Complex thermochromic phase transitions in three polydialkylsilanes with an oxygen atom in the side chain

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Temperature investigations of the UV and Raman spectra of three polydialkylsilanes with an oxygen atom in the side chain have shown that all polymers studied undergo a thermochromic phase transition in the interval from +20 to −70 °C which is not abrupt but is kinetically limited; this transition is of the order–disorder type and is related to a change in the conformation of the polymer main chain from a disordered one to all-*trans*.

Thermochromic phase transitions of high–molecular weight polysilanes are widely studied (see latest review[1] and refs. therein). Recently we have shown that these transitions in the solid state are not abrupt but proceed over a temperature interval, and if such transitions take place on cooling they do not reach completion, being stopped at glassification point T_g.[2–4] We have also noted that the UV band corresponding to the ordered phase has a complex profile or consists of several peaks whose relative intensity depends on the sample prehistory.[4]

Introduction of an oxygen atom into a linear alkyl side chain increases polymer flexibility[5] which leads to lowering of T_g. One can expect that the phase transitions for such polymers may reach completion, so that at low temperature the polymers will exist as only one phase, not a frozen composite mixture. Introduction of an oxygen atom will also change the polarizability of the side chains, thus altering intramolecular as well as intermolecular interactions, which determine the nature of these phase transitions.[6]

With this in mind, we have investigated by variable temperature UV and Raman methods three polymers with an ethoxypentyl group as one or two side chains, namely: $\{Si[(CH_2)_5OEt]_2\}_n$ **1**, $[n\text{-}HexSi(CH_2)_5OEt]_n$ **2** and $[n\text{-}HeptSi(CH_2)_5OEt]_n$ **3**.

The synthesis and some properties of these polymers were recently reported in refs. 5 and 7. In ref. 5, DSC, X-ray and UV data for **2** are presented. At room temperature **2** exhibited an X-ray diffraction pattern characteristic of a hexagonal columnar mesophase (*hcm*), to which a broad UV band at *ca.* 320 nm corresponded. DSC data pointed to a first-order phase transition centered at −21 °C (T_c), which was accompanied by appearance of a new UV band at *ca.* 350 nm whose intensity increased on further cooling to −50 °C while that of the 320 nm band decreased. In ref. 7, thermochromic phase transitions in Langmuir–Blodgett films of **1** and **2** as studied by polarized UV spectroscopy were described.

Here we report the results of a detailed temperature investigation of the UV spectra of solution-grown films of **1**–**3** and of the Raman spectra of solid samples. Experimental conditions were the same as reported in refs. 2 and 3. Experiments were carried out using slow, equilibrium cooling, especially near T_c, as described previously in refs. 3 and 4, because isothermal relaxation of a polymer after temperature lowering near T_c requires not less than several hours. This is illustrated in Figure 1 for the example of polymer **3**. The use of fast cooling misrepresents the real process of the phase transition.

Temperature evolution of the UV spectra of **1**–**3** is presented in Figures 2–4 and shows that all three polymers at room temperature exhibit similar broad UV bands at ~320 nm. On cooling, a second, longer-wavelength absorption, corresponding to a more ordered phase, appears and grows. The temperature at which it appears corresponds approximately to T_c found by DSC and is −15 °C for **1**, −20 °C for **2**, and −5 °C for **3**. The most interesting finding is that the new red-shifted absorption consists of several peaks. These are at ~350, ~360 and ~375 nm, their relative intensity depending on the sample and its prehistory. An analogous picture was recently observed by us for $[n\text{-}Hex_2Si]_n$.[4]

As shown in Figure 2, for **1** three peaks at 351, 359, and 375 nm appear simultaneously, however, the band at 375 does not grow in intensity on further cooling. The band at 359 nm,

