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Synthesis and liquid crystal alignment properties of new cinnamate-based photocrosslinkable polymers

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Because optical buffing can achieve aligning patterns with different azimuthal angles of the liquid crystal directors, photoalignment appears to be a very hopeful technique for designing complex LCD structures. Until recently, most photopolymers provided low anchoring and/or low tilt angles which are unsuitable for industrial applications. In this work, four new photocrosslinkable polymers based on biphenyl and naphthalene moieties have been prepared and characterized. These photopolymers have been irradiated with linearly polarized UV light, and liquid crystal cells have been made. The tilt angles generated by oblique irradiation have been measured as well as the anchoring energies. Finally, the stability of the liquid crystal alignment properties have been studied.

1. Introduction

Since the first reports by Schadt *et al.* [1] and Dyaduysha *et al.* [2], many authors have established that photocrosslinkable polymers irradiated with linearly polarized light can induce liquid crystal alignment. Until these last few years, mainly poly(vinylcinnamate) (PVCi) derivatives have been studied. Qualitatively, the behaviour of the side group chromophores is now rather well understood (scheme 1).

The photochemical mechanism involves both [2 + 2] photocycloaddition and photoisomerization. The side groups whose molecular long axes are in the direction of the linear polarization **P** primarily react. The preferred consumption of *trans*-cinnamate side groups along **P** produces an anisotropic distribution of these groups perpendicularly to **P**, while cycloaddition causes angular reorientation of dimers with their major axes perpendicular to **P** [1]. Simultaneously, *trans* → *cis*-photoisomerization induces successive angular reorientations of the chromophores in the direction perpendicular to **P** [3–5]. Quantitatively, the relative importance of the photoreactions involved is still being argued and seems to be strongly dependent on the exact molecular structure of the photopolymer. In this way, PVCi derivatives give liquid crystal alignment in the direction perpendicular to **P**.

Until recently, no-one could generate a tilt angle higher than 1° by using two cinnamate-based photopolymer films as alignment layers. Even by using oblique irradiation, the measured angle was around 0.3° [6]. Moreover, cells usually had to be filled in the isotropic phase so as to decrease the perturbations induced by flow alignment [1, 7], indicating low anchoring energies. As a consequence, new photocrosslinkable polymers inducing strong anchoring and higher tilt angles needed to be developed for further practical applications.

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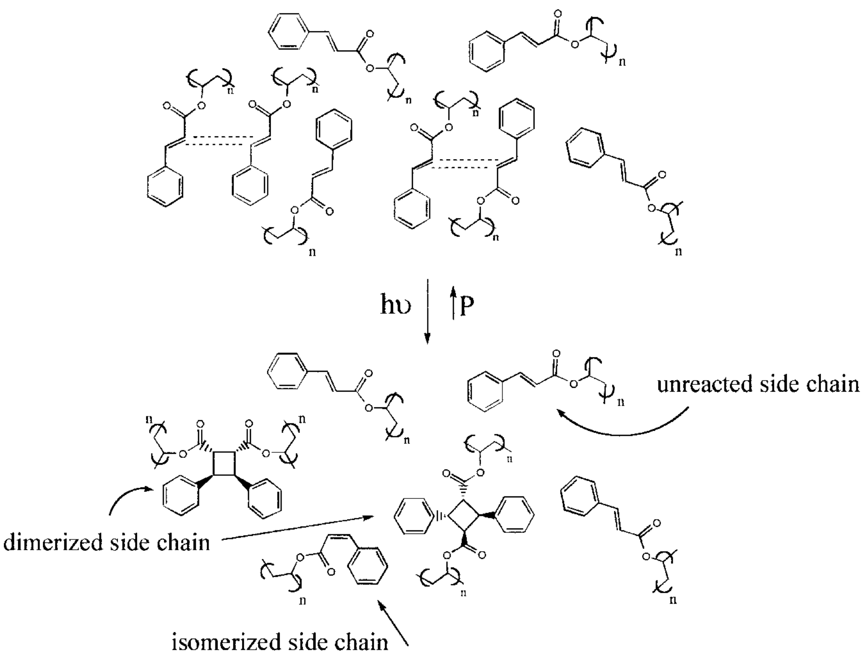
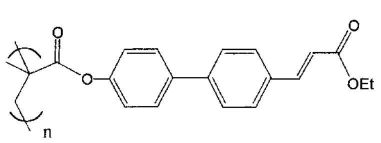


Scheme 1. Polarized light induced changes of a PVCi film surface.

Our goal was to design new cinnamate-based polymers which would be able to induce a tilted alignment determined by one oblique polarized irradiation. For this purpose, the liquid crystals had to be aligned by the dimers preferentially formed along the axis of polarization so that oblique irradiation could induce a tilted easy axis. This result was not likely to be achieved as long a cycloaddition caused an angular reorientation of the molecular axes of the dimers in the direction perpendicular to **P**. Moreover, it seemed necessary to include in the polymer side groups a mesogenic part having a strong affinity with liquid crystals so as to induce stronger anchoring energies.

The structure shown in scheme 2 appears to meet these requirements. The biphenyl moiety resembling the mesogenic core of many liquid crystal materials should generate stronger anchoring energies and higher glass transition temperature (T_g) than PVCi. In addition, exporting the photosensitive double bond to the end of the side group, would prevent rotation of the mesogenic part of the chromophore, blocked by the polymer skeleton as outlined in scheme 3. This point is in agreement with the structure of the coumarine-based photopolymers recently proposed by Schadt *et al.* [8].



Scheme 2. Model compound: poly[ethyl 4-(4-methacryloyloxyphenyl)cinnamate] (Para).

Based on this model three other polymers were synthesized, namely poly[ethyl 3-(4-methacryloyloxyphenyl)cinnamate] (Meta), poly[ethyl 3-(4-methacryloyloxyphenyl)-4-methoxycinnamate] (Metamet) and poly[6-(2-ethoxycarbonylvinyl)-2-methacryloyloxy naphthalene] (Napht). The latter was designed following the same principle but its structure is in this case based on naphthalene (scheme 4).

