Stabilization of the nematic mesophase by a homogeneously dissolved conjugated polymer[†]

Andreas Lohr and Timothy M. Swager*

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A semi-conjugated iptycene polymer containing a special "crankshaft" backbone leading to superior solubility in a nematic LC medium was synthesized. The incorporation of this polymer in the LC leads to thermodynamic stabilization of the nematic mesophase. This effect is attributed to organizational coupling of the LC molecules to the polymer chains.

Introduction

Polymers have always played an important role in liquid crystal devices and are the basis of the alignment layers used in essentially all twisted nematic displays.¹ Polymer networks that extend throughout the LC medium have been extensively studied and are of great importance for commercial display applications.² By far the most popular technique for the production of such polymer networks in the LC medium is free radical polymerization of admixed mesogens that are functionalized with acrylate groups.^{2,3} The cross-linked polymer and the LC medium become phase separated, *i.e.* they are forming a bicontinuous network, and elastic interactions between the polymer network and the LC lead to an orientational stabilization of a particular LC alignment.² If prepared under the right conditions, for example by applying a small electric field during the curing process, such polymer networks can lead to improved electro-optical properties including decreased response times and lower threshold voltage for switching of the liquid crystal display. The polymer network's impact on the LC medium can be enhanced by increasing the polymer content or decreasing the fiber diameter, with the latter leading to a higher surface to volume ratio.² To this end, homogeneously dissolved polymers could be seen as the optimal network "material" if they show high alignment with the LC director and, vice versa, impose strong orientational order on the LC medium.

Previously, our group has shown that dyes and conjugated polymers like poly(*p*-phenylene ethynylene)s and poly(*p*-phenylene vinylene)s equipped with triptycene moieties show high degrees of alignment with the director in nematic liquid crystals, which was attributed to minimization of "internal free volume" between the planes of the triptycene units (Fig. 1a).⁴⁻⁶ Since the iptycene frameworks can obviously create organizational couplings between shape-persistent polymers and the liquid crystal director, we considered applying such polymers for stabilization of particular LC alignments. However, the polymers studied in our group so far suffered from solubility too low to achieve significant effect on the properties of the nematic LCs.



Fig. 1 Schematic representation of (a) iptycene framework (red) alignment in nematic LCs (blue) through minimization of free volume and (b) polymer chain (red) alignment along the director of the nematic mesophase (blue). Polyimide layers (black) lead to planar alignment of the LCs sandwiched between the glass slides (grey) of a test cell.

In this study, we report the synthesis of an iptycene-containing polymer (**P1** in Scheme 1) with a special backbone structure that facilitates superior solubility and alignment in the nematic liquid crystal phase, and show that this polymer has a stabilizing impact on the nematic mesophase. Our design of the polymer in this study is based on the "crankshaft" nature of its backbone that, while maintaining rigidity along the long axis of the polymer, facilitates good solubility by allowing for greater chain dynamics and minimization of the length of the rigid-rod conjugated segments. These factors should lead to lowering of the aggregation propensity of these polymers, which is the main cause for the typically low solubility of fully conjugated polymers. In addition, the polymer is copolymerized from racemic monomers which should further increase disorder along the chain which is again favorable for good solubility.

Results and discussion

Monomer (\pm) -5 was synthesized as shown in Scheme 1. Commercially available 1,5-diaminoanthraquinone (1) was converted into 1,5-dibromoanthracene (2) in an overall yield of 71% by applying a three-step protocol comprising a Sandmeyertype substitution of the amino groups followed by two successive reduction steps *via* the 9,10-dihydro-9,10-dihydroxy-anthracene derivative. In the next step, the iptycene framework was constructed by Diels–Alder reaction of 2 with an excess of *p*-benzoquinone and *in situ* oxidation which gave iptycene quinone (\pm) -3 as a racemic mixture in 56% yield. Subsequently, (\pm) -3 was reduced using zinc under acetic conditions and the formed hydroquinone derivative was alkylated to yield dialkoxyiptycene (\pm) -4 in 59% yield. In the last step, Sonogashira coupling of dibromide (\pm) -4 with trimethylsilylacetylene and subsequent

