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Synthesis and photoinitiated polymerization of diacrylate derivates of halobenzoates

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The synthesis, characterization, mesomorphism and photoinitiated polymerization of new thermotropic derivatives of bis{4-[6-(acryloyloxy)hexyloxy]halobenzoate}-1,4-phenylene were studied. Halogen incorporation in the mesogenic unit decreases the stability of the mesophases of monomers containing three aromatic rings. The monomer **MIII** exhibits a nematic phase which has been macroscopically oriented by surface pre-treatment and fixed by photopolymerization *in situ*, yielding a uniaxially crosslinked network. The molecular ordering of liquid crystalline diacrylate films was visualized by examining the fracture surface by scanning electron microscopy. These films exhibit a fine texture, illustrating the presence of an oriented layered structure.

1. Introduction

Liquid crystal monomers with difunctional polymerizable groups are of great interest as starting materials for the production of anisotropic networks [1–4]. These materials, with anisotropic optical and mechanical properties, represent an area of fundamental research, scientific interest and technologic potential. In particular anisotropic networks have many potential uses in passive solid state optical devices such as colour filters, polarizers, retarders, etc. There are highly promising for use in microelectronics, especially for applications requiring light modulation, for example, in electro-optics, and nonlinear optics [5–8].

Bireactive monomers can be used in the production of these materials by *in situ* photopolymerization [9–13]. This technique of photopolymerization involves the macroscopic orientation of liquid crystal molecules with reactive end groups, such as divinylethers, diepoxides or diacrylates, followed by UV radiation [14, 15]. In this way the molecular orientation within the system becomes fixed by the creation of a three-dimensional anisotropic network.

Broer and coworkers [1, 2] initiated the investigation of anisotropic networks obtained *in situ* by means of photopolymerization of liquid crystal monomers with ultraviolet light. Because of their liquid crystal behaviour, the monomers can be uniaxially oriented by external forces, such as magnetic and electrical fields or surface orientation. One advantage of photopolymerization when compared with thermally activated polymerization is the temperature independence of the photopolymerization process. The temperature of polymerization can be chosen to be in the mesomorphic state, and after the macroscopic direction has been obtained, the polymerization proceeds with a greater degree of conversion. In this way the degree of order and consequently the anisotropic properties of the network can be adjusted as desired. The networks thus obtained behave anisotropically in a number of properties, such as thermal expansion coefficient and refractive index.

In the present work, we describe (i) the synthesis of new diacrylate mesogens with halogen substitution on the rigid mesogenic unit, (ii) the influence of molecular structure on thermotropic properties, (iii) photoinitiated polymerization for the production of an anisotropic network and (iv) the determination of the director profile **n** visualized by scanning electron microscopy (SEM) [16] of films of monomer MIII.

2. Experimental

All starting materials were commercial products of high purity (>99%) and were used without further purification.

The structures of the synthesized compounds were confirmed by FTIR spectroscopy (Nicolet, Magna-IR®550), and ^{1}H and ^{13}C NMR spectroscopy (Bruker AC 250).

Liquid crystalline properties were studied with an Ortholux II Pol-BK, polarizing microscope with a Mettler FP-82 hot stage and Mettler FP-80 central processor.

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The measurement of temperatures and enthalpies of transition was carried out using DSC (STA 625), with a heating and cooling rate of 10°C min^{-1}, operated under nitrogen.

The photopolymerization was initiated using a 350 W mercury lamp; samples for photopolymerization were heated in a furnace model TP91 Linkam. The intensity of radiation of the diacrylate monomers was determined by a Cole–Parmer radiometer. Studies of thermal stability of the monomers and polymers were carried out using a thermobalance (Perkin-Elmer TGA-7) with a heating rate of 10°C min^{-1}. 4-Hydroxy-3-fluorobenzoic acid was prepared according to a method previously described [13].

2.1. *Synthesis of monomers*

The synthesis of all the monomers is outlined in the scheme. Monomers MI and MIV were obtained according to procedures reported in the literature [3]. The synthesis of monomers MII and MIII is described below.

