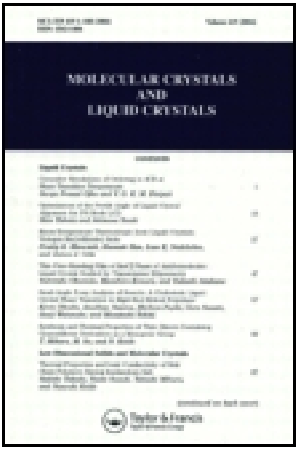

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

To cite this article: E. Chiellini, J. L. Houben, D. Wolff & G. Galli (2000): Chiral Liquid Crystalline Polyacrylates with Side-Chain Fluorescent Mesogens, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 352:1, 439-447

To link to this article: http://dx.doi.org/10.1080/10587250008023202

Mol. Cryst. and Liq. Cryst., 2000, Vol. 352, pp. 439-447
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Printed in Malaysia

Chiral Liquid Crystalline Polyacrylates with Side-Chain Fluorescent Mesogens

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Two new classes of chiral side-chain polymers comprising a variously spaced biphenyl unit as both a mesogenic core and a fluorescent chromophore were investigated. The chiral group was either a 2,3- or a 2,2-disubstituted oxirane ring. The structures of the smectic phases (A, B, or E) were investigated by X-ray diffraction. Excimer fluorescence emission was detected at room temperature in the smectic phase.

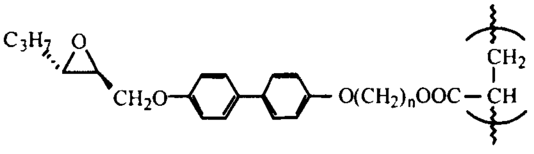
Keywords: chiral polyacrylate; liquid crystalline polymer; mesophase structure; fluorescent mesogen

INTRODUCTION

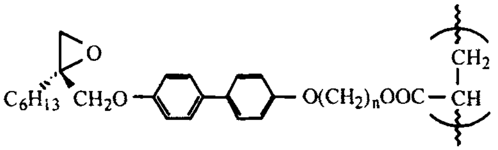
The oxirane ring is a comparatively little used chiral building block of liquid crystals. While the 2,3-disubstituted oxirane ring has been introduced into liquid crystal materials at different positions of the molecular framework[1], very few examples are known of liquid crystal molecules containing a 2,2-disubstituted oxirane ring[2]. To the best of our knowledge, it has never been used as a chiral substituent in side-chain polymers.

The effectiveness of the biphenyl core in promoting liquid crystallinity is well recognized. Its fluorescence emission properties in liquid crystal phases are also documented[3-5]. For instance, it has been shown that the emission properties of alkylcyanobiphenyls strongly depend on the nature of the mesophase[3,5], and that excimer formation is related to the ground-state geometry of the biphenyl chromophores in the nematic phase[5]. Thus, fluorescence investigations of liquid crystal polymers can probe the inter- and intra-molecular interactions which effect the microscopic ordering of the mesogens in the mesophase.

In this work we have characterized two new classes of chiral side-chain polymers **1-n** (*n* = 6, 7, or 11) and **2-n** (*n* = 6, 9, 10, or 11) containing the biphenyl core spaced from the polyacrylate backbone and a 2,3- and 2,2-disubstituted oxirane ring, respectively. We have also started investigations of their fluorescence emission properties in the mesophase.



1-n
(n = 6,7,11)



2-n
(n = 6,9,10,11)

EXPERIMENTAL PART

Synthesis

The synthesis and properties of the acrylate monomers were previously described[6]. The polyacrylates **1-n** and **2-n** were prepared from the corresponding monomers by a free-radical polymerization with AIBN at 60 °C in benzene solution (1 M concentration) for 40 h. They were purified by repeated precipitations from chloroform solution into methanol (yield > 70%).

Characterization

The transition temperatures were taken at a 10 °C/min rate as corresponding to the maximum in the enthalpic peaks of samples that had previously been annealed by cooling from the isotropic melt.

X-ray diffraction measurements were carried out in a custom-made, temperature controlled vacuum chamber with a flat film camera at a distance of 84 mm from the sample. Ni-filtered Cu-Kα radiation was used. The samples were cooled inside the chamber at a 0.4 °C/h rate from the isotropic state to the selected temperature under a magnetic field (2.4 tesla) perpendicular to the incident beam. During all the X-ray experiments the temperature of the sample was controlled within 0.1 °C.

