PII: S0032-3861(98)00052-4

Polymer Vol. 39 No. 21, pp. 5257–5259, 1998
0032-3861/98/$ – see front matter

Structure in amorphous polysilanes determined by diffuse X-ray scattering

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(Accepted 5 January 1998)

Polyphenylsilane, $(HSiC_6H_5)_n$, was synthesised by catalytic coupling of phenylsilane using $Cp_2ZrCl_2/2BuLi$ as a catalyst. Chlorination of the resulting polymer with tetrachloromethane (CCl_4) gave polychlorophenylsilane, $(ClSiC_6H_5)_n$, subsequent substitution of chloride by dimethylamine yielded polydimethylaminophenylsilane, $((CH_3)_2NSiC_6H_5)_n$. The X-ray pattern of the three polysilanes reveal their amorphous state. Due to the similarity of the X-ray pattern of the three polysilanes, diffraction peaks are observed at $s \sim 0.6$, 1.4 and 3.3 $Å^{-1}$, similar conformation and packing of the polysilane chains are concluded. The peaks at 0.6 $Å^{-1}$ are identified as interchain peaks. From a comparison of the reduced scattering functions of polyphenylsilane and liquid benzene, we conclude that the arrangement of phenyl rings in polyphenylsilane is comparable to the statistical disorder of benzene molecules in the liquid state. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: polysilanes; diffuse X-ray scattering; structure)

Introduction

The interesting optical and electronic properties of polysilanes are a result of delocalisation of σ-electrons along the silicon backbone[1]. Synthesis, and structural, optical and electrical properties of polysilanes have been reviewed recently[2].

Polysilanes are potentially useful for a variety of technical applications like microlithography, ceramics and light emitting diodes. On the basis of high photoluminescence quantum yields[3] polysilanes are applied as electroactive layers in electroluminescent devices emitting ultraviolet light[4]. Due to their high hole mobility, polysilanes are also excellent materials as hole transport layers in organic-based light emitting devices[5–7]; polysilanes with a phenyl ring in the monomer unit are used.

Synthesis

The method usually employed for the preparation of polysilanes is the coupling of dichlorosilanes with alkali metals (Wurtz type coupling). The severe reaction conditions strongly limit the number of possible monomers and thus the structural diversity of the synthesised polymers. Since the discovery of the dehydropolymerisation reaction of hydrosilanes a larger field of monomers is accessible[8], and functionalisation of the resulting polymers is easily accomplished.

Polyphenylsilane (PPS) was synthesised by coupling of phenylsilane using $Cp_2ZrCl_2/2BuLi$ as a catalyst. The polymer was dissolved in toluene and filtered over a short Florisil column to separate it from the catalyst. Polyphenylsilane was chlorinated by stirring it with CCl_4 at room temperature for three days affording polychlorophenylsilane (PCPS)[9]. Chlorine was substituted for dimethylamino groups by condensing dimethylamine onto the polymer and refluxing for two days at atmospheric pressure. The polymer was dissolved in toluene and separated from the salt by filtration yielding polydimethylaminophenylsilane (PAPS). The structural formulae of the three polysilanes as well as the synthetic route to PCPS and PAPS are depicted in *Figure 1*. The polymers were characterised by nuclear magnetic resonance, infrared spectroscopy and gel permeation chromatography. M_n values for PPS and PAPS are 2500 and 2250, respectively; this corresponds to 30 monomeric units for PPS and 25 for PAPS. All reactions were performed under an atmosphere of dry argon using Schlenk techniques.

Experimental

The X-ray scattering experiments were performed with a Philips X'PERT system which is integrated in a glove box filled with nitrogen. The purity of the atmosphere was better than 1 ppm for O_2 and H_2O.

The divergence of the primary beam was 0.27°, the beam was focussed by a Bragg-Brentano geometry with a receiving slit of 0.75 mm, CuK_α radiation was used. The experiment on PPS was performed on a 1.5 mm thick bulk sample, small amounts of PCPS and PAPS powder were investigated on a silicon single crystal getting low background from the substrate.

In the case of PPS the experimental intensity was corrected for the polarisation factor. The corrected intensity I_{corr} was transformed to the reduced intensity function $i(s)$ following the procedure suggested by Mitchell[10]:

$$i(s) = kI_{corr} - \sum_{j=1}^{n} f_j^2(s) - I_{Comp} \text{ with } s = \frac{4\pi}{\lambda}\sin\Theta \qquad (1)$$

where k is a normalisation factor of the corrected intensity, s is the absolute value of the scattering vector, $\sum f_j^2(s)$ is the independent coherent scattering of the chemical repeat unit which consists of n atoms, and I_{Comp} is the Compton scattering; values of f_j^2 and I_{Comp} are taken from published tables[11,12].

