

# Synthesis and characterization of reactive liquid crystals and polymers based on terphenyl derivatives

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## Abstract

A series of liquid crystalline methacrylates based on terphenyl derivatives bearing a donor– $\pi$ -acceptor structure has been synthesized. The mesomorphic, optical absorption, photoluminescent and non-linear optical properties of the monomers have been investigated. Polymerization of these monomers was first carried out in solution but the dicyanovinyl group seems to inhibit the reaction despite the fact that the DSC curves of the monomer provide evidence for the occurrence of thermal polymerization. An IR study of this thermal polymerization confirms that only methacrylate groups are involved in the polymerization process. The mesomorphic and thermal properties of the resulting side-chain polymers have also been investigated. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords:* Liquid crystal polymers; Luminescence; Terphenyls

## 1. Introduction

The development of new devices based on the in-situ photopolymerization of liquid crystals (LCs) containing reactive groups has stimulated much interest in the synthesis of new reactive LCs [1–7]. This has been due to the fact that anisotropic polymeric films processed from reactive LCs, in which different types of chromophore can be incorporated within the side chain, have proved to be of interest for optical applications [8,9]. For this reason, we have recently undertaken the synthesis of a series of reactive LCs based on terphenyl derivatives. The terphenyl core has a calamitic structure that is compatible with mesomorphic ordering and is well known to give LCs that have high birefringence [10,11]. Fig. 1 shows the terphenyl monomers synthesized and it can be seen that these have a donor– $\pi$ -acceptor structure. As the donor unit a hexyloxy chain with a terminal methacrylate group was selected and three different acceptors (cyano, nitro and 2,2'-dicyanovinyl groups) were incorporated. Cyanoterphenyl derivatives have been used in the preparation of a wide range of nematic mixtures and, in general, these have high thermal stability as well as chemical and photochemical stability [12]. On the other hand, it has been reported that cyanoterphenyls bearing alkoxy substituents show a high photoluminescence efficiency

[13] ( $\eta = 0.60$  in  $\text{CH}_2\text{Cl}_2$ ), whereas nitro terphenyl derivatives have moderate values of the first-order non-linear hyperpolarizabilities ( $\beta$ ) [14]. In the search of reactive LCs for optical applications the NLO and luminescence properties of the synthesized monomers have been studied.

Furthermore, as an initial step towards the preparation of polymeric films, the polymerization of these monomers has been undertaken giving the side-chain polymers shown in Fig. 1. The mesomorphic and thermal properties of these polymers have also been investigated.

## 2. Results and discussion

### 2.1. Terphenyl reactive monomers

The terphenyl monomers were synthesized according to the synthetic pathways shown in Figs. 2 and 3. The terphenyl core was synthesized by means of a palladium-catalyzed boronic acid coupling reaction [15]. Monomer CNT was synthesized as described in the literature [10] by coupling 4-cyanophenylboronic acid with 4-bromo-4'-hydroxybiphenyl. However, this method only gave the desired product in low yields in the cases of monomers NiT and DCNT and it was found that these systems require the preparation of the boronic acid derivative of the biphenyl unit, which was alkylated with 6-chlorohexanol prior to coupling. The coupling reaction also required protection of the hydroxyl group. All of the described monomers were carefully

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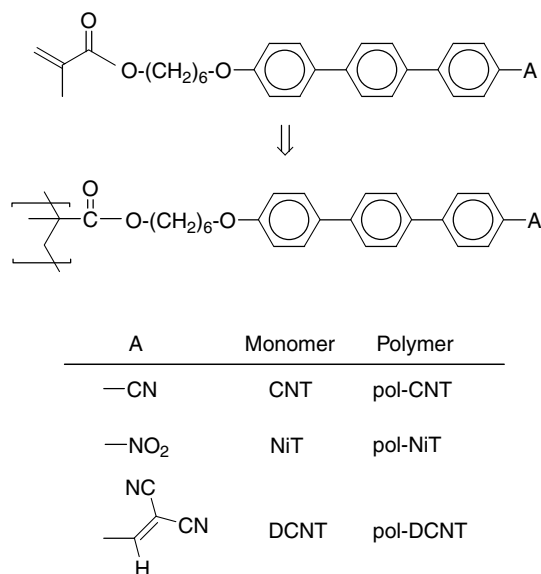


Fig. 1. Terphenyl methacrylate monomers and derived side-chain polymers.

purified by column chromatography and successive recrystallizations before polymerization was undertaken.

The mesomorphic properties of the terphenyl monomers were studied by polarizing optical microscopy and DSC. The results are collected in Table 1. The thermal data correspond to the DSC first heating scan since polymerization was detected in the molten state. This process is remarkable in monomers CNT and DCNT in that a polymerization exotherm is clearly detected, as can be seen in Fig. 4. The polymerization conversion [16] (the reference value for polymerization enthalpy of a methacrylate group has been

