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Conformational changes during the crystallization of poly(di-*n*-hexylsilane)

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Abstract

The conformational changes of the backbone as well as the side chains of poly(di-*n*-hexylsilane) during the isothermal crystallization from the disordered phase was investigated. The backbone reorganization was detected by fluorescence and UV, while the side-chain reorganization was detected by IR. It was found that the backbone reorganization begins to occur prior to the side-chain reorganization. This trend is observed for all the crystallization temperatures investigated. At lower temperatures, the difference in the time of reorganization was not very large, but at higher temperatures the difference becomes larger. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(di-*n*-hexylsilane); Conformation; Isothermal crystallization

1. Introduction

Polysilanes display an intense electronic absorption band in the UV region 300–400 nm, which is assigned to a σ–σ* electronic transition, involving extensive delocalization of electrons along the silicon backbone [1]. The energy of the electronic absorption is strongly correlated with the conformation of the polymer backbone and side chains. Poly(di-*n*-hexylsilane) (PDHS) is one of the most extensively studied polysilanes. In the highly ordered solid phase of PDHS, the silicon backbone adopts an all-*trans* conformation with the side chains oriented perpendicular to the main chain and displays an intense UV absorption at 370 nm. Upon heating, the polymer backbone becomes conformationally disordered, forming a mesophase consisting of hexagonally packed macromolecules and this is indicated by the thermochromic shift of the UV absorption to 315 nm above 42°C [2,3]. It is reported that the driving force for the transition is the side-chain crystallization, which occurs simultaneously [2]. However, Yuan and West reported that poly[(5-ethoxypentyl)-alkylsilane]s undergo an abrupt thermochromic phase transition simultaneously with first-order-like phase transition without side-chain crystallization [4,5]. They proposed that the transformation in poly[(5-ethoxypentyl)-alkylsilane]s is electronically driven, based on the theory suggested by Schweizer [6,7], according to which the thermochromic phenomena can arise from the dispersion interaction of the delocalized electrons along the polymer backbone with the surrounding polarizable medium, which can be the pendant side chains, neighboring polymer chains or solvent molecules. Despotopolou et al. [8] studied the disordering of the hexyl side chain in PDHS films of various thicknesses using grazing incidence reflection FTIR spectroscopy and the backbone disordering using UV absorption spectroscopy. The ratio of the intensity of the IR band at 1469 cm^{-1} to the intensity of the band at 2959 cm^{-1} was taken as the measure of the side-chain disordering. They showed that the disordering of the side chain precedes the backbone disordering as the film thickness is decreased; the side-chain disordering becomes apparent below a film thickness of 2000 Å, while the backbone disordering becomes evident below 500 Å. Although there are a number of studies on the crystallization behavior of PDHS, it is not clearly known whether the side chains and the backbone chains reorganize simultaneously or they reorganize separately [9–11]. In the present work, we examined the reorganization of the backbone as well as the side chains of PDHS during the isothermal crystallization from the disordered state. The backbone conformational change was detected by fluorescence and UV, while the side-chain reorganization was detected by IR.

2. Experimental

PDHS prepared by Wurtz coupling reaction was used for

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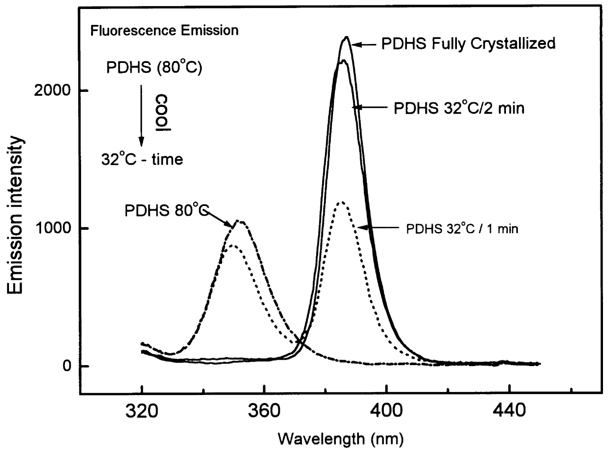

Fig. 1. Fluorescence emission spectra of PDHS at 80 and 32°C for various time periods.

the study. The molecular weight determined by GPC was 6.4×10^5. Thin films of same thickness were prepared by spin casting the hexane solution of PDHS on a quartz plate and were used for fluorescence and UV studies. Fluorescence spectra were recorded using a fluorescence spectrophotometer FP777 (Japan Spectroscopic Co. Ltd.), while the UV spectra were recorded with a UV photometer, Shimadzu UV-2500PC. For IR studies, film was casted on KBr. The FTIR spectra were measured with a Bio-rad FTS-60A1896 FTIR spectrophotometer. Samples were mounted on a hot stage (Mettler FP82HT) and cooled from 80°C rapidly to various crystallization temperatures. Fluorescence emission intensity at 382 nm wavelength and UV absorption intensity at 375 nm were recorded as a function of time at various crystallization temperatures. In the case of IR, the change in intensity at 717 cm^{-1} band, which is assigned to the CH_2 rocking vibration, was followed to monitor the reorganization of the hexyl side chain.

