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Optical properties of the thin films of poly(methylpentoxysilane) homopolymers and copolymers

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Abstract

The optical properties of the thin films of asymmetrically substituted polysilane homopolymers and copolymers were studied. A conformational change in the organopolysilanes having (pentoxy,methyl) or (hexyl,methyl) groups was observed by polarized UV spectrometry and a wide angle X-ray diffraction. The polysilanes and polysilane copolymers having hexyl and pentoxy side chains were crystallized to form oriented films along the direction of the mechanically oriented polytetrafluoroethylene (PTFE) films. The bathochromic shifts were observed for polysilane and the polysilane copolymer having pentoxy side chains when the film thickness was small (ca. < 50 nm). The influence of the thickness of the films on the spectral change was significant when the substituent was a pentoxy group, however, not when it was a hexyl group.

Keywords: Polysilane thin film; Conformation; Alkoxy side chain

1. Introduction

Organopolysilanes have received much attention in recent years due to their unique optical and electrical properties [1]. Such characteristics are caused by the delocalization of electrons along the σ-conjugated silicon backbones and the σ-conjugation system is significantly depends on the conformations and high dimensional structures of the polysilanes.

By controlling the solid state conformation of the polysilane main chain, there occurred many characteristic photophysical abilities using highly oriented polysilane films in the past. The first is the stretching method [2–5], that was useful for many kinds of polymers including polysilanes. The solution cast film of poly(di-*n*-hexylsilane) (PDHS) can also be oriented by the rubbing method [5,6]. The Langmuir–Blodgett (LB) method is useful, however, some new types of polysilanes, bearing bis(butoxyphenyl) [7], phenol [8,9], hydroxyalkyl [10], alkoxyalkyl [11], or amphiphilic ammonium moieties [12], were necessary and actually synthesized in order to use the LB technique. The Si backbone in these LB films tends to aligned parallel to the dipping direction. A vacuum deposition method [13–15] was attempted for fabricating thin films of the polysilanes. The deposited molecular chain was found to be aligned perpendicular to the face of the substrate under appropriate conditions. The friction-transfer technique [16] is superior in terms of not only producing an excellently oriented film but also being applicable for most polysilanes, even the insoluble polysilanes. These five methods were mechanical techniques, while the sixth method was the epitaxial growth method. Such a method is easy to produce highly oriented thin films and the growth directions of the polymers were controlled by the substrates. The surface of the crystal substrate and highly oriented polypropylene (PP) [17] or polytetrafluoroethylene (PTFE) film [18] is commonly used as oriented substrates.

When considering the epitaxial growth method for polysilanes, it was an appropriate method for polysilanes which have high crystallinities such as poly(di-*n*-hexylsilane) (PDHS) [19–21]. On the other hand, polysilanes that have the side chains asymmetrically are low crystallinities. However, such polysilanes were useful for this application

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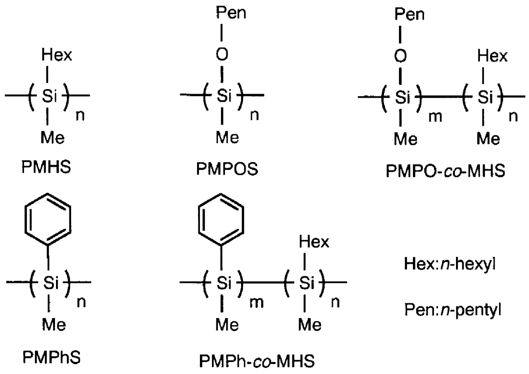
because of the high synthesis yields and good solubilities in organic solvents when compared to the symmetrically substituted polysilanes.

In this study, we focused on the spectral changes in the solid state induced by conformational changes in the asymmetrically substituted polysilanes and polysilane copolymers having pentoxy side chains. The orientation of the molecular chains induced new absorption bands and such effects were largely dependent on their side chains. Therefore, we discuss the optical properties of the polysilanes having different side chains, the alkyl and alkoxy side chains. In addition, the uniaxially oriented films of the polysilanes were prepared by crystallization using a mechanical deposited PTFE highly oriented polymer film as the substrate. Their properties were characterized by polarized UV spectroscopy.