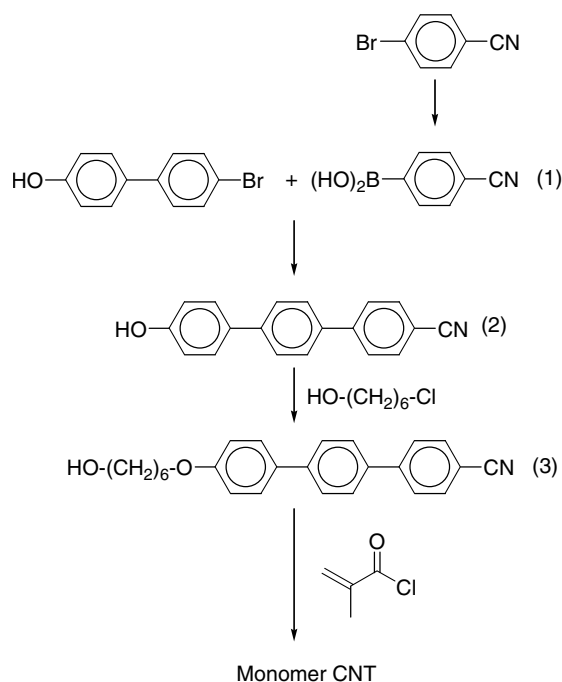


Fig. 2. Synthetic pathway of the monomer CNT.

taken as 57 kJ/mol) measured from these exotherms is about 80% in the case of CNT, which polymerizes in the smectic A phase, and about 47% in the case of DCNT. However, in the latter case we must take into account that the exotherm overlaps with the melting endotherm since the monomer DCNT polymerizes just after melting. In order to establish the mesophase of this monomer, samples of DCNT containing small amounts (<0.5% in weight) of a thermal inhibitor (2,6-di-*tert*-butyl-4-methylphenol) were prepared. The study of this samples, in which thermal polymerization is inhibited, confirmed the nematic nature of the mesophase and revealed that isotropization occurs at around 165°C. The DSC curve of this monomer shows a small exotherm at around 80°C that did not appear when the sample was first heated up to 100°C and then cooled to room temperature. In the case of monomer NiT, the polymerization exotherm was not observed in the DSC study. However, polymerization was detected at around the isotropization temperature when samples of this compound were studied using a polarizing optical microscope equipped with a heating furnace.

The optical absorption (Fig. 5) and photoluminescence (Fig. 6) spectra of the monomers were measured in CH<sub>2</sub>Cl<sub>2</sub>. Absorption is influenced by the electron-withdrawing nature of the terminal substituent. In fact, the absorption spectrum is red-shifted as the electron-withdrawing character of the substituent increases (CNT < NiT < DCNT). The selection of a suitable initiator for the photopolymerization of the formulations based on these monomers should strongly depend on the absorption spectrum. Thus, monomer CNT shows no absorption above 375 nm and, consequently, commercial UV photoinitiators can be used. For NiT and DCNT visible photoinitiators would be recommended. Excitation with light in the absorption band of the monomers gave rise to an emission band at about 410 nm in the case of CNT and at about 535 nm in the case of DCNT. No emission was observed for the NiT compound, probably due to the presence of the nitro group, which is generally a fluorescence quencher [17]. The relative emission intensities of CNT and DCNT compounds were measured using the method described below (experimental techniques). It can be seen that the emission intensity is much higher in the cyano derivative than in the dicyanovinyl compound (see Fig. 6). In both cases the luminescence emission remains stable under light excitation in the absorption band.

The  $\mu\beta$  values obtained by EFISH of the terphenyl chromophores CNT, NiT and DCNT measured in CH<sub>2</sub>Cl<sub>2</sub> are 45, 95 and 170 (in units of 10<sup>-48</sup> esu), respectively. Here  $\mu\beta$  is defined as:  $\mu\beta = \mu_x\beta_x + \mu_y\beta_y + \mu_z\beta_z$  with  $\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$ ;  $\beta_y = \beta_{yxx} + \beta_{yyy} + \beta_{yzz}$ ;  $\beta_z = \beta_{zxx} + \beta_{zyy} + \beta_{zzz}$ , where  $\mu$  is the ground state dipole moment and  $\beta$  is the first-order hyperpolarizability tensor. Increasing  $\mu\beta$  values were obtained on going from the cyano-substituted terphenyl chromophore to the nitro and dicyanovinyl ones. This trend has been attributed to the increasing electron-withdrawing character of the acceptor