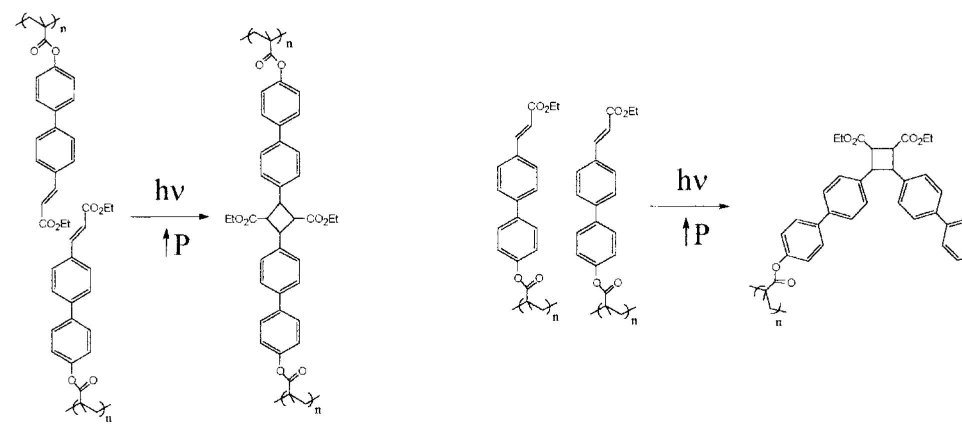
2. Experimental

2.1. *Synthesis of monomers*

2.1.1. *Biphenyl derivatives*

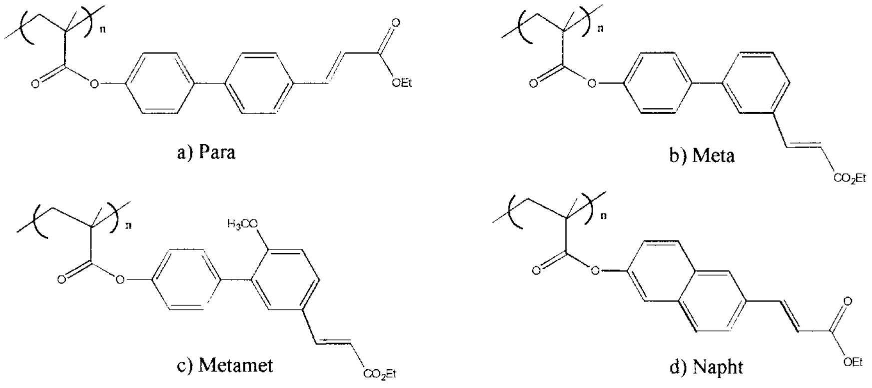
Ethyl methacryloyloxyphenylcinnamates can readily be prepared from the appropriate ethyl hydroxyphenylcinnamates which are commonly obtained from the corresponding hydroxyphenylbenzaldehydes (scheme 5).

The construction of bifunctional biphenyls is more delicate. Although many synthetic routes have been proposed to make biaryls, the palladium-catalysed cross-coupling reaction between aryls seems to be one of the most effective [9]. In a typical Stille biaryl coupling, an aryl electrophile is reacted with a convenient arylstannane in the presence of palladium. This reaction tolerates certain reactive functional substituents such as carbonyl groups, but the phenolic group needs to be protected. The arylstannane is usually obtained from the corresponding bromoaromatic either via the formation of Grignard or organolithium derivatives or directly with hexabutyldistannane and tetrakis(triphenylphosphine)palladium. This last method accepts a wide variety of substituents, but generally leads to a poor yield and substantial



a) Head to tail cycloaddition b) Head to head cycloaddition

Scheme 3. Conformations of dimers of the model compound.



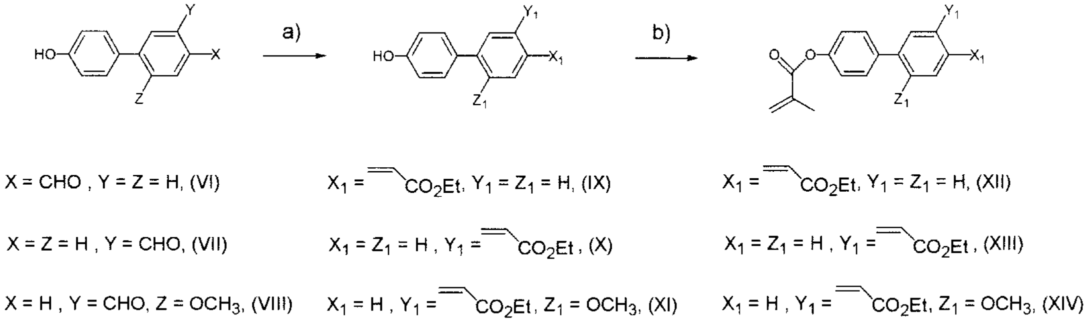
a) Para

b) Meta

c) Metamet

d) Napht

Scheme 4. Structures of the photopolymers synthesized.

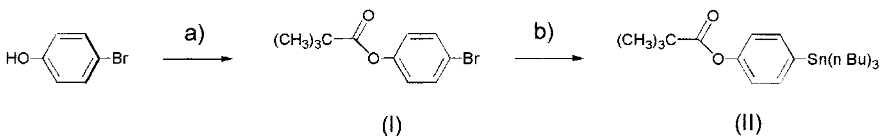


Scheme 5. Method of preparation of the ethyl methacryloyloxyphenylcinnamates; (a) $HO_2CCH_2CO_2Et$, piperidine, pyridine (b) methacryloyl chloride, pyridine.