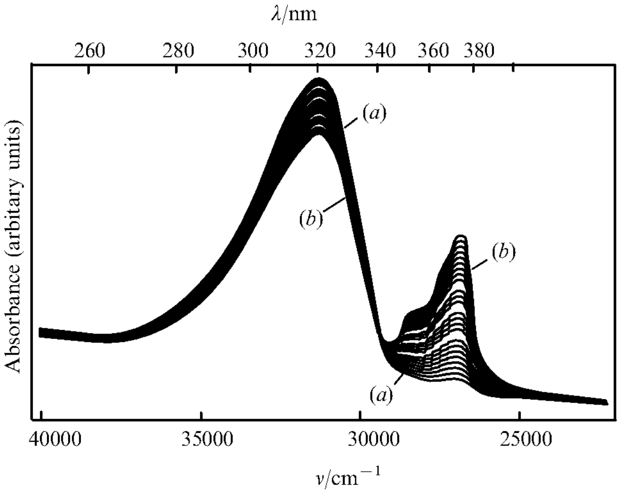

Figure 1 UV spectrum reflecting the process of isothermal relaxation at −5 °C of the polymer **3** during 5 h. Note a gradual increase in the fraction of the modification with all-*trans* conformation of the backbone with time. (*a*) Initial spectrum; (*b*) after 5 h.

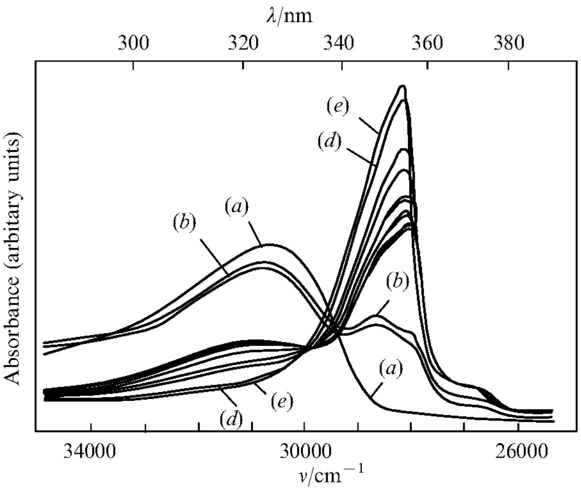

Figure 2 Temperature evolution on cooling of the UV spectrum of the polymer **1**. (*a*) room temperature; (*b*) −20 °C; (*c*) temperature interval from −23 °C to −50 °C; (*d*) −70 °C; (*e*) −220 °C.

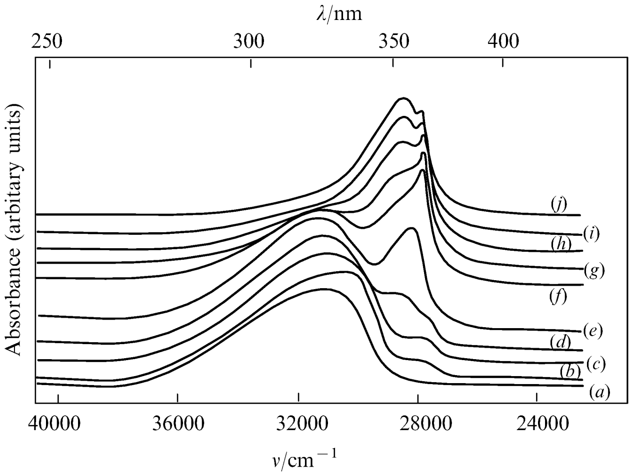

Figure 3 Temperature evolution on cooling of the UV spectrum of the polymer **2**. (*a*) room temperature; (*b*) $-20\,°C$; (*c*) $-23\,°C$; (*d*) $-25\,°C$; (*e*) $-27\,°C$; (*f*) $-30\,°C$; (*g*) $-35\,°C$; (*h*) $-40\,°C$; (*i*) $-50\,°C$; (*j*) $-100\,°C$.

which was initially less intense than that at 351 nm, becomes more intense on further cooling, and at about $-50\,°C$ two peaks merge into one broad band with λ_{max} 355 nm. At $-70\,°C$ the band 320 nm disappears, showing that the phase transition is completed.

For **2** (Figure 3), the red-shifted absorption consists of only two peaks with λ_{max} at 350 and 359 nm. The latter peak appears first. The relative intensity of these peaks depends on temperature. The phase transition reaches completion at $-50\,°C$.