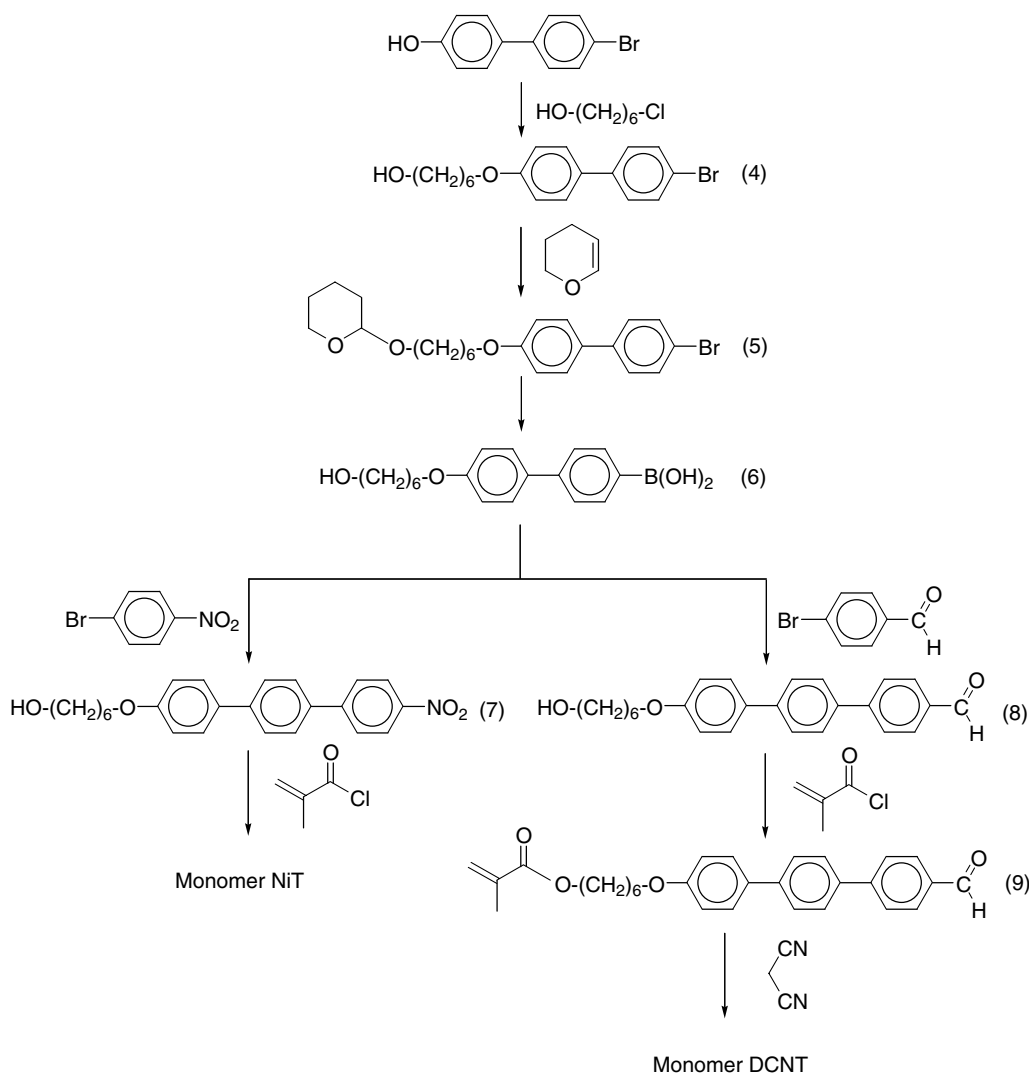


Fig. 3. Synthetic pathway of the monomers DCNT and NiT.

substituents. Similar results for other homologous series of chromophores with these acceptor units have been reported by other authors [18].

## 2.2. Terphenyl side chain polymers

The polymerization of the terphenyl monomers was first carried out by a conventional solution polymerization method using toluene as the solvent and 1% AIBN as the thermal initiator to yield the corresponding side-chain polymers. Polymerization of monomer NiT required extra AIBN (two extra 1% portions of AIBN were added 24 and 48 h after initiating the polymerization) probably due to the presence of the nitro group, which has been reported to retard free radical polymerizations [19]. In the case of monomer DCNT, polymerization did not proceed in reasonable yields when the polymerization was carried out in solution using toluene or DMF as solvent and AIBN or *tert*-butyl peroxide as a thermal initiator. Similar results have been

Table 1  
DSC and polarizing optical microscopy results of terphenyl monomers (data corresponding to the DSC first heating scan, 10°C/min)

Monomer	Phase transition (°C) <sup>a</sup>	$\Delta H$ (kJ/mol)
CNT	C 124 S <sub>A</sub>	6.5
	Polymerization at $T > 140^\circ\text{C}$	-45.1 <sup>b</sup>
NiT	C 72 C'	21.6
	C' 151 N	11.1
	N 180 I	0.4
DCNT	C <sup>c</sup> 138 N <sup>d</sup>	<sup>d</sup>
	Polymerization at $T > 140^\circ\text{C}$	Aprox. -27 <sup>b</sup>

<sup>a</sup> Data corresponding to the onset of the peak.

<sup>b</sup> Data corresponding to the polymerization exotherm.

<sup>c</sup> Before melting a small exotherm is observed around 80°C, which disappears when the sample is heated up to 100°C prior to study.

<sup>d</sup> Melting of the monomer and polymerization overlapped. The nematic nature of the monomeric mesophase was confirmed on samples containing a small amount of a thermal inhibitor (2,6-di-*tert*-butyl-4-methylphenol). Isotropization was detected at around 165°C for these samples (see text).