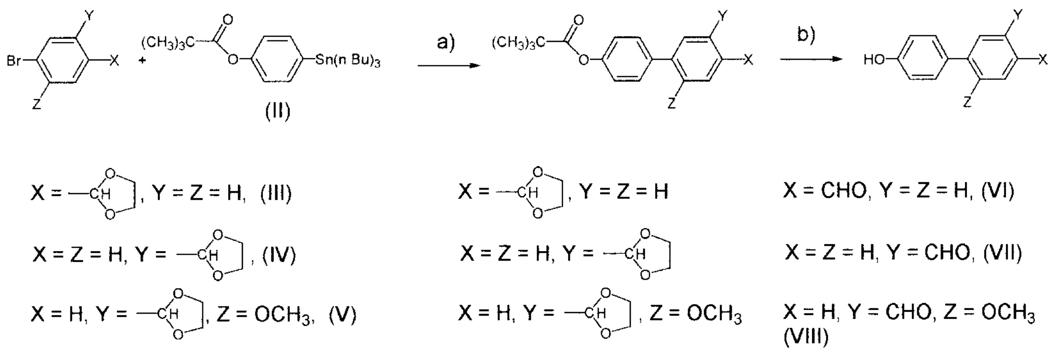
amounts of the diaryl are formed [10]. For this reason, the route involving the Grignard reagent was preferred and led us to choose trimethylacetate (pivaloate) as the protective group for the phenolic derivative: the trimethylacetate group is compatible with the biaryl coupling as well as Grignard reagents (scheme 6).

In addition, ethylene glycol was used for the protection of the carbonyl group in anticipation of the removal in basic medium of the trimethylacetate group. The general method is shown in scheme 7.

2.1.1.1. *4-Bromophenyl pivaloate (I)*. This was prepared by a conventional procedure from 4-bromophenol (Aldrich) and pivaloyl chloride in pyridine to give a white solid (yield 96%). ^1H NMR ($CDCl_3$) δ: 7.5–6.95 ppm



Scheme 6. Method of preparation of 4-tributylstannylphenyl pivaloate: (a) pivaloyl chloride, pyridine (b) Mg, ClSn(n Bu)$_3$, THF.



Scheme 7. Method of preparation of 4-hydroxyphenylbenzaldehydes (a) Pd(PPh$_3$)$_4$, dioxane, 100°C (b) (i) THF/KOH; (ii) H_3O^+.

(2d, 4H, $-C_6H_4-$), 1.47 ppm (s, 9H, $-C(CH_3)_3$). IR ν: 1752 cm^{-1} (C=O), 1485 cm^{-1} (phenyl), 1065 cm^{-1} (Ar–Br).

2.1.1.2. *4-Tributylstannylphenyl pivaloate (**II**).* A solution of 4-bromophenyl pivaloate (24.2 g) in anhydrous tetrahydrofuran (50 ml) was added dropwise to a mixture of tributyltin chloride (31 g) and magnesium (2.5 g) in anhydrous tetrahydrofuran (10 ml) under nitrogen. The solution was stirred at room temperature for 1 h and then overnight at 40°C. The mixture was poured into 3% HCl (100 ml) and three times extracted with light petroleum (100 ml). The combined organic layers were washed successively with 3% HCl (100 ml), saturated aqueous sodium hydrogen carbonate (100 ml) and brine (100 ml). The organic layer was finally dried ($MgSO_4$) and the solvents removed to give a light yellow liquid which was used without further purification (yield 90%). ^{1}H NMR ($CDCl_3$) δ: 7.45–7.02 ppm (2d, 4H, $-C_6H_4-$), 1.5–0.8 ppm (4m, 27H, $-(C_4H_9)_3$). IR ν: 2930 cm^{-1} (C–H), 1756 cm^{-1} (C=O), 1485 cm^{-1} (phenyl).

2.1.1.3. *4-Bromophenyl-1,3-dioxolane (**III**).* This was prepared by a conventional procedure from 4-bromobenzaldehyde and ethylene glycol as described in [11] to give a white solid (yield 88%). ^{1}H NMR ($CDCl_3$) δ: 7.51–7.35 ppm (2d, 4H, $-C_6H_4-$), 5.77 ppm (s, 1H, –OCHO–), 4.2–3.9 ppm (m, 4H, $-OCH_2CH_2O-$).

2.1.1.4. *3-Bromophenyl-1,3-dioxolane (**IV**).* This was prepared by using a similar method to that above (from 3-bromobenzaldehyde) to give a colourless liquid (yield 89%). ^{1}H NMR ($CDCl_3$) δ: 7.64 ppm (s, 1H, $-C_6H_4-$), 7.50–7.40–7.26 ppm (3d, $J = 7.7$ Hz, 3H, $-C_6H_4-$), 5.75 ppm (s, 1H, –OCHO–), 4.2–3.9 ppm (m, 4H, $-OCH_2CH_2O-$).

2.1.1.5. *3-Bromo-4-methoxyphenyl-1,3-dioxolane (**V**).* This was prepared by using a similar method to that above (from 3-bromo-4-methoxybenzaldehyde) to give a colourless liquid (yield 90%). ^{1}H NMR ($CDCl_3$) δ: 7.66 ppm (s, 1H, $-C_6H_3-$), 7.39–6.89 ppm (2d, 2H, $-C_6H_3-$), 5.78 ppm (s, 1H, –OCHO–), 4.2–3.9 ppm (m, 4H, $-OCH_2CH_2O-$), 3.9 ppm (s, 3H, $-OCH_3$). IR ν: 3000–2800 cm^{-1} (C–H), 1607 cm^{-1} (–OCO–).

2.1.1.6. *4-(4-Hydroxyphenyl)benzaldehyde (**VI**).* Compound **III** (0.12 mol) and tetrakis(triphenylphosphine)-palladium (2% mol) were dissolved in 300 ml of degassed anhydrous dioxane. Compound **II** (0.1 mol) was then added neat and the mixture was stirred and kept for 72 h at 100°C under nitrogen. The solvent was removed and the crude mixture dissolved in tetrahydrofuran and poured into aqueous potassium hydroxide (50%, 100 ml). The two phase mixture was heated under reflux with vigorous stirring for 72 h. HCl (33%) was then added dropwise while stirring until a clear mixture formed which was shaken with dichloromethane. The organic phase was washed with brine and dried ($MgSO_4$). After removal of solvent, the viscous liquid was treated with heptane to give a white solid which was crystallized from cyclohexane (yield 44%). ^{1}H NMR ($CDCl_3$) δ: 10.2 ppm (s, 1H, –CHO), 7.97–7.80–7.62–7.0 (4d, 8H, $-C_6H_4-C_6H_4$). IR ν: 3385 cm^{-1} (O–H), 1711 cm^{-1} (C=O).