Massachusetts Institute of Technology, Department of Chemistry, 77 Massachusetts Avenue, Cambridge, MA, 02139, USA. E-mail: tswager@ mit.edu; Tel: +1-617-253-4423

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Scheme 1 Synthesis of polymer P1.

deprotection gave the diyne monomer (\pm)-5 in 46% yield. Copolymerization of monomers (\pm)-5 and 6 under Sonogashira conditions yielded polymer P1 with molecular weight of $M_n =$ 1.9×10^4 g mol⁻¹ and a polydispersity of $M_w/M_n = 2.4$.

Polymer **P1** was found to be nicely and readily soluble in common organic solvents like chloroform and tetrahydrofuran, as well as in the isotropic and nematic phase of the LC material MLC-6884 (negative dielectric anisotropic LC from Merck KGaA) which we used in this study.‡ As can be seen in Fig. 2 and S1†, the polarizing optical micrograph of a non-aligned sample of MLC-6884 containing 10 wt% **P1** taken with crossed polarizers



Fig. 2 Optical micrograph of a solution of P1 in MLC-6884 (10 wt% P1) taken under crossed polarizers after slow cooling of the sample from the isotropic phase to 25 $^{\circ}$ C.

exhibits no evidence of phase separation or micro-crystallization. Furthermore, the observation of a Schlieren texture, which is typical for the nematic mesophase,^{1b} shows that the nematic phase is preserved even with such high content of homogeneously dissolved polymer.

[‡] The composition of commercial LC mixtures like MLC-6884 is usually not published. However, due to its negative $\Delta \varepsilon$ value MLC-6884 consists most presumably of biphenyl and terphenyl cores with lateral fluorine substituents as commonly used in nematic LC materials with negative dielectric anisotropy. (See for example: D. Pauluth and K. Tarumi, J. Soc. Info. Display, 2005, **13**, 693–702). The high polarizability of such aromatic compounds contributes also to the good solubility of the polymer in the LC medium.

Since a high degree of polymer alignment along the LC director is a prerequisite for imposing orientational order on the LC, we first studied whether polymer P1 shows such alignment despite its increased intra-chain disorder and the smaller length of the conjugated rigid-rod segments compared to previously studied polymers.⁶ For this, a solution of P1 (1 wt%) in the LC host (MLC-6884) was prepared and test cells (10 µm cell gap) equipped with parallel rubbed polyimide layers for planar alignment of the LC were loaded with this mixture by capillary force. After slow cooling of the filled cell from a temperature above the clearing point to room temperature, the homogeneous alignment of the nematic LC medium in the cell was confirmed by polarized optical microscopy equipped with a rotatable sample stage. Notably, for these experiments we used LC mixtures containing only 1 wt% polymer to provide suitable absorbance of the polymer for UV/vis absorption measurements. Absorption spectra of these cells were measured with nonpolarized light and also with a polarization direction parallel (0°) and perpendicular (90°) to the LC director orientation, respectively. The dichroic ratio D and order parameter S of the polymer were calculated from the respective absorbance values at the absorption maximum of the polymer (364 nm). The dichroic ratio D is defined as the ratio between the respective absorbance recorded for light polarized parallel and perpendicular to the director orientation and a value of D = 12.9 was obtained in our case. Since it can be safely assumed that the transition dipole moments of the polymer are parallel to its long axis, an order parameter $S = (A_0 - A_{90})/(A_0 + 2A_{90}) = 0.80$ was obtained. Both the values of D and S are in the range of previously studied iptycene-containing polymers that have even higher molecular weight or additional supramolecular chain-extension.⁶ The fact that neither the increased disorder and dynamics in the polymer chain nor the decreased length of the rigid segments affect the



Fig. 3 Black lines: normalized, nonpolarized UV/vis absorption spectra of polymer **P1** in chloroform solution (dotted), as thin film spin-cast on a quartz glass slide (dashed), and dissolved in MLC-6884 (1 wt% polymer) and sandwiched between the glass slides of a test cell equipped with parallel rubbed polyimide layers for planar director alignment (solid). Red lines: absorption spectra of **P1** in the test cell using light polarized parallel (solid) and perpendicular (dashed) to the orientation of the LC director. The shown spectra of **P1** in the LC were obtained by filtering the raw spectra that contain oscillation patterns from interference effects of the rubbed polyimide layer using the FFT filter of Origin 7 (OriginLab Corp.). For a comparison of the original and filtered spectra see Fig. S2 in the ESI[†].