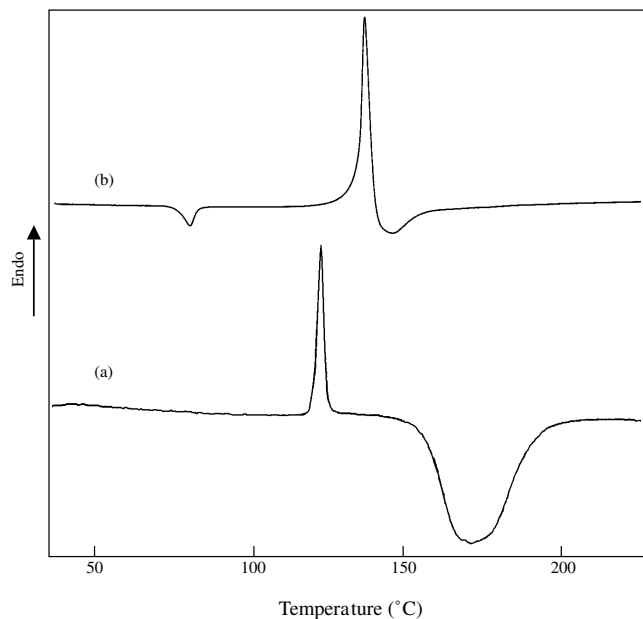


Fig. 4. DSC traces of the monomers: (a) CNT and (b) DCNT. Thermal polymerization is observed after melting.

reported for NLO chromophores containing a tricyanovinyl acceptor [20]. However, the inhibition of the free radical polymerization in solution appears to be in contrast with the spontaneous thermal polymerization detected by DSC at temperatures just above 140°C. On the other hand, the dicyanovinyl group might also be involved in this thermal polymerization to yield a crosslinked or a decomposed material [21] instead of the expected side-chain polymethacrylate. In order to evaluate which groups are really implicated in the polymerization reaction, the IR spectra were recorded of samples (KBr pellets) taken at different temperatures from room temperature (r.t.) to 200°C. Fig. 7 shows the IR spectra taken at r.t., 140°C (maximum of the melting transition of the monomer as detected by DSC) and 200°C. The band at 1630 cm<sup>-1</sup> corresponding to the C=C st of the methacrylate (indicated with an arrow in Fig. 7) disappeared at temperatures  $\geq 140^\circ\text{C}$  and a shift from 1710 to 1724 cm<sup>-1</sup> of the ester C=O st band is observed.

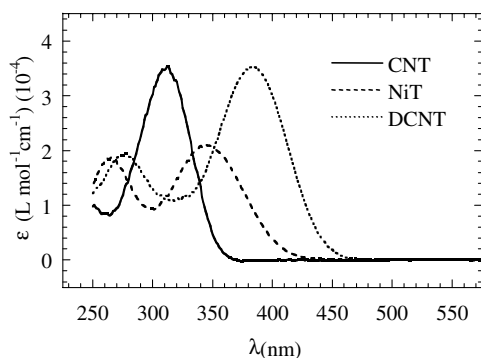


Fig. 5. Absorption spectra (extinction coefficient  $\epsilon$  vs  $\lambda$ ) of the terphenyl monomers in CH<sub>2</sub>Cl<sub>2</sub>.

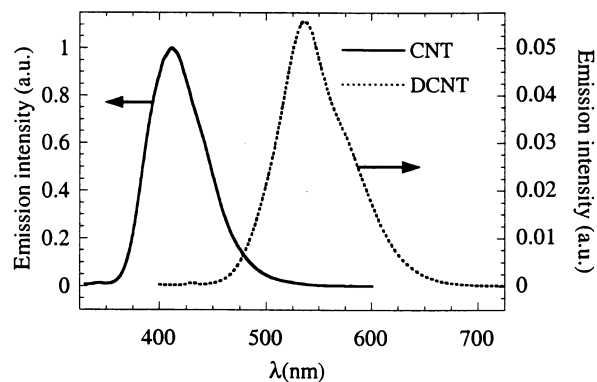


Fig. 6. Emission spectra of the terphenyl monomers CNT and DCNT in CH<sub>2</sub>Cl<sub>2</sub> excited at the lowest energy absorption maximum (CNT, left hand scale; DCNT, right hand scale).

The results are in accordance with the expected reactivity of the methacrylate groups. On the other hand, the band corresponding to the CN st detected at 2224 cm<sup>-1</sup> remained unchanged, as did the band corresponding to the C=C st of the dicyanovinyl group, which was detected as a shoulder around 1603 cm<sup>-1</sup>. If the sample was maintained at 200°C for 1 h, a very similar spectrum was obtained to that taken at 140°C. This fact confirms that only the methacrylate groups were involved in the spontaneous thermal polymerization of the monomer and there was no reactivity of the dicyanovinyl groups at high temperatures. All the terphenyl-derived polymers exhibited poor solubility in conventional organic

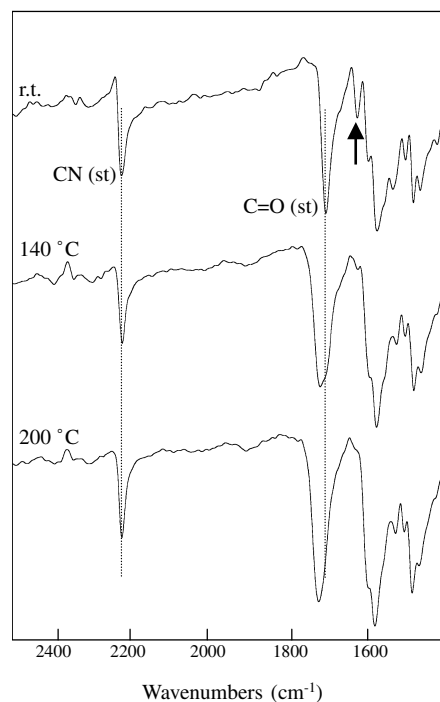


Fig. 7. IR spectra of a sample of monomer DCNT (KBr pellet) taken at different temperatures (see text). The arrow corresponds to the C=C st methacrylate band.

