Macromolecules **2002,** *35,* 327−329

Conformational Transition of End-Grafted Poly(di-*n*-hexylsilane) in Solventless Conditions

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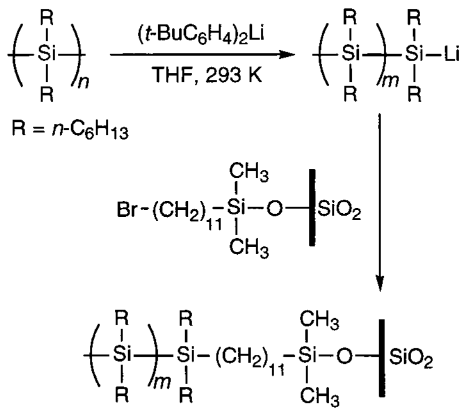
Received August 7, 2001

To study the properties of single polymer chains, we can use a dilute solution of the polymer. This is because we can ignore the interchain interaction in a sufficiently diluted solution. Polymers are usually in the solid phase in solventless conditions. The film form is particularly important for such product applications as photoresists, organic photoconductors, and organic light-emitting diodes. The characteristics of the film are, however, often different from those of the polymer in a dilute solution because of unavoidable interchain interactions. We were intrigued to know what we would observe from an isolated single polymer chain in solventless conditions, for instance in air. Such observations may reveal more of the intrinsic properties of the polymer that are hidden by the quick motion of the polymer in a dilute solution. It is also likely that these observations would attract considerable attention now that single molecular science and engineering are becoming active fields of research. One problem is to find a way of extracting single polymer chains without condensation under solventless conditions.

We recently proposed an approach designed to fix single polymer chains effectively on a substrate surface.[1] This method, which we call the "end-graft" technique, utilizes the formation of a chemical bond between the substrate surface and one of the termini of a polymer chain with a controllable surface density. We have been applying this technique to polysilane, a semiconducting polymer known to exhibit high hole drift mobility[2] and electroluminescence.[3] End-grafted (EG) polysilanes cannot be condensed, even under solventless conditions, if the density is controlled so that it is sufficiently low, which we successfully visualized using atomic force microscopy.[4] In addition, polysilane has a characteristic sharp absorption band in the UV region due to σ-electrons delocalized along the silicon backbone.[5] The degree of this σ-delocalization depends on the backbone conformation, and variations lead to changes in the peak wavelength of the UV absorption band. For many polysilanes this often appears as thermochromism, namely a temperature-dependent spectral change. In this work, we chose poly(di-*n*-hexylsilane) (PDHS) because its thermochromism has been extensively studied in relation to its backbone conformations in dilute solution[6] as well as its solid thin film.[7] We prepared EG-PDHS and measured its temperature-dependent absorption spectra under solventless conditions. We discuss the origin of the characteristic behavior to EG-PDHS by comparing the present result with the thermochromism known for PDHS in dilute solution and for PDHS solid thin film.

Scheme 1



We synthesized EG-PDHS on a quartz substrate as shown in Scheme 1. The idea, which we call the "cut and graft" technique,[1b] is that PDHS with a silyl anion on its terminus is coupled with primary alkyl bromide anchors built in advance on the quartz substrate. We synthesized PDHS by the conventional dehalogenative coupling of R_2SiCl_2 ($R = n\text{-}C_6H_{13}$) in toluene.[5a] Quartz substrates were treated with $Br(CH_2)_{11}Si(CH_3)_2Cl$ (3 wt % toluene solution, 383 K, 1 h). Lithium 4,4′-di-*tert*-butylbiphenylide was prepared by stirring lithium (8 mg) and 4,4′-di-*tert*-butylbiphenyl (5 mg) in dried tetrahydrofuran (3 mL) at 273 K until the solution became dark green. The end-graft reaction took place in dry and oxygen-free conditions in handmade glassware.[4a] We prepared end-lithiated PDHS by adding a drop of lithium 4,4′-di-*tert*-butylbiphenylide into a tetrahydrofuran (10 mL) solution of PDHS (50 mg).[8] The solution became pale yellow as the end-lithiated PDHS was generated. We then transferred the solution to a substrate with the primary alkyl bromide group of $-OSi(CH_3)_2(CH_2)_{11}Br$ on its surface. After a minute, we added a drop of ethanol to quench the excess amount of end-lithiated polysilane. The weight-average molecular weight, as determined by gel permeation chromatography (polystyrene standard) of the quenched PDHS, was 6.6×10^5 (polydispersity, 2.6). That of the initial PDHS was 2.6×10^6 (polydispersity, 3.1). We rinsed the substrates repeatedly in good polysilane solvents to remove any polysilane left on the surface.

Figure 1 shows temperature-dependent electronic absorption spectra of EG-PDHS in a vacuum. It shows an absorption band peaking at 316 nm at 300 K, which is characteristic of the $\sigma-\sigma^*$ transition of PDHS.[6,7] The absorption spectrum was reversibly changed depending on the temperature. The absorption band peaked at 316 nm in the high-temperature region (>250 K) and at 353 nm in the low-temperature region (<220 K). During the transition between 220 and 250 K, we observed a clear isosbestic point (at 332 nm). The change of the spectra can be assigned to the conformational transition known for PDHS.

