ORDER AND THERMOCHROMISM OF POLY(DI-n-ALKYL)SILANE COPOLYMERS

Holger Frey and Martin Möller*
Chemische Technologie, Universiteit Twente
P.O. Box 217, NL-7500 AE Enschede, The Netherlands

Krzysztof Matyjaszewski
Department of Chemistry, Carnegie Mellon University
4400 Fifth Avenue, Pittsburgh PA 15213, USA

ABSTRACT
A series of poly(di-n-alkyl)silane copolymers derived from Poly-(di-n-hexyl)silane, PDHS, was prepared. Mesomorphic phase transitions of these copolymers depend on fraction as well as on the size of the comonomers. DSC and temperature dependent UV-spectroscopy were employed to study the effect of constitutional disorder on the length of all-trans \( \sigma \)-conjugated Si-Si catenated chromophores.

INTRODUCTION
Polysilanes can be described as "one dimensional silicon" with intriguing photoconductive and nonlinear optical properties \[1,2\]. Like other symmetrically substituted inorganic polymers, polysilanes show characteristic transitions from a highly ordered low temperature phase to a partially disordered, hexagonal mesophase \[3\]. The mesomorphic behavior and the related solid state UV-thermo- and piezochromism \[4\] depend strongly on the order of the catena-silicon backbone in the rigid low temperature phase. The conformation of the backbone is determined by the interaction and crystallization of the sidechains. Poly(di-n-hexyl)silane, PDHS, assumes an all-trans conformation, whereas poly(di-n-pentyl)silane, PDPS, and poly(di-n-butyl) silane, PDBS, adopt a 7/3 helical structure. In this paper we describe the investigation of a series of poly(di-n-alkyl)silane copolymers derived from PDHS. The phase transitions were monitored by DSC and temperature dependent UV-spectroscopy.
A. Synthesis and Characterization of the Poly(di-n-alkyl)silane Copolymers

The copolymers were prepared by a Wurtz-type coupling reaction of mixtures of the di(n-alkyl)dichlorosilanes as described previously [5]. Typically, the molecular weight distributions of the polymers were monomodal with a small amount of oligomeric material, which could be separated by fractional precipitation. The molecular weights $M_w$ of the copolymers ranged between 400,000 and 600,000, referred to narrow polystyrene standards. Solution $^{13}$C-NMR spectroscopy showed that the composition of the copolymers equaled the composition of the monomer feed, due to the similar reactivity of the monomers. The $^{13}$C($^1$H) spectra of the copolymers consist of a series of sharp peaks, which could be assigned to the methylene units of the side chains [5].

B. Crystallization and Phase Transitions

A strongly endothermic first order phase transition is observed for PDHS at 42°C [1]. In the low temperature phase, the PDHS molecules are rigidly ordered in a three-dimensional lattice and the alkyl side-chains are packed in an array typical for paraffin molecules. The phase transition has been attributed to subsequent disordering of side chains and the main chain. The incorporation of shorter side chains like n-pentyl, n-butyl or n-propyl leads to defect sites in the lattice of PDHS and introduces intra- as well as intermolecular disorder.

Table 1: Transition Temperatures, Enthalpies and Entropies for the 90/10 and the 80/20 copolymers. Maxima of UV-absorptions of the rigid low temperature phase are also listed.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$T_{\text{trans}}$ [K]</th>
<th>$\Delta H_{\text{trans}}$ [kJ/mol]</th>
<th>$\Delta S_{\text{trans}}$ [J/mol K]</th>
<th>$\lambda_{\text{max}}$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDHS</td>
<td>315</td>
<td>14.8</td>
<td>47.1</td>
<td>372</td>
</tr>
<tr>
<td>90/10 P(DHS/DPS)</td>
<td>307</td>
<td>12.7</td>
<td>41.5</td>
<td>367</td>
</tr>
<tr>
<td>80/20 P(DHS/DPS)</td>
<td>283</td>
<td>10.3</td>
<td>36.6</td>
<td>346</td>
</tr>
<tr>
<td>90/10 P(DHS/DBS)</td>
<td>302</td>
<td>11.5</td>
<td>38.1</td>
<td>365</td>
</tr>
<tr>
<td>80/20 P(DHS/DBS)</td>
<td>295</td>
<td>6.3</td>
<td>21.3</td>
<td>-</td>
</tr>
<tr>
<td>90/10 P(DHS/DPrS)</td>
<td>287</td>
<td>7.0</td>
<td>24.4</td>
<td>362</td>
</tr>
<tr>
<td>80/20 P(DHS/DPrS)</td>
<td>269</td>
<td>3.3</td>
<td>12.1</td>
<td>-</td>
</tr>
</tbody>
</table>

The calorimetric data listed in table 1 show a decrease of transition temperatures and transition enthalpies with increasing fraction of smaller comonomer. In a recent paper we reported on the behavior of P(DHS/DPS) copolymers [5]. In this case, for all
intermediate concentrations the formation of columnar mesophases is observed. The copolymers show isodimorphic mixed crystal formation. This also applies to the copolymers with n-butyl or n-propyl sidechains described here, where large defects are created in the lattice and thus the side chain interactions are lowered considerably. The comparison of the transition enthalpies shows that there are two parameters determining the phase transitions: The fraction as well as the length of the shorter side chains incorporated.

Solid State UV Spectroscopy

PDHS shows a marked UV-thermochromism, when spin-cast films are heated above the phase transition temperature of 42°C. The UV-absorption band shifts from 372 nm to 315 nm [1]. This thermochromism is completely reversible and is ascribed to the onset of mobility of long all-trans ordered, σ-conjugated backbone segments. The long wavelength UV-absorption of PDHS is due to the decrease of the band gap energy between σ-delocalized HOMO and LUMO for trans-sequences compared to gauche Si-Si-bonds of the poly-(di-n-alkyl)silanes. The molecular nature of the sidechain determines the mean free energy of the formation of kinks. Gauche conformations in the Si-Si-backbone in the low temperature phase are favored with increasing number of defects in the paraffin-like array of the side chains.

Fig. 1a, b: Thermochromism of PDHS (left) and 90/10 P(DHS/DBS) (right)
Fig. 1 shows a comparison of the thermochromism of the homopolymer PDHS and the copolymer 90/10 P(DHS/DBS). $\lambda_{\text{max}}$ for the ordered low temperature phase of the copolymers is blueshifted in comparison with PDHS, as also listed in Table 1. This can be explained by the decrease of the length of all-trans conjugated backbone chromophores. The thermochromic transition temperatures correspond to the DSC-data.

Conclusions:
DSC and solid state UV-spectroscopy were employed to study the effect of constitutional disorder on the crystallization and mesophase formation of poly(di-n-hexyl)silylene copolymers. It could be shown, that transition temperatures, UV-thermochromism and UV-absorption maxima can be controlled by the size as well as the fraction of shorter side chain monomer incorporated. In all cases, the formation of a columnar mesophase was little affected by copolymerization of DHS and shorter side chain units. In the disordered high temperature phase, all copolymers seem to have a similar mesophase structure. These results are supported by MAS $^{29}$Si-NMR spectra reported elsewhere [5]. Currently, the effect of copolymerization on photoconductivities is being studied.

ACKNOWLEDGEMENTS
We thank Prof. Dr. H.-J. Cantow, Institut für Makromol. Chem., Universität Freiburg, for supporting this work. K. M. acknowledges support via a Presidential Young Investigator Award as well as from Xerox, Eastman Kodak, and Hoechst Celanese. Financial support for H.F. was provided by the Max-Buchner-Stiftung, FRG.

REFERENCES