2.1.1. *4-(6- Hydroxyhexyloxy)-3-fluorobenzoic acid (**IIb**)*

4-Hydroxy-3-fluorobenzoic acid (10.0 g, 65 mmol) and K_2CO_3 (17.80 g, 0.129 mol) were dissolved in cyclohexanone (250 ml). 6-Chlorohexanol (11.9 g, 87 mmol) was then slowly added to the boiling solution with stirring. Afterwards, the reaction mixture was heated under reflux for 24 h. After filtering off salts and the evaporating the solvent, KOH (2.0 g, 52 mmol) in 100 ml of water/ethanol mixture was added to the cooled solution and the mixture was heated under reflux for a further 10 h. The solvent was evaporated and the **IIb** mixture was acidified with 10 ml of concentrated hydrochloric acid, 50 g of crushed ice and 50 ml of water. The solid product was filtered off and recrystallized from absolute ethanol; yield 9.5 g (65%). IR (KBr) ν cm^{-1}: 3366, 3376–2779, 2940, 1698, 1610, 1551. ^{1}H NMR ($CDCl_3$) δ ppm : 7.98 (d, 1H, aromatic), 7.86 (d, 1H, aromatic), 7.38 (d, 1H, aromatic), 4.33 (t, 2H, $COOCH_2$), 3.68 (t, 2H, $PhOCH_2$), 1.99–1.63 (m, 8H, aliphatic).

2.1.2. *4-[6-(Acryloyloxy)hexyloxy]-3-fluorobenzoic acid (**IIIb**)*

4-(6 Hydroxyhexyloxy)-3-fluorobenzoic acid (10 g, 39 mmol) was added to 1.5 ml of *N*,*N*-dimethylaniline and 0.05 g of 2,6-di-*t*-butyl-4-methylphenol in 200 ml of 1,4-dioxane. At 60°C acryloylchloride (3.51 g, 39 mmol) was slowly added with stirring. To complete the reaction the mixture was stirred for 2 h at 60°C. After cooling, the mixture was poured into ice/water; the white precipitate was filtered off, washed with water and recrystallized from a mixture of 2-propanol/water (7/3): yield 7.24 g (65%). IR (KBr) ν cm^{-1}: 3320–2778, 2940, 1729, 1680, 1610, 1551. ^{1}H NMR (DMS) δ ppm : 8.15 (s, 1H, aromatic), 8.04 (d, 1H, aromatic), 7.02 (d, 1H, aromatic), 6.47 (d, 1H, vinyl), 6.17 (d, 1H, vinyl), 5.86 (d, 1H, vinyl), 4.22 (t, 2H, $COOCH_2$), 4.12 (t, 2H, $PhOCH_2$), 1.90–1.50 (m, 8H, aliphatic).

