A New Cooling-Rate Dependent Thermochromism of Poly(dioctylsilane)

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(Received March 14, 2000; CL-000253)

A rapidly cooled poly(dioctylsilane) (PDOS) is found to exhibit unprecedented thermochromic behavior showing λ_{max} at 353 nm as the major absorption which is accompanied with a minor one at 375 nm. On heating, the absorption at 353 nm begins to decrease at 250 K and, then, the minor one does at 280 K. Similar temperature dependent behavior is observed in the X-ray powder diffraction around $2\theta = 6^{o}$ which is ascribable to inter-chain alignment. On heating diffraction at $2\theta = 6.2^{o}$ (d = 1.43 nm) disappears firstly, and then that at 6.4° (d = 1. 38 nm) is displaced by the diffraction at 5.8° (d = 1.52 nm).

The energy states of poly(organosilane)s are dependent on the conjugation length and the conformation of the backbone. Intramolecular van der Waals interaction through the side-chains is the dominant factor controlling the energy state of polysilanes.[1] Trans zigzag,[2-4] TGTG',[5,6] and 7/3 helix[4] conformations are reported for polysilanes with short, long (> C9), and intermediate alkyl groups, respectively. These crystalline states are transformed into amorphous or hexagonal columnar mesophase (*hcm*) at higher temperatures[3,7] resulting in UV spectral change. Polysilanes with long alkyl groups show, on cooling, a discontinuous thermochromic shift from ca. 320 nm to 345 nm or 375 nm.[8] However, it becomes evident that thermochromism of these polysilanes is more complicated and sensitive toward experimental conditions than ever believed.[9] The structure of poly(dioctylsilane) (PDOS) studied by X-ray analysis is reported to have trans[6] or TGTG',[10] though UV spectrum at low temperature corresponds only to trans form (374 nm). This ambiguity must come from the complicated thermal transitions around room temperature (DSC peaks at –20, 9, and 45 °C).[7d,11] Thus, thermochromic behavior of PDOS was studied under various thermal conditions.

PDOS showed only reported thermochromic behavior exhibiting λ_{max} at 375 nm when cooled slowly (< 0.3 K/min).[13] Unprecedented thermochromic feature was obtained when cooled rapidly (> 3 K/min) (Figure 1). Absorption at 374 nm grows on cooling until 283 K. New absorption at 353 nm begins to grow below 280 K and becomes a major peak at low temperature while the absorption at 374 nm stays almost unchanged. Reverse process was observed in the heating process. The plot of absorbance changes against temperature is shown in Figure 2. The absorption at λ_{max} 353 nm begins to change at 245 K and continues to decrease steady. A negligibly small endotherm (ΔH = 0.11 kJ/mol) was observed at 250 K in a DSC analysis, [11] suggesting that the transition is a very low energy process. An irregular change, which may correspond to the small endotherm, is seen around 265–280 K in Figure 2; unexpected increase of absorption at 374 nm and the deviation from simple decrease of absorption at 353 nm. The absorption at 374 nm turned to decrease at 280 K. A large endotherm (ΔH = 8.7 kJ/mol) in DSC at 280 K must be ascribable to the melting of crystalline part involving trans form (λ_{max} 374 nm) to yield *hcm*. A very minor peak was also detected at 316 K (ΔH = 0.29 kJ/mol) by DSC of a rapidly cooled PDOS, which is consistent with the reported one[11]. We tentatively assigned this as transition from *hcm* to amorphous phase. On further cooling below 240 K, a slight blue shift from 353 to 349 nm is observed for the major peak while absorption at 374 nm stays unchanged. This may imply the conformationaly flexible and thus metastable character of the form at 354 nm even at low temperature.

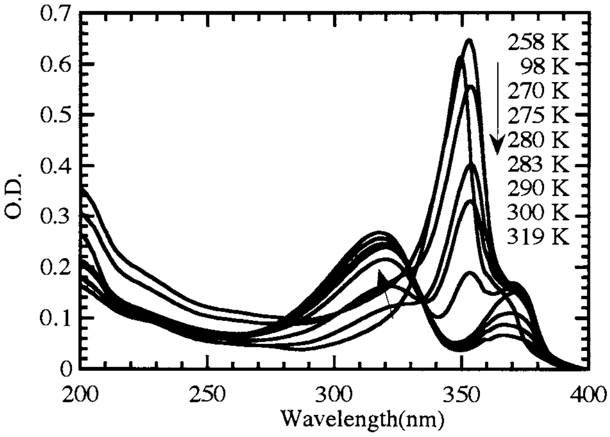

Figure 1. Thermochromism of a rapidly cooled PDOS (7 °C/min)

