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Higher-order structure and thermal transition behaviour of poly(di-n-hexylsilane)

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Poly(di-n-hexylsilane) (PDHS) films cast at various conditions from toluene solutions were studied by X-ray diffraction, d.s.c., u.v.-vis. spectroscopy and fluorescence spectroscopy. The higher-order structure of cast films is discussed in relation to their phase transitions. Films dried slowly at 2°C (film a), quickly at room temperature (film b) and slowly at 36°C (films c and d) have low, moderate and highly crystalline structures, respectively. In thin film c, the (110) plane of the orthorhombic unit cell is oriented parallel to the film surface. The u.v. absorption maxima due to the ordered phase were observed around 357 nm (film a), 370 nm (film b) and 375 nm (film c). The peaks in the fluorescence spectra were observed between 350 nm and 389 nm. The d.s.c. peak temperature for phase transition was observed at 36–49°C.

(Keywords: poly(di-n-hexylsilane); film; high-order structure)

INTRODUCTION

Polysilanes attract a lot of interest with respect to their electronic absorption spectra where the features are attributed to σ-electron delocalization along the main chain, and various polysilanes have been synthesized and investigated[1]. The crystalline polysilanes such as dialkyl-substituted polysilanes are of interest from the structural point of view. Poly(dimethylsilane)[2,3], poly(diethylsilane)[4] and poly(dipropylsilane)[4] have a planar zigzag conformation in the solid state. These high molecular weight polymers are insoluble and their u.v. absorption spectra have not been studied in detail.

The u.v. spectra of poly(dibutylsilane) (PDBS)[1,5,6], poly(dipentylsilane) (PDPS)[6] and poly(di-n-hexylsilane) (PDHS)[5] solutions show the absorption maximum around 315 nm at ambient temperature, and around 354 nm at low temperature. PDBS[6] and PDPS[6,7] in the solid state exist in a 7/3 helical structure which is characterized by the absorption maximum around 313 nm, and the first-order phase transition occurs at ~85 and 70°C, respectively, without drastic changes in the u.v. spectra. The absorption maxima for PDHS in the solid state were observed at 317 and 374 nm, and are associated with a disordered and an ordered phase, respectively, and the phase transition was observed around 41°C[8,9]. According to many studies on PDHS[6–15], the profile of the structure in the solid state is as follows. The backbone chains are locked in a *trans* conformation by crystallization of the side chain in the ordered phase, and the thermal transition results from the side chains melting with subsequent disordering of the planar zigzag conformation in the backbone. Similar thermal transitions were observed in poly(diheptylsilane) and poly(dioctylsilane)[9,12] at 40–50°C. The polysilane backbone is sensitive to pressure, and piezochromism was observed for PDHS[16–18], PDBS[16,18] and PDPS[18] films.

Another crystalline structure characterized by the u.v. absorption maximum of 350 nm was observed for poly(di-n-decylsilane), and the *TGTG'* backbone conformation characterized by the absorption maximum of 347 nm was reported for poly(di-n-tetradecylsilane)[12].

In the conformational study of crystalline polysilanes by u.v. absorption spectroscopy the effect of higher-order structure is also very important because the packing of polymer chains affects the structure of the silicon backbone. PDHS is a well known polysilane, and it was found that the structure of its cast films was affected by the solvents used in preparation[14] and the thermal treatment[14,19]. In this work, the preparation conditions of PDHS films and their higher-order structure are examined. Also, the effect of the higher-order structure on the u.v. absorption spectra and the phase transition behaviour are discussed.

EXPERIMENTAL

Samples and preparation of films

PDHS was synthesized by the Wurtz coupling of dichloro(di-n-hexylsilane) with sodium. The weight-average molecular weights of the samples were 9.6×10^5 (M_1) and 2.1×10^6 (M_2). Thin films ($\leqslant 10\,\mu$m) and thick films (100–140 μm) were cast on a glass or a quartz plate from 0.5–2.0 and 5.5 wt% toluene solutions, respectively. The solvent was evaporated under various conditions as shown in *Table 1*: film b was cast and dried quickly in air at room temperature, and the other films were dried

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Table 1 Preparation conditions of PDHS cast films from toluene solutions

Sample	Concentration of solution (%)	Evaporation temperature (°C)	Evaporation rate
a	0.5–2	2	Slow
b	0.5–2	Room temp.	Quick
c	0.5	36	Slow
d	5.5	36	Slow

in glassware at 2°C (film a) or at 36°C (films c and d). The drying period was 10 h to a few days depending on the concentration of the solution used, the thickness of the films and the evaporation temperature.