2.1.3. *4-[6-(Acryloyloxy)hexyloxy]-3- fluorobenzoyl chloride (**IVb**)*

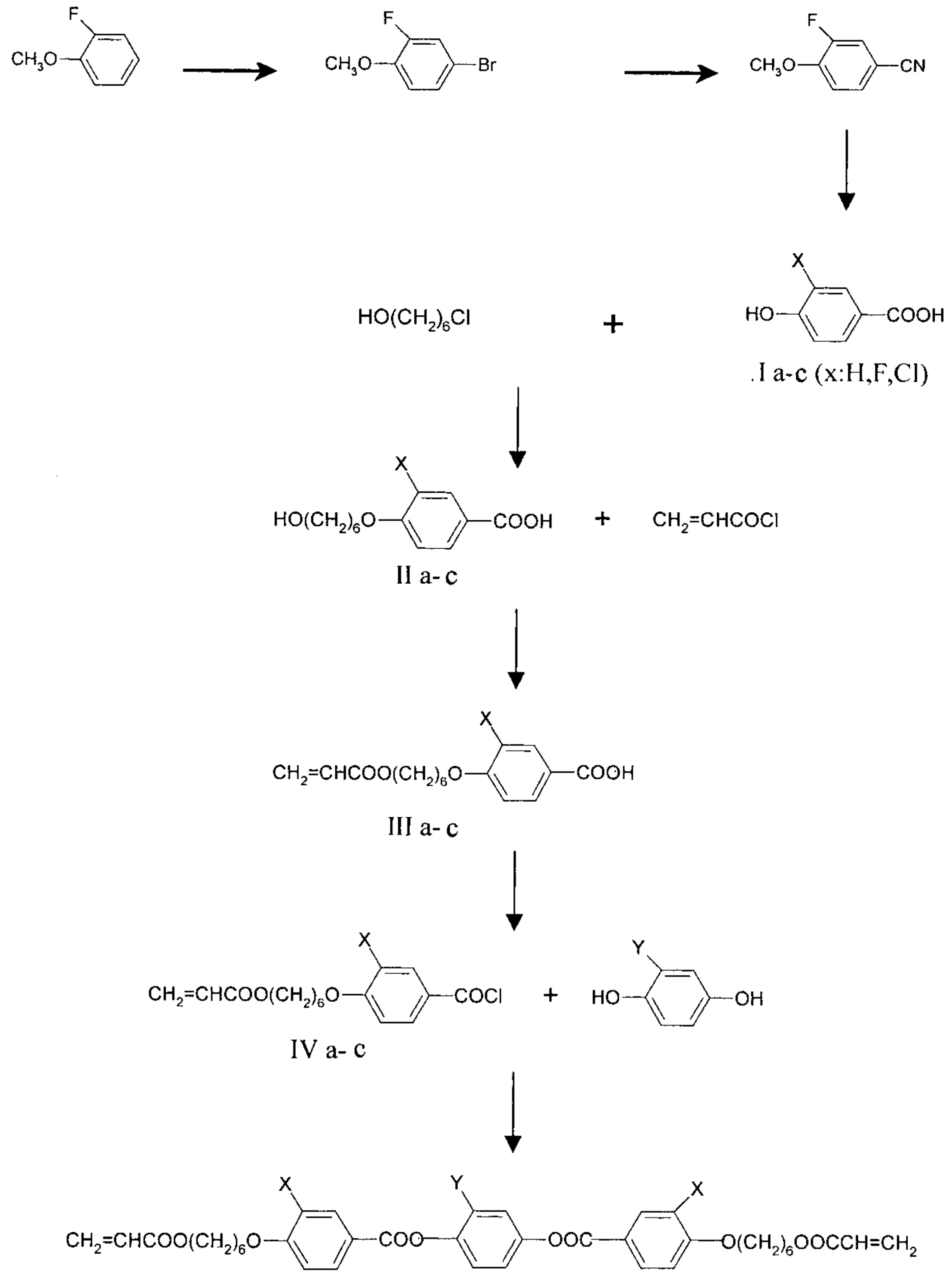
Over a period of 10 min, 2 ml of thionyl chloride were added to 4-[6-(acryloyloxy)hexyloxy]-3-fluorobenzoic acid (2 g, 6 mmol) and of 2,6-di-*t*-butyl-4-methylphenol (0.01 g) in 10 ml of CH_2Cl_2 with a few drops of DMF. After of 24 h at room temperature the dichloromethane and excess thionyl chloride were removed under reduced pressure and the yellow oil obtained was used in the next step without further purification.

2.1.4. *Bis{4-[6-(acryloyloxy)hexyloxy]fluorobenzoate}-1,4-phenylene (MII)*

Hydroquinone (0.32 g, 2.9 mmol) was dissolved in dry THF and the solution cooled to −5°C. At this temperature, acid chloride **IVb** (2.0 g, 5.8 mmol) in 10 ml of THF and 3 ml of triethylamine in 10 ml of THF were added dropwise and simultaneously. After stirring for 3 days at room temperature, a mixture of ice, water and 2 ml of HCl was added. After separation, the organic phase was washed with 50 ml of a concentrated NaCl solution. The organic layer was evaporated and the crude product purified by column chromatography (silica gel, ethyl acetate/hexane 1/9). The oil residue was recrystallized twice from a mixture of diethyl ether and chloroform (4/1); yield 1.1 g (40%). IR (KBr) ν cm^{-1} : 2940, 1720, 1594, 1510, 1500. ^{1}H NMR ($CDCl_3$) δ ppm : 8.20 (d, 2H, aromatic), 8.01 (d, 2H, aromatic), 7.23 (s, 4H, aromatic), 6.94 (d, 2H, aromatic), 6.51–5.83 (m, 6H, vinyl), 4.12 (t, 4H, $COOCH_2$), 4.01 (t, 4H, $PhOCH_2$), 1.90–1.38 (m, 16H, aliphatic). ^{13}C NMR ($CDCl_3$) δ ppm : 162.9, 162.1, 148.8, 148.3, 146.7, 132.1,128.3, 126.7, 124.2, 120.69, 119.8, 116.2, 73,1, 65.6, 30.1, 24.4.

