

# Self-assembled bent-core side-chain liquid crystalline polymers†

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The synthesis of H-bonded bent-core side-chain liquid crystal polymers carried out by two alternative synthetic routes and their properties are reported.

In the last few decades supramolecular chemistry has provided a fantastic tool to create new and ingenious materials with a wide variety of functional properties.<sup>1</sup> In this respect, hydrogen bonding was, is and certainly will be one of the easiest and most useful strategies to build new molecules and supramolecular architectures. In many cases natural motifs—but also more simple systems—can be used to produce artificial biological systems and numerous other functional materials for very different purposes.

Liquid crystals have a place in supramolecular chemistry in their own right, but the H-bonded self-assembly approach has significantly enriched the variety and possibilities of the so-called *fourth state* of matter and provided many types of liquid crystalline phases, either with calamitic or columnar arrangements.<sup>2</sup> Furthermore, the discovery of the new mesophases exhibited by bent-shaped molecules (*i.e.* SmCP) has also been published recently.<sup>3</sup> These bent-materials exhibit similar dielectric and optical behavior to those described for covalent molecules.<sup>4</sup> The majority of H-bonded liquid crystal systems have been developed for low molecular weight materials. However, self-assembled polymers have evolved greatly and, since Kato and Fréchet's pioneering work on side-chain mesogenic polymers,<sup>5a</sup> this approach has gained significance<sup>5b-d</sup> not only in the liquid crystal field but also in the fundamental design of supramolecular side-chain functionalized polymers in general.

In this paper we report our results on the formation of bent-shaped side-chain polymers formed using the self-assembly approach. Bent-core molecules are of prime interest in liquid crystal research due to their special properties, which arise from their unique molecular structure.<sup>4a-e</sup> Features such as the occurrence of polar order within layers or columns as well as the appearance of some supramolecular chiral structures from non-chiral molecules are of fundamental scientific interest, especially given that this chirality can be switched under external electric fields. However, there are very few reports concerning polymers containing bent-core mesogens<sup>4e</sup> and even less on side-chain structures.<sup>4f</sup>

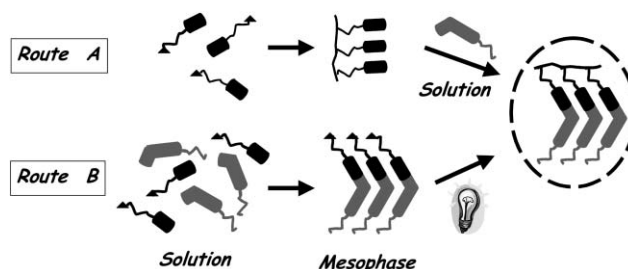
In order to achieve our aim of preparing H-bonded bent-core side-chain polymers, two different strategies were explored: (i) *Route A*, where the self-assembly step follows the polymerization

and (ii) *Route B*, where reactive monomers are created by self-assembly followed by photopolymerization (Scheme 1).

Single pyridine/benzoic acid hydrogen-bonded complexes were selected for this work. Non-mesomorphic stilbazoles **1** and **2** were used as H-acceptors<sup>3</sup> (Scheme 2). Acids **M6**, **M11** and polymers **P6** and **P11** were used as H-donors in order to obtain similar H-bonded-side-chain polymers through both synthetic routes.

*Route A* was used to prepare four self-assembled polymers: **1-P6**, **1-P11**, **2-P6** and **2-P11**.<sup>6a</sup> These polymers were studied by polarizing optical microscopy (OM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD). The results of these studies are collected in Table 1. Despite the non-mesomorphic nature of the components, all of the macromolecules are liquid crystals.<sup>6b</sup> More interestingly, the XRD patterns at variable temperatures reveal features in good agreement with those reported for the mesophases induced by bent-shaped molecules.