Table 2

Thermal and mesomorphic properties of the terphenyl polymers (TGA: Temperature of the onset of the decomposition weight loss curve; DTGA: Maximum of the derivative TGA; Phase transitions corresponding to the DSC first heating scan (10°C/min);  $\Delta H$ : mru, mol of repeat unit)

Polymer	TGA (°C)	DTGA (°C)	Phase transitions (°C)	$\Delta H$ (kJ/mru)
POL-CNT	290	420	C 169 S <sub>A</sub>	3.7
			S <sub>A</sub> 289 I	1.7
POL-NiT	290	350	C 206 S <sub>C</sub>	8.5
			S <sub>C</sub> 290 I <sup>a</sup>	1.5 <sup>a</sup>
POL-DCNT	320	420	C 112 N > 290 <sup>b</sup> I	9.2

<sup>a</sup> Overlapped with decomposition.

<sup>b</sup> No isotropization was detected by DSC. A gradual isotropization was detected by optical microscopy above 290°C, overlapped with decomposition.

solvents, a situation that hinders their characterization and processing into films.

The thermal and mesomorphic polymer properties of the polymers were studied by DSC, polarizing optical microscopy and thermogravimetric analysis (TGA). The results are gathered in Table 2 and it can be seen that the polymers all exhibit good thermal stability. Thus, the thermal decomposition detected by thermogravimetry begins at temperatures around 300°C. The polarizing optical microscopy and DSC measurements confirm the existence of mesomorphism, with the nature of the mesophase depending on the substituent. POL-CNT exhibited large areas of homeotropic and oily streak textures together with a fan-shaped texture corresponding to a smectic A phase. POL-DCNT exhibited *schlieren*, threaded textures that became homeotropic or marbled when they were mechanically stressed. These textures are consistent with a nematic phase. In the case of POL-NiT, a non well-defined *schlieren* texture is observed which becomes pseudohomeotropic when is mechanically stressed. In order to confirm the mesophase nature of this polymer, X-ray diffraction measurements were carried out at 200 (previously heated up to 225°C), 225 and 250°C. The X-ray patterns show a set of three equally-spaced maxima at small angles, which can be assigned to a disordered smectic structure (SmA or SmC) having a layer thickness of 33 Å throughout the temperature range studied. Besides, a large angle ring at a distance of 4.6 Å is also observed, characteristic of the liquid-like arrangement within the layers. The length of the mesogenic group (including the methacrylate group) for a fully-extended conformation measured using Dreiding stereo models is  $30 \pm 1$  Å. Consequently, these results imply that the smectic phase has a bilayer structure. If we suppose an interdigitation of the terphenyl groups, which leads to maximum interactions of the mesogenic cores, the observed layer thickness can be explained by

considering a tilted smectic C phase with a tilt angle of about 40°.

Isotropization of these polymers took place at high temperatures and was accompanied by partial thermal decomposition of the sample. For this reason, phase transition temperatures are based on the first DSC heating scan only and are collected in Table 2. In cases where the thermal decomposition of the sample was avoided, a crystallization exotherm was observed on cooling. The length of the terphenyl mesogens leads to an increase in the interactions between the mesogenic units and consequently to an increase in both the thermal stability and the thermal transition temperatures of the polymers, as well as an increase in the tendency to crystallize on cooling [22].

### 3. Conclusions

A series of terphenyl reactive liquid crystalline monomers have been synthesized having a donor- $\pi$ -acceptor structure. The photoluminescence spectra of the monomers put in evidence that CNT and DCNT exhibit emission bands at about 410 and 535 nm, respectively, and that the emission intensity is much higher for monomer CNT. On the other hand, NiT did not show photoluminescence. The  $\mu\beta$  values (measured by EFISH) depend on the electron-withdrawing character of the acceptor and follows the sequence: CNT < NiT < DCNT.

The free radical polymerization of these monomers was first studied in solution. However, DCNT did not polymerize in solution despite of the thermal polymerization detected by DSC and optical microscopy. The IR study at different temperatures confirms the thermal polymerization, which only affects the methacrylate groups. The terphenyl derived side-chain polymers have a good thermal stability and display a mesophase which nature depends on the acceptor substituent. These polymers crystallize by cooling the mesomorphic melt and show a poor solubility which hinders their characterization and processing. Attempts to obtain anisotropic films by in-situ photopolymerization of mesomorphic samples containing different percentages of the terphenyl monomers and a crosslinking agent are currently in progress. Crosslinking should improve the alignment stability of the chromophores and reduce the optical scattering associated to aggregation processes. The first results on the study of polarized photoluminescence of photopolymerized films containing CNT have been recently published elsewhere [23].

### 4. Experimental

#### 4.1. Monomers

The terphenyl monomers were synthesized according to the synthetic pathways shown in Figs. 2 and 3.

*Monomer CNT*: The intermediate 4-hydroxy-4'-cyano-

terphenyl (2) was synthesized according to the procedures reported in the literature [13] by cross coupling of 4-cyano-benzeneboronic acid (1) [16] and 4-bromo-4'-hydroxybiphenyl (purchased from Aldrich). Recrystallization from absolute ethanol provided a colorless solid in 55% yield.  $^1\text{H NMR}$  (dimethylsulfoxide- $d_6$ )  $\delta$  in ppm: 6.85 (d,  $J = 8.6$  Hz, 2H), 7.56 (d,  $J = 8.6$  Hz, 2H), 7.71 (d,  $J = 8.3$  Hz, 2H), 7.80 (d,  $J = 8.4$  Hz, 2H), 7.91 (s, 4H), 9.60 (s, 1H).