2. Experimental section

2.1. Materials

The polysilanes were prepared by a typical Wurtz coupling reaction. Sodium (twice as much as the monomer in moles) was stirred in dry toluene and heated at 110 °C under a nitrogen atmosphere. The corresponding monomer for homopolymers, or suitable mixture ratios of the monomers for copolymers, were added to the solution and refluxed for 1-h. The reaction was stopped by adding 2-propanol. The crude polymers were washed with water, purified by reprecipitation in toluene by adding 2-propanol, and dried in a vacuum. The preparation of the alkoxy-substituted polysilane homopolymers and copolymers used here was described elsewhere (Scheme 1) [22]. The weight-average molecular weight (M_w) was estimated to be 4.82×10^5, 1.88×10^4, 2.50×10^4, 2.40×10^4, and 1.73×10^5 for poly(methyl-*n*-hexylsilane) (PMHS), poly(methyl-*n*-pentoxysilane) (PMPOS), poly(methyl-*n*-pentoxysilane-*co*-methyl-*n*-hexyl-silane) (PMPO-*co*-MHS), poly(methylphenylsilane) (PMPhS), and poly(methyl-*n*-phenylsilane-*co*-methyl-*n*-hexylsilane) (PMPh-*co*-MHS), respectively, by a size exclusion chromatography measurement calibrated by polystyrene standards. The polydispersity indices (M_w/M_n) were determined to be 3.8, 2.0, 2.2, 2.7, and 4.9 for these polymers, respectively. The composition ratios of the methylpentoxysilane units (MPO) and methylhexylsilane units (MH) of the PMPO-*co*-MHS and methylphenylsilane units (MPh) and methylhexylsilane units (MH) of the PMPh-*co*-MHS were determined by ^{1}H-NMR to be MPO/MH = 55/45 for PMPO-*co*-MHS and the MPh/MH = 53/47 for PMPh-*co*-MHS, respectively.



Scheme 1. Polysilane homopolymers and copolymers studied.

2.2. Sample preparation

The polysilane films between 20–200 nm thicknesses were prepared by spin-casting (1500 rpm) on a flat quartz plate using the $CHCl_3$ solution of the corresponding polysilanes. The thicknesses were controlled by the concentration of the solutions used. The thicknesses of the films were estimated by the absorption intensities integrated in the spectral range of 250–400 nm and compared with the standard films. The standard films were prepared on quartz plates in a area of 10 × 30 mm, and the weight of the films were measured for the corresponding polysilanes. The thicknesses of the reference films were calculated to be around 400 nm for each polysilane from their densities, film weights, and the coated areas. The density of each polysilane is summarized in Table 1.

The quartz and highly oriented PTFE films are used as the substrates. The polysilane films on quartz were isotropic in all directions within the substrate plane, while those on the mechanically deposited PTFE films were oriented in the sliding direction.

2.3. Characterization

The UV absorption spectra were measured using a Hitachi U-3000 spectrophotometer. The oriented thin films were characterized by polarized UV absorption spectroscopy. The Glan–Thompson polarizing prism was used for the polarization measurements.

The wide angle X-ray diffractions (WAXD) of the powdered polysilanes were measured using Ni-filtered Cu Kα radiation (40 kV, 300 mA) generated by a Rint 2500 VH/PC (Rigaku Co., Ltd). The WAXD patterns were taken with an imaging-plate camera. The meridional and equatorial profiles were obtained from the imaging plate.

Table 1
Densities (g/cm^3) of the polysilanes studied

Polymer	Density
PMHS	0.873
PMPOS	0.855
PMPO-*co*-HS	0.865
PMPhS	0.930
PMPh-*co*-HS	0.885

The ab initio MO calculations were carried out using the GAUSSIAN98 program on an IBM-RS/6000-SP. The geometries were fully optimized by the MO calculations at the B3LYP/6-31G** level. The default criteria for convergence were used for the all optimizations. The CIS calculations were performed at the CIS/6-31G* level for the determined geometries.