The following compounds were prepared using a similar procedure to that described for compound **VI**.

2.1.1.7. *3-(4-Hydroxyphenyl)benzaldehyde (VII).* This was prepared from compounds **II** and **IV**, giving a white solid (yield 41%). ^{1}H NMR ($CDCl_3$) δ: 10.06 ppm (s, 1H, $-CHO$), 8.1 ppm (s, 1H, $-C_6H_4-$), 7.92–7.80–7.64 ppm (3d, $J = 7.6$ Hz, 3H, $-C_6H_4-$), 7.57–6.88 ppm (2d, $J = 8.6$ Hz, 4H, $-C_6H_4$).

2.1.1.8. *3-(4-Hydroxyphenyl)-4-methoxybenzaldehyde (VIII).* This was prepared from compounds **II** and **V**, giving a white solid (yield 45%). ^{1}H NMR ($CDCl_3$) δ: 9.92 ppm (s, 1H, $-CHO$), 7.83 ppm (s, 1H, $-C_6H_3-$), 7.42–6.90 ppm (2d, $J = 7.6$ Hz, 3H, $-C_6H_3-$), 3.91 ppm (s, 3H, $-OCH_3$). IR ν: 3240 cm^{-1} (O–H), 1660 cm^{-1} (C=O).

Ethyl hydroxyphenylcinnamates. The hydroxyphenylbenzaldehydes (0.02 mol) were dissolved in anhydrous pyridine (10 ml) with the monoethyl ester of malonic acid (0.045 mol) and a few drops of piperidine. The solution was kept for 48 h at room temperature under stirring in subdued light. A few pieces of porous pot were added and the mixture was heated to 40°C for 24 additional hours. The subsequent work-up was adapted for each compound.

2.1.1.9. *Ethyl 4-(4-hydroxyphenyl)cinnamate (IX).* This was prepared from compound **VI**, and was then precipitated in 3% HCl (300 ml), filtered and crystallized from methanol to give a white solid (yield 77%). ^{1}H NMR ($CDCl_3$) δ: 7.71 ppm (d, $J = 16$ Hz, 1H, $Ar-C\underline{H}=CH-$), 7.56 ppm (s, 4H, $-C_6H_4-$), 7.50/6.92 (2d, $J = 8.6$ Hz, 4H, $-C_6H_4-$), 6.46 ppm (d, $J = 16$ Hz, 1H, $Ar-CH=C\underline{H}-$), 4.28 ppm (q, 2H, $-OCH_2-$), 1.35 ppm (t, 3H, $-CH_3$). IR ν: 3491 cm^{-1} (O–H), 1692 cm^{-1} (C=O), 1633 cm^{-1} (C=C).

2.1.1.10. *Ethyl 3-(4-hydroxyphenyl)cinnamate (X).* This was prepared from compound **VII** and was then poured into 3% HCl (300 ml). The insoluble material was dissolved in dichloromethane, and the solution filtered through silica which was washed twice with dichloromethane. The combined organic layers were dried ($MgSO_4$) and the solvent removed. The resulting residue was finally treated with light petroleum to give a white solid (yield 62.8%). ^{1}H NMR ($CDCl_3$) δ: 7.76 ppm (d, $J = 15.9$ Hz, 1H, $Ar-C\underline{H}=CH-$), 7.47 ppm (s, 1H, $-C_6H_3-$), 7.40–6.89 ppm (2d, $J = 8.6$ Hz, 4H, $-C_6H_4-$), 7.43–6.96 ppm (2d, 2H, $-C_6H_3-$), 6.50 ppm (d, $J = 15.9$ Hz, 1H, $Ar-CH=C\underline{H}-$), 4.28 ppm (q, 2H, $-OCH_2-$), 1.35 ppm (t, 3H, $-CH_3$). IR ν: 3322 cm^{-1} (O–H), 1683 cm^{-1} (C=O), 1637 cm^{-1} (C=C).

2.1.1.11. *Ethyl 3-(4-Hydroxyphenyl)-4-methoxycinnamate (XI).* This was prepared from compound **VIII**, and was obtained as described above for compound **X**. A white solid (yield 55%) was obtained. ^{1}H NMR ($CDCl_3$) δ: 7.67 ppm (d, $J = 16$ Hz, 1H, $Ar-C\underline{H}=CH-$), 7.55 ppm (s, 1H, $-C_6H_4-$), 7.48–6.93 ppm (2d, $J = 8.5$ Hz, 4H, $-C_6H_4-$), 7.53–7.49–7.45 ppm (3d, $J = 7.5$ Hz, 3H, $-C_6H_4-$), 6.50 ppm (d, $J = 16$ Hz, 1H, $Ar-CH=C\underline{H}-$), 4.28 ppm (q, 2H, $-OCH_2-$), 1.35 ppm (t, 3H, $-CH_3$). IR ν: 3349 cm^{-1} (O–H), 1677 cm^{-1} (C=O), 1625 cm^{-1} (C=C).

Ethyl methacryloyloxyphenylcinnamates were prepared by a conventional procedure from the appropriate ethyl hydroxyphenylcinnamate and methacryloyl chloride in pyridine. The following compounds were prepared by using the same procedure.

