The first example of a liquid crystalline side-chain polymer with bent-core mesogenic units: ferroelectric switching and spontaneous achiral symmetry breaking in an achiral polymer

Christina Keith, R. Amaranatha Reddy and Carsten Tschierske*

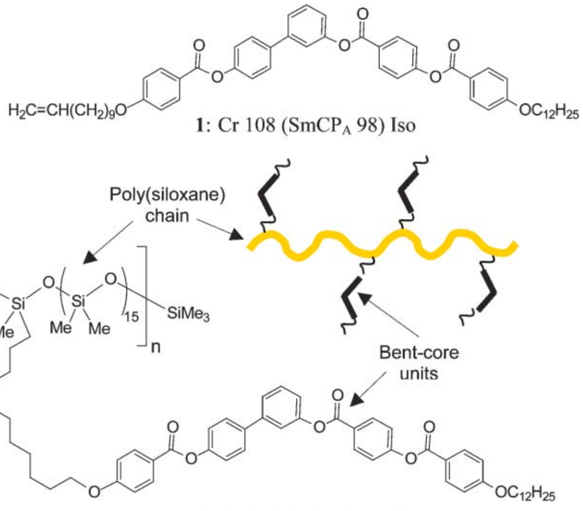
Received (in Cambridge, UK) 7th September 2004, Accepted 18th November 2004
First published as an Advance Article on the web 5th January 2005
DOI: 10.1039/b413643h

A dimethylsiloxane diluted polysiloxane side chain co-polymer with non-chiral banana-shaped mesogenic units shows an optically isotropic ferroelectric switching polar smectic C phase ($SmCP_F$) consisting of a conglomerate of homogeneously chiral domains with opposite handedness.

Liquid crystalline (LC) polymers are of great interest due to their special materials properties combining the typical features of polymers (processability, mechanical properties) with the special application characteristics of LC materials (namely the switching in external fields).[1] Mainly calamitic and discotic mesogenic units have been used for such LC-polymers. These units were either introduced into the polymer main-chain (main-chain polymers) or attached *via* spacer units laterally to the polymer back-bone (side-chain polymers).[1] Polymers with ferroelectric or antiferroelectric switching characteristics have been obtained with optically active chiral mesogenic units, organised in tilted mesophases (*e.g.* SmC* phases).[1,2] Such materials might be useful as flexible light modulating and non-centrosymmetric polar materials (*e.g.* for nonlinear optical, piezoelectric and pyroelectric applications).[1,2] In 1996 Niori *et al.*[3] discovered an alternative way to form (anti)ferroelectric switching LC materials by using achiral mesogenic units with a bent shape, so-called banana-shaped liquid crystals. Since then numerous low molecular mass bent-core liquid crystals have been synthesised and investigated.[4–7] Though first reports about main-chain polymers and derived networks incorporating bent-core units have appeared recently,[8] none of them exhibit switching properties and no side-chain liquid crystalline polymer containing bent-core units has ever been reported, indicating that the design of such materials is not a trivial task. One of the major problems which has to be solved is the high viscosity of such polymers, which makes a response to external stimuli difficult and restricts the application properties.

Herein, we report the first side-chain liquid crystalline polymer with bent-core mesogenic units. Moreover, this polymer exhibits fast ferroelectric switching, and in addition, the highly interesting phenomenon of spontaneous achiral symmetry breaking is observed, which was previously found in LC systems only for few low molecular weight bent-core materials.[5,6]