Fig. 4 DSC thermograms of solutions of P1 in MLC-6884 containing 0 (black), 1 (red), 5 (green), and 10 wt% (blue) P1. The heating/cooling rate was 10 K min⁻¹.

order parameter of the dissolved polymers underlines the general applicability of the iptycene framework and the concept of minimization of free volume to achieve strong solute alignment.⁴ Interestingly, we also observed a red-shift in the absorption spectrum of **P1** in the LC compared to solutions of **P1** in chloroform (Fig. 3). These spectral differences can be explained by planarization of the oligo(phenylene ethynylene) segments (highlighted in blue color in Scheme 1) in the LC medium as suggested by similar nonpolarized absorption spectra of **P1** in the LC medium and in thin-films wherein interchain interactions promote a dense packed planar conformation (Fig. 3, black solid and dashed lines).§

To assess whether the LC-aligned polymer P1 can vice versa impose orientational order on the LC and, thus, stabilize the nematic mesophase, we studied the phase transitions of the LC mixture containing various weight fraction of P1 by differential scanning calorimetry (DSC). As can be seen in the DSC heating curves (upper half of the thermograms in Fig. 4 and S4[†]), the onset temperature T_{N-I} for the nematic-to-isotropic phase transition increases with higher weight fraction of the polymer in the LC material. For the pure LC the onset of the phase transition is at $T_{\rm N-I}$ = 74.3 °C, while an increased onset temperature of 76.7 °C is observed for the P1/LC mixture containing 10 wt% of the polymer. Similarly, upon subsequent cooling (lower half of the thermograms in Fig. 4) the reverse isotropic-to-nematic phase transition sets in at already higher temperature for increasing polymer weight fraction. The increase in the phase transition temperatures of the LC mixtures containing P1 is also confirmed by polarizing microscopy measurements.

The observed thermodynamic stabilization of the nematic mesophase can be related to the organizational coupling of the polymers to the LC molecules which increases the order parameter of the nematic phase. Furthermore, in both halves of the heating/cooling cycle it can be observed that the transitions smear out and the latent heat for the phase transitions decreases with higher polymer content. This behavior was previously

[§] Additional support for aggregation of the polymer in the LC is obtained from temperature-dependent absorption measurements, which show a gradual change of the spectrum with increasing temperature. At high temperature the measured spectrum is similar to that observed for P1 in CHCl₃ solution (see Fig. S3 in the ESI[†]).

Downloaded by UNIVERSITY OF SOUTH AUSTRALIA on 13 June 2012 Published on 12 August 2010 on http://pubs.rsc.org | doi:10.1039/C0JM00621A observed for phase-separated polymer network-stabilized LC materials and explained by the fact that mesogens in proximity to the polymer fibers experience some orientational order through elastic interactions with the polymer fibers even in the isotropic phase.⁷ Thus, an orientational order distribution of the LC molecules is obtained that ranges from (*i*) strongly bound to the network and not showing high latent heat of the nematic-to-isotropic phase transition, to (*ii*) not bound and showing high latent heat for the phase transition as would be the case in the pure LC.

The DSC data show that the incorporation of polymer **P1** in the LC does not disrupt but, moreover, stabilizes the nematic phase, which is in contrast to reports of monomeric triptycene solutes leading to lowering of the clearing temperature of a nematic LC.^{5a} This comparison indicates that, although simple iptycene solutes align very well in the nematic phase, the long-range order imposed by the rigid polymer chain is crucial for stabilization of the nematic phase.

