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Development of non-reactive fluorine-rich biphenyl molecules and their incorporation into a PDLC system

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Novel highly fluorinated molecules containing biphenyl moieties were synthesized via *N*,*N*′-dicyclohexylcarbodiimide esterification reactions. Chemical structures were confirmed by FTIR, NMR and elemental analysis. These non-reactive fluorinated molecules were added in increasing concentrations to a pentaacrylate-based polymer dispersed liquid crystal formulation and thin films were made by homogeneous illumination with a white light source. Refractive index and dynamic scattering measurements, in addition to direct polymerization attempts, indicate that the fluorinated compounds are non-reactive in the photopolymerization process. Electro-optic measurements suggest that the fluorinated molecules preferentially occupy the interface between the crosslinked polymer matrix and the liquid crystal domains. As a consequence, threshold voltages are lowered and relaxation times increased.

1. Introduction

Fluorine-containing polymers are characterized by good thermal stability, low refractive indices and good chemical stability [1, 2]. The low surface energy associated with these polymers makes them candidate materials for anti-fouling coatings and release agents [3]. Our interest in fluoropolymers is focused on potential applications in polymer-dispersed liquid crystal (PDLC) [4] and holographically formed (H-PDLC) [5] films with low electrical switching fields.

PDLCs are composite materials consisting of a liquid crystal phase dispersed within a semi-continuous polymer matrix [4]. In the absence of an electric field, a refractive index mismatch between the polymer matrix and the LC phase ($n_p \neq n_{LC}$) gives rise to the scattering of incident light. When the LC molecules are aligned in the presence of an electric field, a light-transparent film is produced due to matching of the ordinary LC refractive index (n_o) with that of the host polymer (n_p). The switching properties of the LC molecules within the domains depend on many variables including size, shape and chemical interactions. Strong surface anchoring typically results in larger threshold voltages and faster relaxation times. Application of a sufficient strength electric field overcomes the elastic forces anchoring the liquid crystal molecules at the interface. Larger voltages are needed as the strength of anchoring increases. Once the electric field is removed, the relaxation time for the molecules to revert back to the equilibrium distribution is also dictated by the strength of these forces. Stronger anchoring (i.e. larger elastic forces) results in faster relaxation times.

It has been shown that a low surface energy weakens the elastic forces pinning the LC molecules. Such an effect has been demonstrated utilizing fluorine-containing nematic LCs and partially fluorinated polymer matrices [6–9]. In these studies the voltage needed to align the LC molecules decreases while the relaxation times increase. In similar work with H-PDLCs, we have been investigating the incorporation of reactive fluorine-containing monomers into a polymer matrix [10, 11]. This system consists of a highly functional acrylate host that allows for small nanometer sized LC domains to form. Patterning of these domains is possible on a sub-micron periodicity using holographic illumination. The very small LC domains result in high switching voltages due to the small volume/surface ratio. Methodologies to lower this switching voltage are an active area of research in H-PDLC material systems.

Previous work by this group attempted to incorporate both fluorinated acrylate and methacrylate reactive monomers into this system. The latter monomer type was specifically chosen due to its low reactivity relative

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to acrylate-based monomers. This premise is based on previous work [12, 13] which showed that a slow-reacting monomer could be preferentially incorporated at the LC/polymer interface and therefore affect anchoring properties. However in our recent work, no preferential placement of the fluorine molecules at the interface was observed for either study, as indicated by little change in the electro-optical properties of the PDLC films. Instead, their incorporation led to large changes in the host refractive index and subsequently the measured contrast ratios. In addition, incorporation of commercially available non-reactive fluorinated molecules (surfactants) were unsuccessful due to solubility issues with our reactive syrup.

In the work presented here, two non-reactive molecules were designed with chemical structures similar to the LC molecules themselves. These molecules were designed to have aromatic moieties to enhance some limited compatibility with the LC rather than the polymer. Limited compatibility is necessary for homogeneous, one-phase reactive syrups to be formed before curing. Fluorination of the molecules was performed at two different positions. The incorporation of these two molecules into our photopolymer system resulted in substantial changes in the voltage and relaxation times of PDLC films formed via photopolymerization. These measurements in conjunction with real-time measurements on the progression of phase separation in these films indicate that the non-reactive molecules reside near the interface between the LC droplets and polymer matrix. In this report, we describe the synthesis and characterization of two highly fluorinated long chain molecules and their influence on the electro-optical properties upon incorporation into a photopolymerized PDLC.