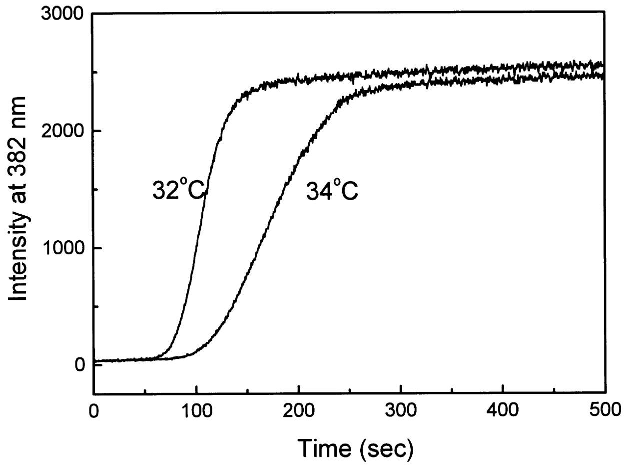

Fig. 2. Fluorescence emission intensity of PDHS at 382 nm as a function of time at 32 and 34°C.

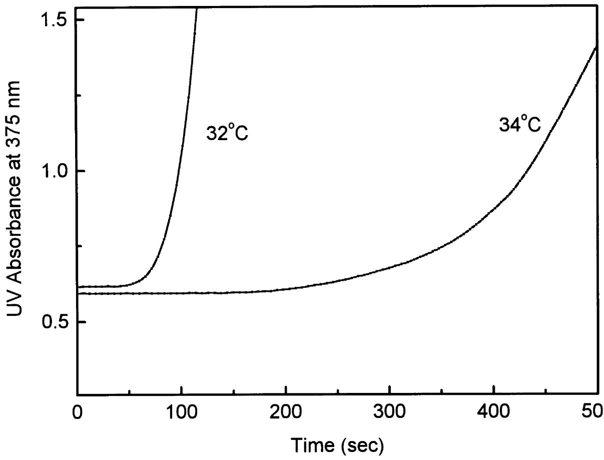

Fig. 3. UV absorbance intensity of PDHS at 375 nm as a function of time at 32 and 34°C.

3. Results and discussion

Fig. 1 shows the fluorescent emission spectra, recorded with time, of PDHS thin film sample cooled to 32°C from 80°C. It is clearly seen that as the PDHS was cooled down to 32°C, the disordered phase changes to the ordered phase and is indicated by the increasing intensity at 382 nm. Fig. 2 shows the fluorescence intensity at 382 nm as a function of time for crystallization temperatures of 32 and 34°C. The initiation of crystallization is indicated by the starting of the steep increase in the intensity. This steep increase in the emission intensity at 382 nm is due to the change of backbone conformation from the disordered state to the ordered all-*trans* conformation. There is some induction period of reorganization depending upon the temperature. The UV absorption at 375 nm with time at various temperatures also showed similar tendency (Fig. 3) as that of the fluorescence intensity, however, there is a difference between the time at which the fluorescence emission intensity begins to show a steep increase and the time at which

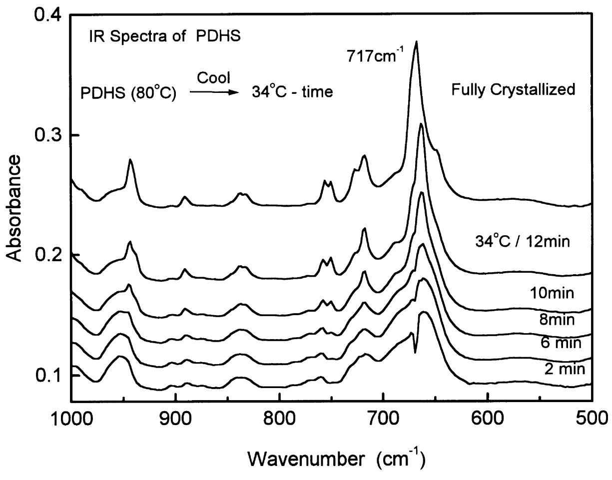

Fig. 4. FTIR spectra of PDHS at 34°C for various time periods.