Measurements

The molecular weights were determined by g.p.c. (Shimazu LC-6A GPC). The thickness of the films was measured with an electric micrometer or by scanning electron microscopy except for the very thin films for u.v. absorption measurement.

X-ray diffraction patterns were measured with Ni-filtered CuKα radiation on a Rigaku X-ray diffractometer. Since it was difficult to peel a film only a few micrometres thick off the glass plate, the film was swollen with toluene for a short time, put into ethanol and filtered. Several tens of small pieces piled in layers were measured. It was confirmed from u.v. absorption spectra that the structure was unaffected by such treatment at room temperature.

Very thin films were cast on quartz plates, and u.v.-vis. absorption spectra were measured using a Jasco Ubest-55 spectrometer. A Jasco FP-777 spectrometer was used to measure the fluorescence spectra of the films.

The phase transition behaviour was examined using a Perkin-Elmer DSC 7 under nitrogen gas flow. The heating and cooling rate used was 10°C min^{-1}. The regeneration behaviour of the ordered phase was isothermally examined as follows. The films were heated to 100°C at a rate of 10°C min^{-1}, and held for 2 min. After quenching to constant temperatures, the exothermic peak was measured.

RESULTS AND DISCUSSION

X-ray diffraction

The packing of molecular chains is greatly affected by the evaporation conditions. *Figure 1* shows the X-ray diffraction patterns of the films. A reflection at the smallest angle ($d = 1.35$ nm) corresponds to the disordered phase[9,13,14,19], and the other reflections are due to the ordered phase. The patterns indicate that films c and d are highly crystalline, film a has low crystallinity and film b has a moderately crystalline structure.

The photographs taken with the beam perpendicular to the film surface show ring diffraction patterns, whereas those taken with a parallel beam show rings (a), arcs (b, d) and spot-like (c) patterns. Thus, the backbone chains have no special orientation in film a, and are parallel to the surface in the other films.

The next problem is how the crystallites are arranged in film c, which gave spot-like diffractions. A monoclinic unit cell containing two molecules with *trans* backbones[11] was proposed as the structure of the ordered part. Recently an orthorhombic unit cell[20] has been reported, which is adopted in the present study. *Figure 2* shows the reciprocal lattice drawing of the X-ray diffraction result on the orthorhombic unit cell ($a = 1.376$,