2. Experimental procedures

N-vinyl pyrrolidinone (NVP), hydroquinone, 4-pentenoic acid, *N*,*N*′-dicyclohexylcarbodiimide (DCCI), *N*,*N*-dimethylacetamide, 2,2′3,3′5,5′6,6′-octafluoro-4,4′-biphenol monohydrate, distilled acetone (dry), 4-dimethylaminopyridine (DMAP), and tetrahydrofuran (dry) were purchased from the Sigma-Aldrich Co. and used as received. 4,4′-Bis(2-hydroxyhexafluoroisopropyl)biphenol was used as received from the Lancaster Co.

2.1. *Synthesis of 2,2′3,3′5,5′6,6′-octafluoro-4,4′-biphenylpent-1-en-4-ate (OBP)*

OBP was prepared via a DCCI coupling reaction using a modification of procedures described previously [14, 15]. 4-Pentenoic acid (2.6 mmol, 0.52 g), 2,2′3,3′5,5′6,6′-octafluoro-4,4′-biphenol monohydrate (2.8 mmol, 1.0 g), DMAP (0.5 mmol, 0.06 g) and hydroquinone (1.3 µmol, 14 mg) were stirred in dichloromethane (50 ml) for 72 h at room temperature. The reaction mixture was vacuum filtered, and the filtrate washed with water, 5% acetic acid and water solution, and again with water. The filtrate was then dried over $MgSO_4$, the mixture filtered, and the solvent removed. Low pressure liquid chromatography was used to isolate the desired product; it was off-white in colour and had a waxy texture. The synthetic scheme for this compound is shown in figure 1 (*a*); yield: 0.73 g (57%), m.p. 48.0°C. FTIR (KBr) ν/cm^{-1}: 1796 (vs ester). ^{1}H NMR: δ 5.9 (2H, $H_2C{=}C\mathit{H}$), 5.2 (2H, $H_2C{=}C$), 5.1 (4H, $H_2C{=}$), 2.8 (4H, $COOC\mathit{H}_2$), 2.5 (4H, H2C=CHCH_2). Elem. anal. for $C_{22}H_{14}F_8O_4$: calc, C 53.4, H 2.63, F 31; found, C 52.90, H 2.7, F 30.61%. The refractive index *n* was estimated as 1.479.

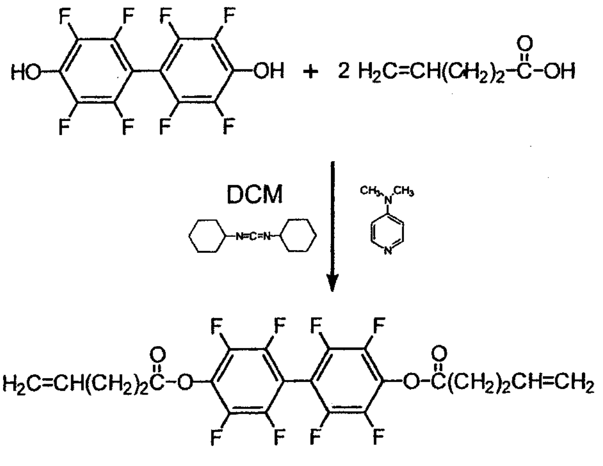


Figure 1a.

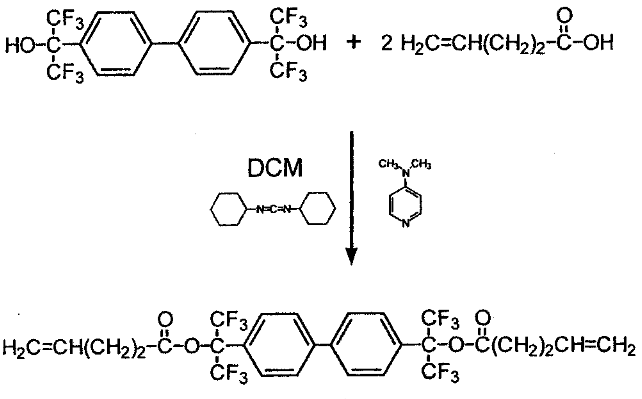


Figure 1b

Figure 1. Scheme for the synthesis of OBP (*a*) and BHP (*b*).

