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Fig. 3. Topology of the exchange interactions according to Fig. 2.

The present results show that indeed the structural data allow us to decide which vanadium centers must be considered formally as +5 and which as +4, at least with respect to the limit of strong localization. In fact, if the V3 and V3a centers were to be considered as vanadium(IV), or as intermediates between vanadium(IV) and vanadium(V), they would be involved in several strong μ-oxo bridges, thus providing a complete change in the exchange pattern. In particular, they would be expected to be involved in strong antiferromagnetic exchange interactions with the V1 and V1a centers, which would then have their spins coupled, contrary to observation. The successful calculation of the magnetic susceptibility confirms that bis μ-oxo bridges are very effective in transmitting antiferromagnetic exchange interactions between oxovanadium(IV) moieties.

The variability of the exchange interactions between vanadium centers and the possibility of fixing the ratio of vanadium(IV) and vanadium(V) centers in the cluster enables us in principle to tune and/or design the topology and as a consequence the magnetic properties of polyoxovanadates (IV/V) through the template effect.[4, 6]

[1] M. T. Pope, A. Müller, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 49. Q. Chen, D. P. Goshorn, C. P. Scholes, X.-L. Tang, J. Zubieta, *J. Am. Chem. Soc.* **1992**, *114*, 4667.
[2] D. Gatteschi, L. Pardi, A. L. Barra, A. Müller, J. Döring, *Nature* **1992**, *354*, 436. D. Gatteschi, L. Pardi, A. L. Barra, A. Müller, J. Döring, *J. Am. Chem. Soc.* **1992**, *114*, 8509.
[3] I. D. Brown, Kang Kun Wu, *Acta Crystallogr.* **1976**, *B32*, 1957.
[4] A. Müller, R. Rohlfing, E. Krickemeyer, H. Bögge, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 909.
[5] D. Gatteschi, B. Tsukerblatt, A. L. Barra, L. C. Brunel, A. Müller, J. Döring, *Inorg. Chem.* **1992**, *31*, 5132; *Inorg. Chem.* **1993**, *32*, 2114.
[6] A. Müller, K. Hovemeier, R. Rohlfing, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1192.

Highly Oriented Poly(di-n-alkylsilylene) Films on Oriented PTFE Substrates

By *Holger Frey, Sergej Sheiko, Martin Möller,** *Jean Claude Wittmann*, and *Bernard Lotz*

Poly(di-n-alkylsilylene)s (polysilanes), catena-Si polymers, are one-dimensional semi- and photoconductors[1] that owe their electronic and photonic properties[2] to the σ-orbital delocalization of the backbone. Hole mobilities of the order of $10^{-5}\,m^2V^{-1}s^{-1}$ on short length scales have been reported[3] for crystalline poly(di-n-hexylsilylene). Generally, symmetrically substituted poly(di-n-alkylsilylenes) are crystalline and form conformationally disordered (two-dimensional) mesophases at elevated temperatures.[4, 5]

Well-oriented polysilene layers are of potential interest for several areas of application: electrophotography,[6] nonlinear optics,[7] display fabrication,[8] and microlithography.[9] In many cases, highly oriented materials may show improved performance in comparison to isotropic films. It was suggested that oriented polysilylenes may show considerably enhanced $\chi^{(3)}$ nonlinear optical (NLO) properties.[1] So far however, there are only a few reports on the manufacture of oriented structures in the literature, either by Langmuir–Blodgett techniques[10] or by co-orientation upon stretching with a drawable polymer matrix[11, 12] in the mesomorphic state.

In this paper it is demonstrated that highly oriented polysilylene films can be prepared by the method of Wittmann and Smith,[13] i.e., crystallization of polymers on a highly preoriented polytetrafluoroethylene (PTFE) substrate. At elevated temperatures, PTFE exists in a partially mobile phase, which upon transfer by friction onto a smooth surface forms a very thin (2–50 nm) film, as the chains in contact with the surface are drawn out of the bulk.[14] The PTFE films used for the work reported here were prepared at 230 °C and a pressure of 15 Pa. Such PTFE layers are suitable as substrates for crystallization of poly(di-n-alkylsilylene)s in a highly oriented film. This is illustrated by Figure 1, which shows optical micrographs of films of (top) poly(di-n-butylsilylene), PDBS, and (bottom) poly(di-n-hexylsilylene), PDHS, which were crystallized on PTFE from $CHCl_3$ solution. The micrographs were taken on the edge of the oriented PTFE film. The left-hand side of the image (recorded with crossed polarizers) shows the typical isotropic spherulites observed for solution- or melt-crystallized poly(di-n-alkylsilylene)s, the right-hand side shows a highly birefringent and homogeneously oriented structure, which indicates the orientation of the PDBS chains upon