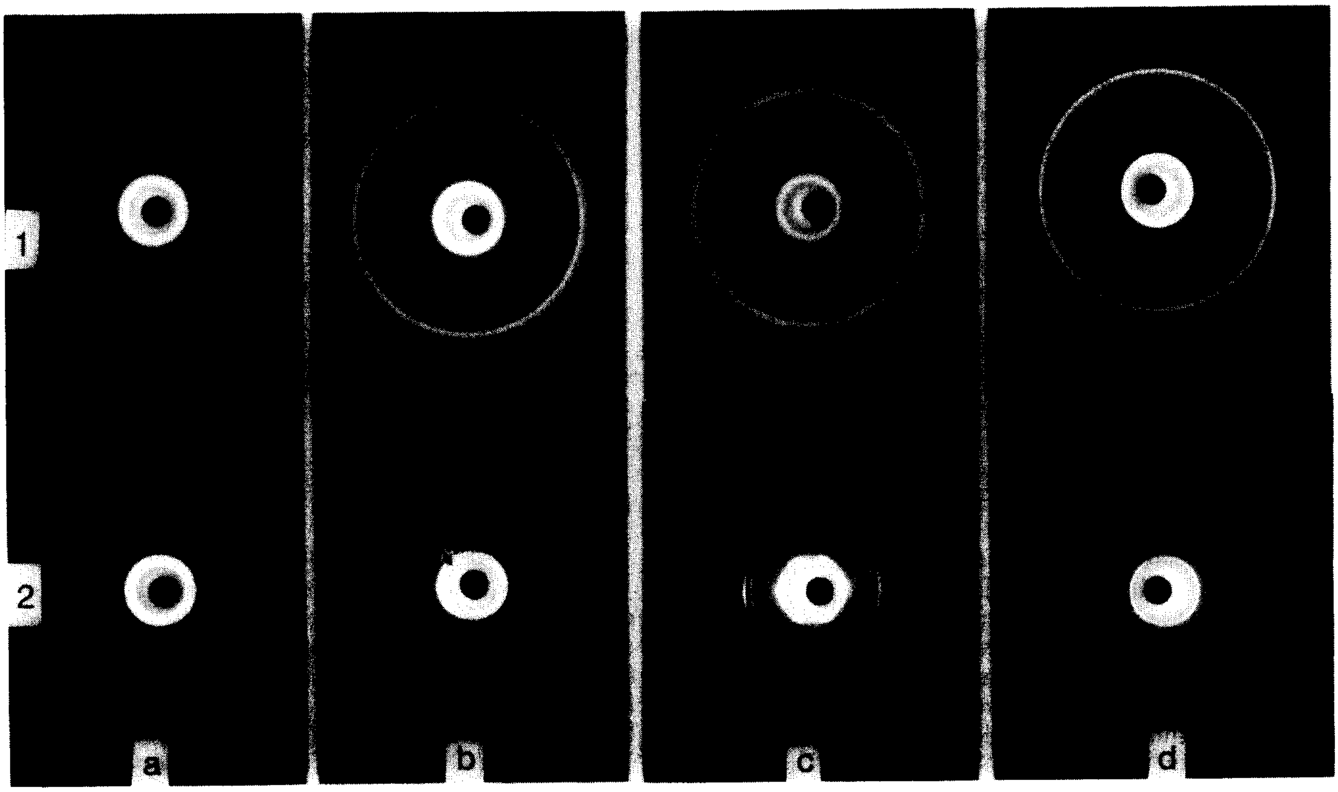

Figure 1 X-ray diffraction patterns of films a–c (M_1) and film d (M_2), taken with beams perpendicular (1) and parallel (2) to the plane of films set vertically. Thickness of film: (a, c): few micrometres; (b) 10 μm; (d) ~140 μm

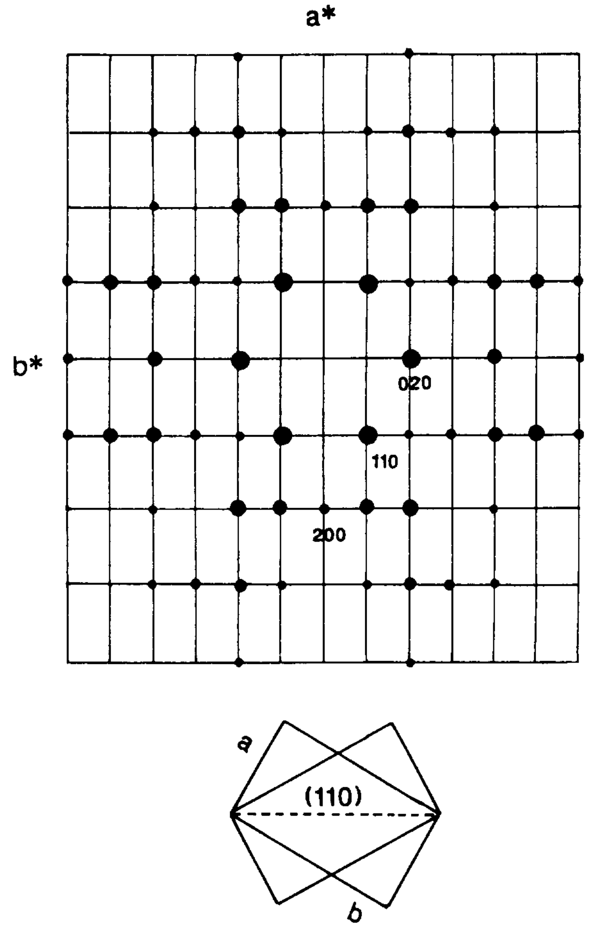

Figure 2 (Top) Reciprocal lattice of the orthorhombic unit cell, where the size of each circle roughly represents the reflection intensities[20]. (Bottom) Arrangement of the unit cell in film c of a few micrometres thickness. The (110) plane is parallel to the film surface

