COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Fluorescent supramolecular liquid crystalline polymers from nucleobase-terminated monomers†

Sona Sivakova and Stuart J. Rowan*

Department of Macromolecular Science and Engineering, Case Western Reserve University, 2100 Adelbert Road, Cleveland, Ohio, USA. E-mail: sjr4@cwru.edu; Fax: +1 216 368 4202; Tel: +1 216 368 4242

Received (in Cambridge, UK) 10th July 2003, Accepted 20th August 2003
First published as an Advance Article on the web 4th September 2003

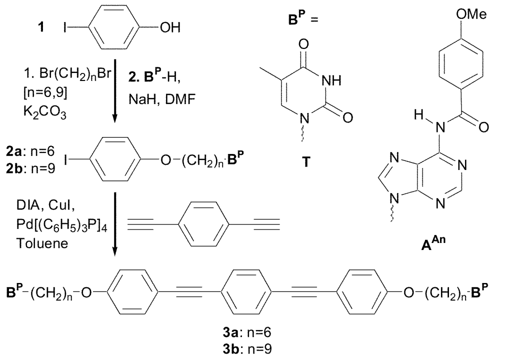
While thymine or *N*^{6}-(4-methoxybenzoyl)adenine terminated bis(4-alkoxy)-substituted bis(phenylethynyl)benzene monomers show no liquid crystalline behaviour by themselves, mixing the complementary nucleobase monomers together results in the formation of thermotropic liquid crystalline phases.

Over the last decade the area of supramolecular polymerisation, *i.e.* the self-assembly of small molecules into polymer-like materials through the use of the non-covalent bond, has received a growing amount of attention.[1] As a result it has been found that material properties of small molecules can be drastically altered by attachment of appropriate binding motifs that induce formation of "supramolecular polymers" by a self-assembly process. In addition, if the binding motif is asymmetric then the desired change in properties should only be expressed when the two complementary binding motifs are present. There are a number of material properties, *e.g.* mechanical, optical, phase organisation and viscosity, that can be altered using such a methodology. One possibility is the use of the non-covalent bond to induce non-mesogenic small molecules to form liquid crystalline phases.[2] In fact, the formation of an ordered liquid crystalline phase will also aid the degree of assembly (or polymerisation) of the small molecules.[2,3] The individual nucleobases are one of natures more interesting binding motifs and the possibility of using them in the material realm has started to gain attention in recent years.[4] In this communication, we present our initial studies on the use of the nucleobase derivatives, based on thymine (**T**) and *N*^{6}-(4-methoxybenzoyl)-adenine (**A^{An}**), to control the assembly of the fluorescent low molecular weight core, bis(4-alkoxy)-substituted bis(phenylethynyl)benzene, and result in the formation of supramolecular polymeric liquid crystalline phases.

While DNA sequences are one of the most predictable supramolecular binding motifs,[5] the individual nucleobases are less well behaved. For example, the purines (adenine and guanine) are able to bind though two different binding sites (Watson–Crick and Hoogsteen),[6] and as a result can form multi-component complexes. Therefore, we decided to investigate the binding capability of *N*^{6}-anisoyl protected adenine (**A^{An}**) which results in one of the binding sites of the adenine moiety being blocked. While such a synthetic modification will reduce the degree of binding of adenine,[7] it is known that the amide group will tend to block the Watson–Crick face of the nucleobase on account of unfavorable interactions between the lone pair electrons of the amide carbonyl and the *N*^{7} of the adenine. We have measured the binding constant in $CDCl_3$ between **T** and **A^{An}** to be *ca.* 22 M^{-1}. While this confirms that the **A^{An}** and **T** still interact with each other it does correspond to a reduction in the binding constant compared to the literature value of the **A–T** interaction ($CDCl_3$ K_{A-T} = 100 M^{-1}).[8] The core units to which the nucleobase derivatives were attached is the known mesogen alkoxy-substituted bis(phenylethynyl)benzene. This mesogen with pendant octyloxy chains and no nucleobases attached has been shown to display both nematic (N) and smectic (S) phases with the following thermal transition temperatures (°C): K–128.3–S_1–167–S_2–182–N–218–I.[9]