4-(6-Hydroxyhexyloxy)-4''-cyanoterphenyl (3) was synthesized by mixing 20 mmol of (2), 24 mmol of 6-chloro-1-hexanol, 20 mmol of  $\text{K}_2\text{CO}_3$  and 4.01 mmol of KI in 200 ml of DMF. The reaction mixture was refluxed overnight and then cooled and poured into 200 ml of water and stirred for 2 h. The crude product was extracted with ethyl acetate and the organic layers were washed with a saturated aqueous solution of NaCl, water, and dried with anhydrous  $\text{MgSO}_4$ . The solvent was removed by evaporation in vacuo and the residue was recrystallized from absolute ethanol to give a colorless solid in 85% yield.  $^1\text{H NMR}$  (dimethylsulfoxide- $d_6$ )  $\delta$  in ppm: 1.30–1.75 (m, 8H), 3.35 (m, 2H), 4.00 (t,  $J = 6.5$  Hz, 2H), 4.36 (t,  $J = 5.0$  Hz, 1H), 7.03 (d,  $J = 8.8$  Hz, 2H), 7.66 (d,  $J = 8.8$  Hz, 2H), 7.76 (d,  $J = 8.5$  Hz, 2H), 7.83 (d,  $J = 8.5$  Hz, 2H), 7.90 (s, 4H).

Monomer CNT, 4-(6-methacryloyloxyhexyloxy)-4''-cyanoterphenyl, was synthesized by mixing 12 mmol of (3), 24 mmol of triethylamine and 130 mg of 2,6-di-*tert*-butyl-4-methylphenol (as a thermal inhibitor) in 250 ml of anhydrous THF under a nitrogen atmosphere. 18 mmol of methacryloyl chloride were added dropwise and the reaction was heated under reflux overnight. The reaction mixture was cooled and poured into 200 ml of an aqueous solution (10% w/w) of  $\text{NH}_4\text{Cl}$ . The crude product was extracted with  $\text{CH}_2\text{Cl}_2$ . The resulting organic layer was washed with a saturated solution of NaCl, water and dried with anhydrous  $\text{MgSO}_4$ . The solvent was evaporated in vacuo and the resulting solid was purified by column chromatography using hexane/ethyl acetate (7:3) as eluent. Recrystallization from absolute ethanol yielded a colorless solid in 70% yield.  $^1\text{H NMR}$  (chloroform- $d$ )  $\delta$  in ppm: 1.45–1.50 (m, 4H), 1.68–1.73 (m, 2H), 1.80 (m, 2H), 1.93 (s, 3H), 4.00 (t,  $J = 6.5$  Hz, 2H), 4.15 (t,  $J = 6.6$  Hz, 2H), 5.30 (m, 1H), 6.08 (m, 1H), 6.97 (d,  $J = 8.8$  Hz, 2H), 7.55 (d,  $J = 8.6$  Hz, 2H), 7.64 (m, 4H), 7.70 (s, 4H). IR (KBr pellet,  $\text{cm}^{-1}$ ): 2227 (CN, st), 1718 (C=O, st), 1635 (C=C methacrylate, st), 1294, 1257, 1225, 1170 (C–O, st), 816 (aromatic,  $\delta$  oop). Elemental analysis (calculated): %C: 79.16 (79.24), %H: 6.82 (6.65), %N: 3.02 (3.19).

Monomer NiT: 4-(6-Hydroxyhexyloxy)-4'-bromobiphenyl (4) was prepared as described for (3) and recrystallized from absolute ethanol. Yield: 80%.  $^1\text{H NMR}$  (chloroform- $d$ )  $\delta$  in ppm: 1.22 (s, 1H), 1.39–1.82 (m, 8H), 3.64 (t,  $J = 6.2$  Hz, 2H), 3.97 (t,  $J = 6.5$  Hz, 2H), 6.95 (d,  $J = 8.8$  Hz, 2H), 7.40 (d,  $J = 8.5$  Hz, 2H), 7.46 (d,  $J = 8.8$  Hz, 2H), 7.51 (d,  $J = 8.5$  Hz, 2H).

Before the preparation of the boronic acid derivative of

(4), the hydroxyl group was protected by using 3,4-dihydro-2H-pyran [24] to provide (5). The boronic acid derivative (6) was prepared according to the literature [16]. Yield 45%.  $^1\text{H NMR}$  (dimethylsulfoxide- $d_6$ )  $\delta$  in ppm: 1.33–1.67 (m, 8H), 3.35 (m, 2H), 3.95 (t,  $J = 6.2$  Hz, 2H), 4.31 (t,  $J = 5.0$  Hz, 1H), 6.96 (d,  $J = 8.5$  Hz, 2H), 7.54 (dd, 4H), 7.79 (d,  $J = 7.5$  Hz, 2H), 7.99 (s, 2H).