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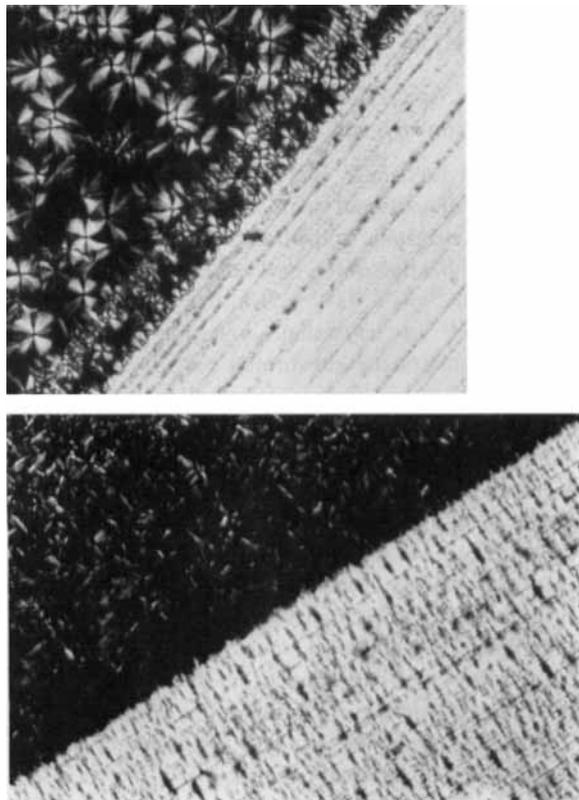
Fig. 1. Micrographs of top) poly(di-*n*-butylsilylene), PDBS, and bottom) poly(di-*n*-hexylsilylene), PDHS, crystallized on the edge of an oriented PTFE film (crossed polarizers); size of the areas imaged: approximately 500 × 420 μm.

crystallization. Similar images have been obtained for poly-(di-*n*-pentylsilylene), PDPS.

The different polysilylenes studied here vary in their crystal structure: PDBS and PDPS form a 7/3 helix,[15] while PDHS has an all-trans planar backbone structure.[1] However, in spite of the different molecular geometries, all materials form similarly oriented layers on friction-transferred PTFE. Optically, we have also observed excellent orientation for various poly(di-*n*-alkylsilylene) copolymers with a fraction of shorter side chains.

In order to evaluate the achievable degree of orientation, the films were characterized by electron diffraction. For this purpose, the polysilylene film cast on PTFE was backed with a carbon support film and floated off the glass. The patterns indicate a high degree of orientation, as demonstrated in Figure 2 for a copolymer derived from PDPS by replacement of 4% of the side chains with chiral (S)-2-methylbutyl substituents.[16] The series of meridional reflections display no significant arcing. The layer line spacing of 13.83 Å is unambiguous evidence for the 7/3 helical structure reported for PDPS,[15] as are the strong third and seventh layer lines at 4.69 Å and 2.04 Å, respectively. Equatorial reflections observed at 11.9–12.0 Å are typical of the interlayer spacing in the hexagonal unit cell (interchain distance of 13.8 Å) of PDPS. No significant amorphous halo indicative of a disor-

dered fraction is detected. The PTFE reflections at 1.30 Å (meridional) and on the equator can be used for the calibration of the polysilylene diffraction patterns.
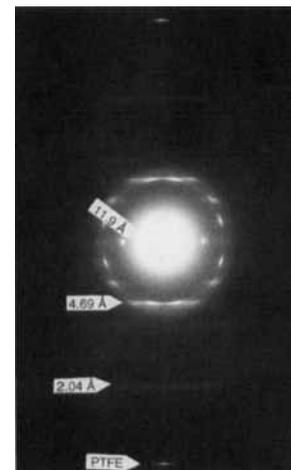

Fig. 2. Electron diffraction pattern of a film of a copolymer derived from poly(di-*n*-pentylsilylene), PDPS, which crystallizes in a 7/3 helix.