2.1.1.12. *Ethyl 4-(4-methacryloyloxyphenyl)cinnamate (XII).* This was made from compound **IX**. A white solid was obtained after purification by column chromatography (SiO_2, dichloromethane) and crystallization from cold methanol (yield 59.3%). ^{1}H NMR ($CDCl_3$) δ: 7.72 ppm (d, $J = 16$ Hz, 1H, $Ar-C\underline{H}=CH-$), 7.62 ppm (s, 4H, $-C_6H_4-$), 7.62–7.21 (2d, $J = 8.6$ Hz, 4H, $-C_6H_4-$), 6.47 ppm (d, $J = 16$ Hz, 1H, $Ar-CH=C\underline{H}-$), 6.38 ppm (s, 1H, $C\underline{H_2}=C(CH_3)-$), 5.78 ppm (s, 1H, $C\underline{H_2}=C(CH_3)-$), 4.28 ppm (q, 2H, $-OC\underline{H_2}-CH_3$), 2.08 ppm (s, 3H, $CH_2=C(C\underline{H_3})-$), 1.35 ppm (t, 3H, $O-CH_2-C\underline{H_3}$). IR ν: 1735 cm^{-1} (unconjugated C=O), 1712 cm^{-1} (conjugated C=O), 1636 cm^{-1} (C=C).

2.1.1.13. *Ethyl 3-(4-methacryloyloxyphenyl)cinnamate (XIII).* This was made from compound **X**. A white solid was obtained after successive crystallizations from cold methanol (yield 26.6%). ^{1}H NMR ($CDCl_3$) δ: 7.75 ppm (d, $J = 16$ Hz, 1H, $Ar-C\underline{H}=CH-$), 7.6–6.9 ppm (m, 8H, $-C_6H_4-C_6H_4-$), 6.47 ppm (d, $J = 16$ Hz, 1H, $Ar-CH=C\underline{H}-$), 6.39 ppm (s, 1H, $C\underline{H_2}=C(CH_3)-$), 5.78 ppm (s, 1H, $C\underline{H_2}=C(CH_3)-$), 4.28 ppm (q, 2H, $-OC\underline{H_2}-CH_3$), 2.08 ppm (s, 3H, $CH_2=C(C\underline{H_3})-$), 1.35 ppm (t, 3H, $O-CH_2-C\underline{H_3}$). IR ν: 1735 cm^{-1} (unconjugated C=O), 1698 cm^{-1} (conjugated C=O), 1636 cm^{-1} (C=C).

2.1.1.14. *Ethyl 3-(4-methacryloyloxyphenyl)-4-methoxycinnamate (XIV).* This was made from compound **XI**. A white solid was obtained after successive crystallizations from cold methanol (yield 39%). ^{1}H NMR ($CDCl_3$) δ: 7.68 ppm (d, $J = 16$ Hz, 1H, $Ar-C\underline{H}=CH-$), 7.6–6.9 ppm (m, 7H, $-C_6H_4-C_6H_3-$), 6.38 ppm (s, 1H, $C\underline{H_2}=C(CH_3)-$), 6.35 ppm (d, $J = 16$ Hz, 1H, $Ar-CH=C\underline{H}-$), 5.78 ppm (s, 1H, $C\underline{H_2}=C(CH_3)-$), 4.28 ppm (q, 2H, $-OC\underline{H_2}-CH_3$), 3.86 ppm (s, 3H, $-OCH_3$), 2.08 ppm (s, 3H, $CH_2=C(C\underline{H_3})-$), 1.35 ppm (t, 3H, $OCH_2-C\underline{H_3}$). IR ν: 1749 cm^{-1}

(unconjugated C=O), 1706 cm^{-1} (conjugated C=O), 1633 cm^{-1} (C=C).

2.1.2. *Naphthalene derivatives*

2.1.2.1. *2-t-Butyldimethylsilyloxy-6-bromonaphthalene (XV)*. This was prepared by a conventional procedure described in [12] from 6-bromo-2-naphthol (Aldrich) and *tert*-butyldimethylsilyl chloride (Aldrich) in DMF. The crude product was purified by column chromatography (SiO_2, light petroleum) to give a white solid (yield 88%). ^1H NMR ($CDCl_3$) δ: 7.91–7.15 ppm (2s, 2H, -naphthyl-), 7.62–7.55 ppm (2d, 2H, -naphthyl-), 7.48–7.10 ppm (2dd, 2H, -naphthyl-), 1.02 ppm (s, 9H, $-C(CH_3)_3$), 0.25 ppm (s, 6H, $-Si(CH_3)_2$). IR ν: 3050–2710 cm^{-1} (C–H), 1270 cm^{-1} (Si–O).

2.1.2.2. *6-t-Butyldimethylsilyloxy-2-naphthaldehyde (XVI)*. This was prepared according to a method described in [13]. Compound **XV** (0.07 mol) was dissolved in dry tetrahydrofuran (350 ml) and cooled to − 80°C under nitrogen. Butyl lithium in hexane (1.6M, 0.14 mol) was added dropwise with stirring over 2 h. Finally, dry dimethylformamide (0.28 mol) was slowly added with stirring and the mixture was allowed to warm to room temperature. The solution was then poured into 3% HCl (300 ml) and shaken three times with light petroleum (100 ml). The combined organic layers were washed with 3% HCl, brine, dried ($MgSO_4$) and the solvents removed. The crude product was purified by column chromatography (SiO_2, dichloromethane/light petroleum 50/50 v/v) to give a colourless viscous liquid (yield 47%). ^1H NMR ($CDCl_3$) δ: 10.10 ppm (s, 1H, −CHO), 8.26 ppm (1s, H, -naphthyl-), 7.92–7.79–7.18 (3d, 5H, -naphthyl-), 1.05 ppm (s, 9H, $-C(CH_3)_3$), 0.3 ppm (s, 6H, $-Si(CH_3)_2$). IR ν: 3050–2710 cm^{-1} (C–H), 1694 cm^{-1} (C=O), 1270 cm^{-1} (Si–O).

