Highly birefringent polymer films from the photo-crosslinking polymerisation of bistolane-based methacrylate monomers

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The photo-polymerisation of mixtures of mono- and di-methacrylates, containing a bistolane moiety with a central fluorine-substituted benzene ring, resulted in the formation of highly birefringent polymer films (Δn = 0.40), which were obtained in a nematic liquid crystal (NLC) phase. While the dimethacrylate forms enantiotropic NLCs at T = 110–138°C, smectic phases at T = 50–138°C and crystallises at T = 50°C, whereas the monomethacrylate forms NLCs at a wider temperature range (T = 98–185°C) and crystallises at a lower temperature (T = 98°C). These methacrylates were infinitely miscible and a 20/80 (w/w) mixture of the dimethacrylate/monoacrylate was able to form an NLC phase over a broad temperature range (T = 73–179°C). The mixed NLC phase exhibited a Δn value of 0.36, even though the Δn values of the mono- and di-methacrylates were determined as 0.35 and 0.25, respectively, suggesting that the Δn of the mixture follows an additivity rule. Furthermore, the Δn of the NLC phase could be increased to 0.40 by photo-polymerisation.

Keywords: nematic phase; rod-like molecules; high birefringence film; photo-cross linking; order parameter

Introduction

Owing to their use in various optical applications such as cholesteric,[1–8] compensating,[9,10] and holographic films,[11–15] as well as polymer-stabilised blue phases,[16] liquid crystalline polymer (LCP) films have attracted considerable attention. For such applications, the employed materials are required to exhibit high birefringence (Δn) at ambient temperature. Columnic LCs, consisting of extended π-conjugated mesogens, for example, exhibit such high birefringence,[17–49] but unfortunately they tend to form thermotropic phases at high temperature, and crystallise at room temperature under the formation of domains that cause light scattering. The polymerisation of LC monomers can prevent such crystallisation, by generating an LC state at high temperature and a vitrification at room temperature. Previously, we reported that the side-chain LCPs with a dinaphthyl-acetylene mesogen exhibit higher Δn values than the corresponding monomeric LCs. The anisotropic alignment of the LCs increased upon polymerisation, ultimately resulting in higher Δn values for the LCP film relative to the monomer LC, and a maximum Δn value of 0.36 was observed for these LCP films at 550 nm.[50]

However, the photo-induced crosslinking of LC monomers is not only an effective method to prepare heat-resistant and highly birefringent films, but it is also able to freeze the assembly states (or alignments) of desirable LC phases. For example, Lub et al. reported highly birefringent polymer films containing bifunctional mesogenic monomers with an olefin and a thiol group.[51] While crosslinking can, similar to polymerisation, increase Δn, it is able to increase the glass transition temperature more efficiently than the polymerisation. Although many photo-crosslinked LC materials, including rod-like and discotic mesogens have been reported,[52–54] photo-crosslinked LCP films with high Δn values (i.e. Δn > 0.4) remain, to the best of our knowledge, undescribed. This scarcity may possibly be attributed to a disarrangement of such highly birefringent LCs due to phase separation or crystallisation during the photo-polymerisation. Moreover, highly birefringent nematic liquid crystals (NLCs) are usually viscous, tend to crystallise, and the polymeric NLCs are less miscible with the monomers.

In this article, we designed and synthesised novel mono- and bi-functionalist bistolane-based monomers with methacrylate groups, and used these as potentially crosslinkable highly birefringent monomers (Scheme 1). These molecules contain a fluorine-substituted central benzene ring, which is expected to broaden the nematic phase and increase the

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miscibility.\cite{55} In addition, mixtures of the two monomers were examined with respect to their birefringence and miscibility.

**Results and discussion**

The di- and mono-methacrylated bistolane-based monomers 1 and 2 were generated via Sonogashira cross-coupling reactions \cite{56,57} as outlined in Scheme 1, and characterised by $^1$H nuclear magnetic resonance (NMR) and high-resolution mass spectroscopy (HRMS) as shown in the ‘Experimental’ section. Representative $^1$H NMR spectra for monomers 1 and 2 are shown in Figures S1 and S2 (Supplemental data).

