

Positive and negative ionochromism and UV sensor properties of oxygen-containing polysilanes

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Addition of lithium trifluoromethanesulfonate (LiOTf) to poly[(4-ethoxyethoxybutyl)octylsilylene] (PEBOS) prevents the normal thermochromic transition to longer wavelength (negative ionochromism), whereas addition LiOTf to poly[bis(5-ethoxyethoxypentyl)silylene] (PEEPS) induces a thermochromic transition (positive ionochromism); the latter effect is reversed in the presence of water or THF vapour, so that LiOTf-doped PEEPS serves as a UV sensor for H₂O or THF.

Recently, polythiophenes having oligoether (OCH₂CH₂O) sidechains have been shown to undergo chromotropic changes in the presence of alkali metal cations.¹ The cations are presumed to bind to the oligoether oxygens and alter the chain conformation, resulting in a strong blue shift of the absorption bands; this type of change we will term 'negative ionochromism.'[†]

Polysilane polymers generally display strong electronic absorption bands in the near ultraviolet region, assigned to $\sigma \rightarrow \sigma^*$ transitions.³ The energy of this transition depends on the conformation of the polymer chain.⁴ Many polysilanes show chromotropic behavior, associated with changes in the backbone conformation which after the σ -conjugation. Thermochromism is especially common, but in selected polysilanes electrochromism,⁵ piezochromism⁶ and solvatochromism⁷ have also been reported.

We have now synthesized several polysilanes containing oxygen atoms in the organic side chains,⁸ and examined the effect of added cations.[‡] The UV spectrum of a thin film of PEBOS as a function of temperature is shown in Fig. 1(a). As the polymer is cooled, the absorption band at 320 nm disappears and is replaced by one at 354 nm; the midpoint of the transition is at *ca.* -32 °C. This sort of thermochromic transition, reflecting a change from a coiled to an all-*trans* conformation, is found for many polysilanes.^{3,4}

The effect of adding lithium trifluoromethanesulfonate to PEBOS is shown in Fig. 1(b)–1(d). With 12.5 and 25.0 mol% LiOTf, the thermochromic transition is progressively inhibited. At 50 mol% LiOTf, no change in the UV spectrum is observed upon cooling, even at -70 °C [Fig. 1(d)]. The lithium-complexed PEBOS thus exhibits negative ionochromism, perhaps because the lithium ions freeze the polymer into a coiled conformation.

The UV spectrum for PEEPS is shown in Fig. 2(a). Like PEBOS, this polymer also undergoes a thermochromic transition from 320 to 352 nm, with a midpoint at *ca.* -38 °C. The effect of added lithium triflate is, however, entirely different. As shown in Fig. 2(b), with 0.75 mol% LiOTf, PEEPS exhibits a thermochromic transition centred at *ca.* 35 °C. Thus in this polymer, lithium complexing causes the bathochromic shift, providing an example of positive ionochromism; the lithium cations apparently serve to lock the polymer into an extended conformation.

For both polymers, these changes in optical absorption upon LiOTf complexing were reflected in the thermal properties. In

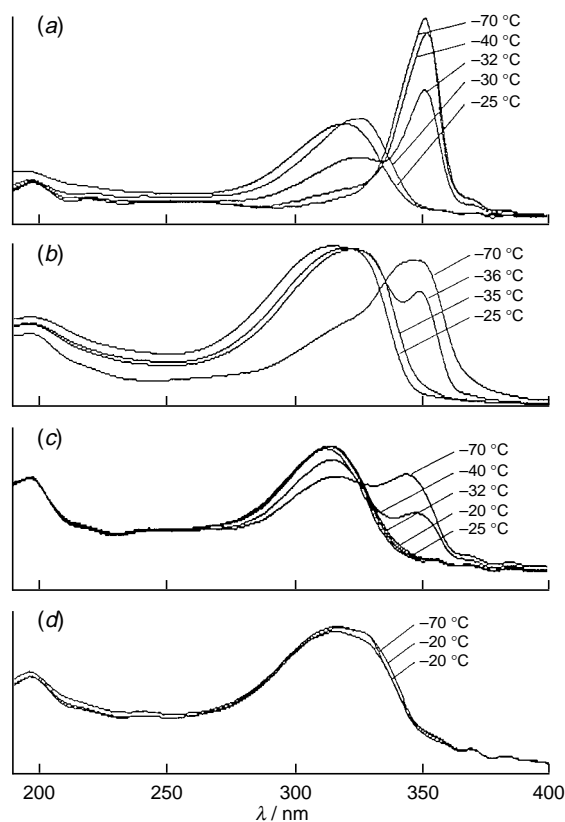


Fig. 1 Thermochromism of PEBOS complexes with LiOTf: Li/Si = (a) 0, (b) 12.5, (c) 25 and (d) 50 mol%

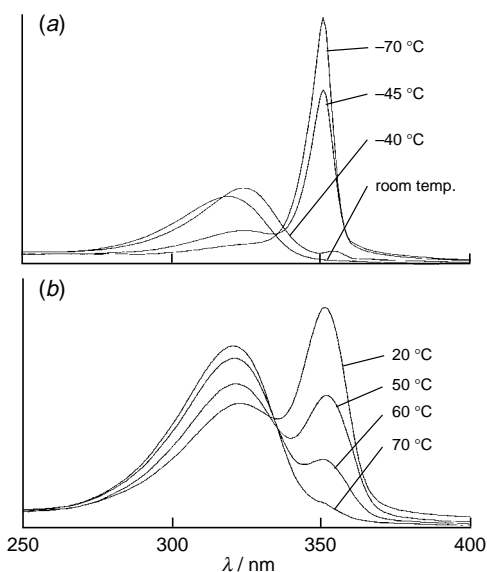


Fig. 2 Thermochromism of (a) a thin film of PEEPS compared to (b) a thin film of PEEPS-LiOTf complex (Li/Si = 75 mol%)

