mechanistic insights. The present system is significantly more sensitive to visible light than either the Belousov-Zhabotinskii[8] or the Briggs-Rauscher[9] reactions, and it should provide an ideal system for experiments on periodic perturbation of chemical oscillators[10] or even for chemical image processing.[11]

Acknowledgment. This work was supported by the National Science Foundation (CHE-8800169) and by a U.S.-Hungarian Cooperative Grant from the NSF (INT-8613532) and the Hungarian Academy of Sciences. We thank Colin Steel for helpful discussions.

---

(8) Gāspār, V.; Bazsa, G.; Beck, M. T. *Z. Phys. Chem. (Leipzig)* **1983**, *264*, 1, S-43.

(9) Kumpinsky, E.; Epstein, I. R.; De Kepper, P. *Int. J. Chem. Kinet.* **1985**, *17*, 345.

(10) Schneider, F. W. *Annu. Rev. Phys. Chem.* **1985**, *36*, 347.

(11) Kuhnert, L.; Agladze, K. I.; Krinsky, V. I. *Nature* **1989**, *337*, 244.

Design and Synthesis of New Ferroelectric Liquid Crystals. 9.[1] An Approach to Creation of Organic Polymer Thin Films with Controlled, Stable Polar Orientation of Functional Groups

David M. Walba*

Department of Chemistry and Biochemistry and
Optoelectronic Computing Systems Center
University of Colorado
Boulder, Colorado 80309-0215

Patrick Keller*

Laboratoire Leon Brillouin
Centre D'Etudes Nucleaires De Saclay
F-91191 Gif-sur-Yvette, Cedex, France

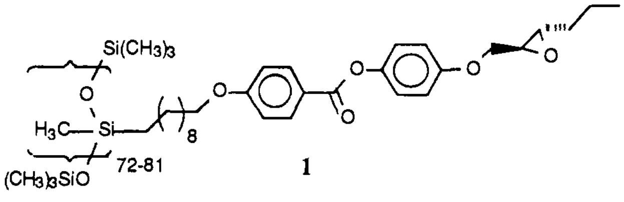
Devendra S. Parmar and Noel A. Clark

Department of Physics, University of Colorado
Boulder, Colorado 80309-0390

Michael D. Wand

Displaytech, Inc., 2200 Central Avenue
Boulder, Colorado 80301

Received March 31, 1989


1

$$X \xrightarrow{95} C^* \xrightarrow{147} I$$
$$\text{"glass"} \xleftarrow{85} C^* \xleftarrow{147} I$$

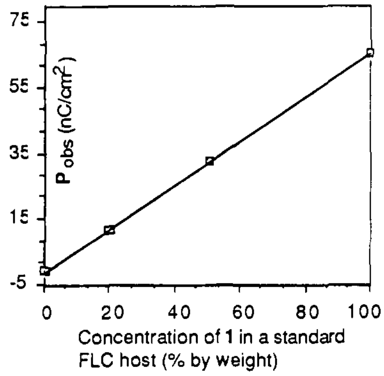


Figure 1. Structure, phase sequence, and polarization of FLC polymer **1** and polarization of some host-guest mixtures.

For many microelectronic and optoelectronic applications, organic thin films with controlled, polar orientation of functional groups relative to a substrate surface hold great potential. Several possible solutions of this problem are currently under active investigation, including the growth of single crystal films,[2] polar deposition of Langmuir-Blodgett multilayers,[3] electrically poled polymer films,[4] and self-assembled multilayers.[5] In this communication, we describe a new approach for achieving designed organic thin films with thermodynamically stable, polar orientation of functional groups using ferroelectric liquid crystal polymers (FLCPs).

Due to the useful physical properties of polymer films and the spontaneous polar order present in ferroelectric liquid crystal assemblies, a large effort has recently been launched directed toward the synthesis of FLCPs.[6,7] The small spontaneous polarization (*P*) observed for materials reported to date coupled with the choice of chiral moieties incorporated into the mesogenic units, however, precludes real insight into the functional group orientation occurring in these systems. Reported herein is the synthesis and characterization of the first FLCP to incorporate a mesogen possessing interpretable sign and large magnitude of *P*.

