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Reverse-mode operation films can be achieved with polymer dispersed liquid crystals by many methods. One method consists in the use of either rough or polyimide treated supports in order to induce homeotropic alignment of the initial mixture that will separate in liquid crystal and polymer rich phases. The major disadvantage is the need for mesogenic monomers to keep a good alignment of the liquid crystal after the polymerization process. In this paper we present results concerning the use of an anisometric, non-mesogenic, tailor-made monomer for the preparation of excellent reverse-mode polymer dispersed liquid crystal shutters cast on rough surfaces. The combined use of rough surfaces and non-mesogenic monomers allows us to exceed earlier limits in physical and chemical properties, cost, and device dimensions by the use of a wider class of monomer molecules.

1. Introduction

Polymer dispersed liquid crystal (PDLC) films are composite materials formed by liquid crystal and polymer, and they have attracted much interest as electrically controlled light shutters [1, 2]. PDLCs can exhibit either a droplet morphology [3], in which the liquid crystal is separated as distinct micron-sized droplets in a continuous polymer matrix, or a reverse morphology [4], in which the liquid crystal fills the voids and crevices in a network structure formed by small polymer balls. PDLCs are generally characterized by an opaque OFF state, which can be turned into a transparent ON state by application of a suitable electric field (normal-mode operation film). In the OFF state light is scattered by the misaligned liquid crystal. In the ON state the mesogenic molecules are characterized by a uniform orientation and do not scatter light provided that the polymer matrix refractive index matches the ordinary refractive index of the liquid crystal (which is characterized by a positive dielectric anisotropy) [3]. On the contrary, reverse-mode PDLCs exhibit a transparent OFF state and an opaque ON state. They have been the subjects of much research for their use in applications where a transparent OFF state is required as the failure-mode of the device. Such particular properties make reverse-mode PDLCs interesting for their possible industrial

applications. They can be useful for the production of both consumer and high technology goods. The delay that industrial production shows in the use of these materials is essentially due to the high costs of components and the particular chemical–physical properties that they must satisfy.

Reverse-mode shutters have been obtained by using dual frequency addressable liquid crystals [5, 6], by polymerizing nematic emulsions [7], by functionalizing the liquid crystal/polymer matrix interface [8] and by using a larger liquid crystal loading [9–11]. These last systems are best known as mesogenic networks. They are characterized by low polymer concentrations (generally less than 5 wt %), a surface treatment of supports in order to induce a homeotropic alignment of the liquid crystal/monomer mixture (i.e. perpendicular to substrates), a low fraction of light scattered out of the normal direction, a bad adhesion to the supports, and the use of mesogenic monomers. More recently, we have proposed a reverse-mode device obtained by the photopolymerization of mixtures containing a low molecular mass liquid crystal with a negative dielectric anisotropy, and a liquid crystal-line diacrylate monomer homeotropically aligned by means of rough surfaces [12]. The use of rough surfaces allows easier and faster preparation since neither surface treatment of supports nor the use of external aligning fields are required. In addition, no limit is theoretically imposed on the dimensions of the devices. The best

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PDLCs are obtained by casting the mixtures on rougher substrates and with a liquid crystalline diacrylate monomer content of about 20 wt % (as they are able to keep a better homeotropic alignment of the liquid crystalline material after the polymerization induced phase separation process). Devices prepared by such methodology show relatively low switching electric fields (~ 2 V μm^{-1}), high contrast ratios (>20), fast response times (some ms) and good adhesion to supports as the monomer concentration is large. Nevertheless, the need for a mesogenic monomer, in order to keep the liquid crystallinity of the initial mixture at high monomer concentrations, represents a limit to further development of reverse-mode PDLCs cast on rough surfaces.

In this work we identify monomer anisometry as the major factor affecting the realization of a reverse-mode PDLC by means of rough surfaces. We show that the lack of mesomorphic properties in the monomer does not affect in a relevant manner the uniform and pre-defined orientation of the liquid crystal, provided that the monomer molecules are anisometric enough. On the contrary, less anisometric monomers prevent the formation of a well defined transparent state.