Fluorescence emission spectra were recorded at room temperature in a front-face geometry with a Greg 200 spectrophotometer (λ_{exc} = 280 nm) with a resolution in excitation and emission of 2 nm on thin polymer films that had been deposited on quartz by cooling from either the isotropic melt or the smectic A phase.

RESULTS AND DISCUSSION

Polymers **1-n** gave rise to different sequences of mesophases above the glass transition temperature, depending on the length *n* of the spacer segment (Tab.I). The structures of the mesophases were studied by X-ray diffraction as illustrated below for **1-6** and **1-7**.

1-6 containing a shorter spacer originated at high temperature a chiral nematic phase. It was impossible to align the sample within a magnetic field (2.4 tesla) because of the difficulty of unwinding the cholesteric helix, that was probably a rather short-pitch one. In fact, no selective reflection of visible light was visually detected from polymer samples that had been aligned by mechanical shear. The underlying smectic A phase exhibited a layer periodicity d = 3.01 nm which compares with the calculated length of the repeat unit (L = 2.90 nm). Therefore, the side chains were organized in a monolayer, fully interdigitated structure in which the mesogens were completely overlapped (intermolecular distance D = 0.46 nm). On further cooling, a smectic B phase was formed with the same layer spacing (Fig.1). The wide-angle signal was rather sharp (a = 0.52 nm), which suggests the phase to be a crystal B rather than a hexatic B.

1-7 and **1-11** formed smectic phases only, with the same SmA-CrB-CrE polymorphism with decreasing temperature. The layer spacing was consistent with the existence of a monolayer structure for each phase and changed slightly across the entire mesophase range, e.g. from

$d = 3.08$ nm in the SmA to $d = 3.03$ nm in the CrE for **1-7**. The X-ray pattern of the CrE phase presented two low-angle Bragg reflections (periodicity 1:2) and three wide-angle sharp signals at periodicities of 0.45 nm, 0.41 nm, and 0.32 nm (relative intensity: strong, medium, weak) (Fig.2). The latter were indexed as the (110), (200), and (210) reflections of an orthorhombic structure, and accordingly the two-dimensional lattice parameters $a = 0.82$ nm and $b = 0.53$ nm were calculated (Fig.3). The surface available per side chain was rather wide ($S = 0.44$ nm^2), which supports the assignment of a CrE phase rather than a truly semicrystalline phase, for which much smaller surfaces of the rectangular lattice are normally observed in side-chain polymers[7].

In complete contrast, polymers **2-n** formed no mesophases but only a semicrystalline phase that transformed directly to the isotropic melt (Tab.I).

TABLE I. Transition temperatures of polyacrylates **1-n** and **2-n**.

sample	M_n (10^{-3})	M_w/M_n	Phase transition temperatures (in K)								
1-6	15	2.7	g	338	CrB	396	SmA	412	N*	438	i
1-7	11	1.7	g	nd	CrE	393	CrB	415	SmA	442	i
1-11	10	1.8	g	352	CrE	391	CrB	404	SmA	426	i
2-6	17	1.5	g	318	k					390	i
2-9	13	2.1	g	326	k					388	i
2-10	15	2.2	g	nd	k					385	i
2-11	18	1.5	g	329	k					397	i

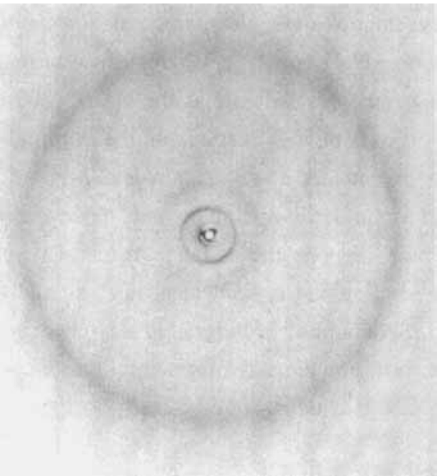


FIGURE 1. X-ray diffraction pattern of **1-6** in the CrB phase at 390 K.

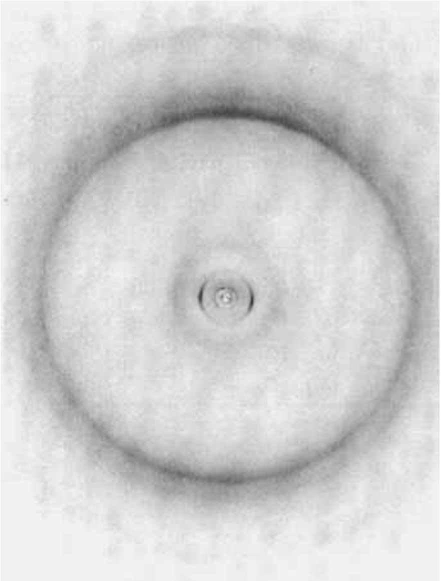


FIGURE 2. X-ray diffraction pattern of **1-7** in the CrE phase at 380 K.