2.1.2.3. *6-Hydroxy-2-naphthaldehyde (XVII)*. This was obtained by cleavage of the *t*-butyldimethylsilylether of compound **XVI**. Compound **XVI** (0.04 mol) was dissolved in tetrahydrofuran (150 ml) and tetrabutylammonium fluoride (0.08 mol) was added. The solution was stirred for 1 h at room temperature. It was then poured into water and shaken with chloroform. The organic layers were washed several times with small portions of water, brine and dried ($MgSO_4$). After removal of solvents, the crude product in chloroform was filtered through silica which was washed twice with chloroform. The organic layers were combined and the solvent removed. Finally, the solid was washed with light petroleum and crystallized from cyclohexane to give a white solid (yield 90%). ^1H NMR ($CDCl_3$) δ: 10.10 ppm (s, 1H, −CHO), 8.26 ppm (1s, H, -naphthyl-), 7.92–7.75–7.21 (3d, 5H, -naphthyl-). IR ν: 3234 cm^{-1} (O–H), 1667 cm^{-1} (C=O).

2.1.2.4. *6-(2-Ethoxycarbonylvinyl)-2-naphthol (XVIII)*. This was prepared by using the same procedure as for compounds **IX** and **X** and a white solid was obtained in 79% yield. ^1H NMR ($CDCl_3$) δ: 7.82 ppm (d, $J = 16$ Hz, 1H, naphthyl–C$\underline{H}$=CH–), 7.84–7.15 (2s, 3H, -naphthyl-), 7.76–7.64 (2d, 3H, -naphthyl-), 6.50 ppm (d, $J = 16$ Hz, 1H, naphthyl–CH=C$\underline{H}$–), 4.30 ppm (q, 2H, $-OCH_2-$), 1.36 ppm (t, 3H, $-CH_3$). IR ν: 3450 cm^{-1} (O–H), 1707 cm^{-1} (C=O), 1687 cm^{-1} (C=O), 1623 cm^{-1} (C=C).

2.1.2.5. *6-(2-Ethoxycarbonylvinyl)-2-methacryloyloxynaphthalene (XIX)*. This was prepared by using the same procedure as for compounds **XIII** and **XIV**; a white solid was obtained in 39% yield. ^1H NMR ($CDCl_3$) δ: 7.82 ppm (d, $J = 16$ Hz, 1H, naphthyl–C$\underline{H}$=CH–), 7.84–7.15 (m, 6H, -naphthyl-), 6.50 ppm (d, $J = 16$ Hz, 1H, naphthyl–CH=C$\underline{H}$–), 6.39 ppm (s, 1H, $C\underline{H}_2=C(CH_3)-$), 5.78 ppm (s, 1H, $C\underline{H}_2=C(CH_3)-$), 4.30 ppm (q, 2H, $-OCH_2-$), 2.08 ppm (s, 3H, $CH_2=C(C\underline{H}_3)-$), 1.35 ppm (t, 3H, $O-CH_2-C\underline{H}_3$). IR: ν: 1728 cm^{-1} (unconjugated C=O), 1702 cm^{-1} (conjugated C=O), 1634 cm^{-1} (C=C).

2.2. *Synthesis of polymers*

Polymers were prepared by radical polymerization of the appropriate monomer in the presence of 2,2′-azobisisobutyronitrile (AIBN). A solution of the monomer (1.0 g) and AIBN (1% by wt) in dry degassed toluene (10 ml) was stirred for 24 h at 60°C under vacuum. The polymer was precipitated into methanol (500 ml) and filtered off. This operation was repeated twice. The polymer was then filtered and dried under vacuum.

2.2.1. *Poly[ethyl 4-(4-methacryloyloxyphenyl)cinnamate]*

$T_g = 200°C$. IR ν: 1751 cm^{-1} (unconjugated C=O), 1712 cm^{-1} (conjugated C=O), 1636 cm^{-1} (C=C), 1605 cm^{-1} (phenyl). λmax: 304 nm; ε: 32 500 l mol^{-1} cm^{-1}.

2.2.2. *Poly[ethyl 3-(4-methacryloyloxyphenyl)cinnamate]*

$T_g = 120°C$. IR ν: 1750 cm^{-1} (unconjugated C=O), 1710 cm^{-1} (conjugated C=O), 1639 cm^{-1} (C=C), 1606 cm^{-1} (phenyl). λmax: 258 nm; ε: 16 000 l mol^{-1} cm^{-1}, shoulder at around 290 nm.

2.2.3. *Poly[ethyl 3-(4-methacryloyloxyphenyl)-4-methoxycinnamate]*

$T_g = 100°C$. IR ν: 1749 cm^{-1} (unconjugated C=O), 1706 cm^{-1} (conjugated C=O), 1633 cm^{-1} (C=C), 1601 cm^{-1} (phenyl). λmax_1: 302 nm; ε_1: 18 800 l mol^{-1} cm^{-1}; λmax_2: 261 nm; ε_2: 22 600 l mol^{-1} cm^{-1}, shoulder at around 320 nm.

Table 1. Nematic liquid crystal materials.

Name	$T_{N\rightarrow I}$/°C	$\Delta\varepsilon$	Δn	Remarks
5CB	35.3	11	0.184	(4-Pentyl-4′-cyanobiphenyl)
ZLI 3086	72	0.1	0.113	Low polarity
ZLI 4792	92	5.2	0.097	Fluorinated terminal groups, medium polarity
ZLI 1132	71	12.9	0.141	Nitrile terminal groups, high polarity

2.2.4. *Poly[6-(2-ethoxycarbonylvinyl)-2-methacryloyloxynaphthalene]*

$T_{N\rightarrow I}$: 200°C, the T_g could not be measured. IR ν: 1749 cm^{-1} (unconjugated C=O), 1710 cm^{-1} (conjugated C=O), 1628 cm^{-1} (C=C). λmax_1: 304 nm; ε_1: 22 700 l mol^{-1} cm^{-1}; λmax_2: 271 nm; ε_2: 33 500 l mol^{-1} cm^{-1}; λmax_3: 262 nm; ε_3: 35 100 l mol^{-1} cm^{-1}.