Monomers 1 and 2 exhibited enantiotropic mesophases. Phase transition temperatures were determined by differential scanning calorimetry (DSC) and the LC phase types were identified by polarised optical microscopy (POM). The results of these measurements are shown in Figures 1 and 2 and summarised in Table 1. The heating DSC thermogram of dimethacrylate monomer 1 (Figure 1(a)) showed one large endothermic peak at $T = 50^\circ C$, corresponding to the melting temperature ($T_m$), as well as two small endothermic peaks at $T = 110$ and $138^\circ C$, which were assigned to the smectic A–nematic (SmA–N) and nematic–isotropic (N–Iso, i.e. isotropisation temperature $T_i$) phase transitions, respectively. Even though the SmC–SmA phase transition could not be detected
by DSC, it was observed by POM. The N phase displayed a Schlieren texture at $T = 120^\circ$C (Figure 2(a)) and a homeotropic dark texture at $T = 95^\circ$C. The SmA phase exhibited a dark texture and the SmA–SmC transition could be detected by the appearance of Schlieren texture as shown in Figure 2(b) and (c). In addition, these phases showed fan-shaped or broken fan-shaped textures in a planar-aligned cell (see Figure S3; Supplemental data). Interestingly, heating monomethacrylated 2 from $T = 98^\circ$C to $T = 185^\circ$C resulted in the exclusive formation of an N phase (Figure 1(b)), which displayed a characteristic marble texture (Figure 2(d)). For both methacrylated monomers, the transition temperatures $T_m$ and $T_i$ were found to be dramatically decreased relative to their respective precursors 4a and 4b. DSC curves and POM images of precursors 4a and 4b are shown in Figures S4–S6 (Supplemental data).

Monomers 1 and 2 are infinitely miscible, and Figure 3 shows the POM-based phase diagram for the monomer mixtures upon heating at 5°C min$^{-1}$ (see the ‘Experimental’ section). The phase diagram upon cooling is shown in Figure S7 (Supplemental data). Therein, the Sm phase represents both SmA and SmC phases in order of decreasing temperature. $T_m$ values below 50°C could not be determined by POM, and are therefore not shown in the phase diagram. The observed phase transition temperatures were consistent with a well-defined additivity rule. Increasing the fraction of monomer 2 resulted in a decreased Sm–N transition temperature and an increased $T_i$, thus widening the N temperature range. An 20/80 w/w mixture of 1 and 2 formed an N phase over a temperature range of more than 100°C ($T = 73$–179°C).

Subsequently, the uniaxially aligned 20/80 w/w mixture of 1 and 2 was subjected to UV-induced ($\lambda_{\text{max}} = 365$ nm; 57.2 kJ m$^{-2}$) photo-polymerisation at $T_m + 10^\circ$C. A small quantity of hydroquinone (5 wt%) was added to the mixture in order to prevent any heat- and light-induced polymerisation of the methacrylates. Polarised optical micrographs of the UV-irradiated mixture obtained by rotating the crossed nicoles are shown in Figure 4. The high
contrast between the diagonal and extinction positions indicated that the alignments were fixed tenaciously. Similar results were also observed for a 30/70 w/w monomer mixture of 1 and 2, as well as for monomer 1. Even though UV-irradiated films of a 10/90 w/w monomer mixture of 1 and 2 as well as of monomer 2 exhibited lower contrast relative to other mixtures, these were still sufficiently aligned in order to enable a measurement of their birefringence. As the reactivity of monomethacrylated 2 is lower than that of dimethacrylated 1, its LC alignment could not be locked readily.

Figure 2. (colour online) Polarised optical micrographs of (a) Schlieren texture of the N phase of 1 at \( T = 120^\circ\text{C} \); (b) extinction of the homeotropic-aligned SmA phase of 1 at \( T = 95^\circ\text{C} \); (c) Schlieren texture of the SmC phase of 1 at \( T = 80^\circ\text{C} \); (d) marble texture of the N phase of 2 at \( T = 180^\circ\text{C} \).

Table 1. Phase transition temperatures (in °C) for 1, 2, 4a and 4b obtained from heating DSC thermograms (10°C min\(^{-1}\)).

| Sample | Cr | SmC | SmA | N   | I   |
|--------|----|-----|-----|-----|-----|
| 4a     | 173| 231 *|     |     |     |
| 1      | 50 | 95a | 110 | 138 |     |
| 4b     | 134| 235 |     |     |     |
| 2      | 98 | 185 |     |     |     |

Note: *Determined by POM.

Figure 3. POM-derived phase diagram for monomer mixtures of 1 and 2. Circles, triangles and squares represent the N-Iso, Sm-N and Cr-Iso transition, respectively.
Finally, \( \Delta n \) values were measured according to the previously reported procedures.\cite{58, 59} The measurements were unified at \( T_m + 10^\circ C \) for all the mixtures prior to polymerisation, and at room temperature for the polymer films. The \( \Delta n \) values observed for 1 or 2, as well as for 30/70, 20/80 and 10/90 w/w mixtures of 1 and 2 are summarised in Table 2. The concomitant increase of \( \Delta n \) with a proportional increase of 2, the \( \Delta n \) value of which is higher than that of 1, suggested an additive rule for the \( \Delta n \) values of the binary mixtures that had not been photo-irradiated. However, the 20/80 w/w mixture exhibited a \( \Delta n \) value of 0.36, which is higher than that of 2 (\( \Delta n = 0.35 \)). Moreover, the monomer mixture exhibited a wider temperature range for the N phase and formed an SmA phase at lower temperature (\( T = 73^\circ C \)), which should result in a higher N order of the mixture relative to monomer 2. Photo-crosslinking polymerisations of the mixture increased its \( \Delta n \) value to 0.40. Representative wavelength dispersion values of \( \Delta n \) for the mixture prior and posterior to photo-polymerisations are shown in Figure S8 (Supplemental data).