$b = 2.386$ and $c = 0.399$ nm). Since the d-spaces of the two strong reflections, 110 and 020, are almost the same, the reflection photograph has a hexagonal pattern. When two reciprocal lattices are overlapped as shown in the lower part of *Figure 2* where the (110) planes are parallel to the film surface, the diffraction pattern corresponds with that shown in *Figure 1c2*. This indicates that the (110) plane is well oriented parallel to the film surface through slow evaporation in the thin film of a few micrometres. Takeuchi *et al.* prepared a thin film using a drop of dilute solution of PDHS on a Si wafer substrate, in which the (020) or the (110) plane was parallel to the surface of film[21]. The orientation of the (110) plane in our thin film c is not due to any epitaxial effect, but probably due to the small thickness of film. The arrangement of the (110) plane of crystallites is considered to be almost parallel to the surface in the thin film c, but a little scattered in the thick film d prepared by evaporation of the concentrated solution.

Thermal transition behaviour

Figure 3 shows the typical d.s.c. curves of films of M_2. An endothermic and an exothermic peak correspond to the order–disorder phase transition and the reverse transition, respectively. The peak becomes larger and shifts to higher temperature for the films with a highly crystalline structure, although the exothermic peak is affected by the structure regenerated. The endothermic peak is observed around 36°C for film a, and in the range of 46–49°C for the other films. Similar d.s.c. curves were obtained for films made of M_1, though the peak temperature of films b–d was observed at 42–43°C (not shown). The largest enthalpy value obtained for the endothermic peak was $98\,\mathrm{J\,g^{-1}}$ for film d, M_2 (the value for film d, M_1 was $85\,\mathrm{J\,g^{-1}}$).

PDHS exists in a hexagonal lattice structure above the transition temperature[14], in which the backbone and the side chain conformations are randomized by the introduction of *gauche* bonds[10], however, some local order is

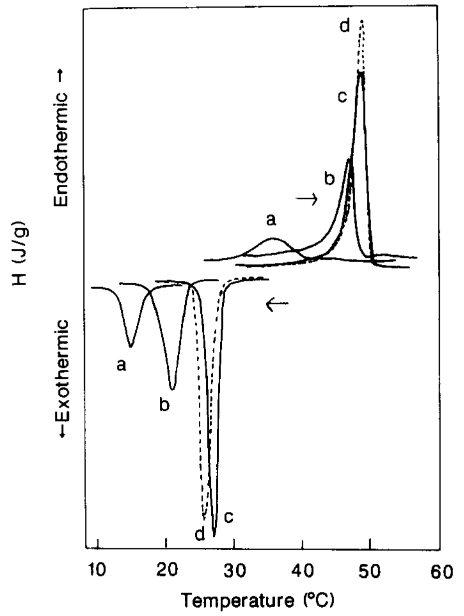

Figure 3 Heating to 100°C and successive cooling d.s.c. curves of films a–d (M_2)

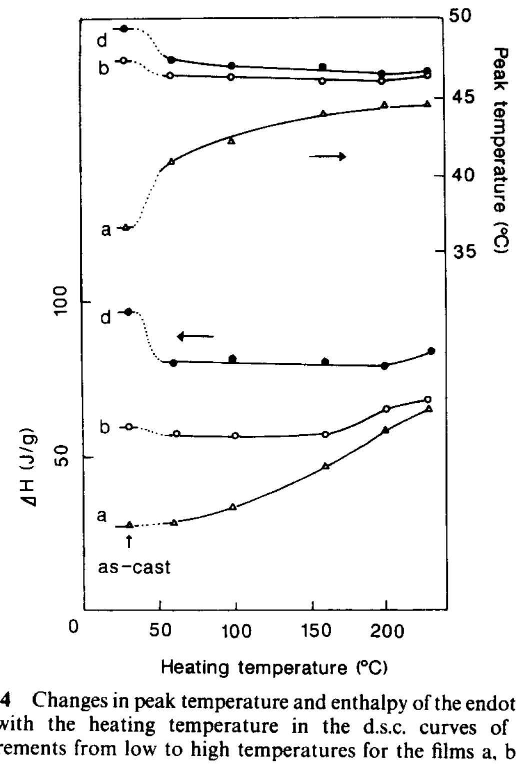

Figure 4 Changes in peak temperature and enthalpy of the endothermic peak with the heating temperature in the d.s.c. curves of repeat measurements from low to high temperatures for the films a, b and d (M_2)

retained at high temperature[9]. The lateral packing correlation (or coherence length) of the disordered part is improved with heating through the transitions, and the regenerated ordered phase after cooling shows an increase in size as a result of the heat treatment[5,14].