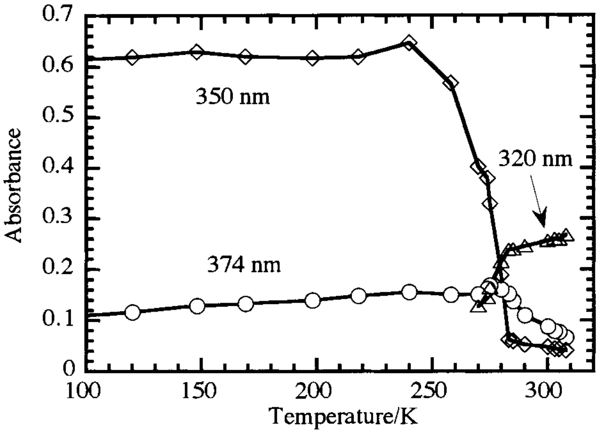

Figure 2. Plot of absorbance change in a rapidly cooled PDOS.

As shown in Figure 3, a rapidly cooled PDOS shows several X-ray diffractions at 240 K.[14] Here, interesting temperature

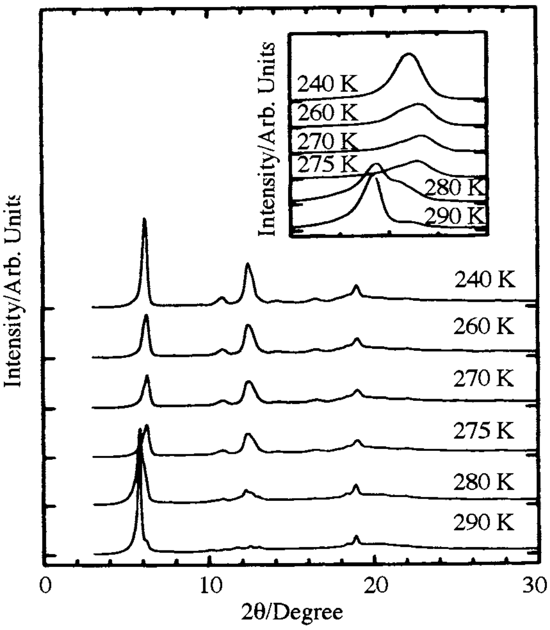

Figure 3. X-Ray diffraction of a rapidly cooled PDOS

dependency is seen around $2\theta = 6^\circ$ (insert in Figure 3). The temperature dependent behavior of diffractions at $2\theta = 5.8^\circ$ (d = 1.52 nm), 6.2° (d = 1.43 nm), and $2\theta = 6.4^\circ$ (d = 1.38 nm) apparently corresponds to those of the absorption bands at 320, 353, and 374 nm in the UV spectra, respectively. Similar temperature dependent behavior was also found in the X-ray diffraction of polysilane co-polymers and was attributed to conformational mixture.[12] The diffraction is essentially related only to the inter-column packing determined mainly by the side chain alignment. The lower the diffraction angle, the wider the inter-column distances. Thus, the diffraction at $2\theta = 5.8^\circ$ must be responsible to *hcm* part in PDOS and the that at $2\theta = 6.4^\circ$ being the crystalline part packed with well-aligned side chains which must accompany the main chains of trans conformation.

A meridional diffraction at 0.42 nm, in addition to diffractions detected in Figure 3, was observed in an uniaxially extended PDOS film at 240 K,[6,11] but showed no diffraction attributed to the 7/3 helix. No direct information on the conformation giving the absorption at 353 nm was obtained. Since the absorption at 353 nm is transformed to *hcm* as well as trans form with very low energy barrier around 270 K, we prefer to assign the form as an intermediate conformer between trans and gauche, probably more trans-like one. [16]

This study was supported from the Ministry of Education, Science, Sports, and Culture (Japan) for Grant-in-Aid for Scientific Research on Special Promote Research No.09239244 and C No. 10640564.

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16 New theoretical calculation suggests that poly(dialkylsilane)s take stable conformations with dihedral angles around ± 120 °, ± 150 °, and ± 165°.[17] The existence of TGTG' form is also doubted for poly(dialkylsilane)s.[18].

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