2.1.5. *Bis{4-[6-(acryloyloxy)hexyloxy]-3-chlorobenzoate}1,4-phenylene (MIII)*

This compound was synthesized in the same way as monomer MII. 4-(6-Acryloyloxyhexyloxy)-3-chlorobenzoic acid **IVc** (2.00 g, 6 mmol) was reacted with excess thionyl chloride (2 ml) containing a drop of DMF in 10 ml of dichloromethane for 4 h. The solvent and excess thionyl chloride were removed under reduced pressure to produce the crude acid chloride. The product was dissolved in 10 ml of dichloromethane and added slowly to a cold solution of (0.32 g, 3 mmol)



MI, MII, MIII, MIV, MV

Scheme. Synthesis of monomers.

of hydroquinone and 1.30 g (0.13 mol) of trietylamine in 50 ml dichloromethane. The solution was stirred at room temperature for 10 h and was then washed with water and dried over anhydrous $MgSO_4$. After removing the solvent the crude product was purified by column chromatography (silica gel, *n*-hexane/

dichloromethane 1/9) and recrystallized from methanol/dichloromethane to give colourless white crystals; yield 1.4 g (60%). IR (KBr) ν cm^{-1} : 2945, 1720, 1598, 1278, 890. ^{1}H NMR (CDCl$_3$) δ ppm : 8.21 (d, 2H, aromatic), 8.00 (d, 2H, aromatic), 7.26 (s, 4H, aromatic), 6.44 (d, 2H, vinyl), 6.19 (d, 2H, vinyl), 5.84 (d, 1H, vinyl), 4.21 (t, 4H, COOCH$_2$), 4.13 (t, 4H, PhOCH$_2$), 1.89–1.51 (m, 8H, aliphatic). ^{13}C NMR (CDCl$_3$) δ ppm : 163.4, 162.1, 149.8, 148.2, 147.7, 131.1,128.3, 126.7, 124.2, 120.9, 116.8, 115.5, 73.1, 65.0, 30.4, 24.4.

Monomers MIV and MV were synthesized in the same way as monomers MII and MIII, to give colourless crystals; yield 65% and 68% respectively.

2.2. *Polymerization procedures*

As an example, the photopolymerization of monomer MIII is described. The monomer was dissolved in chloroform with an additional 1 wt% of a photoinitiator (2,2-dimethoxy-2-phenylacetophenone) and subsequent evaporation of the solvent under vacuum.

The polymerization mixtures were oriented macroscopically in a glass test cell provided with rubbed polyimide layers. Subsequently, the monomer layers held in the nematic temperature range were crosslinked by irradiation with a UV lamp of intensity 0.5 mW cm^{-2} at 350 nm for 15 min, yielding transparent polymer networks with a macroscopic orientation. The crosslinked reaction was verified by IR measurements, showing disappearance of the vinyl group absorption band.

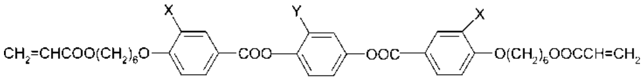
3. Results and discussion

3.1. *Synthesis of monomers*

Photopolymerizable monomers that are halobenzoate derivatives can be formed from reactive mesogens incorporating a polymerizable end group at the end of a flexible spacer attached to each end of a molecular core. The crosslinked polymer network is formed by polymerization of each of the photoreactive end groups with nearest neighbours.

The chemical structures of the monomers synthesized possess a mesogenic unit of three phenyl rings linked by ester bonds, functionalized on each side with an acrylate group connected to the mesogen by a flexible hexamethylene spacer. These monomers formed a high network density after photopolymerization. The synthesis of the monomers involved firstly the formation of 4-(6-hydroxyhexyloxy)-3-halobenzoic acid derivates by etherification of the 4-hydroxy-3-halobenzoic acid derivates with 6-chlorohexanol. The required acrylates were obtained by reaction with acryloyl chloride, with dimethylaniline to neutralize the HCl formed.

Table. Transition temperatures of diacrylates monomers.



Monomer	*X*	*Y*	Transition temperature/°C
MI	H	H	Cr 108 N 155 I
MII	F	H	Cr 99 N 129 I
MIII	Cl	H	Cr 86 N 106 I
MIV	H	Cl	Cr 100 N 117 I
MV	Cl	Cl	Cr 83 I

3.2. *Properties of the monomers*

The transition temperatures of the diacrylates are given in the table. The melting and clearing points were determined on the second heating. The monomer MI had been previously synthesized and was used as reference [2].

