Thermochromism of Polysilanes Bearing Non-Ionic Polar Side Chains and Some $LiClO_4$ Salt[1]

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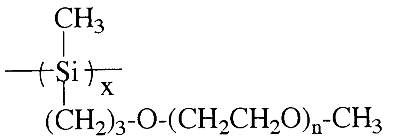
(Received October 23, 1996)

The titled polysilanes, $\{CH_3\text{-}O(CH_2CH_2O)_n\text{-}CH_2CH_2CH_2\text{-}Si\text{-}CH_3\}_x$ (n=1~3), are thermochromic both in the solid state and in solution. In the solid state these polysilanes all show a continuous bathochromic shift until nearly the same kink point temperature(190 K), then blue shift slightly. A water-soluble polysilane, n=3, forms a complex with $LiClO_4$. The thermochromic behavior of the complex is highly dependent on Li content. The complex of higher Li content shows only a blue shift on cooling while complexes of low Li content display red shift initially till T_g and then blue shift. An unexpected hyperchromic effect accompanied by the blue shift is observed for the complex of Si:Li=1:1 on cooling.

Thermochromism is one of the most unusual optical characteristics among the diverse physical properties that polysilanes display.[2] The nature of side chain is the most critical factor to determine the type of the thermochromism; in solution polysilanes with highly asymmetric dialkyl side chains show continuous bathochromic shift and those having symmetric long dialkyl side chains show abrupt transition on cooling.

Thermochromism of polysilanes has been discussed based on the phase transition of the main chain induced by the side chain ordering. A polarization interaction between polymer main chain and its surroundings was also proposed recently.[3] West[4] has presented data supporting this theory by demonstrating that polysilanes having ethereal side chains still display abrupt thermochromic transition without showing any side chain crystallization. Recently, we have prepared polysilanes bearing long oxyethylenic side groups, $\{CH_3\text{-}O(CH_2CH_2O)_n\text{-}CH_2CH_2CH_2\text{-}Si\text{-}CH_3\}_x$ (where n=1~3).[5] It is of interest to know the effect of the extremely flexible side chain as well as the effect of some guest compounds on the thermochromic behavior of these polysilanes. We report herein the temperature dependent UV spectra of polysilanes **1-3** and complexes of polysilane **3** with $LiClO_4$.



$$\text{-}\!\!\left(\underset{(CH_2)_3\text{-}O\text{-}(CH_2CH_2O)_n\text{-}CH_3}{\overset{CH_3}{\mathrm{Si}}}\right)_{\!x}\!\!\text{-}$$

Table1. Physical properties of polysilanes **1-3**

Polysilane	n	Mw ($x10^3$)[a]	λmax [b]	Tp (K)
1	1	3.5	303	243
2	2	5	306	197
3	3	4.3	307	193

[a] Refered to polystyrene standard. [b] In THF at 297 K.

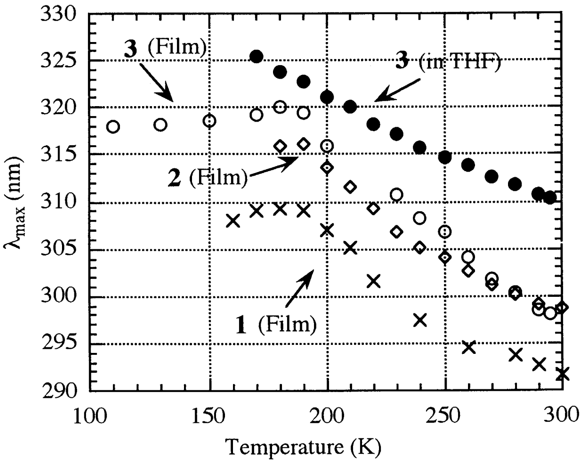


Figure 1. Themperature dependence of the λ_{max} of polysilanes **1-3**.

Polysilanes **1-3** are soft, elastic solid in their appearance. Glass transition temperatures(T_g) for these polysilanes **1-3** obtained by DSC analyses are summarized in Table 1 together with the molecular weight (M_w) and the absorption maximum (λ_{max}) in THF. The temperature dependence of λ_{max} of polysilanes **1-3** in the solid state as well as that of **3** in THF are shown in Figure 1.[6] The continuous bathochromic shift on cooling resembles the thermochromic behavior of poly(hexylmethylsilane).[2] A distinct kink for each polysilane is commonly observed at ca. 195 K in the plot. The kink temperatures of polysilanes **1-3** are almost consistent with T_g determined by DSC analysis. It is of interest that polysilanes **1-3**, in spite of the defferent side chain lenght, have nearly the same T_g which is in agreement with T_g of polyethylene oxide. This may reflect the very flexible nature of polysilanes **1-3**.

The shifts for polysilanes **1-3** are nearly the same at 245-195 K. A slight blue shift below T_g is commonly observed for polysilanes **1-3**. All conformations of polysilanes freeze at T_g and iso-free-volume change is only allowed. Thus, a thermal shrinkage of the main-chain without significant conformational deformation may account for this blue shift.