3. Results and discussion

The WAXD profiles of the polysilane powder are shown in Fig. 1. Two broad peaks are observed at $2\theta = 7$ and 20° in the WAXD profile of PMHS, which shows that the amorphous structure with disordered conformation dominantly exists in PMHS. Chunwachirasiri et al. analyzed the WAXD of PMHS and reported the presence of a number of polymorphic structures below room temperature [23]. But, the crystalline reflections were not observed in the PMHS at room temperature. A small sharp reflection is observed at $2\theta = 8°$ in PMPOS, suggesting that a small amount of crystalline phase or mesomorphic phase is formed. The crystallinity of PMPOS is, however, very low and molecular chains of PMPOS exist mainly in the amorphous phase at room temperature. The amorphous structure of PMPOS is considered to be different from that for PMHS in the packing of main-chain and side-chain and molecular conformation, because the WAXD profile of the PMPOS is very different from that of PMHS. The electrostatic interaction between the alkoxy side chains is considered to affect the amorphous structure of alkoxy-substituted polysilanes. PMPO-*co*-MHS has an almost similar structure to the structure of PMHS, as shown in Fig. 1(b) and (c), although the relative intensities of the two broad peaks ($2\theta = 7$ and 20°) are slightly different.

Fig. 2 shows the thickness dependence of the UV spectra of the spin-cast film on quartz. A broad absorption band is observed around 300 nm for the thick film of PMHS, whereas a new peak around 340 nm appeared for the thin

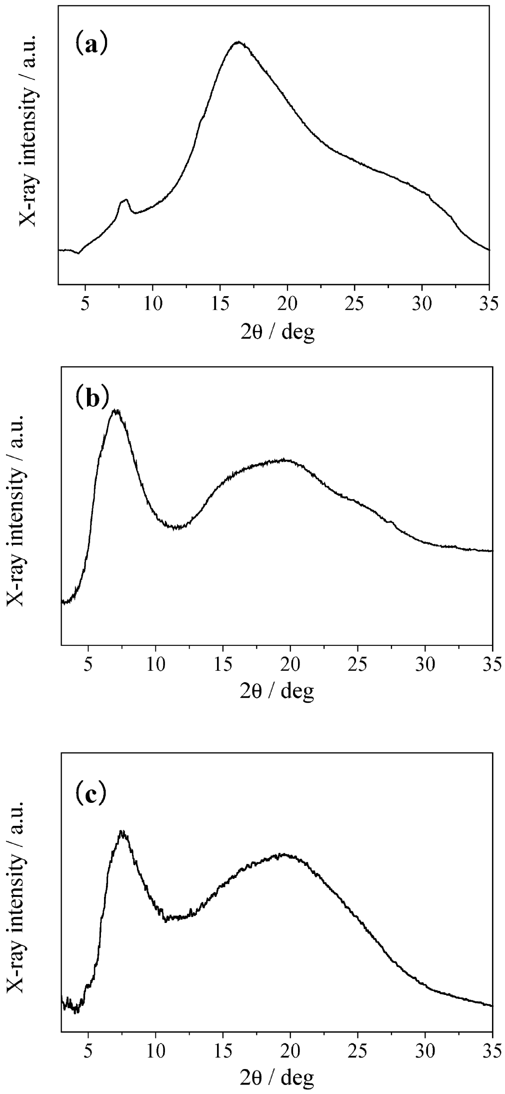


Fig. 1. WAXD profiles of polysilane powder. (a) PMPOS, (b) PMHS, and (c) PMPO-*co*-MHS.