The effect of heat treatment on these films was examined by repeating the d.s.c. measurements. The peak temperatures and the change in enthalpy of the endothermic peaks are plotted against the heating temperature in *Figure 4*. The highly crystalline structure of film d became a little disordered by heat treatment above the transition temperature, but recovered slightly with treatment above 200°C. The less ordered films became more ordered by heat treatment at low temperature but never achieved the highly ordered structure of film d.

The regeneration behaviour of the ordered phase was examined isothermally by d.s.c. The films were repeatedly quenched from 100°C to constant temperatures to measure the subsequent exothermic peak caused by regeneration of the ordered phase. *Figure 5* is a plot of the change in heat against time after quenching. In the film with an ordered structure, regeneration occurred quickly even at high temperature. By repeating the measurement, regeneration was delayed for film d and became faster for film b. Both results suggest that the highly ordered structure of film d is gradually disordered by heating, while the less ordered film b became ordered.

U.v.-vis. absorption spectra

The absorption maximum of the u.v. spectrum depends upon the conformation of the backbone and the length of the Si–Si bonds[1]. *Figure 6* shows the u.v.-vis. absorption spectra of the films. The low crystalline film a is characterized by the strong absorption at 314 nm, which is associated with the disordered phase, and the small one at 357 nm. The red shift from 316 to 353 nm was observed when the PDHS solution was cooled to low temperature, and was ascribed to a coil-to-rod transition[5,19]. The PDBS film prepared at −78°C contains the *trans* backbone chains characterized[16] by the absorption maximum at 355 nm. An absorption maximum at 350 nm for unsymmetrically substituted alkyl polysilanes in the solid state was ascribed to the shorter planar sequence caused by the mismatch of side-chain length[22]. The 357 nm absorption in the spectrum of film a is ascribed to the shorter *trans* sequence.

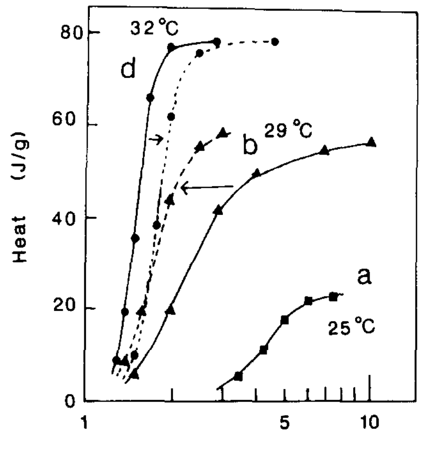

Figure 5 Change in heat generated by the isothermal disorder–order phase transition with time after quenching from 100°C for films a, b and d (M_2): (——) first run; (– – –) fourth (b) and seventh (d) runs

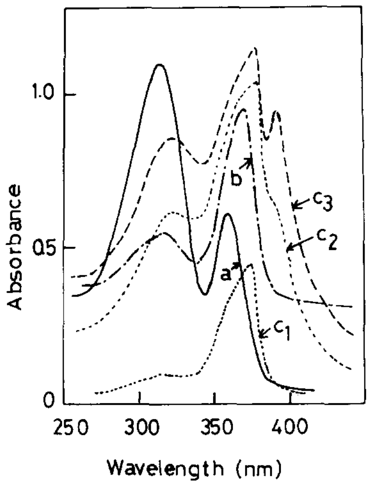

Figure 6 U.v.-vis. spectra of films a–c (M_1)