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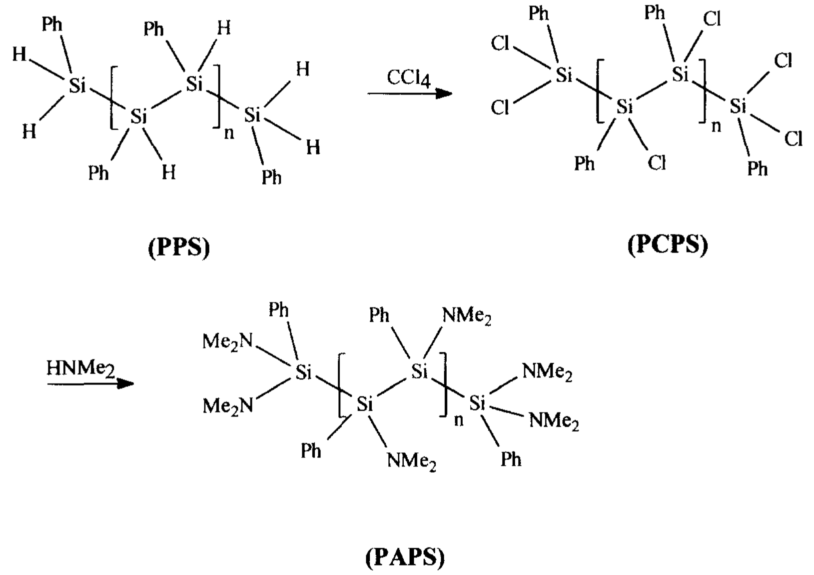

(PPS)

(PCPS)

(PAPS)

Figure 1 Chemical structure of polyphenylsilane (PPS), polychlorophenylsilane (PCPS), polydimethylaminophenylsilane (PAPS) and the synthetic route to PCPS and PAPS

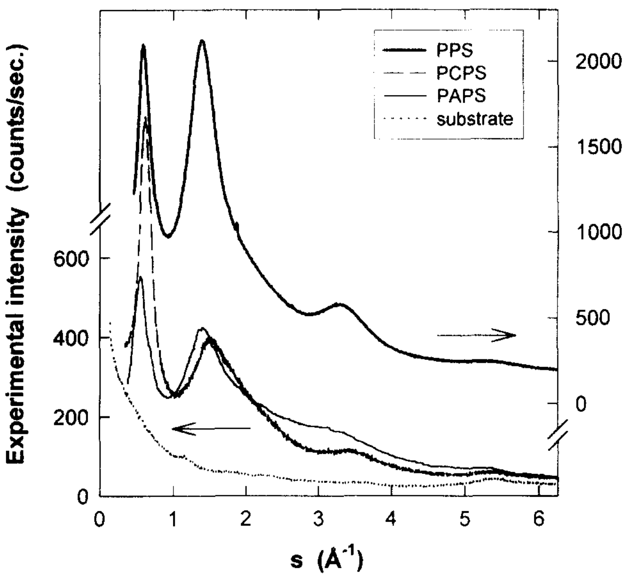

Figure 2 Experimental intensity *versus* absolute value of the scattering vector *s* of PPS, PCPS and PAPS

Results and discussion

The results for PPS, PCPS and PAPS are shown in *Figure 2*; the intensity scale for PPS is given on the right-hand side, for PCPS and PAPS on the left-hand side. Since only small amounts of PCPS and PAPS powder were investigated, the diffuse scattering of the substrate is plotted for comparison. *Table 1* gives the position of the diffraction peaks as observed in the experiment. Additionally, the intensity ratios of the two main peaks, $I(s{\sim}0.6)/I(s{\sim}1.4)$, are given; in this case the influence of the substrate is corrected.

Similar X-ray patterns are observed for all three polysilanes. The peak positions as well as the relative intensities (except for PCPS at $s = 1.52$ Å^{-1}) do not change significantly; therefore, we conclude that the conformational packing of these three polysilanes is similar.

Table 1 Positions of the peaks within the X-ray diffraction pattern and the intensity ratios of the first two peaks $I(s{\sim}0.6$ Å$^{-1})/I(s = 1.4$ Å$^{-1})$ of PPS, PCPS and PAPS

	s (Å^{-1})	s (Å^{-1})	s (Å^{-1})	s (Å^{-1})	Intensity ratio
PPS	0.59	1.40	3.3	5.4	1.0
PCPS	0.61	1.52	3.4		2.3
PAPS	0.57	1.40	3.2		1.0