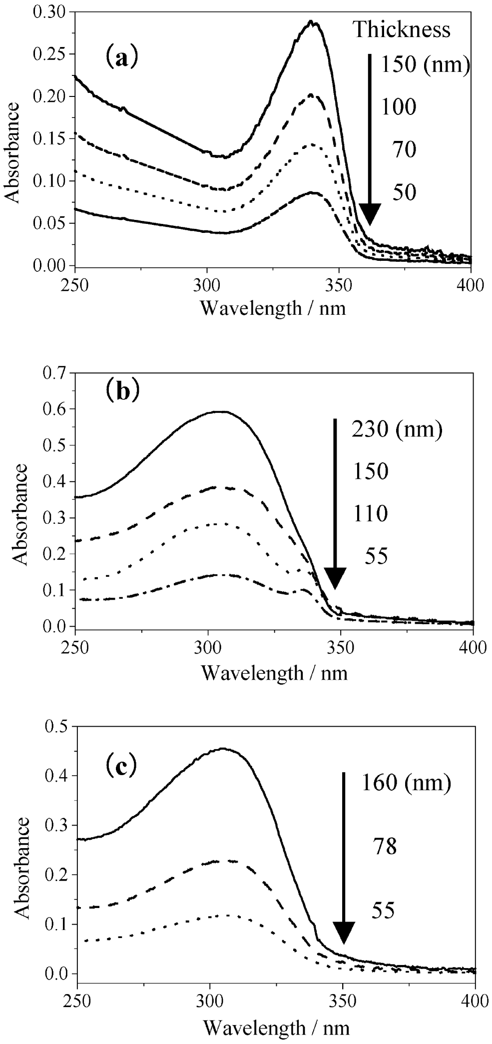


Fig. 2. Thickness dependence of UV spectra of spin cast films of polysilanes on quartz. (a) PMPOS, (b) PMHS, (c) PMPO-*co*-MHS.

film, similar to the results reported by Kaito et al. [18,24]. The new peak is attributed to the more extended conformation, which might be caused by the increase in the population of the *disoid* and *trans* conformations as reported in the study of Chunwachirasiri [23]. On the other hand, there is not any significant thickness dependence of the UV spectra for PMPOS, PMPO-*co*-MHS. The ordered structure was not induced even in the thin films owing to the electrostatic interaction between alkoxy side-chains and substrate.

PDHS has been known to take structure with the main chain lying-down on the substrate plane, and therefore, the hexyl groups are aligned perpendicular against the plane [21]. An increase in the thickness is an important factor for expanding the main chain of PDHS, because a sufficient thickness of the film induces a higher population of the trans segments in the main chains through the three-dimensional growth of the packing of the side chains. On the other hand, the side-chains of PMHS were oriented parallel to the substrate plane [18]. For PMPOS, the determination of the side-chain orientation was difficult because such polysilanes have side chains substituted asymmetrically and therefore, three-dimensional growth was inefficient. The structural organization of the thin film of the polysilane having asymmetric substituents is then decided by alignment between each Si-backbone or is in agreement with the unperturbed (no effect from the environment) conformation of the individual main chain itself. After these alignments of the main chains, the ordered conformation decreases the interaction between the side chains. According to such an assumption, two methods are important for inducing the high orientation of these polysilanes. One trial is to decrease the film thickness in order to reduce ambiguous structures due to the overlaying of the polysilanes, and this may clarify the effect of the deposited surface and the nature of the polysilane itself. Another is to crystallize polysilane on highly oriented substrates.

However, the first method was appropriate for PMHS, but not for PMPOS as shown in Fig. 2. It is difficult to self-align PMPOS because of the high electrostatic repulsion between the substituents. The second method was then expected to be effective for PMPOS to extend the conformation of the Si-backbone. Fig. 3 shows the polarized UV absorption spectra of polysilanes crystallized on highly oriented PTFE substrates. The thicknesses of the films were about 50 nm for all the polysilanes. For PMHS, the absorption bands were observed at 300 and 337 nm, similar to the spectrum for the same thickness spin cast film (Fig. 2(a)). The band at 337 nm has a higher intensity than the 300 nm band in the parallel polarized absorption spectrum, while the reverse is true in the perpendicular polarized spectrum. The dichroic ratio at 337 nm was stronger than that at 300 nm, therefore, this result shows that the Si-backbone of PMHS was extended along the orientation direction of the PTFE film.