2.2. *Synthesis of 4,4′-biphenylhexafluoroisopropylpent-1-en-4-ate (BHP)*

The synthesis scheme is the same as for OBP wherein 4,4′-bis(hydroxyhexafluoroisopropyl)biphenol is replaced for octafluorobiphenol monohydrate. Initially, 4-pentenoic acid (20 mmol, 2 g), DCCI (22 mmol, 5 g), 4,4′-bis(hydroxyhexafluoroisopropyl)biphenol (5.0 mmol, 2.5 g), 135 ml 1,2-dichloromethane, and DMAP (20 mmol, 24 g) were added. The solution was stirred for 12 h at 23°C. The reaction mixture was vacuum filtered to remove the dicyclohexyl urea precipitate. Column chromatography was employed to isolate the desired product which was translucent and tan-yellow in colour; yield 2.5 g (75%). The chemical structure of the compound is shown in figure 1 (*b*); at room temperature it was a liquid. FTIR (KBr) ν/cm^{-1}: 1796 (vs ester). ^{1}H NMR (CDCl$_3$): δ 7.6 (4H, aromatic), 7.5 (4H, aromatic), 5.9 (2H, $H_2C{=}CH$), 5.2 (2H, $H_2C{=}$), 5.1 (2H, $H_2C{=}$), 2.7 (4H, $COOCH_2$), 2.5 (4H, $H_2C{=}CHCH_2$). Elem. anal. for $C_{28}H_{22}F_{12}O_4$: calc, C 51.7, H 3.4, F 35.0; found, C 51.37, H 3.29, F 30.86%. Refractive index: $n = 1.467$.

2.3. *Characterization*

^{1}H NMR spectra were recorded using a Varian VXR-300 spectrometer with a Varian VXR-4000 processor. A Perkin-Elmer FTIR 1725X spectrometer equipped with a GC-IR 1700X interface was used to obtain infrared transmittance spectra. Refractive index measurements were made using an ABBE-3L refractometer, model 33-46-10. The standard recipe for PDLC films consisted of 50 wt% inert liquid crystal E7 (EM Industries) and 50 wt% prepolymer solution consisting of a dye, co-initiator, a reactive diluent NVP, and dipentaerythritol hydroxypentaacrylate [10]. Standard formulation specimens were prepared in the absence of difunctional allyl additives. PDLC films were cured for 5 min using a floodlit incandescent lamp. The threshold voltage (V_{90}) was determined by measuring the voltage required for the thin film cell to achieve 90% of its maximum transmittance ($T_{\max}$). The measurements utilized a 1 kHz square wave across the thickness of the film using a HP3245A Universal Source in series with a 130x power amplifier. Relaxation time measurements—defined as the time necessary for a cell at $T_{\max}$ to return to a value of $T_{\min} + 0.1(T_{\max} - T_{\min})$ when the field is switched off—were made using a HP 54111D digitising oscilloscope. Low voltage, high resolution scanning electron microscopy LVHRSEM was employed for morphology studies using a Hitachi S-900 scanning electron microscope with a 1 keV accelerating voltage. A 2–5 nm thick coating of tungsten was deposited using a dual ion beam sputter coating apparatus to minimize artifacts associated with sample charging.

3. Results and discussion

Both POM and DSC studies indicated that neither neat BHP nor OBP formed a liquid crystal phase. Attempts to photo- and thermally-polymerize BHP and OBP were unsuccessful, confirming that their reactivities were much lower than that of the penta-acrylate monomer mixture. Photopolymerization was attempted using a high pressure mercury vapour arc lamp. Thermal polymerization (using AIBN) was attempted in differential scanning calorimetry. These results indicated weak polymerization above 120°C prior to thermal degradation of either molecule. This lack of reactivity was expected as allyl monomers of this type are known to be non-reactive due to autoinhibition [16]. At the higher temperatures, these types of monomers polymerize at very low rates with low degrees of polymerization. The inactivity is also attributed to degradative chain transfer; the allylic C–H bond adjacent to the double bond is very weak, facilitating the chain transfer to the monomer. Because of this process, the polymer chains are terminated by transfer after the addition of only few monomer units. The allylic radicals which are formed by chain transfer are resonance-stabilized and hence less efficient in initiating free radical polymerization. The allylic radicals combine with each other or terminate the propagating radicals [16].