Typically, PDHS in dilute solution shows abrupt thermochromism at the transition temperature (T_c) of 242 K between two phases: one peaking at 317 nm and the other peaking at 353 nm.[6a] Although thermochromism is also observed for a solid thin film of PDHS, its T_c is relatively higher (315 K), and one of the phases

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10.1021/ma011421j CCC: $22.00

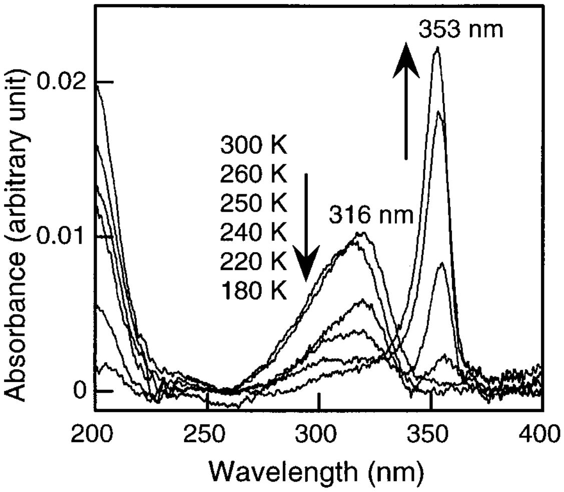

Figure 1. Temperature-dependent electronic absorption spectra of EG-PDHS in a vacuum.

has a different absorption peak at 374 nm.[7] Our present result is very interesting in that EG-PDHS chains behave like PDHS in dilute solution even in solventless conditions: T_c is comparable to that in dilute solution, and more obviously, the longer wavelength absorption band appears at the same wavelength as that of PDHS in dilute solution (353 nm) but for PDHS solid thin film (374 nm).[9]

The result in Figure 1 shows that the interchain interaction between the EG-PDHS chains is as low as it is in solution. We can simply understand this is because the EG-PDHS chains are isolated from each other even in solventless conditions and are thus free from complex interchain interactions that occur in bulk. The relatively wide temperature range needed for completing the transition in EG-PDHS is probably due to the lower degree of freedom of motion for a polymer with one terminus fixed on solid surface than that for a free polymer chain in solution. Other possibilities include the interaction of the EG-PDHS chains with the substrate and the assistance of the solvent in promoting such an abrupt transition in solution. Many papers have already discussed the thermochromic phase transition of PDHS, although the origin of the abrupt transition in dilute solution and the difference between the absorption peak wavelength in solution and that of solid thin film have remained undetermined.[5a,c] The difference has often been discussed by considering the solvent effect to be an essential factor. Our present experiment reproduces solution thermochromism even under solventless conditions, and this result demands a reconsideration of such models.

We should mention that in some cases with a high surface grafting density EG-PDHS can aggregate to form specific structures on a flat Si(111) surface.[4b] Unfortunately, we cannot completely ignore the possibility of the formation of such structures in the vicinity of the SiO_2 surface.[10] This motivated us to compare our present result with the thermochromic transitions of PDHS films confined in two-dimensional space: ultrathin films fabricated by either the spin-coating[11] or Langmuir–Blodgett (LB) technique.[12] Spin-coated films thinner than 50 nm exhibit a change in population of the two phases due to the restricted geometry in the film thickness direction. The PDHS LB film had a lower T_c (288 K) than the PDHS solid film. However, the peak wavelengths for long-wavelength absorption bands of both films are observed at about 370 nm, which is the same as that of a PDHS solid film. The absorption peak wavelength at 353 nm observed for EG-PDHS can, therefore, most likely be assigned to a monomolecular event, or at least we can say that few EG-PDHS chains are involved.[13]

The fact that we still observed thermochromism in EG-PDHS means that EG-PDHS chains are still mobile in a vacuum. We can say that grafting one of the polymer chain termini is insufficiently strong to prevent temperature-driven motion and that the interaction between the EG-PDHS chain and the quartz surface is also insufficiently strong to prevent it. Furthermore, there was no obvious change in the electronic absorption wavelength. This means that the electronic structure of PDHS was not affected by grafting on the substrate. We think this is because quartz is an insulator, meaning that we can expect a certain electronic interaction between the end-grafted polysilane and the substrate if a metal or semiconductor substrate was chosen.

In conclusion, we studied the temperature dependence of the electronic absorption spectra of EG-PDHS. We found that EG-PDHS behaves like PDHS in a dilute solution, and this is due most likely to a monomolecular event. This may be characteristic not only of EG-PDHS but also of a variety of polymers end-grafted on a solid surface.

Acknowledgment. The authors thank Prof. N. Matsumoto at Shonan Institute of Technology and Dr. M. Fujiki for fruitful discussions. They also thank Dr. M. Morita, Dr. K. Torimitsu, and Dr. H. Takayanagi for their encouragement.

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(8) We found that dialkylpolysilanes, in which the silyl anions are not very stable, required a lithium reagent with stronger electron-transfer ability. We also found that methyllithium was effective for cleaving the Si–Si bond of polysilanes containing phenyl groups such as poly(methylphenylsilane) and poly[bis(*p*-*n*-butylphenylsilane)], in which the silyl anions are more stable.

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(10) We did not succeed in imaging EG-PDHS on SiO_2 substrates, mainly due to the surface roughness of the substrates. However, we were able to estimate the surface density as $\sim 10^{10}$ EG-PDHS chains in 1 cm^2 (one chain in 100 × 100 nm) on average by using the following data: molar absorption coefficient per Si unit for PDHS in dilute solution ($\sim$10 000 cm^{-1} dm^3 mol^{-1}), weight-average molecular weight for EG-PDHS (660 000), and absorbance for EG-PDHS ($\sim$0.01). We can eliminate aggregate formation by using EG-PDHS with a much lower surface density, but this prevents us from observing the absorption spectra.

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MA011421J