2. Experimental

^{1}H NMR spectra were obtained on a Bruker WM-300 spectrometer. MS spectra were recorded on a Hewlett-Packard GC-MSD 5972 instrument and IR spectra on a Perkin Elmer FTIR Paragon 1000 PC spectrophoto-meter. Monomer **I** was synthesized according to the procedure outlined in [13]. 2,5-Thiophendicarbonyl chloride was prepared according to a known procedure [14]. The preparation of monomer **II** (see the scheme) is described below.

2.1. *4-(2-Tetrahydropyranyloxy)phenol*

Hydroquinone (10.21 g, 90.0 mmol) was dissolved in 100 ml of dry diethyl ether with a catalytic amount of *p*-toluenesulphonic acid (0.7838 g, 4.1 mmol). 3,4-Dihydro-2H-pyran (7.65 g, 90.0 mmol) was added drop-wise and the solution was stirred for 18 h at room
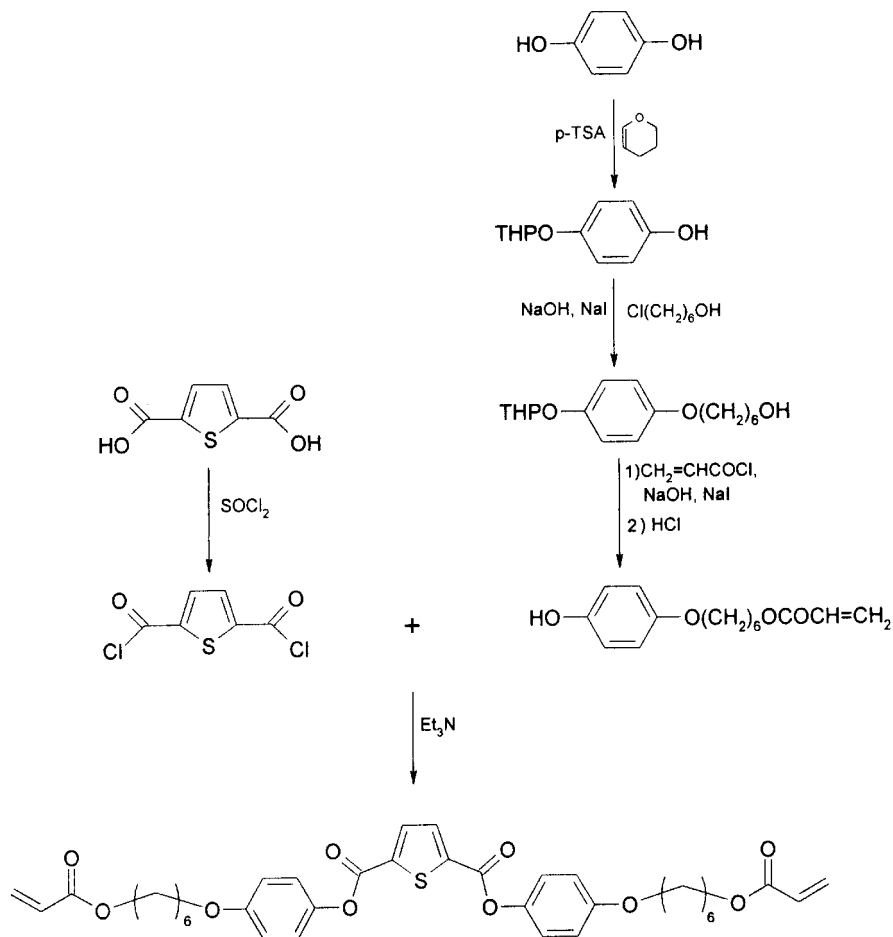
Scheme. Synthesis of bis{4-[6-(acryloyloxy)hexyloxy]phenyl} 2,5-thiophenedicarboxylate.