Thus, following literature procedures,[7a,8] hydrosilylation of 4-[(*S*,*S*)-2,3-epoxyhexyloxy]phenyl 4-(ω-decenyloxy)benzoate[9] with commercially available polymethylhydrosiloxane[10] (MW = 4500-5000) catalyzed by dicyclopentadienylplatinum(II) chloride gave a white, crystalline solid after precipitation from a benzene solution with methanol. The ^{1}H NMR ($CDCl_3$) and infrared spectra ($CHCl_3$) of the new material are consistent with the desired polymer **1** (Figure 1). Optical microscopy on the neat polymer, mixing studies with a low molar mass smectic C* host, and dielectric spectroscopy combine to show unequivocally that the new

---

(1) Previous papers in this series: (a) Walba, D. M.; Clark, N. A.; Razavi, H. A.; Eidman, K. F.; Haltiwanger, R. C.; Parmar, D. S. A Novel Application of the Molecular Recognition Paradigm: Design of Ferroelectric Liquid Crystals. *Liquid Crystal Chemistry, Physics, and Applications*; Doane, J. W., Yaniv, Z., Eds.; Proc. SPIE 1080, 1989; pp 115-122. (b) Walba, D. M.; Clark, N. A.; Razavi, H. A.; Parmar, D. S. A Novel Application of the Host-Guest Paradigm: Design of Organic Optoelectronic Materials. In *Proceedings of the 5th International Symposium on Inclusion Phenomena and Molecualr Recognition*; Atwood, J. L., Ed.; Plenum Publishing Corp., in press. (c) Walba, D. M.; Eidman, K. F.; Haltiwanger, R. C. *J. Org. Chem.*, in press. (d) Walba, D. M.; Razavi, H. A.; Clark, N. A.; Parmar, D. S. *J. Am. Chem. Soc.* **1988**, *110*, 8686-8691, and references therein.

(2) For a general discussion of the factors controlling crystal shape, see: Berkovitch-Yellin, Z. *J. Am. Chem. Soc.* **1985**, *107*, 8239-8253. For a relevant specific example, see: Itoh, H.; Hotta, K.; Takara, H.; Sasaki, K. *Opt. Commun.* **1986**, *59*, 299-303.

(3) Popovitz-Biro, R.; Hill, K.; Landau, E. M.; Lahav, M.; Leiserowitz, L.; Sagiv, J. *J. Am. Chem. Soc.* **1988**, *110*, 2672-2674, and references therein.

(4) (a) Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 690-703. (b) Leslie, T. M.; Demartino, R. N.; Choe, E. W.; Khanarian, G.; Haas, D.; Nelson, G.; Stamatoff, J. B.; Stuetz, D. E.; Teng, C.-C.; Yoon, H.-N. *Mol. Cryst. Liq. Cryst.* **1987**, *153*, 451-477.

(5) Tillman, N.; Ulman, A.; Schildkraut, J. S.; Penner, T. L. *J. Am. Chem. Soc.* **1988**, *110*, 6136-6144.

(6) (a) Shibaev, V. P.; Kozlovsky, M. V.; Beresnev, L. A.; Blinov, L. M.; Plate, N. A. *Polym. Bull.* **1984**, *12*, 299. (b) Decobert, G.; Soyer, F.; Dubois, J. C. *Polym. Bull.* **1985**, *14*, 179. (c) Decobert, G.; Dubois, J. C.; Esselin, S.; Noel, C. *Liq. Cryst.* **1986**, *1*, 307. (d) Zentel, R.; Reckert, G.; Reck, B. *Ibid.* **1987**, *2*, 83. (e) Esselin, S.; Bosio, L.; Noel, C.; Decobert, G.; Dubois, J. C. *Ibid.* **1987**, *2*, 505. (f) Uchida, S.; Morita, K.; Miyoshi, K.; Hashimoto, K.; Kawasaki, K. *Mol. Cryst. Liq. Cryst.* **1988**, *155*, 93-102.

(7) (a) Keller, P. *Ferroelectrics* **1988**, *85*, 425. (b) Suzuki, T.; Okawa, T. *Makromol. Chem., Rapid Commun.* **1988**, *39*, 755.

(8) Keller, P. *Mol. Cryst. Liq. Cryst. Inc. Nonlin. Opt.* **1988**, *157*, 193.

