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Role of the Restricted Geometry on the Morphology of Ultrathin Poly(di-*n*-hexylsilane) Films[†]

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The properties and morphology of thin films critically depend on the chain conformation and organization near the substrate. Presently, the trend toward structure miniaturization, especially in the microelectronics industry, dictates the use of ultrathin polymer films, and, hence, understanding the effect of the restricted geometry on the organization of the polymer chains near the interface is of great current scientific and technological importance.

To study the effect of thickness on the properties of ultrathin (0−1000 Å thick) polymer films, we have elected to work with the polysilanes, and specifically poly(di-*n*-hexylsilane) $-[(C_6H_{13})_2Si]_x-$. The electronic structure of these materials depends on the polymer chain conformation,[1] and, therefore, they are ideally suited for the study of the polymer chain conformation in a restricted geometry. UV−visible absorption spectroscopy, a simple and well understood technique, can be used for this purpose.

In this study, poly(di-*n*-hexylsilane) with a M_w of 2.6 × 10^6 and a polydispersity of 2.4 was used. The films were prepared by spin-casting a solution of an appropriate concentration (0.1−2 wt %) of the polymer in isooctane (Aldrich Chemical Co.) on a freshly cleaned and dried quartz disk (Esco Products Inc.). After deposition, the samples were annealed at 100 °C for 10−15 min. The thickness of a polymer film under specific casting conditions was estimated by preparing a similar film on a Si wafer and measuring its thickness by ellipsometry on an Auto EL^R-II automatic ellipsometer (Rudolph Research). It should be noted that both the surfaces of the clean quartz substrate and the silicon wafer, which is covered by a native silicon oxide layer, are chemically similar, each having many hydroxyl groups on the surface. The UV−visible spectra of films whose thicknesses ranged between 50 and 3450 Å were recorded using a Cary 3 (Varian) UV−vis spectrometer.

The poly(di-*n*-hexylsilane) bulk films show two strong UV absorption maxima, one around 27 470 cm^{-1} (364 nm) and one around 31 650 cm^{-1} (316 nm). It has been suggested that the low-energy peak (27 470 cm^{-1}) corresponds to an extended all-trans conformation of the Si backbone, with the side chains largely extended but not completely all-trans. The high-energy absorption (31 650 cm^{-1}) arises from a conformationally disordered backbone in a presumably helical conformation.[2] In thick films the low-energy absorption has been correlated with the presence of a crystalline phase, while the low-energy one corresponds to a disordered phase.[3] Thus, by following the UV absorption of the polymer films, the change in the backbone conformation as well as the chain organization in the film can be studied as a function of thickness.

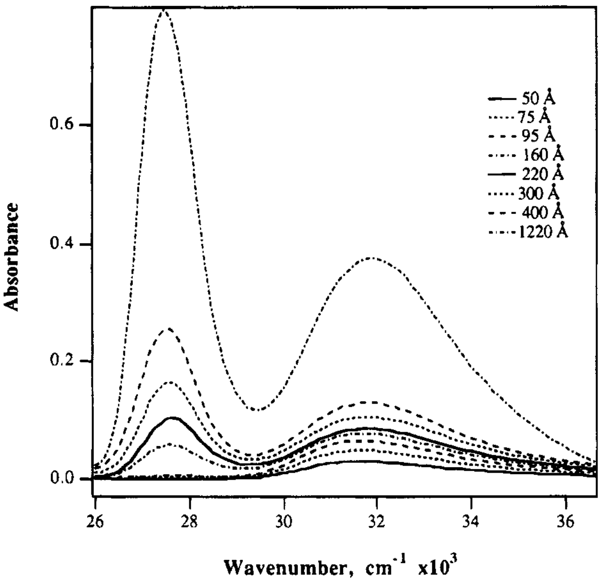

Figure 1. UV absorption spectra of poly(di-*n*-hexylsilane) films: 50−1220 Å.

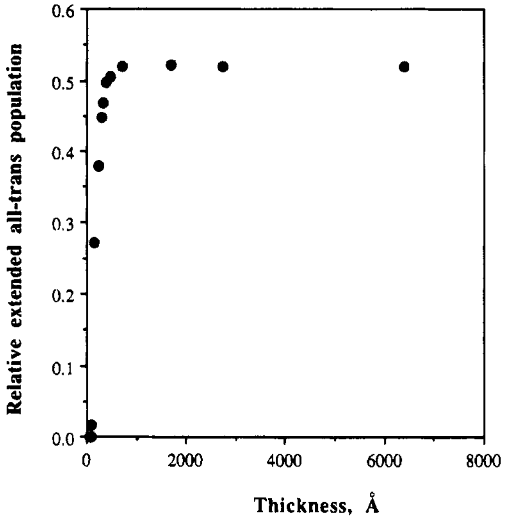

Figure 2. Dependence of the relative all-trans population on film thickness.