In order to get a low viscous material, the rather flexible polysiloxane polymer backbone was chosen. In addition, it was decided to synthesise a co-polymer in which the mesogenic repeat units are highly diluted by nonmesogenic dimethylsiloxane units (ratio *ca.* 1 : 15) to reduce the viscosity even more. The synthesis was achieved by grafting the olefin-terminated bent-core mesogen **1**[6] to a random methylhydrosiloxane–dimethylsiloxane copolymer (molecular weight 1900–2000 g mol^{-1}, 6–7 mol% SiH, HMS-071, Gelest, Inc.) by means of a hydrosilylation reaction in the presence of Karstedts catalyst.[6] **Poly-1** was purified by repeated filtration over silica gel ($CHCl_3$) to remove catalyst and excess **1** and was dried *in vacuo*. The absence of the Si–H group and the olefinic C–H signals as well as the correct ratio of the protons in the ^{1}H-NMR spectrum indicate complete reaction.† The polymer was studied by polarised light microscopy, X-ray scattering and electro-optical investigations. Upon heating **Poly-1** melts at 67 °C and shows a LC phase which changes to the isotropic liquid state at 119 °C. At 29 °C a glass transition can be found in the cooling cycle as well as in the second and the following heating cycles. It is really surprising that the mesophase stability of this highly diluted LC polymer (it should be remembered, that there is only one mesogenic unit among 15 non-mesogenic dimethylsiloxane units!) is significantly (20 °C) higher than the mesophase stability of the olefinic precursor **1**[6] (see Fig. 1).



1: Cr 108 ($SmCP_A$ 98) Iso

Poly-1: Cr 67 (g 29) $SmCP_F$ 119 Iso

Fig. 1 Comparison of the mesophases and phase transition temperatures (*T*/°C) of the low molecular weight banana molecule **1** with the polymer **Poly-1**, as determined by DSC (first heating scan, 10 K min^{-1}) and confirmed by polarising microscopy; abbreviations: Cr = crystalline solid state, g = glassy state, $SmCP_A$ = antiferroelectric switching polar tilted lamellar LC phase, $SmCP_F$ = ferroelectric switching polar tilted lamellar LC phase, Iso = isotropic liquid state; *n* is the number of repeat units in the polymer backbone, which is about 16–17.

---

*carsten.tschierske@chemie.uni-halle.de

The X-ray powder diffraction pattern of the liquid crystalline phase of **Poly-1** (Fig. 2b) is characterised by one sharp reflection and the corresponding 2nd order reflection, indicating a layer structure with d = 7.3 nm. The length of the mesogenic unit including the terminal alkyl chain, the aromatic core and the spacer unit amounts to L = 5.0 nm (assuming a 120° bent-shape and an *all-trans* conformation of the alkyl chains). The mesogenic cores are strongly tilted (40–45°, as measured by electro-optical investigations, see below) leading to an effective length of the mesogenic units of *ca.* 3.5 nm. The remaining space is the contribution from the polysiloxane sublayer. In the wide angle region two diffuse scattering with maxima at d_1 = 0.46 nm, and d_2 = 0.77 nm can be found, corresponding to the mean distances between the hydrocarbon parts and the dimethylsiloxane units, respectively, indicating the segregation of the polysiloxane backbones into distinct sublayers. Hence this mesophase represents a micro-segregated triple layer structure composed of alternating aromatic, aliphatic and oligosiloxane sublayers as shown in Fig. 2a.

The mesophase of **Poly-1** appears optically isotropic between crossed polarisers, but by rotating the polariser, regions of different brightness can be observed (Fig. 2c). Rotating the polariser in the other direction reverses the brightness of the domains (Fig. 2d), which is a clear indication of a chiral superstructure.[5,6]

The switching behaviour of this polymer was investigated using the triangular wave method. Only one very sharp peak per half period of an applied triangular wave voltage was observed in a simple triangular wave field even at a very low frequency (1.0 Hz, see Fig. 3a). The spontaneous polarisation is 500 nC cm^{-2}. This single peak does not split in a modified triangular wave voltage, where a plateau is introduced at zero voltage (Fig. 3b).[7] This is a strong indication of a ferroelectric switching process where the switching occurs directly between two oppositely polarised macroscopic polar states. Additional confirmation for this kind of switching behaviour was obtained from the optical investigations of the switching process. Circular domains (see Fig. 4) were grown by slow cooling under an applied dc field. A switching process can be seen by the rotation of the extinction crosses of these domains upon changing the sign of the applied field. However, the extinction brushes do not relax at zero voltage (even after 30 min at 0 V there is no change of the position of the brushes). Rotation takes place only upon application of the opposite field and this behaviour clearly confirms the bistable (ferroelectric) switching process (Fig. 4).