The position of the first peak at $s = 0.57\ldots0.61$ Å^{-1} is more or less equal for the three polysilanes, the s-value does not change considerably by replacing the hydrogen atom of PPS by a chlorine atom or an amino group. However, the intensity ratios listed in *Table 1* differ considerably. The fact that we observe an intensity ratio of 1 for PPS and PAPS and an intensity ratio of 2.3 for PCPS indicates that the first peak of the three X-ray patterns is due to interchain scattering. Interchain scattering in PPS and PAPS arises mainly because of scattering between the silicon backbones, in the case of PCPS the chlorine atom gives an additional main contribution to the interchain scattering. From a rough comparison of the quadratic form factors at $s = 0.6$ Å^{-1} between PPS and PCPS we derive a 2.25 times higher value for PCPS. The bond distance between the silicon backbone and the chlorine atom of approximately 2.0 Å should give an additional broadening of the diffraction peak; however, the width of the peak is too broad to detect such an influence.

The reduced intensity $s^*i(s)$ was calculated for PPS, and the result is depicted in *Figure 3*. Also the reduced intensity of liquid benzene is plotted taken from previous work[13]. Strong similarities are observed between PPS and liquid benzene. Of course, the interchain peak of PPS at $s = 0.59$ Å^{-1} cannot be observed in liquid benzene. Due to the excellent agreement of $s^*i(s)$ of liquid benzene at the peak at 1.4 Å^{-1} and some agreement at higher s-values we conclude that the phenyl rings within amorphous PPS are similarly arranged as benzene molecules in the liquid state. The disagreement at $s{\sim}3.3$ Å^{-1} is probably due to interchain scattering within the polysilane chain. Note that the reduced intensity contains inter- as well as intramolecular scattering. It should be noted that an excellent agreement was found between liquid benzene and polystyrene[14].

The crystal structure of benzene reveals that neighbouring molecules are perpendicular to each other, this T-stacking of

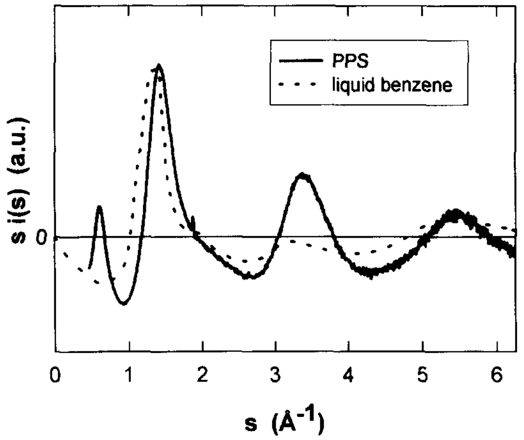

Figure 3 Reduced intensity function *i*(*s*) in a *s***i*(*s*) *versus* *s* plot (*s* = absolute value of the scattering vector) of PPS in comparison with liquid benzene[12].

aromatic molecules is the main interaction between the molecules in crystalline benzene[15]. Calculations show that even benzene molecules interact as a dimer in a T-shape manner[16]. In liquid benzene the preferred conformation of two benzene rings is reported as a T-shape and only a small number of the benzene molecules are arranged parallel to each other[13]. Since the X-ray diffraction patterns of liquid benzene and PPS show similar features, we assume a T-shape packing of the phenyl rings within PPS. The T-shape interaction between phenyl rings is dominant in polyphenylsilane; it is also probably the dominant interaction in PCPS and PAPS.

Due to the steric hindrance within one polymer chain the interacting phenyl rings are mainly from different polymer chains. The electrical conductivity in polysilanes is one-dimensional along the silicon backbones; the T-stacked π-conjugated phenyl rings of neighbouring polymer chains can be the cross-over links for electrons (or holes) between two silicon backbones. Therefore, the T-stacking of the phenyl rings is probably the reason for the good performance of polyphenylsilanes as hole transport layers.

Conclusion

The amorphous state of PPS, PCPS and PAPS, synthesised by catalytic coupling and substitution reactions, was investigated by X-ray diffraction. Despite the different substituents on the silicon backbone the order within the amorphous state is similar for the three polysilanes.

The dominant peak at around 0.6 Å^{-1} could be referred to interchain scattering between the silicon backbones. From a comparison with liquid benzene we conclude that the diffraction pattern of PPS at higher *s*-values is determined by the scattering between phenyl rings. The T-stacking of the phenyl rings is the dominant interaction which determines the amorphous states of these three polyphenylsilanes. The phenyl rings are probably the link for the electrical transport between two silicon backbones of polyphenylsilanes.

Acknowledgements

We thank M. Braun for the installation of the Philips X'PERT system within a glove box and Philips for help in overcoming the technical problems of operating an X-ray diffractometer in a glove box. We thank the Austrian Fonds zur Förderung der wissenschaftlichen Forschung, project number 9747-CHE for financing the experimental equipment. This work was performed within the Spezialforschungsbereich Elektroaktive Stoffe.

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