temperature. A mixture of EtOH/NH₃ (1/1) was added until the solution was basic. The reaction mixture was poured into water and shaken with CH_2Cl_2. The organic phase was separated, washed with 75 ml of water, dried with anhydrous Na_2SO_4, and evaporated. The product was purified by column chromatography (silica gel, hexane/EtOAc as eluent), and gave a white crystalline powder. Yield 9.37 g (52%), m.p. 96–98°C. IR (KBr, v cm^{-1}): 3346, 1509, 1180. ¹H NMR (CD₃OD, δ ppm): 1.59–1.99 (m, 6H), 3.57 (m, 1H), 3.92 (m, 1H), 5.21 (t, 1H, $J = 3.60$ Hz), 6.68 (d, 2H, $J_o = 6.72$ Hz), 6.87 (d, 2H, $J_o = 6.72$ Hz).

2.2. 4-(2-Tetrahydropyranyloxy)-1-(6-hydroxyhexyloxy)benzene

4-(2-Tetrahydropyranyloxy)phenol (7 g, 36.1 mmol) in 150 ml of dry butanone was added to 1.7 g (42.5 mmol) of sodium hydroxide. After a clear solution was obtained, sodium iodide (5.4 g, 36.1 mmol) and 6-chlorohexanol (5.76 g, 42.2 mmol) were added. The solution was maintained under reflux for 12 h and for another 12 h at room temperature, filtered, and evaporated. Then 200 ml of diethyl ether and 100 ml of water were added to the remaining oil. After separation, the organic phase was washed with 50 ml of 10% aqueous sodium hydroxide and 50 ml of saturated aqueous sodium chloride; it was then dried over anhydrous Na_2SO_4 and evaporated. The crude product was washed with *n*-hexane to remove unreacted 6-chlorohexanol, and the white powder recrystallized from *n*-hexane. Yield 5.48 g (51%), m.p. 54–55°C. IR (KBr, v cm^{-1}): 3300, 1513, 1196. *M/Z*: 294 (m$^+$, 1%), 210 (30%), 110 (100%). ¹H NMR (C₆D₆, δ ppm): 1.20–1.38 (m, 14H), 3.34 (t, 2H, $J = 6.10$ Hz), 3.36 (m, 1H), 3.63 (t, 2H, $J = 6.10$ Hz), 3.84 (m, 1H), 5.25 (t, 1H, $J = 3.2$ Hz), 6.85 (d, 2H, $J = 9.00$ Hz), 7.17 (d, 2H, $J_o = 9.00$ Hz).

2.3. 4-[6-(Acryloyloxy)hexyloxy]phenol

A solution of acryloyl chloride (1.05 g, 29.6 mmol) in 6 ml of dry dichloromethane was added dropwise to a solution of 4-(2-tetrahydropyranyloxy)-1-(6-hydroxyhexyloxy)benzene (6.93 g, 23.55 mmol), triethylamine (3.6 g, 36 mmol) and a catalytic amount of *tert*-butylcatechol in 20 ml of dry dichloromethane. After the mixture had been stirred for 48 h at room temperature and the solvent evaporated, the residue (dissolved in 20 ml of EtOH) was treated with concentrated HCl (5 ml) for 1 h with stirring at 0°C. The reaction mixture was shaken with dichloromethane, and the extract dried over anhydrous sodium sulphate, distilled under reduced pressure to remove the solvent, and the residue column chromatographed (silica gel, EtOAc/*n*-hexane as eluent). Yield 4.05 g (65%), white solid. IR (KBr, v cm^{-1}): 3402, 1723, 1509, 1196, 989–972. *M/Z*: 264 (M$^+$, 9%), 110

(100%). ¹H NMR (CDCl₃, δ ppm): 1.44–1.77 (m, 8H), 3.89 (t, 2H, $J = 6.51$ Hz), 4.17 (t, 2H, $J = 6.50$ Hz), 5.83 (dd, 1H, $J_{cis} = 10.38$ Hz, $J_{gem} = 1.23$ Hz), 6.13 (dd, 1H, $J_{trans} = 17.07$ Hz, $J_{cis} = 10.38$ Hz), 6.41 (dd, 1H, $J_{trans} = 17.07$ Hz, $J_{gem} = 1.23$ Hz), 6.77 (s, 4H).