Conclusions

In summary, we have shown that the integration of iptycenecontaining polymers into a nematic LC medium leads to a stabilization of the nematic mesophase. This effect is attributed to organizational coupling of the LC molecules to the polymer strands leading to an enhanced order parameter of the LC medium. In the future we plan to apply such polymers in devices wherein the polymer organization is stabilized by cross-linking and attaching the ends of the polymers to the electrodes of the cell. In devices containing such an iptycene polymer network strong elastic forces work on the LC molecules throughout the device. As a result, a faster electro-optical response is expected upon release of the electric field compared to conventional devices wherein the equilibrium re-alignment is only imposed from the surface.

Experimental section

General

Solvents and reagents were obtained from commercial suppliers and, if not otherwise stated, used as received. The liquid crystal material MLC-6884 was obtained from Merck KGaA Column chromatography was performed on silica gel (SiliCycle, particle size 40-63 µm). NMR experiments were conducted on a Bruker Avance 400 spectrometer with TMS or residual solvent signal as internal standard. High-resolution mass spectrometry was carried out on a Bruker Daltonics apex IV FTMS instrument with an EI or DART ion source. Molecular weight and polydispersity index of the polymer were obtained from an HP series 1100 gel permeation chromatography system with THF as solvent and calibrated with polystyrene standards. UV/vis absorption spectra were measured on a Cary 50 instrument. DSC measurements were performed using a TA Q100 calorimeter and sample quantities of the order of 5 mg were used. Melting points were measured and polarizing optical micrographs were taken on a Leica DM RXP Optical Microscope equipped with a rotatable Linkham 350 hot stage controlled by a Linkham TMS 94 temperature controller.

Polymer–LC solutions with different wt% of polymer were prepared by mixing the respective amount of polymer and MLC-6884 in a small vial and heating the mixture into the isotropic phase with a heat gun. Cooling to room temperature resulted in generation of a homogeneous LC solution. For the preparation of the test cells KSRO-10 test cells (manufactured by E.H.C. Co. Ltd, Japan, cell gap 10 μ m, with parallel rubbed polyimide coating) were heated to 90 °C on a Linkham 350 hot stage and the LC-polymer solutions were infused by capillary action. The cell was slowly cooled to 75 °C, equilibrated at this temperature for 30 min, and then slowly cooled to room temperature.

1,5-Dibromoanthracene (2)

1,5-Diaminoanthraquinone (10.0 g, 42.0 mmol) and CuBr₂ (21.2 g, 94.6 mmol) were suspended in MeCN (200 mL). tert-Butyl nitrite (12.5 mL, 90%) was added under vigorous stirring and the mixture was heated to 65 °C for 2.5 h. The mixture was cooled to room temperature (rt) and hydrochloric acid (3 M, 100 mL) and H₂O (100 mL) were added. After stirring the mixture for additional 20 min the solid was filtered, washed with water (4 \times 100 mL) and EtOH (50 mL), and dried in vacuo. Subsequent filtration of the material through a plug of silica gel using CHCl₃ as eluent and drying in vacuo yielded 13.7 g of crude 1,5-dibromoanthraquinone as an orange powder. This material was suspended in *i*-PrOH (250 mL) and the mixture was cooled to 0 °C. NaBH₄ (3.59 g, 95 mmol) was added and stirring was continued for 1.5 h at 0 °C and additional 2 h at rt. The mixture was poured into water (500 mL) and the resulting suspension was stirred for 3 h until the green color disappeared. The solid was filtered, washed with water (2×100 mL), and dried in vacuo. The off-white solid was suspended in AcOH (200 mL) and SnCl₂ (19.0 g, 100 mmol) was added. The mixture was refluxed for 2 h, cooled to rt, and poured into water (500 mL) under stirring. After filtration the solid was washed with water $(3 \times 100 \text{ mL})$ and the crude product was dried in vacuo. The material was finally subjected to column chromatography (SiO₂, CHCl₃) to yield the product as a pale yellow powder. Yield 10.0 g (29.8 mmol, 71%). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 8.82 (s, 2H), 8.07 (dd, J = 8.4 Hz, J = 0.8Hz, 2H), 7.84 (dd, J = 7.2 Hz, J = 0.8 Hz, 2H), 7.36 (dd, J = 8.4 Hz, J = 7.2 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ 133.1, 130.6, 130.2, 128.9, 127.3, 126.2, 122.7. HRMS (DART, pos. mode, solvent): calcd m/z for C₁₄H₈Br₂ ([M]⁺) 333.899, found 333.899.