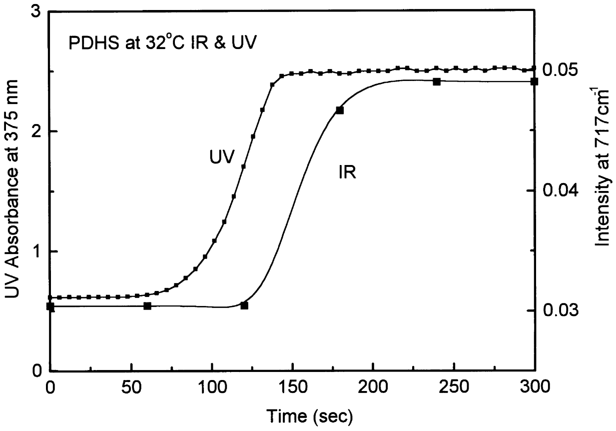

Fig. 5. UV absorbance intensity at 375 nm and intensity of IR band at 717 cm^{-1} as a function of time at 32°C.

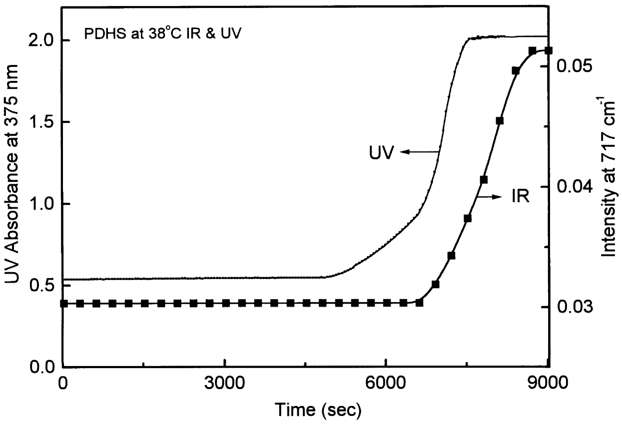

Fig. 6. UV absorbance intensity at 375 nm and intensity of IR band at 717 cm^{-1} as a function of time at 38°C.

the UV absorbance shows a steep increase. The analysis of the data in a shorter time scale showed that the UV absorbance at 375 nm also started increasing very gradually at the same time as that of the fluorescence emission intensity at 382 nm. The steep increase in the fluorescence intensity prior to the UV intensity may be attributed to the reported energy transfer between the chromophores in PDHS [8,12,13]. It was shown that most of the emission results from the low energy chromophores with all-*trans* conformation even when the crystallinity is low and this is an indication of the occurrence of energy transfer from the disordered phase to the crystalline phase. In the present case, due to the energy transfer, the fluorescence intensity shows disproportionately large increase even when the content of the ordered *trans* segments, which appears as a result of the reorganization, is very low. However, the UV absorbance at 375 nm is proportional to the concentration of the *trans* segments generated during the reorganization.

IR spectra can provide information on the reorganization of the side chain as molecular vibrations of *n*-alkyl side chains give rise to absorptions in the infrared region. We recorded the IR spectra of PDHS samples cooled to various temperatures and crystallized isothermally. Fig. 4 shows the IR spectra of PDHS cooled to 34°C and crystallized isothermally. The spectra were recorded every 1 min after reaching the crystallization temperature. The change in IR spectra with time is clearly visible. The change in intensity of the 717 cm^{-1} band, which is attributable to CH_2 rocking vibration, can be considered as an indication of side-chain reorganization. The intensity at 717 cm^{-1} was found to increase with time at each crystallization temperature. This is plotted along with the UV absorption intensity measured at 375 nm which indicates the backbone ordering (Figs. 5 and 6). It can be seen that the backbone reorganization indicated by the steep increase in the UV absorption at 375 nm begins to occur prior to the side-chain reorganization deduced from the increase in the intensity of the 717 cm^{-1} band. This trend is observed for all the crystallization temperatures investigated. At lower temperatures, the difference in the time of reorganization was not very large (Fig. 5), but at higher temperatures the difference becomes larger (Fig. 6). This observation indicates that the thermochromism in PDHS is a manifestation of the backbone reorganization to the all-*trans* conformation and the side-chain reorganization seems to be slower as compared to the backbone reorganization.

Acknowledgements

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