2.4. Bis{4-[6-(acryloyloxy)hexyloxy]phenyl} 2,5-thiophenedicarboxylate (monomer II)

A mixture of 4-[6-(acryloyloxy)hexyloxy]phenol (3.27 g, 12.4 mmol), a catalytic amount of *tert*-butylcatechol, 5 ml of dry dichloromethane, and dry triethylamine (1.78 ml, 17.67 mmol) was treated dropwise under N₂ and with stirring with a solution of 2,5-thiophene-dicarbonyl chloride (1.27 g, 6.19 mmol) in CH_2Cl_2. The reaction mixture was stirred at room temperature for 48 h, hydrolysed with a mixture of ice and concentrated HCl (1/1), and finally extracted with CH_2Cl_2. The organic phase was washed with 50 ml of saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and the solvent removed under reduced pressure. The crude product, a white solid, was recrystallized from aceto-nitrile. Yield 1.68 g (41%), white crystalline powder, m.p. 91–92°C. IR (KBr, v cm^{-1}): 1732, 1511, 1202, 926, 984. ¹H NMR (CDCl₃, δ ppm): 1.47–1.85 (m, 16H), 4.04 (t, 4H, $J = 6.51$ Hz), 4.16 (t, 4H, $J = 6.51$ Hz), 5.85 (dd, 2H, $J_{gem} = 1.77$ Hz, $J_{cis} = 10.65$ Hz), 6.11 (dd, 2H, $J_{cis} = 10.65$ Hz, $J_{trans} = 17.19$ Hz), 6.32 (dd, 2H, $J_{trans} = 17.19$ Hz, $J_{gem} = 1.77$ Hz), 7.02 (d, 4H, $J_o = 8.88$ Hz), 7.24 (d, 4H, $J_o = 8.88$ Hz), 8.05 (s, 2H).

2.5. Mixtures

ZLI 4788-00, a commercially available and patented nematic liquid crystal material with a negative dielectric anisotropy ($\Delta\varepsilon = 5.7$), was supplied by E. Merck. Mixtures were prepared by weighing appropriate amounts of monomer and liquid crystal in vials and subsequently stirring them at 100°C. About 1.5 wt % of photoinitiator (2,2-dimethoxy-2-phenylacetophenon, Aldrich) was added. Then, a small quantity of the mixture was introduced by capillarity into home made cells whose thickness was set to be 20 μm by glass spheres. The cells had a 120 nm indium tin oxide conductive substrate (Balzers) with an average roughness of 2.6 nm as determined by atomic force microscopy (Nanoscope III, Digital Instruments). Optical investigations were performed with a polarizing optical microscope (Laborlux 12 POL, Leitz). The sample temperature was changed with a programmable hot stage (PR600, Linkam) at a rate of 1°C min^{-1}. The polymerization of aligned samples was achieved at a controlled temperature (80°C) by UV radiation from a 125 W high pressure mercury lamp for 10 min. Longer exposure times do not change the electro-optical properties of cells, but cause a yellowing of films because of

probable photodecomposition of the organic materials. The electro-optical transmittance of mixtures was measured at room temperature using the optical line described previously [15]. The intensity of the incident light measured with no sample in place was assumed to be full-scale intensity. The rise and decay times of transmittance, defined, respectively, as the time required to drop to 10% of the maximum transmittance and to reach 90% of the optical response after the external field is removed, were determined by monitoring the drive signal ($v = 1\,kHz$, Vpp $= 200\,V$) and the response of the photodiode using a digital storage oscilloscope.

3. Results and discussion

The monomers chosen for this study are reported in figure 1.