(9) 4-[(*S*,*S*)-2,3-epoxyhexyloxy]phenyl 4-(ω-decenyloxy)benzoate was prepared by coupling of 4-[(*S*,*S*)-2,3-epoxyhexyloxy]phenol with 4-(ω-decenyloxy)benzoyl chloride promoted by triethylamine/DMAP. Synthesis of the enantiomerically enriched epoxy phenol and a similar coupling to 4-(decyloxy)benzoyl chloride are described in the following: Walba, D. M.; Vohra, R. T.; Clark, N. A.; Handschy, M. A.; Xue, J.; Parmar, D. S.; Lagerwall, S. T.; Skarp, K. *J. Am. Chem. Soc.* **1986**, *108*, 7424-7425. 4-[(*S*,*S*)-2,3-epoxyhexyloxy]phenol is commercially available from Displaytech, Inc., 2200 Central Avenue, Boulder, CO 80301.

(10) Petrarch Systems, Inc. Cat No. PS 122.

material possesses the desired C* phase over a broad temperature range, as indicated by the phase sequence shown in Figure 1.[11]

Our approach for probing functional group orientation in low molar mass FLCs is to measure the sign and magnitude of the ferroelectric polarization in an aligned thin film between conducting glass plates.[1d,12] This is done by switching the ferroelectric with an applied voltage step and measuring the current response of the cell. By a novel combination of interaction with a rubbed polymer alignment layer on the surface of the electrodes and shear, it proved possible with compound **1** to achieve excellent alignment, affording a monodomain of ordered polymer film 3 μm thick, with an electrode area of 1.17 cm^2.[11]

Switching in the standard geometry[12] was relatively slow (3 ms at 85 °C, 15 V/μm driving field) but easily allowed measurement of P for the material. In fact, neat compound **1** showed a polarization of +65 nC/cm^2 (85 °C). The sign and magnitude of P for the (*S*,*S*)-epoxide-containing polymer are consistent with the model presented earlier for the low molar mass mesogen itself (+45 nC/cm^2), where polar orientation of the epoxide dipole is the major contributor to the macroscopic polarization.[9] Previously reported FLCPs showed polarizations (measured in unaligned samples) on the order of 6 nC/cm^2.[6,7]

Small-angle neutron diffraction studies of achiral, deuterium labeled smectic A polymethylsiloxane side chain LCPs similar to **1** indicate that the backbone orients as a random coil between the layers of mesogen molecules (i.e., in the smectic layers), with the mesogenic units oriented relative to the layers much as they would be in a low molar mass A phase.[13] The reasonable extrapolation of this result to smectic C phases, in combination with the observed polarization of polymer **1**, suggests that the polar orientation of molecular dipoles in **1** is similar to that obtained in the analogous low molar mass material.

It is thus expected that when bound in the "crystal" lattice of a low molar mass C* host, the mesogenic units of the FLCP should orient in the bent cylinder binding site according to our model for the molecular origins of P,[1,9,12] and the observed polarization of host–guest mixtures (complexes) should be a linear function of concentration of the polar component (the FLCP in this case), since the presence of the backbone in the smectic layers is not expected to affect the shape of the binding site. Indeed, polymer **1** is miscible in all proportions with the standard C* host 4-[(*S*)-(+)-(4-methylhexyl)oxy]phenyl 4-(decyloxy)benzoate,[14] and the observed polarization for aligned samples of mixtures possessing 20% and 50% by weight of polymer **1** in the host (+11 nC/cm^2 and +33 nC/cm^2, respectively) are linear with concentration, as indicated by the plot shown in Figure 1. In total, the data presented here provides good evidence that the molecular recognition model for functional group orientation in low molar mass materials may be extended to the FLCP films of the present study.

In conclusion, an organic polymer ferroelectric thin film showing good global functional group orientation in a large-area monodomain has been created. Evidence is presented for a molecular-level interpretation of dipole orientation occurring in the FLCP phase which is similar to that for the analogous low molar mass material, with the slight modification that the polymer backbone is now present in the smectic layers. While by our interpretation the polymeric nature of the FLCP does not dramatically affect functional group orientation, obvious advantages with respect to processibility in some applications accrue from achieving this orientation in a polymer film relative to the low molar mass materials.

Acknowledgment. This work was supported in part by the Office of Naval Research, by the NSF Engineering Research Center program (Optoelectronic Computing Systems Center, Grant No. CDR-8622236), and by the National Science Foundation (Grant No. DMR-8611192).

---

(11) The alignment technique, optical microscopy, miscibility studies, and dielectric spectroscopy of **1** are detailed in: Parmar, D. S.; Clark, N. A.; Keller, P.; Walba, D. M.; Wand, M. D. *J. Phys. (Les Ulis, Fr).* Submitted for publication.

(12) Walba, D. M.; Slater, S. C.; Thurmes, W. N.; Clark, N. A.; Handschy, M. A.; Supon, F. *J. Am. Chem. Soc.* **1986**, *108*, 5210–5221.