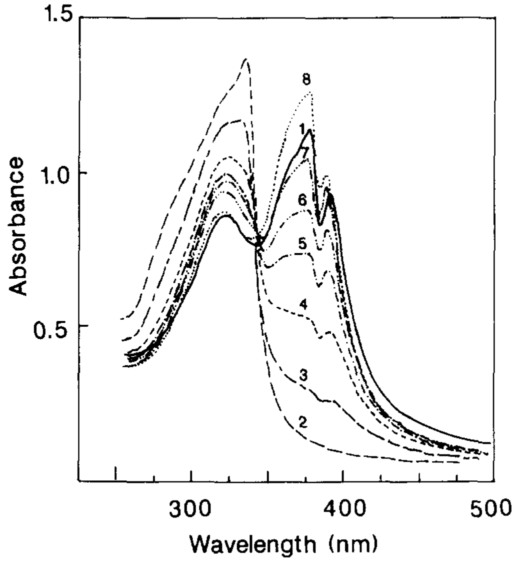

Figure 7 Repeat of u.v.-vis. measurement from 1 to 8 after heat-treatment at 80°C for 10 min on film c (M_1)

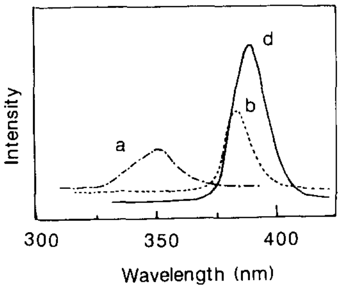

Figure 8 Fluorescence (extinction 280 nm) spectra of films a, b and d (M_2)

The absorption maximum of the ordered phase shifts to longer wavelength with increasing crystallinity, and was observed around 370 nm (film b) and 375 nm (film c). Films c were generally not uniform in thickness and structure, and their spectra varied from sample to sample as indicated by curves c_1–c_3 in *Figure 6*, in which a shoulder or another maximum is observed at a wavelength a little longer than 375 nm. In addition, these films were not transparent as a fine crystalline structure was generated through slow evaporation, causing scattering and affecting the spectrum.

Figure 7 shows the spectra of film c, which were measured repeatedly after heat treatment. The absorption maxima are observed at 322, 378 and 391 nm for the as-cast film (spectrum 1) and at 334 nm for the heat-treated film (spectrum 2). In the regeneration process of the ordered phase, the absorption around 390 nm was quickly recovered with disappearance of the 334 nm absorption, while the 378 nm absorption was slowly recovered. This suggests that the structure of the film was not uniform, and the absorption spectrum became broad. Since the quickly recovered part has a more ordered structure than the slowly recovered part as discussed before, the absorption maximum for the former is expected at a little longer wavelength than for the latter. It is reasonable to associate the more ordered part with the fine crystalline structure, but the absorption spectrum of the more ordered part is probably disturbed near the absorption maximum by the dispersion of the refractive index. Another possible effect of the fine structure is the tailing to the longer wavelength in the spectra.

It is difficult to determine the true absorption maximum for the highly crystalline film c, though it could be at a wavelength a little longer than 375 nm but less than 390 nm. The absorption maximum at 334 nm in spectrum 2 (*Figure 7*) might also be explained in a similar way because the films were still opaque after heat treatment.

Figure 8 shows the effect of the higher-order structure on the fluorescence spectra, in which peaks are observed at 350 nm (film a), 383 nm (film b) and 389 nm (film d). Here film a had a disordered phase. The peak position, which may show the overall property of the backbones, changed with time for the less ordered films. Although the details have not been examined yet, the peak shifted to longer wavelength for such a film even kept in a refrigerator for a long period. This result suggests that the main chains become ordered very slowly with relaxation of the molecular chains in the less ordered films.

CONCLUSIONS

The packing of the molecular chains in the PDHS films cast from toluene solutions greatly depends upon the temperature and rate of evaporation of solvent and the thickness of the films.

When the solvent is slowly evaporated at a little below the order–disorder phase transition temperature, the films, especially thick films of high molecular weight, have a highly crystalline structure. In contrast, films are more disordered when evaporated at 2°C. The molecular chains are oriented parallel to the film surface except for the film evaporated at low temperature, and the (110) plane of the orthorhombic unit cell is also arranged parallel to the film surface for thin film c (a few micrometres).

The order–disorder phase transition occurs at higher temperature in film of more ordered structure, and the regeneration of the ordered phase quickly proceeds on cooling. The less ordered films became ordered by the heat treatment, while the highly ordered film tends to be disordered by the treatment.

The absorption maximum in the u.v. spectra for the more ordered phase was observed at longer wavelength between 357 nm and 380 nm, although the upper limit is not certain because the spectra are probably disturbed by the fine crystallites generated through slow evaporation. The peak in the fluorescence spectra of these films was between 350 nm and 389 nm.

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