At a thickness of 1220 Å the UV−visible spectrum is the same as the one obtained with a bulk film, showing the two typical intense maxima. As the thickness is decreased, the relative intensity of the low-energy absorption decreases, while that of the high-energy one increases. Figure 1 shows the absorbance plotted vs wavenumber for a range of film thicknesses. At 50 Å, there is no detectable absorption at 27 470 cm^{-1}, and thus no extended all-trans backbone segments are present; instead, the polymer chain is conformationally disordered[3] and presumably helical.[2] The relative amount of extended all-trans conformers in the ultrathin films can be estimated by integrating the area under the low-energy peak and dividing it by the total area under both peaks; this is shown in Figure 2 as a function of thickness. It is clearly evident from Figure 2 that there is a decrease in the amount of conformational extension of the backbone as the thickness of the films is decreased below 500 Å.

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In thick films this ratio is a measure of both the backbone extension and the magnitude of intermolecular interactions that exist[2] in the ordered crystalline phase. From the UV measurements, the extent of chain extension of a bulk film is estimated to be around 52%. Although, in this work, we have not attempted to relate the chain extension information obtained spectroscopically with crystallinity, it is interesting to note that the above-mentioned estimate of crystallinity from chain extension (52%) for bulk films is in good agreement with crystallinity measurements using X-ray diffraction[3] or DSC analysis.[4] In preliminary results of work in progress we have related the local chain conformation, as determined from the spectroscopic results, to the bulk morphology and have been able to analyze the kinetics in terms of the Avrami–Evans theory of crystallization.[5]

In spin-cast poly(di-*n*-hexylsilane) thin films, the in-plane refractive index (TE) has been measured[6] to be 1.578, while the out-of-plane (TM) value was 1.538. This anisotropy in the refractive index leads to a significant birefringence of 0.04 which clearly shows that the poly(di-*n*-hexylsilane) chains are extended parallel to the plane of the film. In addition, the polymer chains in spin-cast poly(pentylhexylsilane) films were found to be oriented predominantly parallel to the film surface.[7] In the UV absorption experiments carried out in this work, with light propagating along the film normal, the electric vector is parallel to the plane of the film, and, thus, maximum absorption is observed from the $\sigma-\sigma^*$ transition (along the polymer backbone) that gives rise to the UV absorption.[1] Consequently, the spectral changes observed in Figure 1 as the film thickness is decreased reflect a change in the chain conformation of the polymer and cannot be attributed to a changing orientation of the backbone relative to the substrate in the ultrathin films.

For comparison, low molecular weight samples of poly(di-*n*-hexylsilane) (M_w = 42 600) were also examined. The final percentage of extended all-trans segments in the bulk films, as measured by the UV analysis, was around 82%, significantly higher than that of the high molecular weight samples. Nevertheless, a reduction in the relative low-energy absorption below a thickness of 500 Å was observed for these films as well. The low molecular weight chains contain substantially fewer repeat units compared to the high molecular weight samples. The achievement of higher conformational extension by the low molecular weight material may be due to the faster diffusion of the short chains. For the low molecular weight chains the local segmental motion necessary for the rearrangement of the conformationally disordered backbone to an extended all-trans conformation is, thus, easier to achieve. There is a change in the radius of gyration R_g from 100 nm for the high molecular weight material to about 6 nm for the low molecular weight material.[8] It is striking that the onset of the change in molecular organization occurs slightly below 500 Å for both materials, indicating that it is not the overall chain length or the R_g that is important but a feature with a characteristic size of a few hundreds of angstroms. Since poly(di-*n*-hexylsilane) is known to crystallize in thick films, such a feature could possibly be related to a crystallite or the critical nucleus from which a crystallite is formed.

We have shown that geometrical confinement has a dramatic effect on the chain conformation of poly(di-*n*-hexylsilane). In ultrathin films the overall extent of molecular organization of the polymer backbone into an extended all-trans conformation falls precipitously below 500 Å. It is therefore evident that thickness can be used as an alternate way, besides temperature and pressure,[9-11] to control the chain conformation and the resulting morphology and related properties in ultrathin films.

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