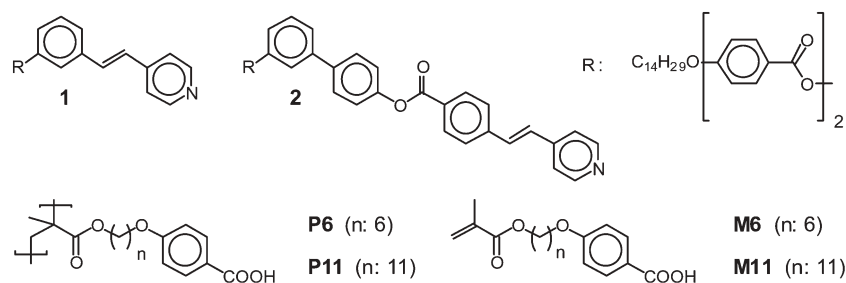
Very similar patterns were observed for polymers **1-P11**, **2-P6** and **2-P11**. In the wide-angle region there is diffuse scattering, whereas in the small-angle regions there are sharp layer reflections up to third order (Table 2 and ESI†). This indicates well-defined layer structures for the mesophase in all cases, *i.e.*, the macromolecules arrange themselves in smectic phases without in-plane order. Differences between the estimated length of the side-structures [from 57 Å (**1-P6**) to 70 Å (**2-P11**)] and the interlayer distances measured suggest a tilted molecular disposition within the liquid crystalline phase. These data, the grainy textures observed by OM and the large enthalpic changes determined for their mesophase–liquid transitions are consistent with a SmCP phase rather than with a conventional SmC mesophase. (see Figure S6† and refs. 4b–e). However no further experimental evidence to support the polar nature of these lamellar phases could be achieved; thus the label SmC has been used for these mesophases.<sup>7</sup> The large interlayer distance measured for **2-P6**, compared both to the other polymers and to the estimated length of its side-structure, is noteworthy. This can be explained in terms of a bilayer structure. Bilayer smectic phases (*i.e.*, SmA<sub>2</sub>) have been described for side-chain polymers possessing short spacers.<sup>8</sup> The



Scheme 1 Alternative synthetic routes followed to prepare the polymers.

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**Scheme 2** General structure of the H-acceptors and H-donors used.

**Table 1** Liquid crystalline properties of the studied materials

Material	Phase transition (°C, [kJ mol <sup>-1</sup> ]) <sup>a,b</sup>
<b>1-P6</b>	g <sup>c</sup> 62 Col <sub>r</sub> 126.7 [24.3] I
<b>1-P11</b>	g <sup>d</sup> 73 SmC 133.0 [25.7] I
<b>2-P6</b>	g <sup>d,e</sup> SmC 213.6 [34.3] I
<b>2-P11</b>	g <sup>d,e</sup> SmC 201.3 [21.8] I
<b>1-M6</b>	Crys 93.6 [35.1] I
<b>1-M11</b>	Crys 92.2 [18.2] SmCP 97.2 [18.0] I
<b>2-M6</b>	Crys 118.3 [15.4] SmCP 164.6 [16.2] I
<b>2-M11</b>	Crys 122.6 [10.5] SmCP 160.5 [13.1] I
<b>P/I-M11</b>	Crys 85.7 [8.1] SmC 130.1 [13.6] I

<sup>a</sup> From DSC second heating scans (10 °C min<sup>-1</sup>). <sup>b</sup> Crys, crystalline phase; SmC, tilted smectic mesophase without in plane order; SmCP, SmC polar mesophase; Col<sub>r</sub>, columnar rectangular mesophase; g, glassy phase; I, isotropic liquid phase. <sup>c</sup> Glass with Col<sub>r</sub> order. <sup>d</sup> Glass with SmC order. <sup>e</sup> T<sub>g</sub> not detected by DSC.

**Table 2** X-Ray data for some studied materials

Material	Phase	Measured spacings/Å	Miller index	Parameters/Å
<b>1-P6</b>	Col <sub>r</sub>	47.7	101	a = 69
		32.9	002	c = 66
		21.7	301	
		14.6	204	
		11.8	404,503	
<b>1-P11</b>	SmC	54.1	001	c = 54.2
		27.4	002	
		17.9	003	
<b>2-P6</b>	SmC	89.6	001	c = 89.6
		44.8	002	
		29.9	003	
<b>2-P11</b>	SmC	63.6	001	c = 64.0
		21.5	003	
<b>1-M11</b>	SmCP	51.4	001	c = 51.8
		17.5	003	
<b>P/I-M11</b>	SmC	55.3	001	c = 55.4
		27.8	002	
		18.4	003	

presence of the short spacer also seems to promote the columnar rectangular arrangement—also characteristic of low-molecular weight bent-mesogens—found for the shortest polymer **1-P6**. Additionally, XRD and OM of all these polymers at room temperature indicate columnar and lamellar glasses that all are stable over weeks.