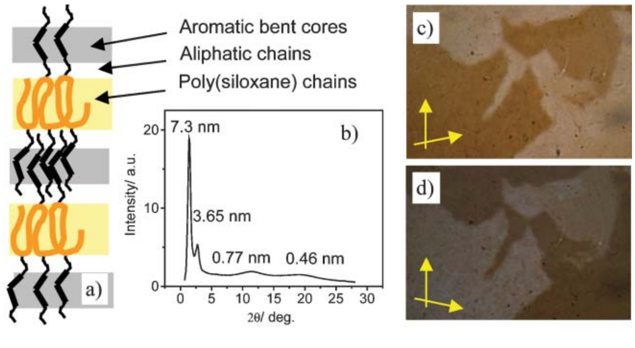


Fig. 2 (a) Model of the organisation of **Poly-1** in the mesophase (the bent cores are tilted with respect to the projection plane); (b) X-ray diffractogram at 100 °C; (c, d) texture obtained by cooling the isotropic liquid without applied field, characterised by chiral domains of opposite handedness (there is a slight deviation of the polarisers from a 90° angle, either positive or negative).

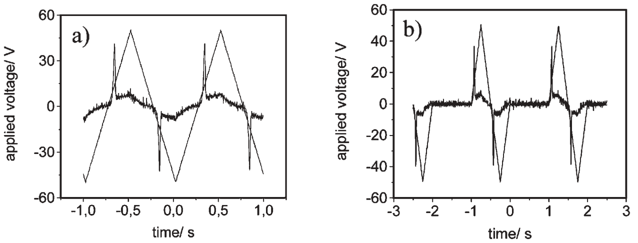


Fig. 3 Switching current response of **Poly-1** (T = 90 °C, ±50 V, 1 Hz, 5 μm ITO coated cell, EHC, Japan). The occurrence of only one peak in each half period on applying (a) a simple and (b) an alternating simple and modified triangular wave voltage is an indication of a ferroelectric switching process.

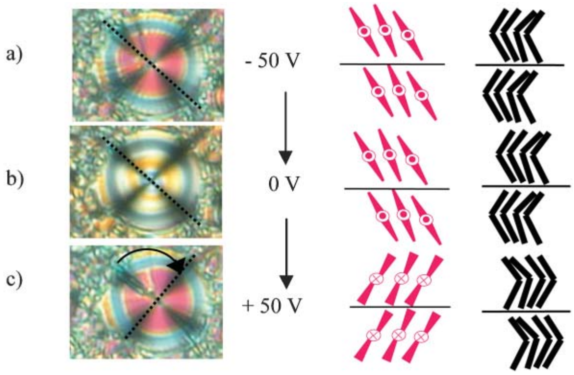


Fig. 4 Textures (between crossed polarisers) obtained by cooling the isotropic liquid under an applied dc voltage (50 V). The direction of the extinction brushes of the circular domains remains unchanged by terminating the field (a → b) and these brushes rotate by *ca.* 40–45° (corresponding to the tilt angle of the mesogenic cores) upon applying the opposite field (b → c), indicating a bistable (ferroelectric) switching of **Poly-1**. (T = 95 °C, 6 μm polyimide coated ITO cell).

In summary, the first side chain LC polymer with bent-core mesogenic units was synthesised and this material shows ferroelectric switching behaviour as well as spontaneous achiral symmetry breaking into domains with chiral supramolecular structures of opposite handedness, properties which are of actual interest. In this respect the properties of this polymer are clearly distinct from the structurally related low molecular weight compound **1**[6] (see Fig. 1) which does not show any chiral domains and which is an antiferroelectric switching material. On the other hand, the polymer behaves very similarly to siloxane substituted low molecular mass LC.[6] Therefore, it can be concluded that in low molecular mass systems as well as in polysiloxane polymers the siloxane units are responsible for these special properties. Micro-segregation of the polysiloxane backbone from the mesogenic segments into distinct sublayers appears to be a main factor leading to these special properties.

The authors are grateful to the Deutsche Forschungsgemeinschaft (GRK 894) and the Fonds der Chemischen Industrie for financial support. R. A. Reddy is grateful to the Alexander von Humboldt Foundation for a research fellowship.