Thus, close to perfect orientation can be concluded from electron diffraction. However, electron diffraction is a very local method and limited to thin layers. Therefore, we have studied films with a thickness up to 1 μm crystallized on PTFE. Randomly selected areas were investigated by polarized transmission Fourier transform infrared (FTIR) spectroscopy. This also allows the orientation quality to be compared with the orientation observed in a drawn ultra high molecular weight polyethylene (UHMWPE)/PDPS blend reported before.[12] The aligned PTFE films were prepared on silicon wafers, which are transparent to infrared light. Subsequently, the polysilylene films were solution crystallized on the PTFE. Polarized FTIR spectra of PDPS and PDHS, as shown in Figure 3, confirm a high degree of orientation even in quite thick films. The PTFE films on silicon are too thin to be detected by FTIR transmission spectroscopy and thus do not show up in the spectra presented here. Both PDPS and PDHS display strongly dichroic behavior, depending on whether the polarization direction is parallel or perpendicular to the orientation of the layers.

At least two dichroic band regions are evident (Fig. 3): i) the region from 600 to 700 cm^{-1}, with a very strongly dichroic band at 660–670 cm^{-1} (Si–C stretching vibration, highly orientation sensitive), and ii) the CH$_2$ and CH$_3$ stretching vibrations between 2800 and 2900 cm^{-1}, which are weakly dichroic in PDPS and strongly dichroic in PDHS. The strong dichroism of the 660 cm^{-1} band reflects the good backbone orientation, since the transition moment of the Si–C stretching vibration is parallel to the polysilylene chain. The dichroism observed for the side chain stretching vibrations in PDHS and PDPS demonstrates much more pronounced orientation of the side chain matrix in PDHS,
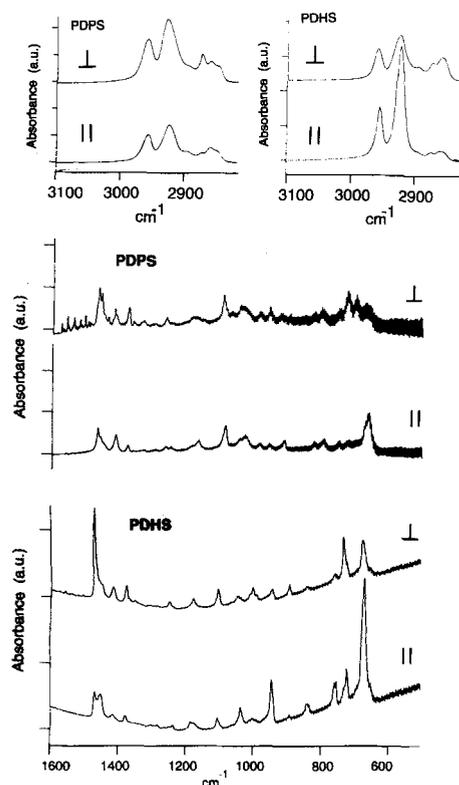
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Fig. 3. Polarized transmission FTIR spectra of PDPS and PDHS, recorded parallel (∥) and perpendicular (⊥) to the orientation direction. The spectra exhibit periodic fringes, which are due to interference of the IR beam in the thin material layer and thick Si-wafer substrate.

with its three-dimensionally ordered side chains,[17] than in the less ordered helical PDPS. A more detailed discussion of the polarized FTIR spectra is in preparation. Comparison with the FTIR data from [12] shows that the degree of orientation in the present films is comparable to that reached by ultradrawing (drawing ratio $\lambda \geq 30$) in a UHMWPE matrix.