To explore the alternative *Route B*, the “reactive monomers” **1-M6**, **1-M11**, **2-M6** and **2-M11** were prepared and characterized.<sup>6a,9a</sup> These complexes exhibit a switchable SmCP mesophase—with the exception of complex **1-M6**, which does not form a mesophase (Tables 1 and 2). Photopolymerization studies were focused on **1-M11**.<sup>9b</sup> The conversion vs. irradiation time and the

polymerization rate vs. conversion relationship in the SmCP mesophase were evaluated from the photopolymerization exotherms of the DSC curves.† From these data, a final conversion of around 74% in the polar mesophase was determined. Furthermore, free thin films of this photopolymer (**P/I-M11**) were also prepared and studied by MO, DSC and XRD. These studies show that **P/I-M11** exhibits rather similar mesogenic properties to polymer **1-P11** prepared by *Route A*, but with a more crystalline nature. This fact is clearly observed from the DSC thermograms (Table 1 and ESI†). Likewise, significant stabilization of the liquid crystalline order is achieved upon polymerization and, in agreement with previous results,<sup>10</sup> polymerization leads to a 10% increase in the layer spacing (*c*) in the smectic order (Table 2). Interestingly *Route B* allowed to prepare thin films of **P/I-M11** in ITO coated-cells by the *in situ* polymerization of **1-M11** within the cells. However, neither electrooptic switching nor second harmonic generation activity were detected for these samples in the mesophase.<sup>11,12</sup> Thus, the polar order of the lamellar liquid crystalline phase of this material could not be proven. Both synthetic routes afford highly viscous polymethacrylates. To overcome this drawback different alternatives to prepare more flexible H-bonded polymers containing bent-core mesogens are now being addressed.

In summary, we have shown that the versatility of non-covalent side-chain functionalized polymers could be extended to bent-core mesogenic materials. These results can help to design a range of different materials based on the unique bent-shaped molecules and their remarkable liquid crystalline phases, a new field that has a very exciting future. Furthermore, the work reported here concerns not only the synthesis of this type of polymer in solution, but also support the synthetic possibilities of *soft* phases, providing a bank of alternatives from which to choose.

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- 6 (a) The synthesis of the desired bent-complexes required the H donor and H acceptor to be mixed in precise equimolecular proportions in a common solvent (THF), followed by slow removal of the solvent. The formation and thermal stability of the complex was confirmed by IR spectroscopy (see ESI) and through OM measurements: the solid samples melted cleanly without the appearance of biphasic regions; (b) In some cases, virgin semicrystalline samples of these polymers did not form mesophase on heating but all of them were mesomorphic on successive thermal treatments after they had first been melted to the isotropic liquid.
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- 9 (a) To avoid premature thermal polymerization of the reactive complexes 200 ppm of a thermal inhibitor (2,6-di-*tert*-butyl-4-methylphenol) was added to the samples, but partial thermal polymerization of the complexes **1-M6**, **2-M6** and **2-M11** was observed on heating, limiting any comparative study; (b) The photopolymerization of **1-M11** was carried out using a photo-DSC experimental setup equipped with a 365 nm lamp and samples containing 1% (w/w) of Irgacure 369 and 200 ppm of the thermal inhibitor 2,6-di-*tert*-butyl-4-methylphenol. The liquid crystalline properties of the monomer were not noticeably modified for the blends.
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- 11 Samples of **1-M11** were subjected to electric fields to ensure a ferroelectric SmCP order before polymerization. However, despite the proven switching of the monomer, as soon as a DC voltage was applied, the sample polymerized to give opaque films without SHG activity under a 1064 nm laser.
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