(±)-6,11-Dibromotriptycene-1,4-quinone (±)-3

1,5-Dibromoanthracene (6.00 g, 17.9 mmol), freshly sublimed *p*-benzoquinone (8.77 g, 80.6 mmol) and CuCl (1.77 g, 17.9 mmol) were suspended in AcOH (100 mL) and refluxed for 2 h. After cooling to rt the solid was filtered and washed with hot water. After drying, the crude product was purified by two column chromatography runs (SiO₂) using CHCl₃/MeOH = 99 : 1 and CHCl₃ as eluent, respectively. The product was obtained as a yellow powder. Yield 4.44 g (10.0 mmol, 56%), mp > 300 °C. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 7.42 (d, *J* = 7.2 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.93 (m, 2H), 6.65 (s, 2H), 6.25 (s, 2H). ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ 183.0, 151.7, 145.1, 143.2, 135.6, 129.8, 127.5, 124.0, 119.8, 47.4. HRMS (EI,

Downloaded by UNIVERSITY OF SOUTH AUSTRALIA on 13 June 2012 Published on 12 August 2010 on http://pubs.rsc.org | doi:10.1039/C0JM00621A 70 eV): calcd m/z for ([M – Br]⁺) 360.986, found 360.987 (100%), calcd m/z for ([M]⁺⁺) 441.903, found 441.904 (54%).

(±)-1,6-Dibromo-11,14-ditetradecyloxytriptycene (±)-4

Iptycene quinone (\pm) -2 (3.5 g, 7.92 mmol) was dissolved in a mixture of AcOH (35 mL) and THF (105 mL). Zinc dust (7 g) was added and the mixture was stirred at rt for 2 h. After filtration of the mixture through a pad of silica gel using MeOH as solvent, the yellow filtrate was poured into water (500 mL) and the formed white solid was filtered, washed with water, and dried in vacuo. This material, K₂CO₃ (3.74 g, 27 mmol), and KI (900 mg, 5.4 mmol) were suspended in 2-butanone (20 mL) and C14H29Br (8.0 mL, 27 mmol) was added. The mixture was refluxed for 22 h. After cooling to rt the mixture was poured into water (30 mL) and extracted with diethyl ether (2 \times 50 mL). The combined organic phases were washed with HCl (0.05 M), H₂O, and brine and dried over MgSO4. After removal of the solvent the residue was subjected to column chromatography (SiO₂, CH_2Cl_2/n -hexane = 1 : 9) and recrystallized from THF/acetone to yield a colorless powder. Yield 3.90 g (4.66 mmol, 59%), mp 159 °C. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 7.37 (d, J = 7.2Hz, 2H), 7.18 (dd, J = 8.2 Hz, J = 0.8 Hz, 2H), 6.85 (dd, J = 8.0 Hz, J = 7.6 Hz, 2H), 6.52 (s, 2H), 6.35 (s, 2H), 3.93 (t, J = 6.7 Hz, 4H), 1.84 (m, 4H), 1.55 (m, 4H), 1.4–1.2 (m, 40H), 0.88 (t, J = 7.0 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ 148.9, 147.6, 145.3, 134.5, 129.1, 126.8, 123.5, 119.4, 111.3, 69.9, 47.4, 32.1, 30.0-29.9 (6×), 29.8, 29.7, 29.6, 26.4, 22.9, 14.3. HRMS (EI, 70 eV): calcd m/z for ([M - 2C₁₄H₂₉]⁺) 443.918, found 443.918 (100%), calcd m/z for ([M - C₁₄H₂₉]⁺) 640.137, found 640.138 (15%), calcd m/z for ([M]⁺) 836.358, found 836.356 (10%).