The synthesis of the **B^P-3-B^P** monomers (Scheme 1) was achieved by reacting, under basic conditions, either thymine (**T**) or *N*^{6}-anisoyl adenine (**A^{An}**) with either **1a** or **1b**, which contain a C6 or C9 alkyl chain, respectively. The resulting product **2** (**a** or **b**) was then reacted with 1,4-diethynylbenzene under Heck coupling conditions to yield the desired bis(phenylethynyl)benzene-derived supramolecular monomers. Using this synthetic route we prepared four different monomers which not only varied the nucleobase they contained but also the length of the alkyl chain between the nucleobase and the bis(phenylethynyl)benzene core.

Individually, the four monomers show no propensity for LC behavior and have very high melting points. For example, Figs 1a,b show the DSC thermograms for **A^{An}–3a–A^{An}** and **T–3a–T**. However, upon mixing and melting these two complementary nucleobase-terminated monomers, a dramatic decrease in the melting temperature is observed (Fig. 1c) along with concurrent formation of a viscous bifringent phase between 125–154 °C. Fig. 2a shows the polarized optical



Scheme 1 Synthesis of the nucleobase terminated monomers.

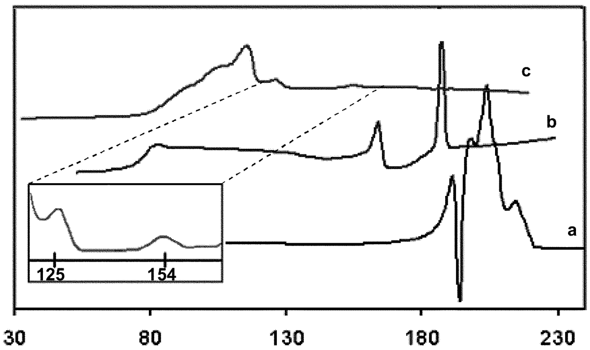


Fig. 1 DSC thermograms of the second heating of (a) **T–3a–T**; (b) **A^{An}–3a–A^{An}**; and (c) **A^{An}–3a–A^{An}**: **T–3a–T** (1 : 1 molar ratio) with an expansion of the bifringent region (inset).

---

† Electronic supplementary information (ESI) available: This includes ^1H NMR and DSC data for all monomeric compounds, as well as DSC data of the mixtures, the NMR titration data for the binding study and photoluminescence spectra of the **A^{An}–3a–A^{An}** : **T–3a–T** mixture and its individual components. See http://www.rsc.org/suppdata/cc/b3/b307877a/

DOI: 10.1039/b307877a

Table 1 Thermal transitions observed upon mixing complementary monomers of **B^{P}–3a–B^{P}** and **B^{P}–3b–B^{P}**

Monomer mixture (1 : 1)	Transitions heating/°C^{a,b}	Transitions cooling/°C^{a,c}	Bifringent range/°C^{a,b}
A^{An}–3a–A^{An} : T–3a–T	94, 105, 116, 125, 154, 172	154, 115, 110, 101	125–154
A^{An}–3a–A^{An} : T–3b–T	77, 96, 119, 137, 146, 166, 179	176, 161, 142, 134, 117, 95	120–178
A^{An}–3b–A^{An} : T–3a–T	88, 110, 174	162, 86	110–175
A^{An}–3b–A^{An} : T–3b–T	75, 84, 117, 163, 184, 192	182, 163, 117, 80	117–185

^{a} DSC and POM measurements. ^{b} Second heating. ^{c} Second cooling.