Christina Keith, R. Amaranatha Reddy and Carsten Tschierske*
Institute of Organic Chemistry, Martin-Luther-University Halle-Wittenberg, Kurt-Mothes Str. 2, D-06120 Halle, Germany.
E-mail: carsten.tschierske@chemie.uni-halle.de;
Fax: +49(0)345 5527346; Tel: +49(0)345 5525664

Notes and references

† ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, J = 8.8 Hz, 2H, ArH), 8.14 (d, J = 8.7 Hz, 4H, ArH), 7.63 (d, J = 8.9 Hz, 2H, ArH), 7.49 (d, J = 4.9 Hz, 2H, ArH), 7.43 (m, 1H, ArH), 7.36 (d, J = 8.9 Hz, 2H, ArH), 7.27 (d, J = 8.7 Hz, 2H, ArH), 6.98 (m, 1H, ArH), 6.95 m, 4H, ArH), 4.04 (m, 4H, OCH_2), 1.83 (m, 4H, CH_2), 1.47 (m, 4H, CH_2), 1.26 (m, 32H, CH_2), 0.87 (t, J = 6.7 Hz, 3H, CH_3), 0.51 (broad, 2H, $SiCH_2$), 0.07 (s, 78H, $Si(CH_3)_2$), 0.05 (s, 12H, $Si(CH_3)_2$), 0.01 (s, 3H, Si–CH_3).

1 *Handbook of Liquid Crystals*, ed. D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill, Wiley-VCH, Weinheim, 1998, vol. 3.

2 S. T. Lagerwall, *Ferroelectric and Antiferroelectric Liquid Crystals*, John Wiley & Sons, New York, 1999.

3 T. Niori, T. Sekine, J. Watanabe, T. Furukawa and H. Takezoe, *J. Mater. Chem.*, 1996, **6**, 1231.

4 D. R. Link, G. Natale, R. Shao, J. E. Maclennan, N. A. Clark, E. Körblova and D. M. Walba, *Science*, 1997, **278**, 1924; G. Pelzl, S. Diele and W. Weissflog, *Adv. Mater.*, 1999, **11**, 707; C. Tschierske and G. Dantlgraber, *Pramana*, 2003, **61**, 455.

5 J. Thisayukta, Y. Nakayama, S. Kawauchi, H. Takezoe and J. Watanabe, *J. Am. Chem. Soc.*, 2000, **122**, 7441; G. Heppke, D. D. Parghi and H. Sawade, *Liq. Cryst.*, 2000, **27**, 313; R. A. Reddy and B. K. Sadashiva, *Liq. Cryst.*, 2003, **30**, 1031; J. Ortega, C. L. Folcia, J. Etxebarria, N. Gimeno and M. B. Ros, *Phys. Rev. E*, 2003, **68**, 11707; W. Weissflog, M. W. Schröder, S. Diele and G. Pelzl, *Adv. Mater.*, 2003, **15**, 630; A. Jakli, Y.-M. Huang, K. Fodor-Csorba, A. Vajda, G. Galli, S. Diele and G. Pelzl, *Adv. Mater.*, 2003, **15**, 1606.

6 G. Dantlgraber, A. Eremin, S. Diele, A. Hauser, H. Kresse, G. Pelzl and C. Tschierske, *Angew. Chem., Int. Ed.*, 2002, **41**, 2408; G. Dantlgraber, S. Diele and C. Tschierske, *Chem. Commun.*, 2002, 2768.

7 J. P. Bedel, J. C. Rouillon, J. P. Marcerou, M. Laguerre, H. T. Nguyen and M. F. Achard, *J. Mater. Chem.*, 2002, **12**, 2214.

8 S. Demel, C. Slugovc, F. Stelzer, K. Fodor-Csorba and G. Galli, *Macromol. Rapid Commun.*, 2003, **24**, 636; A. C. Sentman and D. L. Gin, *Angew. Chem., Int. Ed.*, 2003, **42**, 1815; E.-J. Choi, J.-C. Ahn, L.-C. Chien, C.-K. Lee, W.-C. Zin, D.-C. Kim and S.-T. Shin, *Macromolecules*, 2004, **37**, 71; J. Barbera, N. Gimeno, L. Monreal, R. Pinol, M. B. Ros and J. L. Serrano, *J. Am. Chem. Soc.*, 2004, **126**, 7190.