Refractive index measurements of films formed from syrups with different amounts of each fluorinated molecule confirm these results. The refractive indices of BHP and OBP are 1.467 and 1.479, respectively, while that of the standard polymerized films is 1.539. A very small decrease in the refractive index is observed; however the decrease is not of the magnitude expected if full incorporation into the standard films was occurring. These results are a definite indicator that the fluorinated compounds are not incorporated in the polymer matrix, consistent with the low reactivity of these compounds. Solubility up to 10 mol% of either additive in the reactive syrup was easily achieved.

Real-time monitoring of the phase separation kinetics supports the notion that the fluorinated molecules are instead affecting the separation of the LC phase. Shown in the table and figure 2 are the onset times for the appearance of a LC phase as obtained from real-time transmittance curves. The appearance of the LC phase causes a sharp decrease in transmitted light through the film due to scattering. The LC phase appeared slightly after one minute into the curing process. The addition of OBP resulted in a gradual increase in the onset time to a maximum of 10.4 min for 10.75% addition. The delay in the onset time for BHP was much more pronounced with a maximum of 34 min for 8.3% addition. This data is indicative of the presence of the fluorinated molecules in the LC phase during the cure process.

Table. Floodlit PDLC film optical performance parameters as a function of fluorinated alkenyl monomer concentration.

Additive	Additive concentration/mol %	LC phase onset time/min	Threshold voltage/V μm^{-1}	Relaxation time/μs	Matrix refractive index
Standard	0	1.23	10.8	156	1.539
OBP	0.5	1.3	11.7	159	1.539
	2.4	2.2	9.5	163	1.538
	5.0	4.9	6.1	299	1.538
	10.7	10.4	2.9	312	1.537
BHP	0.4	1.7	11.0	141	1.539
	1.9	3.2	6.4	228	1.538
	3.9	8.5	2.6	433	1.538
	8.3	34	1.9	339	1.537

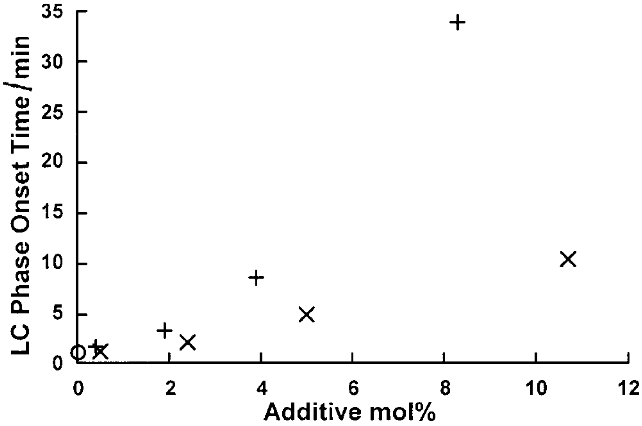


Figure 2. Onset of the liquid crystal phase as a function of additive concentration as determined by non-polarized light scattering obtained from the PDLC during curing. O is the standard formulation (no additive), X is for OBP samples, + is for BHP samples.