Monomer **I** is a liquid crystal, while **II** and **III** do not show any mesomorphism even though **I** and **II** have comparable molecular lengths. **III** is less anisotropic in shape than **I** and **II**. In fact, it is characterized by a lower ratio, R, between its long and short molecular axes ($R_{\mathbf{I}} \sim R_{\mathbf{II}} \sim 8 > R_{\mathbf{III}} \sim 5$) as determined by molecular modelling with the aid of a software package (MOPAC V6.0).

Figure 2 shows the AFM image and the section profile along the diagonal of the image of the substrates used in this work. Such supports are characterized by an average roughness of about 2.6 nm and are known to give well aligned reverse-mode PDLCs using a liquid crystalline monomer.

The molecular alignment of nematic mixtures generally depends on the physical–chemical and mechanical interactions, which are related to both surface topology and the elastic properties of the liquid crystal [16, 17]. As a consequence, the alignment of polymerized mixtures will depend on a balance between the initial molecular alignment and the disorder induced by photopolymerization. Once the cells were filled, the alignment of nematic mixtures held between crossed polarizers was observed. It was found that the surfaces were able to
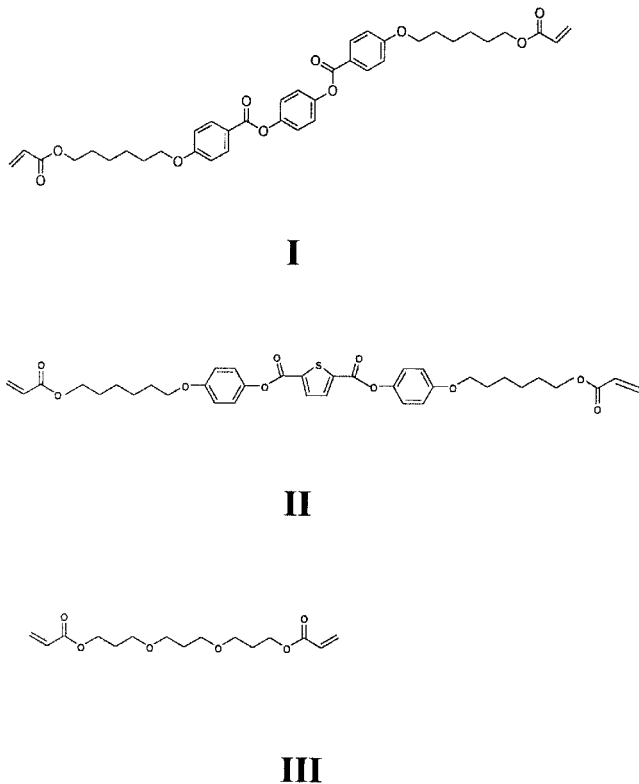

Figure 1. Monomers used in this work: 1,4-bis{4-[6-(acryloyl-oxy)hexyloxy]benzoyloxy} benzene (**I**), bis{4-[6-(acryloyl-oxy)hexyloxy]phenyl} 2,5-thiophenedicarboxylate (**II**), and tri(propylene glycol) diacrylate (**III**).
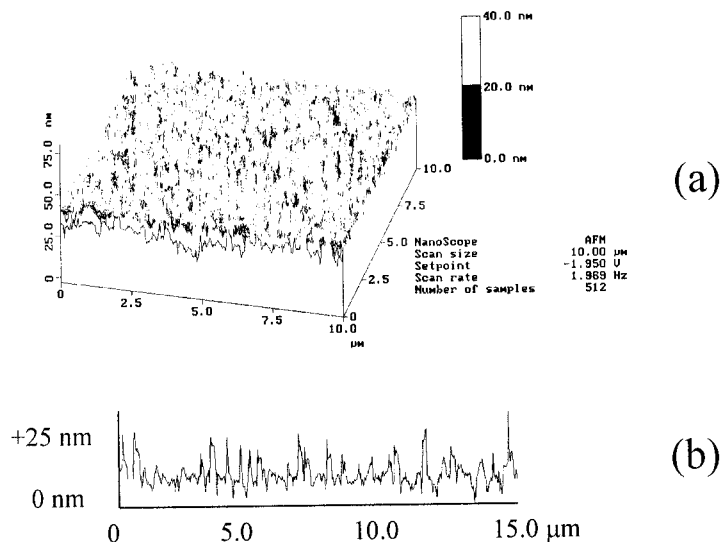