The synthesis of 4-(6-hydroxyhexyloxy)-4''-nitroterphenyl (7) was carried out according to the procedure described for (2). The compound was recrystallized from absolute ethanol to yield an orange solid. Yield: 50%.  $^1\text{H NMR}$  (chloroform- $d$ )  $\delta$  in ppm: 1.22 (s, 1H), 1.44–1.65 (m, 4H), 1.77–1.84 (m, 2H), 3.70 (m, 2H), 4.00 (t,  $J = 6.4$  Hz, 2H), 6.98 (d,  $J = 8.5$  Hz, 2H), 7.55 (d,  $J = 8.6$  Hz, 2H), 7.67 (s, 4H), 7.76 (d,  $J = 8.5$  Hz, 2H), 8.30 (d,  $J = 8.6$  Hz, 2H).

Monomer NiT was synthesized by reaction of (7) with methacryloyl chloride according to the procedure described for monomer CNT. The monomer was purified by column chromatography using methylene chloride as eluent to give a pale yellow solid, which was washed with hexane and recrystallized from absolute ethanol to give a yellow solid. Yield: 60%.  $^1\text{H NMR}$  (chloroform- $d$ )  $\delta$  in ppm: 1.45–1.52 (m, 4H), 1.69–1.85 (m, 4H), 1.93 (s, 3H), 4.00 (t,  $J = 6.3$  Hz, 2H), 4.15 (t,  $J = 6.4$  Hz, 2H), 5.50 (m, 1H), 6.00 (m, 1H), 6.97 (d,  $J = 8.8$  Hz, 2H), 7.55 (d,  $J = 8.6$  Hz, 2H), 7.70 (s, 4H), 7.75 (d,  $J = 8.8$  Hz, 2H), 8.29 (d,  $J = 8.6$  Hz, 2H). IR (KBr pellet,  $\text{cm}^{-1}$ ): 1716 (C=O, st), 1635 (C=C methacrylate, st), 1522, 1340 ( $\text{NO}_2$ , st), 1292, 1257, 1217, 1169 (C–O, st), 818 (aromatic,  $\delta$  oop). Elemental analysis (calculated): %C: 73.07 (73.18), %H: 6.28 (6.36), %N: 3.18 (3.04).

Monomer DCNT: 4-(6-Hydroxyhexyloxy)-4''-formylterphenyl (8) was prepared by adding, under nitrogen atmosphere, a solution of 0.33 mmol of tetrakis(triphenylphosphine)palladium(0) in 10 ml of DMF to a previously degassed solution of 11 mmol of the boronic derivative (6), 10 mmol of 4-bromobenzaldehyde and 30 mmol of  $\text{K}_3\text{PO}_4$  in 20 ml of DMF at room temperature. The reaction mixture was stirred under a nitrogen atmosphere at 80°C during 24 h. The reaction mixture was then shaken with ethyl acetate and brine, and the insoluble materials were filtered off through celite. The organic layer was washed with water, dried with anhydrous  $\text{MgSO}_4$ , and the solvent removed by evaporation in vacuo. The final product was recrystallized from ethanol. Yield: 40%.  $^1\text{H NMR}$  (dimethylsulfoxide- $d_6$ )  $\delta$  in ppm: 1.35–1.47 (m, 4H), 1.71–1.75 (m, 4H), 3.30 (m, 2H), 3.98 (t,  $J = 6.4$  Hz, 2H), 4.30 (t,  $J = 5.0$  Hz, 1H), 7.01 (d,  $J = 8.8$  Hz, 2H), 7.64 (d,  $J = 8.8$  Hz, 2H), 7.73 (d,  $J = 8.4$  Hz, 2H), 7.82 (d,  $J = 8.6$  Hz, 2H), 7.91–7.99 (m, 4H), 10.06 (s, 1H).

4-(6-Methacryloyloxyhexyloxy)-4''-formylterphenyl (9) was prepared as described for monomer CNT (see above). Yield: 80%.  $^1\text{H NMR}$  (chloroform- $d$ )  $\delta$  in ppm: 1.45–1.55 (m, 4H), 1.69–1.82 (m, 4H), 1.92 (s, 3H), 4.00 (t,  $J = 6.4$  Hz, 2H), 4.15 (t,  $J = 6.6$  Hz, 2H), 5.50 (m, 1H), 6.08

(m, 1H), 6.96 (d,  $J = 8.6$  Hz, 2H), 7.55 (d,  $J = 8.6$ , 2H), 7.66 (m, 4H), 7.78 (d,  $J = 8.2$  Hz, 2H), 7.95 (d,  $J = 8.2$  Hz, 2H), 10.04 (s, 1H).