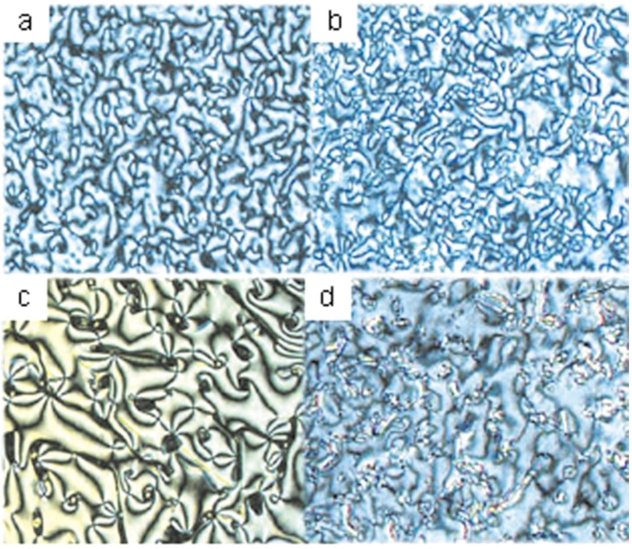


Fig. 2 Polarized optical micrographs of bifringent textures observed for (a) **A^{An}3a^{An}** : **T–3a–T** at 130 °C; (b) **A^{An}3a^{An}** : **T–3b–T** at 160 °C; (c) **A^{An}–3c–A^{An}** : **T–3a–T** at 155 °C (d) **A^{An}–3b–A^{An}** : **T–3b–T** at 120 °C (magnification 500×). See ESI for optical micrographs (×100).†

micrograph of this material at 130 °C. Above 175 °C, the material behaves as a free-flowing liquid, which becomes more viscous again upon cooling below 175 °C. At 153 °C, a viscous bifringent phase was observed which became solid below 120 °C. It should be noted that these phenomena are not observed on the first heating of the 1 : 1 samples obtained either from solid or solution-state mixing, but are consistently present upon subsequent heating and cooling cycles. Similar observations were made for the nine carbon monomers **A^{An}–3b–A^{An}** and **T–3b–T**. Individually, these monomers exhibit high melting temperatures which decrease upon mixing, and a viscous bifringent phase (Fig. 2b) can be observed between 118 °C and 180 °C. In both cases, it is postulated that the formation of the viscous bifringent phase occurs as a result of the monomers aggregating into a supramolecular polymer.

Intermixing of the C6 and C9 monomers with complementary moieties in 1 : 1 ratios also produced similar results with viscous bifringent phases forming at lower temperatures compared to the high melting, non-bifringent individual monomers. For example, the **A^{An}–3b–A^{An}** : **T–3a–T** material shows a texture indicative of a nematic phase at 155 °C (Fig. 2c). All mixtures showed numerous transitions as measured by DSC (Table 1) of which most could be attributed to transitions between crystalline, viscous bifringent, and isotropic states. Most transitions were observed as extremely broad peaks consistent with the presence of a polydispersed polymeric mixture.

In addition to forming viscous bifringent phases the mixed materials also displayed polymer-like properties. For example, fibres could be obtained from the LC phase of these systems. Fig. 3a shows an optical micrograph of a fibre obtained from the bifringent phase of the **A^{An}–3a–A^{An}** and **T–3a–T** mixture at *ca*. 145 °C. Fig. 3b shows the X-ray fibre diffraction data which confirm that these fibres are oriented.

Furthermore, these fibres are also fluorescent. Fig. 3c shows the fibre when it is excited with UV light (365 nm). Fluorescence spectra of films of the individual components,

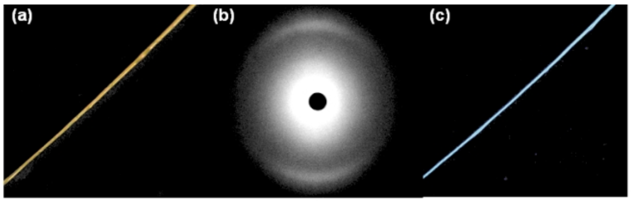


Fig. 3 (a) Optical micrograph (×10) of a fibre obtained from the LC phase of **A^{An}–3a–A^{An}** and **T–3a–T** under non-polarized light, (b) fibre diffraction pattern of the fibre and (c) optical micrograph (×100) of the fibre when excited with UV light (365 nm).