Surprisingly, for PMPOS, a new band at 350 nm was observed as shown in Fig. 3(b), and this was not seen in the spin-cast film on quartz (maxima at 340 nm). The band at 350 nm has a higher intensity in the parallel polarized absorption spectrum than in the perpendicular polarized spectrum. This means that the highly oriented PTFE film strongly influenced the alignment of the Si-backbone of PMPOS, although the shift in the band maxima is smaller than that of PMHS. The thickness dependence of the film was examined as shown in Fig. 4. If the thickness of the films was increased more than 90 nm, the absorption of the 350 nm band disappeared. These results show that the conformational change in the main chains of the PMPOS induces such a bathochromic shift. In addition, only a very small effect on PMPO-*co*-MHS by the PTFE oriented film is observed in Fig. 3(c). The parallel polarized absorption spectrum and the perpendicular polarized absorption spectrum are almost identical. Trials to make the spin-cast film on the oriented PTFE film for PMPO-*co*-MHS having different ratios of MPO and MH units produced similar results. These results showed only little conformational

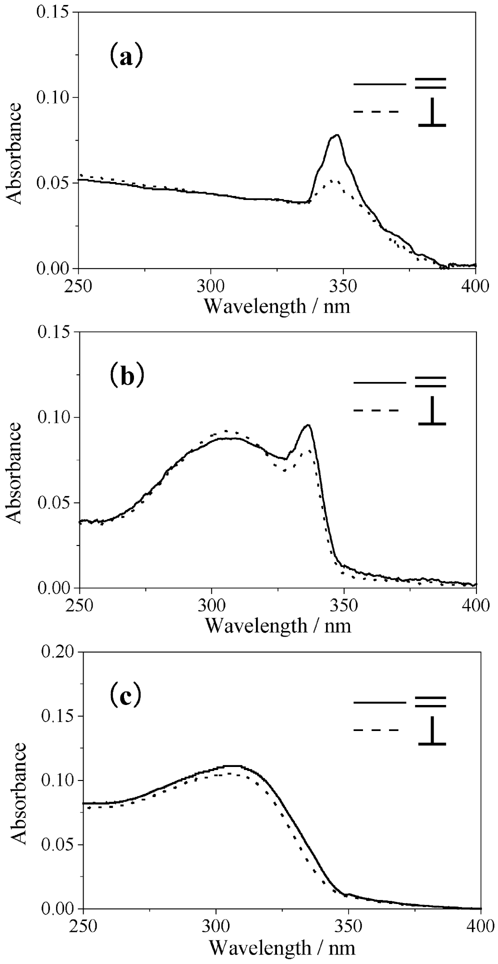


Fig. 3. Polarized UV spectra of polysilanes spin-casted on highly oriented PTFE substrate, solid line: parallel polarization, and dotted line: perpendicular polarization. (a) PMPOS (48 nm), (b) PMHS (50 nm), and (c) PMPO-*co*-MHS (38 nm).

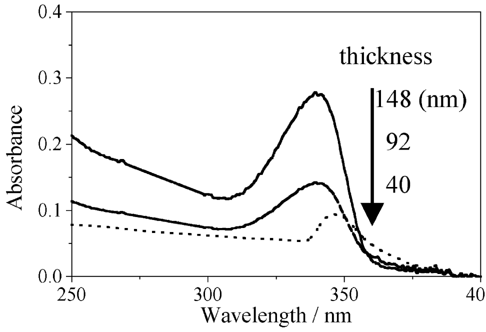


Fig. 4. Thickness dependence of UV spectra of spin cast films of PMPOS on highly oriented PTFE film. The thicknesses of the films were 148, 92, 40 nm, respectively.

change of the main chains of PMPO-*co*-MHS was induced by the highly oriented PTFE film.