| 1:2 w/w | \( \Delta n \) (prior)\(^a\) | \( \Delta n \) (posterior)\(^b\) |
|---------|-----------------|-----------------|
| 100:0   | 0.25            | 0.27            |
| 30:70   | 0.32            | 0.36            |
| 20:80   | 0.36            | 0.40            |
| 10:90   | 0.37            | 0.37            |
| 0:100   | 0.35            | 0.36            |

Figure 4. (colour online) POM images from a uniaxially aligned cell of the 20/80 w/w monomer mixture of 1 and 2, which the rubbing directions are (a) 45° and (b) parallel to the polarisation directions, respectively.

### Table 2. \( \Delta n \) values for 1, 2 and mixtures thereof, prior and posterior to photo-polymerisation.

**Conclusion**

Bistolane-based mono- and di-methacrylate monomers 1 and 2, containing a fluorine-substituted central benzene ring, were synthesised and used for the preparation of highly birefringent LC films via photo-crosslinking polymerisations. Both monomers exhibited enantiotropic N phases at relatively low temperatures (\( T < 200^\circ C \)). Dimethacrylate monomer 1 exhibited a N phase in a narrower temperature range (\( T = 110–138^\circ C \)) than monomethacrylate monomer 2 (\( T = 98–185^\circ C \)), and both monomers were infinitely miscible. A 20/80 w/w mixture of 1 and 2 exhibited an NLC phase in a temperature range of more than 100°C (\( T = 73–179^\circ C \)). Even though moderate birefringence was observed for dimethacrylate 1 (\( \Delta n = 0.25 \)), that of monomer mixtures between 1 and 2 increased with an increasing proportion of monomethacrylate 2 (\( \Delta n = 0.35 \)), suggesting an additivity rule to be operative. The uniaxial alignment of the monomer mixture was successfully fixed by photo-polymerisation, which increased the birefringence even further (\( \Delta n = 0.40 \)). This study thus provides a synthetic avenue to highly birefringent polymeric LC films for various optical applications.

**Experimental**

**Methods, materials and instruments**

Chemical reagents were obtained from TCI or Wako (Japan) and used as received. \(^1\)H NMR and \(^13\)C NMR spectra were recorded in CDCl\(_3\) or DMSO-\(d_6\) on a Brucker DPX300S spectrometer at room temperature, and tetramethylsilane was used as an internal standard. The optical textures of LCs were examined by POM on a Leica DM2500P microscope with a Mettler FP90 hot stage. Transition temperatures and enthalpy changes were measured by DSC on a Perkin Elmer DSC7 employing a heating/cooling gradient of 10°C min\(^{-1}\). Photo-polymerisations were carried out using a USHIO SP9-250UB (\( \lambda = 365 \text{ nm} \); \( t = 10 \text{ min} \)). Measurements of \( \Delta n \) were performed within a uniaxially aligned nematic cell, which
4-(6-Hydroxyhexyloxy)-1-(2-trimethylsilylethynyl)benzene (1a)

A mixture of 4-bromophenol (5.20 g, 30.0 mmol), K2CO3 (12.4 g, 90.0 mmol) and MeCN (70 mL) was heated to reflux for 24 h. The reaction mixture was extracted with ethyl acetate, washed with water, brine, and dried over MgSO4. After filtration and evaporation of the solvent, the residue was purified by column chromatography on silica gel (ethyl acetate/hexane = 1/2) to afford 1a as a colourless solid. Compound 1a was obtained as a pale brown liquid. Yield: 98%; 1H NMR (300 MHz, CDCl3) δ 7.36 (d, J = 9.0 Hz), 6.77 (d, 2H, J = 9.0 Hz), 3.95 (t, 2H, J = 9.0 Hz), 3.66 (t, 2H, J = 6.6 Hz), 1.79 (tt, 2H, J = 6.5 and 6.7 Hz) ppm.