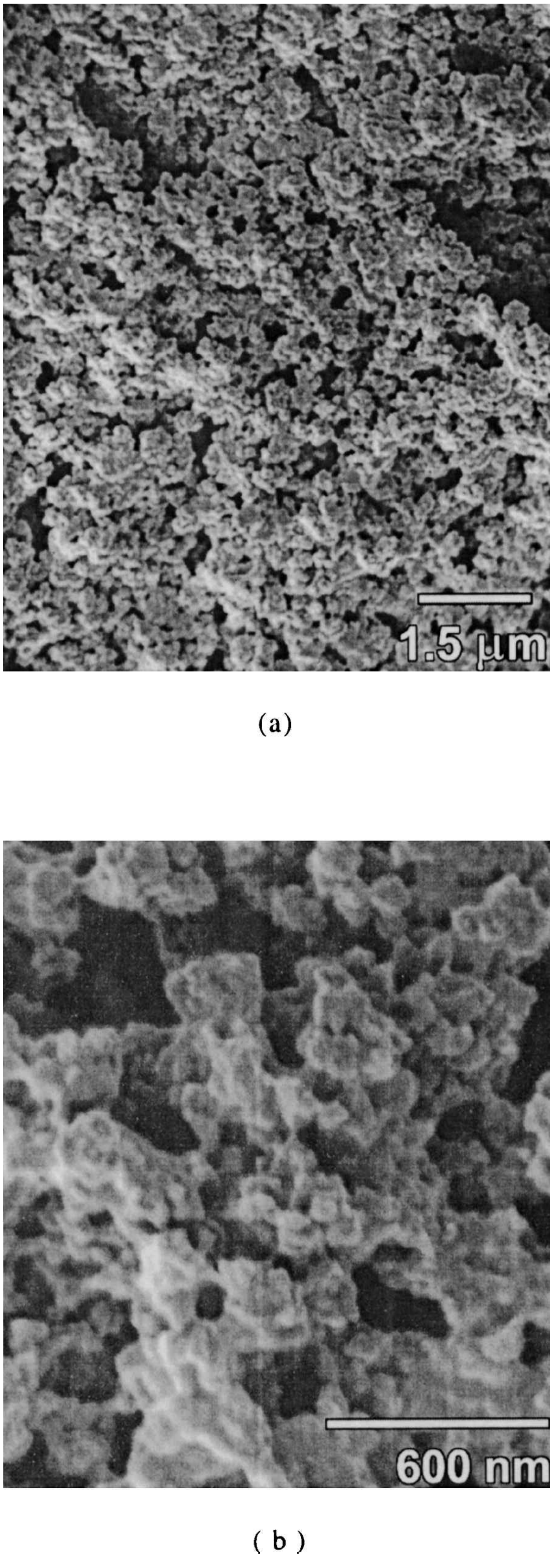
Being preferentially in the reactive syrup, rather than the growing polymer network, contaminates the LC phase. As is well known, the appearance of a LC phase is highly sensitive to the presence of non-mesogenic contaminants. Studies of mixing with bulk LC indicated suppression of the clearing temperature. As an example, 4.5% BHP reduces the clearing temperature to 56.5°C while 9.5% reduces it to 53°C. Thus, by preferentially residing in the fluid phase from which the LC phase must form, the additive molecules delay the appearance of the LC phase. The OBP molecule, due to the presence of fluorine on the aromatic ring is excluded earlier from the reactive phase thereby delaying the onset of LC less than BHP.

Although differential photocalorimetry measurements (unpublished) indicate that the polmerization rate decreases with the addition of BHP and OBP to the reactive syrup, this magnitude is no larger than observed when adding methyl acrylate and methyl methacrylate monomers. In addition, in a separate DPC experiment, the addition of reactive fluorinated acrylates caused no decrease in reaction rate as compared with similar concentrations of methyl acrylate. Thus, no significant chain transfer to BHP or OBP occurs. This is also consistent with the fact that the least effective chain transfer agents among halogenated derivatives [17] are those of fluorinated compounds.

The morphology of all formulations consisted of a highly interconnected porous matrix with liquid crystal-filled interstices as shown in figure 3. The polymer matrix is composed of aggregated polymer ‘beads’, consistent with high monomer functionality systems described by Rejaram *et al.* [18, 19]. Thus as polymerization proceeds, high molecular mass networks are rapidly formed. The nodular characteristics of the polymer indicate that these highly crosslinked ‘beads’ phase separate out of the reactive syrup. Little difference in the overall morphology was observed with incorporation of the fluorinated molecules.