We already reported that PMHS and PMPOS take similar conformations in solution. The UV absorption spectra of PMHS and PMPOS in CH_2Cl_2 [22] were very similar to their spectra of the spin-cast films. Therefore, the conformations of PMHS and PMPOS might be similar in solution and in the spin-cast film, although PMPOS has a lower crystallinity than PMHS. The difference of these two polymers is the smaller bathochromic shift of the absorption maxima of PMPOS and PMPO-*co*-MHS than that of PMHS when they crystallize on the highly oriented PTFE films. Two reasons were considered; the first is that the differences in the singlet excitation energies (*E*s) between the trans-rich and gauche-rich conformations for PMPOS and PMHS are not similar. In order to estimate such a possibility, we carried out the ab initio MO calculation of the model compounds of these polysilanes. The racemo(meso)-dihydroxyloctamethyltetrasilane (OS4R) and decamethyltetrasilane (MS4) (Fig. 5(a) and (b), respectively) were used as model compounds in this study, because polysilanes were too large to perform the ab initio MO calculations. The calculation was performed similarly to our previous oligosilanes work [25]. Fig. 5(c) and (d) show the results of the CIS/6-31G* calculations of the *E*s for the dihedral angles of the Si-backbone around the *trans-disoid* (120–180°) and *ortho-gauche* (50–110°) conformational regions of which oscillator strengths are the highest. The transitions having the highest oscillator strengths in the *ortho-gauche* region did not have the lowest transition energies. The *E*s of MS4 and OS4R in the *trans-disoid* dihedral angle region are similar, except for the values at 180°. On the other hand, the *E*s of OS4R had flat values over all the regions of the *ortho-gauche* conformations, and the absolute values of the *E*s are smaller than MS4. Considering the polymer structure as an extension of these oligomer structures, these above results imply that the difference in the *E*s between the *trans*-rich and *gauche*-rich conformations for PMPOS is smaller than that of PMHS.

Another reason is closely related to the difference in the number of *trans*-rich segments due to the alignment of the main chains on the substrate planes between PMPOS and PMHS. PMPOS has electron-rich substituents. If the molecular chains aligned to each other are similar to PMHS, the electrostatic repulsive interaction between the molecular chains is so large that PMPOS has a low crystallinity, and a conformational change in the Si-backbone is difficult to occur. One is able to estimate by X-ray measurements the dependence of the thickness, however, it is too difficult to observe WAXD peaks of a thin film because the reflections of the polysilanes were too weak and that of the substrate was too strong.

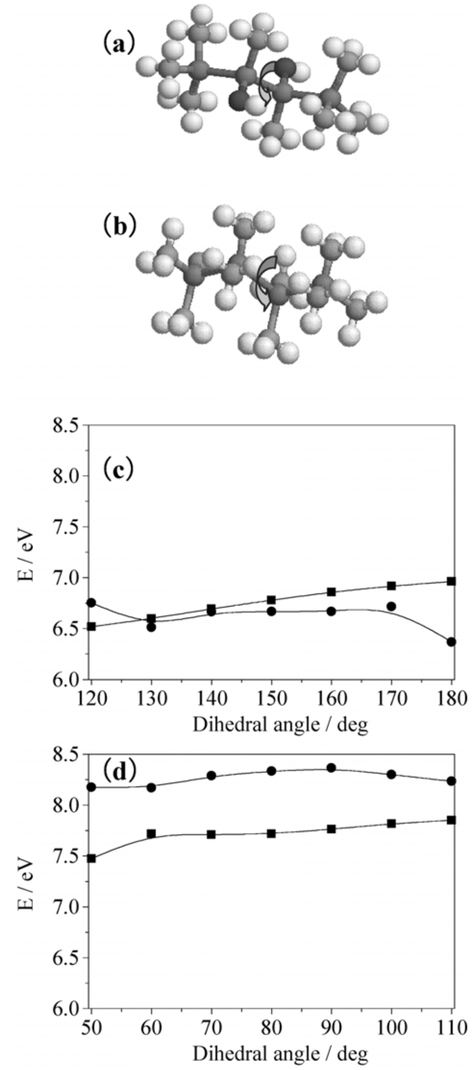


Fig. 5. Schematic representation of calculated model compounds of oligosilanes; (a) MS4 and (b) OS4R. Variable dihedral angles of Si–Si–Si–Si for calculations are indicated in the figures. Calculated (CIS/6-31G*) singlet excitation energies as a function of dihedral angles for MS4 (●) and OS4R (■); (c) the *trans-disoid* conformational region and (d) the *ortho-gauche* conformational region.