4-(6-Hydroxyhexyloxy)-1-(2-trimethylsilyl ethenyl)benzene (2a)

A mixture of trimethylsilylacetylene (8.10 mL, 58.6 mmol), triethylamine (35 mL) and THF (35 mL) was degassed with argon bubbling, before being washed consecutively with aqueous HCl (2 M) and brine, and being dried over MgSO4. The reaction mixture was filtered and the filtrate was extracted with ethyl acetate, before being washed with ether, being dried over MgSO4. After evaporation of the solvents, the residue was purified by column chromatography on silica gel (ethyl acetate/hexane = 1/2) to afford 2a as a pale brown liquid. Yield: 81%; 1H NMR (300 MHz, CDCl3) δ 7.39 (d, 2H, J = 9.0 Hz), 6.80 (d, 2H, J = 9.0 Hz), 3.95 (t, 2H, J = 6.6 Hz), 3.66 (t, 2H, J = 6.5 Hz), 1.79 (tt, 2H, J = 6.6, 6.9 Hz), 1.67–1.36 (m, 6H), 1.26 (s, 1H) ppm.

2-Fluoro-1,4-bis(2-[4-(6-methacryloylhexyloxy)phenyl]ethynyl)benzene (4a)

Compound 4a was generated by applying generic Sonogashira-coupling conditions, using 3a (2.00 g, 9.16 mmol), 4-bromo-2-fluoriodobenzene (1.38 g, 4.58 mmol), TEA (20 mL), THF (20 mL), Pd(PPh3)4 (0.318 g, 0.275 mmol) and Cu (52.4 mg, 0.275 mmol). Yield: 25%. Colourless solid. 1H NMR (300 MHz, CDCl3) δ 7.51–7.38 (m, Ar-H, 5H), 7.24–7.12 (m, Ar-H, 2H), 6.87 (d, J = 9.0 Hz, Ar-H, 2H), 3.98 (t, J = 6.5 Hz, Ar-OH2, 4H), 3.67 (t, J = 6.5 Hz, CH2-OH, 4H), 1.81 (tt, J = 6.5 and 6.7 Hz, 4H), 1.67–1.35 (m, 12H), 1.24 (s, 2H) ppm. HRMS-FAB+ (m/z): [M]+ calcd for C34H37FO4, 528.2676; found, 528.2686.
1H), 5.55 (s, C = CH2, 1H), 4.16 (t, J = 6.6 Hz, CH2-O-C = O, 4H), 3.67 (t, J = 6.5 Hz, Ar-OH2, 4H), 1.94 (brs, CH3 = C(CH)2COO, 3H), 1.81 (tt, J = 6.6 and 6.9 Hz, 4H), 1.72 (tt, J = 6.5 and 7.3 Hz, 4H), 1.55–1.41 (m, 8H) ppm. HRMS-FAB+ (m/z): [M] calcd for C45H43FO4, 664.3200; found, 664.3199.

4-(2-Trimethylsilyl)ethynyl-1-methoxybenzene (1b)

Compound 1b was synthesised by applying generic Sonogashira-coupling conditions, using 4-bromoanisole (5.0 g, 26.7 mmol), trimethylsilylacetylene (5.6 mL, 40.1 mmol), TEA (20 mL), THF (20 mL), Pd(PPh3)4 (0.62 g, 0.53 mmol) and CuI (0.10 g, 0.53 mmol). Yield: 85%. Pale yellow liquid. 1H NMR (300 MHz, CDCl3) δ 7.40 (m, Ar-H, 2H), 6.82 (d, J = 9.0 Hz, Ar-H, 2H), 3.80 (s, O-CH3, 3H), 0.24 (s, Si-CH3, 9H) ppm.

1-Ethynyl-4-methoxybenzene (2b)

Compound 2b was synthesised following the general procedure for the deprotection of trimethylsilyl groups as described for 3a, using 1b (4.6 g, 22.5 mmol), K2CO3 (9.3 g, 67.5 mmol), MeOH (20 mL) and THF (20 mL). Yield: 97%. Pale yellow liquid. 1H NMR (300 MHz, CDCl3) δ 7.53–7.40 (m, Ar-H, 5H), 7.27–7.19 (m, Ar-H, 2H), 6.89 (d, J = 9.0 Hz, Ar-H, 2H), 6.87 (d, J = 9.0 Hz, Ar-H, 2H), 6.10 (s, C = CH2, 1H), 5.55 (s, C = CH2, 1H), 4.16 (t, J = 6.8 Hz, CH2-O-C = O, 2H), 3.98 (t, J = 6.2 Hz, Ar-O-CH2, 2H), 3.84 (s, O-CH3, 3H), 1.94 (brs, CH2 = C(CH3)2COO, 3H), 1.81 (tt, J = 6.4 and 6.8 Hz, Ar-O-CH2-CH2, 2H), 1.72 (tt, J = 6.2 and 6.7 Hz, -CH2-CH2-CH2-O-C = O, 2H), 1.56–1.41 (m, O-CH2-CH2-CH2, 4H) ppm. HRMS-FAB+ (m/z): [M] calcd for C33H31FO4, 510.2206; found, 510.2220.

Disclosure statement

No potential conflict of interest was reported by the authors.

Supplemental data

Supplemental data for this article can be accessed here.

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