Monomer DCNT was prepared by mixing 6 mmol of (9), 6 mmol of malonitrile and a few drops of piperidine (2–5) in 40 ml of ethanol. The mixture was refluxed until completion of reaction, as monitored by TLC (about 20 min). The solvent was evaporated in vacuo and the monomer was purified by column chromatography using methylene chloride/hexane (9:1) as eluent and then recrystallized from ethanol to give a yellow solid. Yield 60%.  $^1\text{H}$  NMR (chloroform- $d$ )  $\delta$  in ppm: 1.45–1.58 (m, 4H), 1.67–1.85 (m, 4H), 1.92 (s, 3H), 4.00 (t,  $J = 6.4$  Hz, 2H), 4.15 (t,  $J = 6.6$  Hz, 2H), 5.53 (m, 1H), 6.10 (m, 1H), 6.97 (d,  $J = 8.8$  Hz, 2H), 7.56 (d,  $J = 8.8$  Hz, 2H), 7.68 (dd, 4H), 7.78 (d,  $J = 8.3$  Hz, 2H), 7.98 (d,  $J = 8.3$  Hz, 2H). IR (KBr pellet,  $\text{cm}^{-1}$ ): 2225 (CN, st), 1710 (C=O, st), 1632 (C=C methacrylate, st), 1281, 1249, 1205, 1171 (C–O, st), 816 (aromatic,  $\delta$  oop). Elemental analysis (calculated): %C: 78.40 (78.34), %H: 6.02 (6.16), %N 5.68 (5.71).

#### 4.2. Polymers

POL-CNT and POL-NiT were synthesized by free-radical polymerization in solution. The monomer and AIBN (1% w/w in the case of POL-CNT and 3% w/w for POL-NiT, see text), as a thermal initiator, were dissolved in 15 ml of dry toluene in a Schlenk tube. The solution was degassed, heated to 70°C under an argon atmosphere and stirred for 48 h (POL-CNT) or 72 h (POL-NiT). After cooling to room temperature, the reaction mixture was poured into methanol and the solid was isolated by filtration. The polymer was purified by thoroughly washing with chloroform and ether. Yield: 60–70%. POL-DCNT could not be synthesized by this method and was obtained by spontaneous bulk polymerization at a temperature  $\geq 140^\circ\text{C}$  (melting temperature of the monomer) in the absence of a thermal initiator.

IR (KBr pellet,  $\text{cm}^{-1}$ ). POL-CNT: 2225 (CN, st), 1726 (C=O, st), 1288, 1252, 1176, 1151 (C–O, st), 816 (aromatic,  $\delta$  oop); POL-NiT: 1722 (C=O, st), 1520, 1340 ( $\text{NO}_2$ , st), 1286, 1254, 1211, 1174, 1149 (C–O, st), 818 (aromatic,  $\delta$  oop); POL-DCNT: 2225 (CN, st), 1724 (C=O, st), 1282, 1247, 1200, 1171, 1151 (C–O, st), 814 (aromatic,  $\delta$  oop).

Elemental analysis (calculated): POL-CNT: %C: 78.95 (79.24), %H: 6.78 (6.65), %N: 3.14 (3.19); POL-NiT: %C: 72.87 (73.18), %H: 6.48 (6.36), %N: 2.95 (3.04); POL-DCNT: %C: 78.10 (78.34), %H: 6.24 (6.16), %N: 5.57 (5.71).

#### 4.3. Techniques

Elemental analyses were carried out using a Perkin-Elmer 240 C microanalyzer. IR spectra were obtained using a ATI Mattson Genesis Series FTIR.  $^1\text{H}$ -NMR measurements of the samples were obtained with a Varian Unity-300 spectrometer operating at 300 MHz and using deuterated chloroform or dimethylsulfoxide as solvent. UV-Vis spectra were

recorded using a Hitachi U-3400-UV-Vis-NIR spectrophotometer. Luminescence measurements were performed using a Perkin-Elmer LS50B spectrofluorimeter. The relative emission intensities of the CNT and DCNT compounds in  $\text{CH}_2\text{Cl}_2$  (see Fig. 6) were obtained as follows. After measuring the absorption spectrum the solutions were diluted to give an optical density of 0.01 in the maxima of the lowest energy absorption band (311 nm in CNT and 382 nm in DCNT). In this way we avoided the attenuation of the exciting beam across the cell and thus emission intensity was uniform. Afterwards the emission spectra were recorded under excitation in the absorption maximum.

The second-order NLO properties of the chromophores were measured in  $\text{CH}_2\text{Cl}_2$  solution using the EFISH technique. This technique allows the determination of the  $\mu\beta$  product when an electric field is applied to a solution of NLO-active species. Measurements of  $\mu\beta$  were carried out with a nonlinear optics spectrometer from SOPRA S.A. The fundamental light at 1907 nm came from the first Stokes peak of a hydrogen Raman cell pumped by the 1064 nm light of a Q-switched Nd:YAG laser (Quantel YG 781, 10 pps, 8 ns pulse). That light was passed through a linear polarizer and focused on the EFISH cell. The applied DC electric field (parallel to the light polarization) was 7 kV. The output light of the cell was passed through an interference filter to select the second harmonic light, which was detected with an R642 photomultiplier from Hamamatsu. The estimated errors in  $\mu\beta$  values are  $\pm 10\%$ .

Mesomorphic behavior was confirmed by optical microscopy using a Nikon polarizing microscope fitted with a Mettler FP-82 hot stage and a Mettler FP-80 control unit. A Perkin-Elmer DSC-7 differential scanning calorimeter was used to determine the thermal transitions. Transition temperatures were read at the maximum or the onset of the transition peaks for the polymers and model compounds, respectively, at a scanning rate of  $10^\circ\text{C}/\text{min}$ . TGA was performed using a TA STD 2960 simultaneous DTA-TGA instrument at a heating rate of  $10^\circ\text{C}/\text{min}$  in the range 40–600°C under a nitrogen atmosphere.

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