Figure 2. AFM image (*a*) and section profile along the diagonal (*b*) of the substrates used in this work. The average roughness is 2.6 nm.

align nematic mixtures containing monomer **I** almost perpendicular to the substrates. On the contrary, highly birefringent samples were obtained with mixtures containing monomer **III**. An intermediate situation was achieved in cells filled with monomer **II**. Such samples were UV irradiated in their nematic state at 80°C. After polymerization we obtained PDLC films characterized by different values of the zero field transmittance. The electro-optical behaviour of such cells was investigated by observing their optical transmittances as a function of the applied field and tilt angle. In addition, the response times were measured.

Figure 3 reports the optical transmittances of PDLC samples containing the three different monomers.

Highly transparent PDLCs (zero-field transmittance about 78%) were obtained using the liquid crystalline monomer **I**. Almost opaque cells were achieved using monomer **III** (around 15%). Intermediate values of transmittance were obtained with the anisometric, non-mesogenic, tailor-made monomer **II** (about 30%). We cannot exclude the possibility that a non-perfect matching between the refractive index of the non-mesogenic material and of the ordinary liquid crystal exists and that one determines a reduced value of the zero-field transmittance in the latter samples. All the transmittances decrease with increasing applied electric field as it gives rise to a 90° tilt of the liquid crystal director because of the negative dielectric anisotropy of the liquid crystal.

All samples are characterized by a decreasing behaviour of the OFF state transmittance as a function of viewing angle. The decrease is lower than in conventional PDLCs (see figure 4) and suggests the presence of a polymer ball morphology for our PDLC films.

Morphology analysis confirms this situation. Figure 5 shows the polymer ball typical morphology exhibited by all our samples.

Each of the materials presents a reverse morphology, i.e. their matrix consists of small polymer balls (average
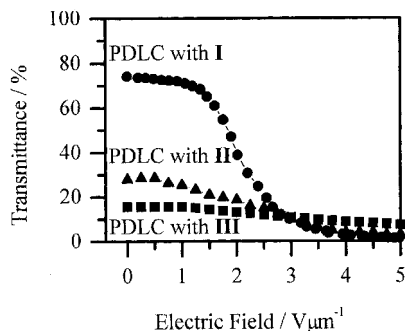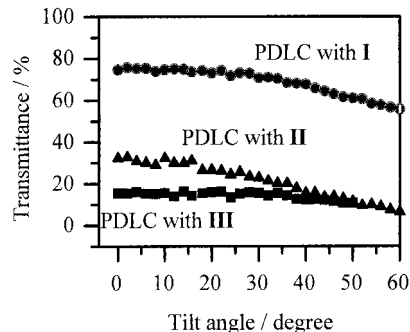

Figure 4. Viewing angle dependence of the OFF state transmittances of PDLCs containing the three different monomers.
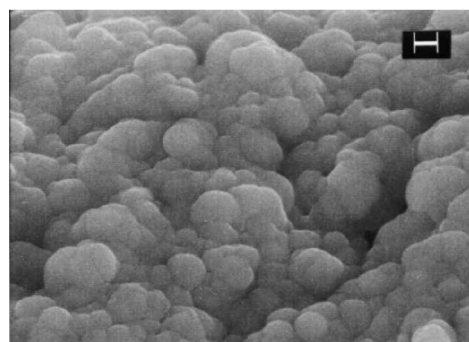

Figure 5. SEM picture of the typical morphology shown by the PDLC cells. Each monomer gives rise to a polymer ball morphology characterized by small spherical polymer seeds, with an average radius of 100 nm, merging in a network structure. The bar is 200 nm.

radius about 100 nm) merging in a network structure, whose voids and crevices are filled by liquid crystal. Such a structure is not affected by a significant loss in angular transmittance even at large tilt angles, as the thin liquid crystal layers around the polymer droplets do not give rise to a sufficient phase shift of the light [3].