For **3**, the long-wavelength absorption also consists of two peaks but with λ_{max} 352 and 376 nm. Figures 1 and 4, in which the data for **3** are presented, clearly demonstrate the dependence of the phase transition process on the sample prehistory. When the film of **3** was first prepared, its spectrum at room temperature contained only the *hcm* band at 320 nm. It was necessary to cool the film to $-5\,°C$ to obtain the red-shifted band, which first exhibited the peak at 375 nm but in the process of isothermal relaxation the peak at 352 nm also emerged (Figure 1). However, the next experiment with the same film (Figure 4) showed that a small amount of the red-shifted band was present even at room temperature. The interplay between the intensity of the two peaks during the process of cooling is reflected in Figures 1, 4. The phase transition for **3** reaches completion at $-50\,°C$. Further cooling to $-248\,°C$ leads to a noticeable blue shift of both peaks in the complex band corresponding to the more ordered phase [Figure 4 (*d*)].

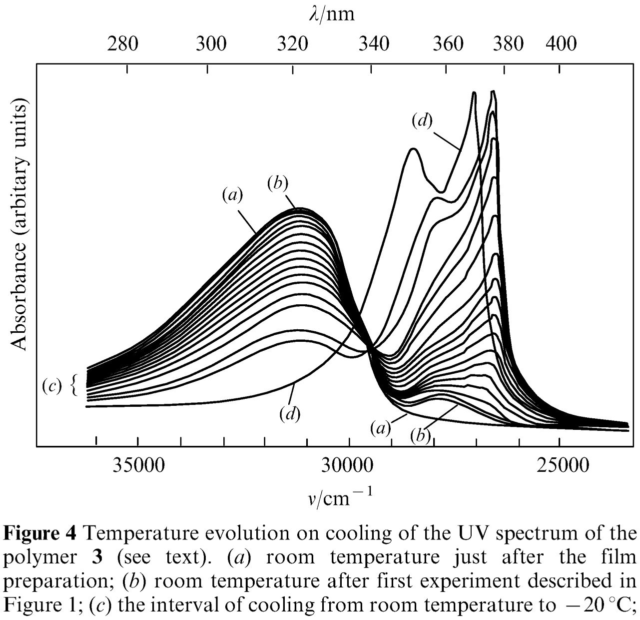

Figure 4 Temperature evolution on cooling of the UV spectrum of the polymer **3** (see text). (*a*) room temperature just after the film preparation; (*b*) room temperature after first experiment described in Figure 1; (*c*) the interval of cooling from room temperature to $-20\,°C$; (*d*) $-248\,°C$.

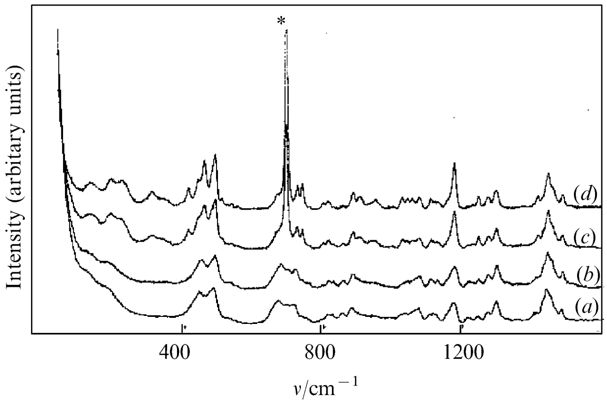

Figure 5 Temperature evolution of the Raman spectrum (excited by 514.5 nm line) of the polymer **1**. (*a*) room temperature; (*b*) $-30\,°C$; (*c*) $-70\,°C$; (*d*) $-180\,°C$. * The line of the νSi–C vibration corresponding to the all-*trans* configuration of the backbone.

Thus, all three polymers with an ethoxypentyl side group studied here undergo a thermochromic phase transition on cooling, which is not abrupt but kinetically limited. Its onset (T_c) is in the interval from $+20$ to $-20\,°C$ and its completion is in the interval -50 to $-70\,°C$. Between these temperatures, coexistence of the two forms takes place; the fraction of each form was shown to be not a single-valued function of temperature, but dependent instead on the sample prehistory and on the rate of cooling.