Electro-optic measurements were performed to examine the influence of OBP and BHP on the films. The threshold voltage of standard formulation films was determined to be 10.8 V μm^{-1}, as shown in figure 4. The addition of OBP resulted in a substantial decrease in threshold voltage to a minimum value of 2.9 V μm^{-1} for a 10.7 mol % concentration. The addition of BHP also resulted in a similar decrease in driving voltage with surfactant concentration. A minimum of 1.9 V μm^{-1} was reached at a concentration of 8.3 mol %. This is also consistent with real-time measurements that indicated that the BHP preferred the LC phase over the polymer phase. The substantial decrease in switching voltages further confirms the presence of the non-reactive molecules at the interface between the pure LC phase and the polymer matrix interface.

Relaxation time measurements are also consistent with this conclusion, as the addition of either of the molecules results in longer relaxation times. The addition of OBP resulted in a gradual increase in relaxation times with additive concentrations for a maximum value of 312 μs for 10.7 mol %. Again, a stronger effect occurs for



(a)

(b)

Figure 3. LVSEM micrographs of the typical bead-like morphology. Note the LC phase is continuous and not isolated into spherical domains.

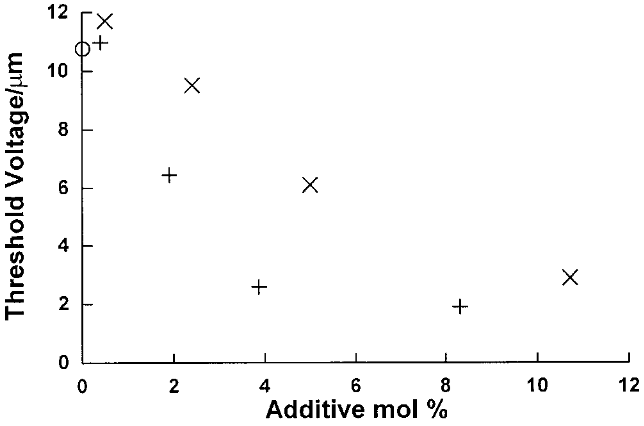


Figure 4. Threshold voltage as a function of additive concentration. O is the standard formulation (no additive), X is for OBP samples, + is for BHP samples.

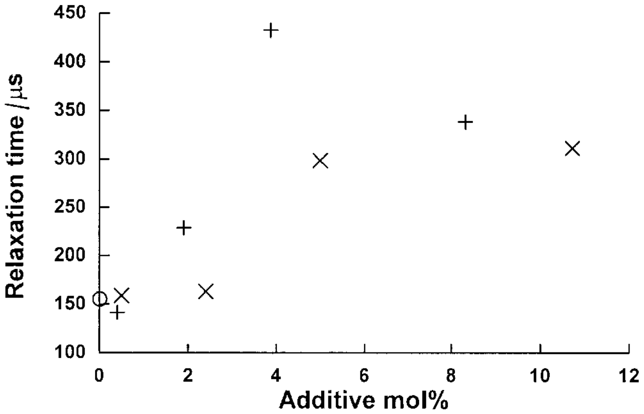


Figure 5. Relaxation time as a function of additive concentration. O is the standard formulation (no additive), X is for OBP samples, + is for BHP samples.

BHP as even longer relaxation times of >400 µs were observed. This is in agreement with the PDLC behaviour in general where the field-off times are known to increase with decreasing threshold voltage [4]. Threshold voltages are known to decrease with increasing droplet sizes and τ_{off} scales quadratically with droplet size [4]. In general, if the strength of the anchoring of the LC molecules to the polymer matrix is weakened, less force (voltage) is needed to overcome the elastic forces pinning the initial molecular distribution. As a consequence, the restoring force (when the voltage is turned off) is weakened and thus the time to relax back to the initial distribution is lengthened.

In summary, two new fluorine-containing molecules which are non-reactive and similar in shape to the native LC molecules have been designed and incorporated into a photopolymerized PDLC system. The increase in the delay times for the onset of LC phase appearance, in addition to the measured refractive index data, confirm no or little incorporation of these molecules into the polymer matrix. The delay in LC appearance is due to contamination of the LC phase with non-mesogenic monomers. Once the LC phase is formed, these molecules are present at the interface between the LC domains and the polymer matrix. This results in a substantial weakening of the anchoring, yielding lower switching voltages and longer relaxation times.

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