2.3. *Liquid crystal alignment properties: sample preparation*

The polymers were deposited onto glass substrates by spin coating with a 2 wt % solution in 1,1,2-trichloroethane. The films were dried at 120°C for 2 h under vacuum. Irradiation of the polymers was performed by exposing the films to linearly polarized UV light at 300 nm. A metal halide lamp in series with an Oriel UV visible sheet polarizer and a 300 nm interferential filter provided 0.25 mW cm^{-2} light intensity at 300 nm. The film thickness was about 100 nm.

Liquid crystals cells were constructed by sandwiching a liquid crystal mixture between two photopolymer coated glass substrates. The thickness was set by 10 µm thick mylar spacers. The cells were then sealed in a plastic bag under vacuum so as to prevent the glue from entering the cell by capillarity while the polymerization of the glue proceeded. The final thickness of the cells was around 12 µm.

The cells were filled with different commercial nematic liquid crystal materials or mixtures 5CB, ZLI 4792, ZLI 3086 or ZLI 1132 (E. Merck, table 1) at a temperature at which the material was in the nematic state.

The direction of the preferential alignment of the liquid crystals was determined using an optical compensator. Tilt angles were measured by using the crystal rotation method [14]. The azimuthal anchoring energies were measured by the method developed by Dozov and Polossat [15].

3. Results and discussion

3.1. *Liquid crystal alignment*

We made antiparallel cells for characterization of the alignment properties of the synthesized photopolymers. The homogeneity of the texture was studied by polarized microscopy as a function of the irradiation time. The results are reported in table 2.

Table 2. Polymers' photoalignment properties.

Polymer	Irradiation time	Flow direction[a]	Alignment direction[a]	Quality[b]
Para	2 min	⊥	⊥	1
	15 min	⊥	⊥	1
	2 h	∥	⊥	1
		⊥	⊥	2
	16 h	⊥	⊥	2
Meta	2 min	∥	∥	1
	15 min			1
	2 h	⊥		0
		∥	∥	1
	16 h			1
Metamet	2 min	∥		0
	15 min		∥	1
	2 h	⊥		1
		∥		2
	16 h			2
Napht	2 min	∥	∥	1
	15 min			1
	2 h	⊥		0
		∥	∥	1
	16 h			1

[a] Relative to the direction of polarization.

[b] 0 is for randomly aligned liquid crystals, 1 is for disturbed by flow alignment, 2 is for homogeneous alignment.

All polymers induced a preferential alignment direction once irradiated with polarized UV light. The homogeneity of the texture was improved when the UV exposure time was prolonged. No alterations of the textures were noticed for exposures as long as 16 h. The optimum irradiation time and alignment direction depended on the polymer.

Meta, Metamet and Napht gave an orientation of the liquid crystals in the direction of polarization, whereas Para aligned the liquid crystals perpendicularly like PVCi derivatives. This must mean that in the case of Para no preferential alignment is due to dimers. Of all the polymers, Metamet induced the most homogeneous alignment with no perturbation provoked by the flow of the liquid crystals in the nematic phase. On the contrary, Meta showed rather poor alignment properties irrespective of the irradiation conditions. These results will be discussed in detail elsewhere [16].

3.2. *Azimuthal anchoring energy*

To characterize the anchoring energy of our photopolymers, we studied the azimuthal anchoring energy. We used a measurement technique described elsewhere [15]. The principle is to create a mechanical torque in a thin twisted cell, made up by the substrate and a counterplate with strong planar anchoring (a lens of known curvature). The cell thickness varies from 0 at the contact point up to 30 µm, and we measured the deviation of the nematic director as a function of the thickness.

In the Rapini–Papoular approximation, one obtains:

$$\frac{K_{22}}{d}(\varphi_{\mathrm{twist}} - \varphi_{\mathrm{S}}) = \frac{W_{\mathrm{a}}}{2}\sin(2\varphi_{\mathrm{S}})$$

where K_{22} = twist elastic constant, d = cell thickness, φ_{twist} = twist angle of the thick cell, φ_{S} = liquid crystal director deviation in the sample, and W_{a} = azimuthal anchoring energy.

The results for the azimuthal anchoring energy are presented in table 3.

The cells used for anchoring energy measurements were filled in the isotropic phase so as to reduce flow-induced alignment. In these conditions, the alignment is expected to be due only to the interactions between the liquid crystal and the anisotropic photopolymer film. On the contrary, the cells made for the alignment characterization were filled in the nematic phase. In this case, the orientation of the liquid crystal is due both to elastic interactions with the anisotropic polymer and to memorized flow alignment. Due to the orientational memory on the surface of the polymer, one can easily understand that the final alignment strongly depends on the filling temperature. Consequently, it is hardly possible to link the quality of the texture of our cells, influenced by the memory, to the memory independent values of the azimuthal anchoring energy.

From a qualitative point of view, it is interesting to note that the liquid crystal director does not return exactly to its original position when the bulk torsion is removed. In other words, the deviation is not purely elastic and is influenced by surface memory effects. This easy axis reorientation under applied torque (anchoring gliding), has been already observed for other photoaligned layers [17].

Nevertheless, one can remark that, as expected, our photopolymers induced a higher anchoring energy than PVCi. Moreover, it is important to notice that Metamet induced a higher anchoring energy than SiO_x. This confirms that photopolymers can generate strong anchoring.

Table 3. Anchoring energy of 5CB on the photopolymers at 22–23°C.

Polymer	Irradiation time/h	Anchoring energy/J m^{-2}
PVCi	2	2.5×10^{-6}
Meta	16	3.2×10^{-6}
Para	2	9.2×10^{-6}
Metamet	2	$> \mathrm{SiO}_x$

3.3. *Tilt angle*

To induce a tilted alignment, we exposed our photopolymers to oblique polarized UV light. The angle of incidence was either 10°, 30° or 50° relative to the normal of the cell. The chosen irradiation time was always higher than 1 h, where most cells were homogeneous. The cells were filled with various liquid crystals from highly polar to non-polar. Whatever the polymer, the irradiation conditions and the liquid crystal, no significant tilt angle was measured.