From the X-ray data for $\mathbf{2}^5$ and from the literature data,[1] it is obvious that the high-temperature phase with its ~320 nm UV band is *hcm*. Longer wavelength UV absorption in the region 350–375 nm is usually assigned to a modification with the all-*trans* backbone conformation. For instance, the crystalline all-*trans* phase of $[n\text{-Hex}_2\text{Si}]_n$ absorbs at 375 nm, those of $[\text{Et}_2\text{Si}]_n$ and $[n\text{-Pr}_2\text{Si}]_n$ at *ca.* 350 nm.[8,9] By analogy, we can assume that the UV bands in the same region observed for the polymers studied also correspond to a phase with an all-*trans* backbone conformation.

It is well established[10,11] that the Raman spectrum of the polysilanes with an all-*trans* backbone conformation is enhanced by pre-resonance, when excited in the visible region, and exhibits a sharp intense line at *ca.* 690 cm^{-1}. which is used as a criterion of *trans*-conformation. To check the assumption made above, we have studied the temperature dependence of the Raman spectra of solid samples **1**–**3**. The spectra were excited by a 514.5 nm line. The results were similar for all samples and demonstrate the emergence and growth of the Raman line near 690 cm^{-1} during the phase transition. These results are examplified in Figure 5 for **1**. There confirm that the low-temperature modification of **1**–**3** exhibiting UV absorption in the region 350–375 nm corresponds to a form with the all-*trans* backbone conformation.

However, the nature of the complex structure of the latter UV bands remains still unclear and is being throughly studied. It has been argued that the more long and perfect is the all-*trans* sequence of silicon atoms, the more stable it is and the more red-shifted is its UV band due to maximal σ–σ conjugation.[1] However, the results presented here show that the most red-shifted peak in the UV absorption in question is not always the most intense. For instance, the peak near 375 nm in the UV spectrum of **1** remains very weak compared to that at 355 nm even at low temperature.

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References

1 R. West, in *Comprehensive Organometallic Chemistry* II, eds. E. Abel, F. G. A. Stone and G. Wilkinson, Pergamon Press, Amsterdam, 1995, vol. 3, pp. 77-109.

2 L. A. Leites, S. S. Bukalov, R. West and T. Asuke, *Mendeleev Commun.*, 1994, 205.

3 S. S. Bukalov, L. A. Leites, R. West and T. Asuke, *Macromolecules*, 1996, **29**, 907.

4 S. S. Bukalov, L. A. Leites, R. West and R. Menescal, *Macromolecules*, in press.

5 C.-H. Yuan and R. West, *Macromolecules* 1993, **26**, 2645.

6 K. S. Schweizer, L. A. Harrah and J. M. Zeigler, in *Silicon-Based Polymer Science*, eds. J. M. Zeigler and F. W. G. Fearon, Advances in Chemistry, Series 224, ACS Washington, 1990, p. 79.

7 R. Kani, Y. Nakano, Y. Majima, S. Hayase, C.-H. Yuan and R. West, *Macromolecules*, 1994, **27**, 1911.

8 L. A. Leites, T. S. Yadritseva, S. S. Bukalov, B. A. Antipova and V. V. Dement'ev, *Vysokomol. Soedin.*, 1992, **34A**, 104 [*Russ. Polym. Sci.* (*Engl. Transl.*), 1992, **34**, 980].

9 R. Menescal, J. Eveland, R. West, L. A. Leites, S. S. Bukalov, T. S. Yadritseva and M. Blazso, *Macromolecules*, 1994, **27**, 5885.

10 E. K. KariKari, A. J. Greso, B. L. Farmer, R. D. Miller and J. F. Rabolt, *Macromolecules*, 1993, **26**, 3937.

11 S. S. Bukalov, L. A. Leites, V. A. Morozov, R. West and R. Menescal, *Mendeleev Commun.*, 1994, 41.

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