A^{An}–3a–A^{An} and **T–3a–T**, and the 1 : 1 mixture, which were solution cast from chloroform onto glass slides, show only slight differences in the shape of the emission peaks.†

In conclusion, we have shown that while addition of the nucleobase thymine and the nucleobase derivative *N*^{6}-(4-methoxybenzoyl)adenine to a mesogenic alkoxy-substituted bis(phenylethynyl)benzene results in a loss of liquid crystal phase formation, simple mixing and annealing of the two complementary nucleobase-derived monomers results in the formation of relatively stable LC phases. Concurrent with the formation of the viscous bifringent phases the material also demonstrates the ability to form oriented fluorescent fibres. Thus we have utilized the functionality of the core unit to aid LC formation and impart fluorescent behaviour, in conjunction with the self-assembly capability of the nucleobases, which not only aids LC formation but also imparts polymer-like properties to the material, *i.e.* fibre formation.

We thank the Case School of Engineering and the Dow Chemical Company for helping to fund this work. We also thank Professor C. Weder for useful discussions. SJR also thanks the NSF for a CAREER Award (CHE-0133164).

Notes and references

1 L. Brunsveld, B.J. B. Folmer, E. W. Meijer and R. P. Sijbesma, *Chem. Rev.*, 2001, **101**, 4071; A. Ciferri, *Macromol. Rapid Commun.*, 2002, **23**, 511; *Supramolecular Polymers* ed. A. Credi, Marcel Dekker, New York, 2000.

2 J.-M. Lehn, *Polym. Int.*, 2002, **51**, 825; T. Kato, N. Mizoshita and K. Kanie, *Macromol. Rapid Commun.*, 2001, **22**, 797; C. M. Paleos and D. Tsiourvas, *Liq. Cryst.*, 2001, **28**, 1127; A. Cifferri, *Liq. Cryst.*, 1999, **26**, 489.

3 T. Gulik-Krzywicki, C. Fouquey and J.-M. Lehn, *Proc. Natl. Acad. Sci. USA*, 1993, **90**, 163; P. Bladon and A. C. Griffin, *Macromolecules*, 1993, **26**, 6604; M. Kotera, J.-M. Lehn and J.-P. Vigneron, *J. Chem. Soc., Chem. Commun.*, 1994, 197; M. Kotera, J.-M. Lehn and J.-P. Vigneron, *Tetrahedron*, 1995, **51**, 1953; C. St. Pourcain and A. C. Griffin, *Macromolecules*, 1995, **28**, 4116; M. L. Bushey, T.-Q. Nguyen and C. Nuckolls, *J. Am. Chem. Soc*, 2003, **125**, 8264.

4 T. Shimizu, R. Iwaura, M. Masuda, T. Hanada and K. Yase, *J. Am. Chem. Soc.*, 2001, **123**, 5947; K. Yamaguchi, J. R. Lizotte and T. E. Long, *Macromolecules*, 2002, **35**, 8745; R. Iwaura, K. Yoshida, M. Masuda, K. Yase and T. Shimizu, *Chem. Mater.*, 2002, **14**, 3047; S. J. Rowan, P. Suwanmala and S. Sivakova, *J. Polym. Sci., Part A: Polym. Chem.*, in press.

5 E. A. Fogleman, W. C. Yount, J. Xu and S. L. Craig, *Angew. Chem., Int. Ed.*, 2002, **41**, 4026.

6 C. M. Paleos and J. Michas, *Liq. Cryst.*, 1992, **28**, 773.

7 J. S. Nowick, J. S. Chen and G. Noronha, *J. Am. Chem. Soc.*, 1993, **115**, 7636.

8 J. Sartorius and H.-J. Schneider, *Chem. Eur. J.*, 1996, **2**, 1446.

9 A. R. A. Palmans, M. Eglin, A. Montali, C. Weder and P. Smith, *Chem. Mater.*, 2000, **12**, 472.