Polysilane **3** is soluble not only in polar organic solvents such as acetonitrile and alcohols but in water. The oligo-ethylene oxide-like side chains can form complexes with alkali metal ions. Polysilane **3** -$LiClO_4$ complexes were in fact prepared from THF solution,[7] and the thermochromic behavior of the complexes in the solid state was examined. Shifts of λ_{max} and relative change of absorbance[8] are shown in Figures 2 and 3, respectively.

Thermochromic behavior of the complex is highly dependent on the Li content. A complex with low Li content behaves similarly to the original polysilane **3**. Complexes with high Li

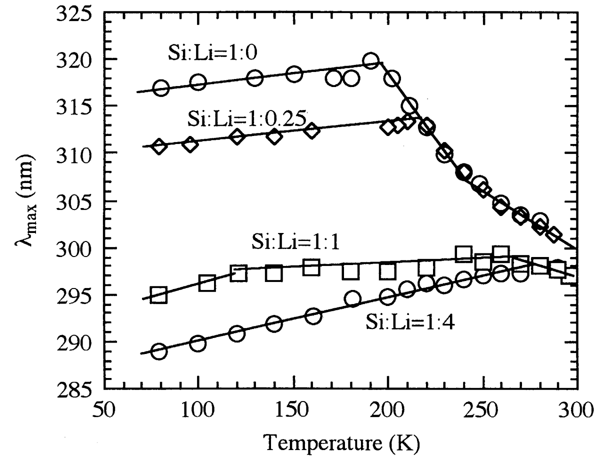


Figure 2. Themperature dependence of λ_{max} of **3**-$LiClO_4$ complexes.

content(Si:Li=1:1) show a red shift only a narrow temperature range and then show near constant λ_{max}, or no red shift was observed for the complex of Si:Li=1:4. This can be explained by Li ions fixing the ethereal side chain, restricting its free movement. The kink temperature which corresponds to T_g determined by DSC analyses, therefore, rises with increasing Li content in the complexes. Similar increase of T_g with increasing Li salt was observed in poly(ethylene oxide) or polymers having olig-oethylene oxide side groups.[9] This increase can be attributed both inter- and intrachain bridging effect by lithium salts.

The bathochromic shift in the thermochromism of polysilanes is usually accompanied by hyperchromic effect. As shown in Figures 2 and 3, λ_{max} and the O.D. of polysilane **3** and the complex of Si:Li=4:1 behave as expected. However, though a slight blue shift takes place below T_g for the complex of Si:Li=1:1, an unexpected further hyperchromic effect is observed below the kink temperature. Since four oxygen atoms in a polyethylene oxide contribute to make a fairly stable complex with lithium ions, each side group in polysilane **3** can fix a lithium ion in Si:Li=1:1 complex though inter-sdie chain fixing is also possible.

Polysilane **3** complex(Si:Li=1:1) takes its most stable conformation at T_g(260 K), the "freezing point" of iso-free volume. Further lowering the temperature causes thermal shrinkage of the complex resulting in thickening the film and, thus, yields a hyperchromic effect. A slight conformational deformation also may take place to resulti in a slight blue shift.

With excess of the salt presented(Si:Li=1:4), the polysilane is "frozen" in salt matrix and the film becomes more firm. Thus, thermal shrinking will be less than in the polysilane of lower Li content and accordingly no intensification of the absorbance is expected.

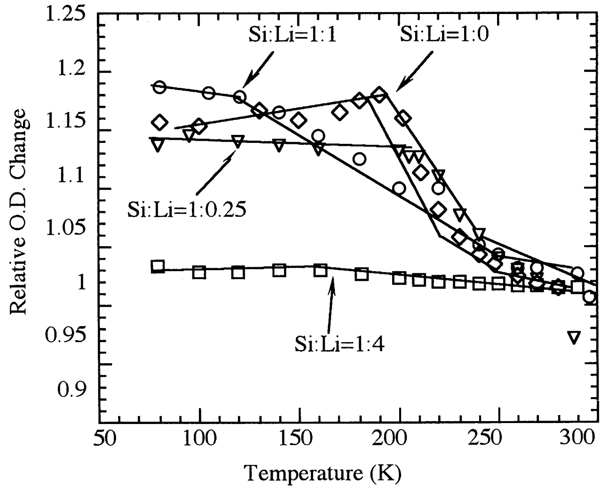


Figure 3. Relative O.D. change of **3**-$LiClO_4$ complex.

The study of ionic mobility of these unusual polysilane-$LiClO_4$ complexes is of interest for future study.

The authors are grateful to Prof. R. Nakao and Prof. T. Horii for the help of variable temperature UV measurement. Thanks are also given to Shin-etsu Chemical Co. Ltd and Tohre Dow Chemical Co, Ltd. for their generous gift of chlorosilanes.

References and Notes

1 Part of this paper have been reported at 69th Spring Annual Meeting of CSJ, Kyoto(March, 1995), Abstr. 3F819.
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6 λ_{max} in THF occurs longer wavelength than that of film on quartz. The study of this solvent-polysilane interaction will be reported elsewhere.
7 Polysilane **3**-$LiClO_4$ complexes were prepared from THF solution and dried under high vacuum at 60 °C.
8 Because preparation of polysilane films with the same absorbance is difficult, the O.D. values are normalized by taking the O.D. value at 280 K as unity for the purpose of comparison.
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