Monomers MII, MIII and MIV all present a thermotropic nematic phase, which in the region of the nematic–isotropic transition shows a classic schlieren texture. The substitution of a hydrogen by a chlorine atom (monomer MIV) in the central aromatic ring of the mesogenic unit destabilizes the mesophase. This is due to the loss of symmetry of the mesogen, which causes a decrease in the intermolecular interaction between neighbouring molecules and a decrease in degree of orientation in this phase, resulting in a decrease in transition temperatures.

Monomer MIII, unlike monomer MI, was substituted in both of the outer aromatic rings. This substitution of hydrogen by chlorine does not change the symmetry of the molecule, nevertheless it produces a change in its dipole moment and the length to breadth ratio (geometric anisotropy), causing a decrease in intermolecular interactions, thereby, affecting the mesophase transition temperatures. The mesomorphic behaviour of the mesogen MII is essentially the same as for the other monomers, demonstrating that substitutions with chlorine, fluorine and hydrogen, increase the order of the mesophase as the size of the substituent decreases.

Monomer MV exhibited no mesogenic properties; all three aromatic rings are substituted with chlorine, modifying intermolecular interactions and the geometric anisotropy, and thus producing changes in the mesogenic range. Thus an asymmetric substitution of the central aromatic ring causes a drastic decrease in the packing of molecules, destabilizing the formation of a mesophase.

3.3. *Ordering visualized by SEM*

It has been demonstrated that the molecular liquid crystal order can be visualized by scanning electron

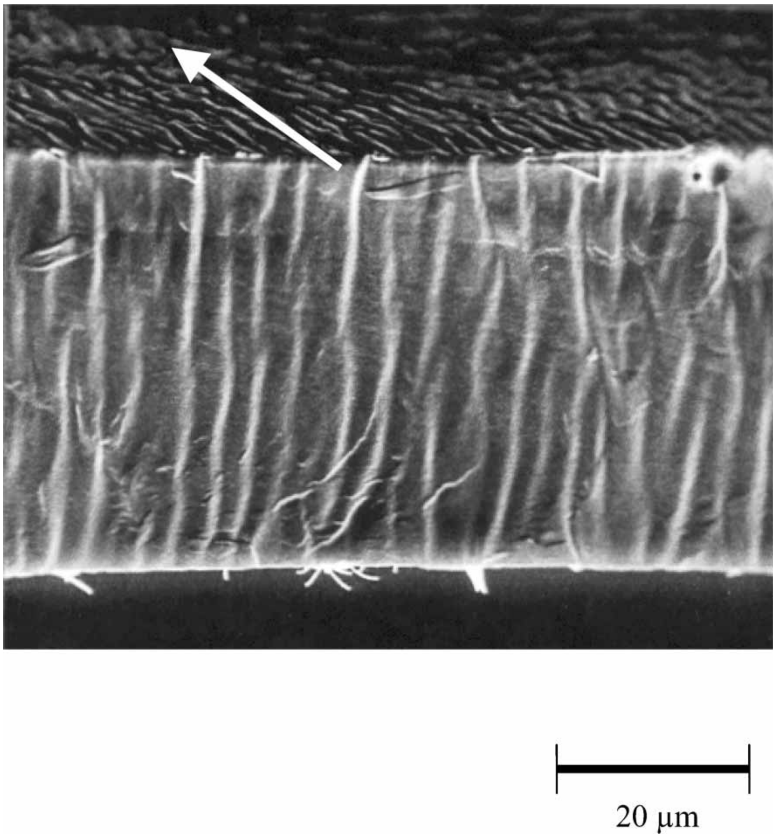


Figure 1. SEM image of a MIII film photopolymerized in the nematic phase at 90°C. The fractured surface is perpendicular to the molecular orientation.