To summarize, crystallization of poly(di-n-alkylsilylene)s on an oriented PTFE substrate yields highly oriented poly-(di-n-alkyl-silylene) films of several square centimeters, even when the film thickness exceeds 1 μm. The degree of orientation is assessed by optical birefringence, electron diffraction and dichroic IR experiments. The PTFE-induced orientation technique can be extended to poly(di-n-alkylsilylene)s with different crystalline structures. The underlying cause of the high orientation achieved on aligned PTFE substrates is not yet clear. Epitaxy is not very plausible, given the different molecular geometries and cell parameters of PTFE and the polysilylenes. Alternatively, oriented grooves on the PTFE surface may act as a nanometer-scale grating, inducing anisotropic nucleation of the mesomorphic polysilylenes.[13]

[1] N. Matsumoto, K. Takeda, H. Teramae, M. Fujino, in *Silicon Based Polymer Science* (Eds: J. M. Zeigler, F. W. G. Fearon), Advances in Chemistry, Vol. 224, American Chemical Society: Washington, DC **1990**.

[2] R. D. Miller, J. Michl, *Chem. Rev.* **1989**, *89*, 1359, and references cited therein.

[3] H. Frey, M. Möller, M. P. de Haas, N. J. P. Zenden, P. G. Schouten, G. P. van der Laan, J. Warman, *Macromolecules* **1993**, *1*, 89.

[4] F. C. Schilling, A. J. Lovinger, J. M. Zeigler, D. D. Davis, F. A. Bovey, *Macromolecules* **1989**, *22*, 3055.

[5] M. Varma-Nair, J. Cheng, Y. Jin, B. Wunderlich, *Macromolecules* **1991**, *24*, 5442.

[6] K. Yokoyama, M. Yokoyama, *Chem. Lett.* **1989**, 1005. M. A. Abkowitz, M. J. Rice, M. Stolka, *Phil. Mag. B* **1990**, *61*, 25.

[7] J. C. Baumert, G. C. Bjorklund, D. H. Jundt, M. C. Jurich, H. Looser, R. D. Miller, J. Rabolt, R. Sooriyakumaran, J. D. Swalen, R. J. Twieg, *Appl. Phys. Lett.* **1989**, *53*, 1147.

[8] J. Kido, K. Nagai, Y. Okamoto, T. Skotheim, *Chem. Lett.* **1991**, 1267.

[9] R. D. Miller, S. A. Macdonald, *J. Imaging Sci.* **1987**, *31*, 43.

[10] F. W. Embs, G. Wegner, D. Neher, P. Albouy, R. D. Miller, C. G. Willson, W. Schrepp, *Macromolecules* **1991**, *24*, 5068.

[11] L. A. Harrah, J. M. Zeigler, *Macromolecules* **1987**, *20*, 601.

[12] M. Möller, H. Frey, S. Sheiko, *Colloid Polym. Sci.* **1993**, *271*, 554.

[13] J. C. Wittmann, P. Smith, *Nature* **1991**, *352*, 414.

[14] C. M. Pooley, D. Tabor, *Proc. R. Soc. London* **1972**, *A329*, 251.

[15] R. D. Miller, B. L. Farmer, W. Fleming, R. Sooriyakumaran, J. Rabolt, *J. Am. Chem. Soc.* **1987**, *109*, 2509.

[16] H. Frey, M. Möller, K. Matyjaszewski, *Macromolecules* **1993**, in press.

Ultrathin Films of Cellulose on Silicon Wafers**

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Efforts to construct supramolecular architectures of polymers have led to the development of a novel, non-amphiphilic class of polymers—so called hairy-rod materials—which are excellently suited for the Langmuir–Blodgett (LB) technique.[1] Hairy-rod polymers consist of an inherently stiff backbone to which short flexible side chains are attached so as to provide the backbone with a permanently fixed hydrophobic solvent shell.

Examples are substituted phthalocyaninatopoly(silox-ane)s[2] and co-poly(glutamate)s,[3] both of which are well-suited for the preparation of supramolecular architectures by the LB-technique. Ultrathin films of the pure materials or of composites of the components are of interest for their application as sensor devices,[4] in optoelectronics[5] or as orientation layers in the manufacture of liquid-crystal displays (LCDs).[6]

Monolayers of cellulose derivatives[7, 8] or pure cellulose[9] at the air–water interface have been studied for more than 60 years. For example, Kawaguchi et al. investigated

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