacrylate **5** below 0°C confirmed the presence of a fluid phase. In figure 8, the kinetics of polymerization of **5** in the isotropic and monotropic (discotic) nematic phase are compared. At − 5°C in the liquid crystalline phase, **5** polymerized readily, as the sharp polymerization isotherm testifies (figure 8). The final degree of conversion obtained in the monotropic fluid phase was 30% according to DSC, which indicates that only one acrylate per molecule reacted on average. At 100°C, in the isotropic phase, a final conversion of 75% was obtained, very close to the 78% yield obtained in the N_D phase at the same temperature for a discotic triacrylate reported previously [14].

Triacrylate **5** in the monotropic phase was not studied further in the pure form, because of the limits imposed by working at low temperatures (below 0°C), but we used it in mixtures with non-reactive triphenylene benzoate **3**.

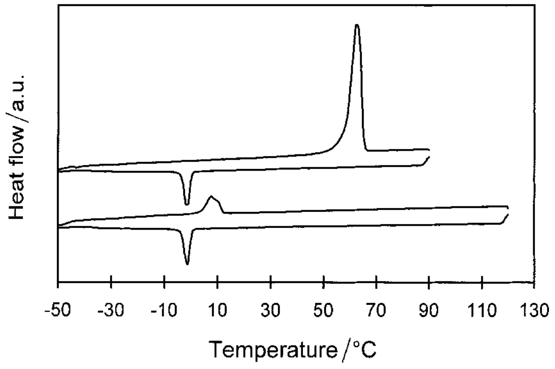


Figure 7. DSC curves of triacrylate **5** (from top to bottom: first heating, first cooling, second heating, second cooling runs).

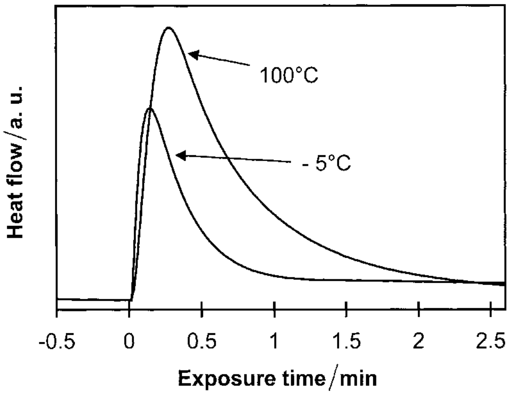


Figure 8. Isothermal DSC curves of the photopolymerization of triacrylate **5** at − 5 and 100°C.

3.6. *Mixtures of compound **5** with non-reactive discotic **3***

Figure 9 shows part of the binary phase diagram of **5** in **3**. These two compounds are only miscible at small percentages of triacrylate **5**. We polymerized 5 and 10 wt % mixtures of **5** in **3**. Curing of the 10% mixture between 90 and 120°C led to final degrees of conversion of 93%, whereas an average of almost 100% conversion was reached for the 5% mixture.

To determine the proportion of **3** fixed by **net-5**, we recorded DSC thermograms of the polymerized mixtures and measured the melting peak enthalpy of **3** at 109°C. The DSC scans show that 82% of **3** was crystallized in the 5% mixture, and 75% in the 10% mixture. This means that only about 14% of **3** was incorporated in the polymeric phase during polymerization and phase separation.

The results obtained with triacrylate **3** are similar to those obtained with mixtures containing hexa-acrylates **1** or **2**. The crosslinker was not able to freeze-in significant proportions of a non-reactive discotic. Thus, this is not a method to make thermally stable anisotropic materials. This phase separation during polymerization might be useful when making discotic polymer dispersed liquid crystals or discotic liquid crystalline gels.

4. Conclusion

The liquid crystalline properties of discotics **1** and **2** with a triphenylene hexabenzoate central core and six acrylate end groups make those compounds suitable for photoinitiated polymerization in the N_D phase.

Photocrosslinking of hexa-acrylates **1** and **2** macroscopically oriented in the N_D phase produces thermally stable and anisotropic thin films. Shorter monomer spacers and lower polymerization temperatures lead to polymer networks with a higher order. The curing temperature can be used to vary the birefringence of the resulting polymer films between − 0.03 and − 0.08.

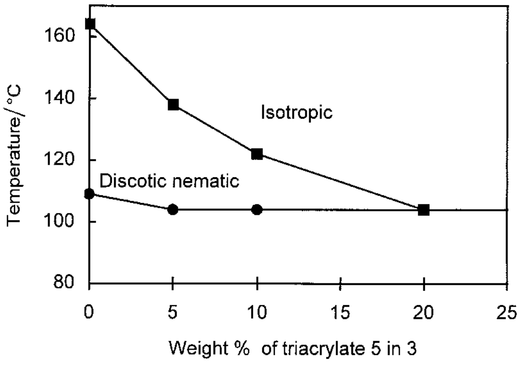


Figure 9. Binary phase diagram of **5** in **3** (only the left part of the diagram is shown).

Using a phenyl 1,3,5-benzenetricarboxylate ring instead of triphenylene hexabenzoate as central core greatly simplifies the synthetic and purification procedures of reactive discotics. The triacrylate of the phenyl 1,3,5-benzenetricarboxylate derivative we synthesized displays a monotropic nematic phase similar to its non-reactive counterpart. However, discotics with a larger central core display LC phases that remain stable over much broader and more convenient temperature ranges and are therefore the first choice in preparing anisotropic materials.

Polymerization of mixtures of a discotic crosslinker with non-reactive discotic compounds results in high degrees of conversion. Very little of the non-reactive discotic compound is incorporated into the final polymer network because of phase separation, resulting in polymer rich regions and polymer free regions.

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