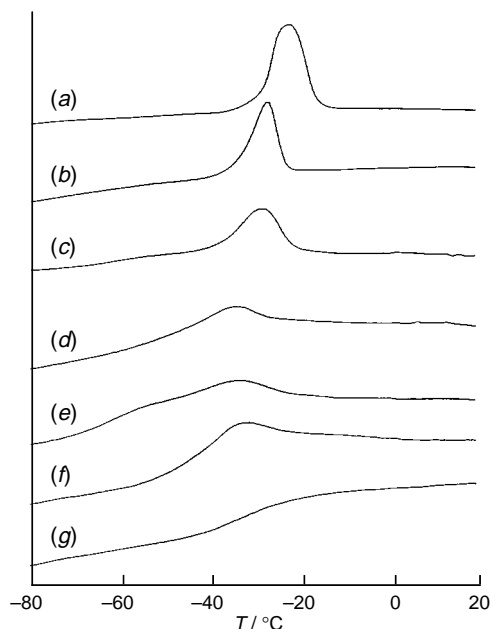


Fig. 3 DSC thermogram of PEBOS–LiSO₃CF₃ complexes. Li/Si = (a) 0, (b) 12.5, (c) 25, (d) 40, (e) 50, (f) 60 and (g) 80 mol%.

the differential scanning calorimetry (DSC) thermogram for PEBOS, shown in Fig. 3(a) a first order transition is found at a temperature near that of the thermochromic change.† As LiOTf is added, the thermal transition weakens and moves to lower temperature [Fig. 3(b)–(d)]; with 50 mol% LiOTf, only a second-order transition is seen. For PEEPS, a thermal transition is found at –35 °C (Fig. 4). As LiOTf is added this transition weakens and a new thermal transition appears above 0 °C. With 75 mol% LiOTf, the thermogram is dominated by a transition at 35 °C, corresponding to the UV thermochromic transition.

PEEPS exhibits yet another unexpected phenomenon involving a new type of chromotropic behavior. The spectra in Fig. 2 were determined in a cryostat, out of contact with the atmosphere. If the cryostat is opened to admit moist air (at 25 °C) the long wavelength band at 352 nm disappears and is replaced by the higher energy, 320 nm absorption. This change is reversible; pumping on the sample to remove moisture regenerates the long wavelength band. Exposure to THF vapour likewise reversibly shifts the absorption band from 352 to 320 nm. Thus PEEPS behaves as an ultraviolet sensor for small basic molecules. We theorize that water and THF compete with the oxygen atoms in the PEEPS sidechains for the lithium cations,¹⁰ allowing the polymer to relax into the coiled form which it normally adopts at room temperature. The effect is quite structure-specific, since diethyl ether vapour does not induce the hypsochromic shift.

Similar, but much weaker, effects were observed when salts of Na⁺ or K⁺ were added to PEBOS and PEEPS. The reason for the striking difference in behaviour between these two polymers is not clear; we are now synthesizing other (OCH₂CH₂O)-containing polysilanes to explore the effect of structural variability on these novel chromotropic effects.

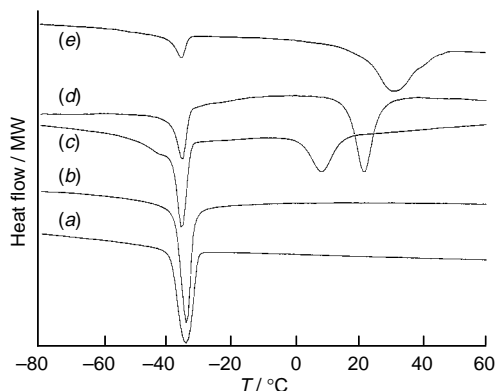


Fig. 4 DSC curve of PEEPS–LiSO₃CF₃ complexes. Li/Si = (a) 0, (b) 25, (c) 50, (d) 75 and (e) 100 mol%.

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Footnotes and References

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† Positive ionochromism has been observed for polythiophenes having calixarene substituents with Na⁺ ion (ref. 2).

‡ The preparation of PEBOS and PEEPS was carried out by sodium condensation of diorganodichlorosilanes, as described in an earlier paper (ref. 9). PEBOS was precipitated from PhMe solution with MeOH, and PEEPS was precipitated from PhMe with MeCN–H₂O (1 : 2). The structures of the polymers were confirmed by ¹H, ¹³C and ²⁹Si NMR spectroscopy. Gel permeation chromatography indicated a bimodal *M_w* distribution for PEBOS (*M_w* 1.4 × 10⁶ and 2 × 10⁴ vs. polystyrene standard) and a monomodal distribution for PEEPS (*M_w* 1.6 × 10⁶).

§ Differential scanning calorimetry thermograms were determined at a heating and cooling rate of 10 °C min^{–1} under a dry helium atmosphere over the temperature range from 100 to –100 °C.

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