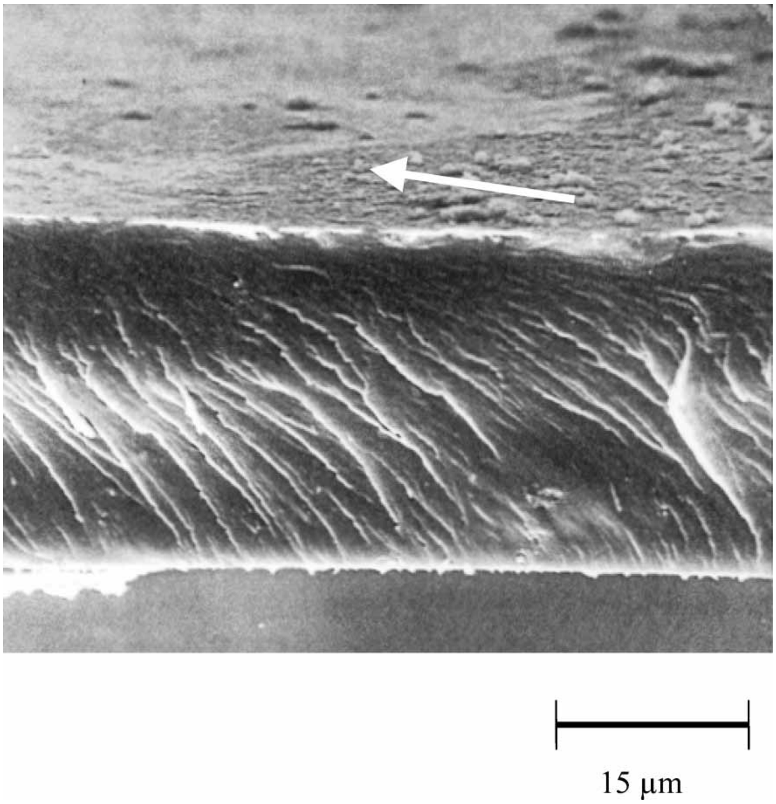


Figure 2. SEM image of a MIII film of fractured parallel to the director orientation, photopolymerized in the nematic phase at 90°C.

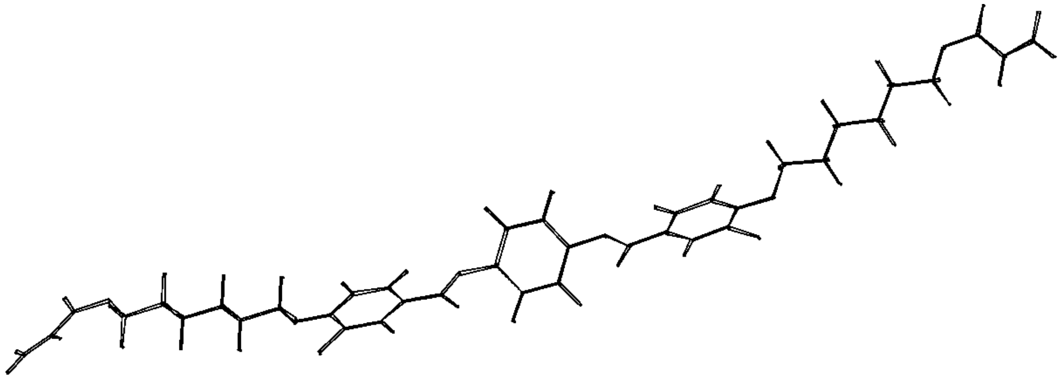


Figure 3. Conformation of MIII in monomeric state.

microscopy (SEM) which is based on the fixation of the director **n** by UV photopolymerization of diacrylate monomer [16]. Visualization of the molecular order was made with the polymeric film obtained from monomer MIII, after special processing of the surface. We fixed the director of a previously oriented monomer; the films were placed in liquid nitrogen to give fracturing perpendicular and parallel to the direction of the director (figures 1 and 2). A fine gold layer was deposited on the fractured surfaces. Figure 1 is a micrograph of the fractured surface of polymer MIII of 40 µm thickness, that has been planarly oriented after surface treatment with polyimide, and polymerized in the nematic mesophase at 90°C. The polymer fractures perpendicularly to the direction of observation, with microtextures in vertical lines. This texture is characteristic of a perpendicular molecular alignment to the surface fractured. From a micrograph of higher resolution the distance between two lines can be deduced as 120–150 nm. From conformational analysis of the monomer (figure 3), the nearest-neighbour distance is approximately 0.50 nm, corresponding to 240–300 molecules between two continuous lines.

The micrograph of figure 2 shows the fractured surface of a polymer film of 30 µm thickness, polymerized in the nematic phase at 90°C and oriented by processing the surface. The film is fractured parallel to the director direction, giving a grid texture, with a line separation of 100–120 nm. This type of texture is characteristic of a molecular order parallel to the plane, confirming the direction planar when using processed surfaces [16].

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