In order to clarify the effects of the MPO units on the conformational changes in the main chain, we examined other polysilanes, PMPhS and PMPh-*co*-MHS, which have MPh units instead of MPO units. PMPhS, consisting of only MPh units, has a higher crystallinity and more rigid main-chain than PMPOS and PMHS [26]. The higher rigidity of the main-chain inhibits its conformational change similar to the MPO units. The thickness dependence of the UV spectra of PMPhS and PMPh-*co*-MHS are shown in Fig. 6. No dependence of the film thickness was observed for PMPhS. It is considered that the interaction between Si-backbone and phenyl groups and the conformation of main chain affect the electronic state of PMPhS. Since there is no regularity in tacticity of PMPhS, it should be considered that the extended conformation has also been disturbed to some extent, and molecular chain of disturbed and not extended conformation has packed in the crystal. This is the regular reason of the longer wavelength shift than polyalkylsilanes, then, the packing and rigidity of the main-chain definitely suppressed the conformational change in the main chains for PMPhS. Therefore, it was also estimated that one of the reasons for the small bathochromic shift in the absorption band for PMPOS is the small conformational change in the Si-main chain.

On the other hand, for PMPh-*co*-MHS, there was remarkable dependence of the film thickness on the UV spectra similar to PMHS, but has not been seen in PMPO-*co*-MHS. The peak maximum at 322 nm shifted to 334 nm. The conformational change in the main chains were slightly suppressed by the rigidity of the main-chain, because the wavelength of the new peak maximum (334 nm) was shorter than that observed for PMHS (338 nm). However, these results show the stretched conformation of the main chain and increase in the alignments between the main chains. In a thick film, PMPh-*co*-MHS takes two conformations, one conformation is the origin of the 290 nm shoulder and the other is a more extended conformation which is the origin of the 322 nm band. However, there were no peaks around 290 nm in the thin film of PMPh-*co*-MHS, though the homopolymer with MH units, PMHS, takes two conformations shown by the 305 and 338 nm absorption bands in the thin film. This may reveal that the conformational change in the main chain from the conformation at 290 nm shoulder to that at 334 nm band was induced.

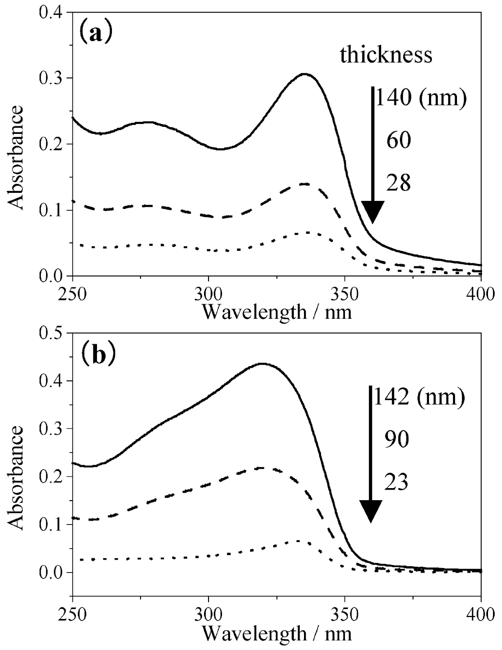


Fig. 6. Thickness dependence of UV spectra of spin-cast films of polysilanes (a) PMPhS, (b) PMPh-*co*-MHS) on quartz.