(±)-6,11-Diethynyl-1,4-ditetradecyloxytriptycene (±)-5

Dibromide (±)-4 (300 mg, 358 µmol), Pd(PhCN)₂Cl₂ (9.90 mg, 25.8 µmol), (t-Bu₃PH)BF₄ (16.2 mg, 55.9 µmol), and CuI (3.28 mg, 17.2 µmol) were placed in an oven-dried Schlenk tube. Subsequently, the tube was evacuated and refilled with argon (5 cycles). THF (1.5 mL) and *i*-Pr₂NH (144 μ L, 1.03 mmol) were added through a septum and the mixture was stirred at rt for 15 min. Trimethylsilylacetylene (145 µL, 1.03 mmol) was added and the septum replaced by a glass stopper. The mixture was heated to 50 °C for 70 h and additional 100 µL portions of trimethylsilylacetylene were added every 24 h. The solvent was evaporated in vacuo and the residue was chromatographed (SiO₂, CH_2Cl_2/n -hexane = 2 : 8). After evaporation of the solvent, the residue was taken up in a mixture of THF (3 mL) and MeOH (1.5 mL), and K₂CO₃ (180 mg, 1.30 mmol) was added. The mixture was stirred for 2 h at rt and diluted with diethyl ether and water. The aqueous phase was separated and extracted with Et₂O. The combined org. phases were washed with HOAc (10%), water and brine and dried over MgSO₄. Column chromatography (SiO₂, CH_2Cl_2/n -hexane = 2:8 and hexanes/EtOAc = 98:2) and recrystallization from EtOH yielded (\pm) -4 as colorless powder.

Yield 120 mg (165 µmol, 46%), mp 134–137 °C. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 7.43 (d, J = 7.6 Hz, 2H), 7.14 (dd, J = 7.8 Hz, J = 1.0 Hz, 2H), 6.94 (dd, J = 7.6 Hz, 2H), 7.14 (dd, J = 7.8 Hz, J = 1.0 Hz, 2H), 3.92 (t, J = 6.2 Hz, 4H), 3.30 (s, 2H), 1.83 (m, 4H), 1.55 (m, 4H), 1.4–1.2 (m, 40H), 0.88 (t, J = 7.0 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ 149.0, 148.2, 145.8, 135.0, 128.9, 125.0, 124.9, 117.7, 111.5, 81.6, 80.1, 70.1, 45.6, 32.1, 29.9 (6×), 29.8, 29.7, 29.6, 26.3, 22.9, 14.3. HRMS (DART, pos. mode): calcd *m*/*z* for C₅₂H₇₀O₂ ([M + H]⁺) 727.545, found 727.546.

Polymer P1

Diyne (\pm) -5 (59.0 mg, 106 µmol), diiodide 6 (77.4 mg, 106 µmol), Pd(PPh₃)₄ (5.78 mg, 5 µmol), and CuI (0.95 mg, 5.0 µmol) were placed in a flame-dried Schlenk tube. The tube was transferred into a glove box and toluene (1.75 mL) and *i*-Pr₂NH (0.75 mL) were added. The tube was sealed and the mixture was heated to 60 °C for 24 h. Sat. NH₄Cl solution and CHCl₃ were added and the org. phase was separated. After washing the org. phase with sat. NH₄Cl solution $(2\times)$, H₂O and brine it was dried over MgSO₄. After filtration the solvent was removed and the residue taken up in CHCl₃. Precipitation by slow addition to MeOH and filtration yielded the polymer. Yield 90 mg (88 µmol, 83%). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 7.6–7.3 (br m, 4H), 7.23 (br m, 2H), 7.00 (br m, 2H), 6.6-6.4 (br m, 4H), 3.95 (br m, 4H), 3.1-2.6 (br m, 4H), 1.93 (br m, 2H), 1.78 (br m, 4H), 1.5-1.1 (br m, 60H), 1.0–0.7 (br m, 18H). GPC (THF, polystyrene): $M_{\rm n} = 1.9 \times$ 10^4 Da, $M_w/M_n = 2.4$.

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