(13) (a) Moussa, F.; Cotton, J. P.; Hardouin, F.; Keller, P.; Lambert, M.; Pēpy, G.; Mauzac, M.; Richard, H. *J. Physique* **1987**, *48*, 1079–1083. (b) Hardouin, F.; Noirez, L.; Keller, P.; Lambert, M.; Moussa, F.; Pēpy, G. *Mol. Cryst. Liq. Cryst.* **1988**, *155*, 389–397.

(14) Keller, P. *Ferroelectrics* **1984**, *58*, 3–7. Our measurements give a value of −1 nC/cm^2 for this host, which is commercially available from Aldrich.

UV Photoisomerization of *N*-Methylacetamide and Resonance Raman Enhancement of a New Conformation-Sensitive Amide Mode

Yang Wang, Roberto Purrello,[†] and Thomas G. Spiro*

Department of Chemistry, Princeton University
Princeton, New Jersey 08544

Received April 27, 1989

Ultraviolet resonance Raman (UVRR) spectroscopy is being developed as a structure probe for proteins.[1,2] Near resonance with the first allowed electronic transition (ca. 190 nm) of the peptide bond, strong enhancement is seen for amide modes, particularly amide II (~1560 cm^{-1}), whose intensity is sensitive to the α-helix content in polypeptides and proteins.[3] Song et al.[4] have recently called attention to another peptide UVRR band, near 1390 cm^{-1}, which disappears in D$_2$O and may be a conformation marker. For the peptide model compound, *N*-methylacetamide (NMA), they identified this band at a much higher frequency, 1496 cm^{-1}, and assigned it to the overtone of the out-of-plane NH bend, amide V. A previous suggestion[2] that the 1496-cm^{-1} band arises from photoisomerized *cis*-NMA was rejected by Song et al.[4]

In Figure 1 we demonstrate, however, that the 1496-cm^{-1} band is indeed photoinduced. At low laser power incident on a flowing sample of aqueous NMA this band is *absent* in the 200-nm-excited RR spectrum (D), but it grows in when the power is increased (C) and particularly when the sample is stationary (B) even at low power. Its frequency is the same as the IR band assigned to amide II of *cis*-NMA prepared by matrix quenching from a high-temperature nozzle[5] and is the same as that of the intense amide II band in the 200-nm-excited RR spectrum of aqueous caprolactam (Figure 1A), a secondary amide for which the cis isomer is enforced by its cyclic structure. The 1496-cm^{-1} band can therefore be assigned with confidence to *cis*-NMA produced by photoisomerization from the stable trans form. Supporting this inference is the observation of intensity loss in the amide II and III bands of the trans isomer.

Importantly, photoisomerization is also observable in D$_2$O and is especially evident when the *N*-methyl group is replaced by CD$_3$ (Figure 2). For this isotopomer H/D exchange collapses the amide II and III bands of the trans isomer, arising from coupled C–N stretching and N–H bending coordinates,[6] into a single strong band at 1496 cm^{-1} which is essentially pure C–N stretching (amide II′). At high laser power levels, a new band grows in at 1471 cm^{-1},

---

* Author to whom correspondence should be addressed.

[†] Permanent address: Dipartimento oli Scienze Chimiche Universita di Catania, Catania, Italy.

(1) Hudson, B. S.; Mayne, L. C. In *Biological Applications of Raman Spectroscopy*; Spiro, T. G., Ed.; Wiley: New York, 1987; Vol. II, Chapter 4.

(2) Harada, A. I.; Takeuchi, H. *Spectroscopy of Biological Systems*; Clark, R. J. H., Esther, R. E., Eds.; Wiley: New York, 1986; pp 113–175.

(3) (a) Copeland, R. A.; Spiro, T. G. *Biochemistry* **1985**, *24*, 4960–4968. (b) Copeland, R. A.; Spiro, T. G. *J. Am. Chem. Soc.* **1986**, *108*, 1281–1285.

(4) Song, S.; Asher, S. A.; Krimm, S.; Vandekar, J. *J. Am. Chem. Soc.* **1988**, *110*, 8548–8550.

(5) Ataka, S.; Takeuchi, H.; Tasumi, M. *J. Mol. Struct.* **1984**, *113*, 147–160.

(6) Sugawara, Y.; Hirakawa, A. Y.; Tsuboi, M. *J. Mol. Spectrosc.* **1984**, *108*, 206.