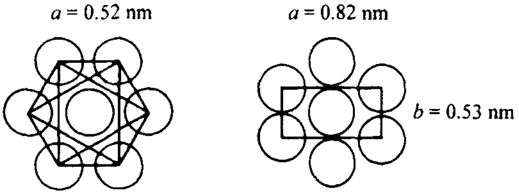
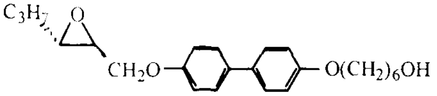


FIGURE 3. Schematic of the packing in the layers of the CrB (left) and CrE (right) phases of **1-7**.

As one example, the X-ray diagrams of **2-11** exhibited five low-angle reflections (periodicity 1:2:3:4:5) typical of a rather well correlated lamellar structure (d = 6.10 nm). In the wide-angle region, four signals were detected at periodicities of 0.47 nm, 0.45 nm, 0.40 nm, and 0.33 nm (relative intensity: weak, strong, medium, very weak) that, however, could not be indexed.

We assume that the bulky, protruding 2,2-oxirane ring inhibited the formation of a mesophase, although a rather high-melting semicrystalline phase was retained for any given length of the spacer segment, e.g. T_m = 397 K and ΔH_m = 25 kJ/mol for **2-11**.

The fluorescence emission properties of the polymers and the low-molar-mass model compound **3** were investigated in solution and in the bulk at room temperature (Fig.4). In contrast to what is observed for biphenyl where the vibrational structure of the emission spectra is quite marked[8], the spectra of **3** were structureless and the maximum was at 342-343 nm. The fluorescence spectra of the polymers showed a small red-shift of the maximum emission and a significant spectral broadening on the low-energy side which can be associated with an excimer emission.



3

While for 3 the $I_{400}/I_{\max}$ ratio was 0.04 to 0.05, greater values were measured for the polymers, e.g. 0.16 to 0.18 for **1-6** ($\lambda_{\max}$ = 350 nm). Comparison of these data with experiments on structurally related polymers suggests an incomplete formation of excimer structure[9]. Thermal treatments appeared to have little effect on excimer emission. More ordered smectic polymers **1-n** and semicrystalline polymers **2-n** were less effective in forming emitting excimers, as estimated by the lower values of $I_{400}/I_{\max}$, e.g. 0.11 for **1-7** ($\lambda_{\max}$ = 345 nm) and 0.10 for **2-6** ($\lambda_{\max}$ = 346 nm).

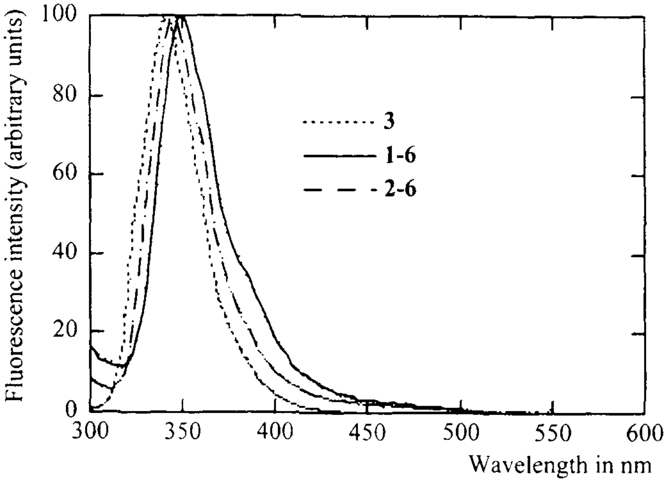


FIGURE 4. Fluorescence emission spectra of model compound **3** (in solution) and polymers **1-6** and **2-6** (in bulk at room

temperature) (λ_{exc} = 280 nm).

CONCLUSIONS

New chiral polyacrylates were synthesized which incorporated side-chain biphenyl mesogens bearing either a 2,3- or a 2,2-disubstituted oxirane ring substituent. Excimer formation was evidenced in the polymers, although the interaction between the biphenyl chromophores appeared to be rather small. This could be ascribed to either restricted conformational freedom and diffusion or steric hindrance of the chromophores in the highly ordered room-temperature phase.

Acknowledgments

Work performed with financial support from the EC, *Training and Mobility Research Programme*, CT97-0119.

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