Fig. 7 shows the polarized UV absorption spectra of these polysilanes crystallized on a highly oriented PTFE substrate. For PMPhS, no effects were observed on its alignment by the oriented substrate. The parallel polarized absorption spectrum and the perpendicular polarized absorption spectrum are almost identical to the sample spin-casted on quartz. It was also predicted that the conformation of the main chain was essentially determined by the bulky substituents for PMPhS. The thickness dependence of the UV spectra of PMPh-*co*-MHS oriented on the PTFE films is shown in Fig. 6(b) and (c). The polarization at the 334 nm band was obviously different in

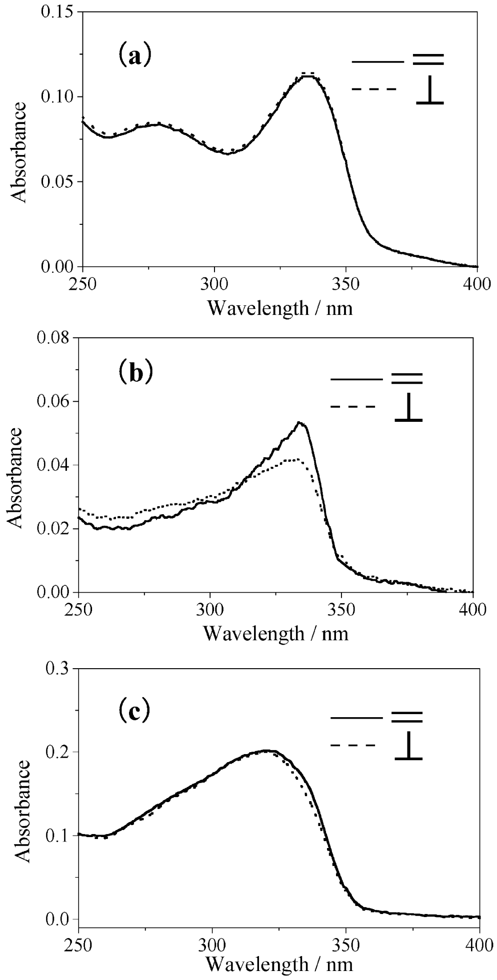


Fig. 7. Polarized UV spectra of polysilanes spin-casted on highly oriented PTFE substrate, solid line: no polarized UV spectra, broken line: parallel polarization, and dotted line: perpendicular polarization. (a) PMPhS (57 nm thickness), (b) thin film of PMH-*co*-MPhS (25 nm), and (c) thick film of PMH-*co*-MPhS (110 nm).

the thin film, while the difference became smaller in the thick film. In addition, the polarization was smaller in the range of 300 nm band than that around 334 nm. These results showed that the 334 nm band was highly oriented in the orientation direction of the PTFE and assigned to the extended Si-backbone. This implies that PMPh-*co*-MHS has a conformational change in the main chain, though it has bulky side chains. Compared the results of the PMPO-*co*-MHS with that of PMPh-*co*-MHS, it was also estimated that the electrostatic interactions between the molecular chains of PMPOS inhibit any conformational change in the main-chain much stronger than the steric interactions between the side chains.

4. Concluding remarks

The effects of the side chains of the polysilanes having asymmetric substituted side chains on their optical properties of thin films were studied. The conformations of the polysilanes and polysilane copolymers were controlled by the thickness of the films and crystallization on the highly oriented PTFE substrates. The highly oriented films of the polysilanes and the polysilane copolymer having hexyl side chains were prepared on quartz by the spin-cast method, and the orientation was significantly affected by the thickness of the films. However, for the polysilane and polysilane copolymer having pentoxy substituents, the alignment was only observed by the method crystallizing on the oriented PTFE films. It was considered that the reasons why bathochromic shifts induced by the orientation on surface for polysilane and polysilane copolymer having pentoxy side chains were smaller than that for polysilane and polysilane copolymer having hexyl side chains. Two effects of the pentoxy side chains on the optical properties in solid states are estimated. Ab initio MO calculations predicted that the difference in the *E*s between the extended and twisted conformations becomes smaller when the side-chains were alkoxy groups. It was also estimated that the pentoxy side chains suppressed the conformational change in the main chain. The orientation of the main chains might be caused by the electrostatic interactions between the main chains. This is in contrast to the orientation of the polysilanes having aryl groups caused by the steric interactions between the bulky side chains.

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