Figure 6 shows the electro-optical response of our PDLC samples to a modulated sine wave.

All the samples are characterized by a fast rise time (less than 2 ms) as the drive field determines this. In contrast, different decay times are measured (2, 8 and 16 ms for monomers **I**, **II** and **III**, respectively). A lower decay time is usually an index of larger restoring forces acting on the liquid crystal dispersed in the matrix. In our opinion, such a difference in the decay times of our three PDLC cells can be attributed to the local environments with different degrees of order which the liquid crystal experiences. In fact, it is expected that a liquid crystalline monomer, such as **I**, can give a local environment more ordered than **II** and **III** can, resulting in a shorter restoring time.

Figure 3. Electric field-dependent transmittances of PDLCs containing the three different monomers.
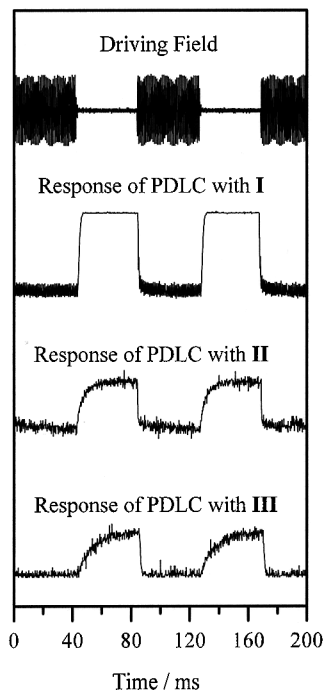
Figure 6. Electro-optical response shown by PDLCs containing the three different monomers. The rise times are always faster than 2 ms as they are dependent on the external drive field. The largest decay time is obtained for the response of the PDLC with monomer **III**.

4. Conclusions

In this work we have synthesized a new monomer characterized by a lower melting point and an easier and cheaper synthetic procedure, which would facilitate eventual industrial scale up. Such a monomer is not a liquid crystal, but it has an elongated shape and a rigid core like a liquid crystal. If it is mixed with a liquid crystal, the mixture can be homeotropically aligned by a clean (i.e. without any treatment) rough surface. The alignment is achieved through the typical grooves present in the substrates, which promote excellent anchoring and an easy axis almost perpendicular to the glass plates of the cell. Such preferential alignment can be stored if crosslinkage of the polymerizable component is performed. The application of a suitable electric field gives an opaque ON state as the liquid crystal directors are tilted by 90°. Even if the synthesized monomer **II** does not give as high an optical contrast as the liquid crystalline monomer **I**, it gives rise to PDLC films characterized by good adhesion to the supports and rather fast response times. The electro-optical properties of reverse-mode PDLCs prepared with this new monomer **II** are similar to those shown by PDLCs obtained with

liquid crystalline monomers such as **I**. Consequently, the liquid crystallinity of the monomer component is unimportant for the preparation of reverse-mode PDLCs cast on rough surfaces; it must simply have an adequate shape anisometry. Indeed, most anisometric monomers give a transparent state. Such results will allow the preparation of new monomers from commercially available precursors without requiring that they have mesomorphic properties. Lower costs, a higher chemical stability, easier preparation and easier scale-up could be gained in this way. The use of anisometric, non-mesogenic, tailor-made monomers can therefore give easier and cheaper production of large area displays and light shutters, made by means of the alignment promoted by rough surfaces. Further synthesis work is in progress in order to obtain refractive index-matched monomers, so gaining larger OFF state transmittances.

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