For our photopolymers, this result could mean that the geometry of the dimers formed during oblique UV irradiation is not suitable to induce a pretilt angle. Actually, most authors who have reported a significant tilt angle with photopolymer-based cells used fluorinated [18–20] or alkyl branched [21] chromophores. For example, by using poly(vinylfluorocinnamate) (PVFCi), Dyaduysha *et al.* obtained a tilt angle as high as 8°. For these experiments, they had to make hybrid cells (one substrate coated with rubbed polyimide, and one substrate coated with irradiated PVFCi) so as to avoid flow-induced degeneracy of the tilt angle on their ‘soft’ substrates [18]. In this case, the need for a conventional alignment layer strongly reduces the alignment patterning. Significant tilt angles with two photopolymer films were obtained by Grüneberg *et al.* [22] and Schadt *et al.* [8]. Grüneberg grafted cinnamate moieties onto a self-assembled silane layer. This method gave tilt angles from 0.5° to 3.5° when cinnamates were substituted with long alkoxy chains ($-\mathrm{OC}_4\mathrm{H}_9 \rightarrow -\mathrm{OC}_{10}\mathrm{H}_{21}$). Nevertheless, the process seems to be hardly suitable for industrial applications. Schadt *et al.* were able to achieve any desired tilt angle by oblique irradiation of coumarin-based polymers, but no detailed descriptions of the chemical structures responsible for the pretilts were reported.

In our study, degeneracy of the tilt angle is not likely, at least as far as Metamet is concerned, because of the measured azimuthal anchoring energy. On the contrary, the absence of fluorinated or hindered alkyl (alkoxy) groups may be responsible for the 0° tilt angle obtained. These substituents also appear in polyimides which induce high tilt angles [23, 24], and they may be of interest for further improvement of photopolymer alignment properties.

3.4. *Stability of the photoalignment*

The stability of the liquid crystal alignment on the photopolymers synthesized was evaluated. Irradiation time as well as liquid crystal were varied to check their influence on ageing. Moreover, rubbed and hybrid cells (one substrate coated with rubbed photopolymer, one with untreated photopolymer) were made in order to determine the influence of the polymer treatment. The results are reported in table 4. Times indicate the delay before the appearance of the observed defects.

The results can be summarized as follows. We noticed two processes of degeneracy. The first one involved the appearance of randomly aligned microdomains which increased slowly in size. It occurred with rubbed photopolymers and irradiated Metamet; thus the surface anisotropy was not stable. The second was due to the appearance of thin lines which grew at the interface between liquid crystal and the alignment layer of irradiated Meta, Napht and Para. The longer the polymers were exposed to UV light the more stable the alignment. Finally, the stability depended on the liquid crystal; ageing was faster when 5CB was used.

When carefully observed between crossed polarizers, the lines were identified as polymer splits. Besides, by profiling the behaviour of a drop of 5CB at the surface of Napht by ellipsometry, we were able to check that liquid crystals diffused into the film [25]. Consequently, the cracks are likely to be due to the diffusion of the liquid crystal molecules into the photopolymer. As crosslinking proceeds, the polymer films become stressed and brittle. When liquid crystals diffuse into this polymer matrix, capillarity forces are so huge that the polymers crack. On the contrary, if UV exposure is long enough, crosslinking increases polymer cohesion and slows down liquid crystal diffusion. In these conditions we expect a different behaviour of the liquid crystals, depending on their swelling properties. This explanation is in agreement with the fact that cracks are only observed with irradiated photopolymers and with the better stability of the longest irradiated films. In the case of Metamet, the diffusion of liquid crystals seems to be strongly reduced, but the alignment is not stable.

Little is said about ageing of the alignment induced by photopolymers, and the behaviour of our polymers may be very peculiar given their mesogenic structure. Nevertheless, the swelling effect of liquid crystals is a very common problem and partly justifies the use of alignment layers, such as polyimides, which hardly swell at all.

4. Conclusion

We prepared four new photocrosslinkable polymers for liquid crystal photoalignment. Parallel alignment along the direction of polarization of UV light was achieved by moving the photosensitive double bond to the end of the biphenyl-based side groups. Only one polymer showed a stronger anchoring than SiO_x but all of them gave stronger anchoring than PVCi. Whatever the irradiation conditions, the liquid crystal and the polymer used, no significant tilt angle was measured.

Table 4. Stability of the alignment induced by the photopolymers synthesized. The liquid crystal used is generally 5CB.

Polymer	Treatment	Stability	Observation
Metamet	UV exposure: 2 min → 16 h	3 months	Randomly aligned microdomains
Para	2 min exposure	few min	Lines
	15 min exposure	few h	
	2 h exposure	24 h	
	16 h exposure	> 1 month	
	2 h exposure ZLI 3086	1 month	
	Rubbed	> 1 month	Randomly aligned microdomains
	Rubbed + 2 h exposure	48 h	Lines
Meta	2 min exposure	few days	Lines
	15 min exposure	few weeks	
	2 h exposure	1 month	
	16 h exposure	> 3 month	
	2 h exposure ZLI 3086	> 1 month	Lines + randomly aligned microdomains
Napht	2 min exposure	few days	Lines
	15 min exposure	few days	
	2 h exposure	3 weeks	
	16 h exposure	> 1 month	
	2 h exposure ZLI 3086	1 month	
	Rubbed	> 1 month	Randomly aligned microdomains
	Rubbed + 2 h exposure	48 h	Lines
	Hybrid cell: 1 surface rubbed 1 surface untreated	> 1 month	Randomly aligned microdomains

Therefore no pretilt is induced with oblique polarized irradiation of the polymers synthesized. High tilt angles were obtained by other workers with coumarin-based side chains and fluorinated or hindered alkyl (alkoxy) branched side groups. These structures may be necessary to generate significant tilt angles when using photocrosslinkable polymers as alignment layers. Moreover, the alignments induced by our irradiated polymers were not stable for longer than three months because of swelling caused by the liquid crystals.

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