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Structural Studies on Highly Oriented Thin Films of Silicon–Based Polymers

A Doctoral Thesis

by

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of Science, Osaka University

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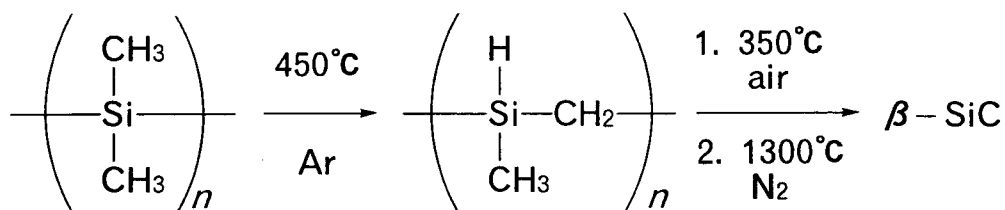
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Chapter 1

General Introduction

Silicon is an element which positions just below carbon in the periodic table, so that it is expected to be analogous to carbon in chemical properties. Actually, an Si atom usually has four valence bonds and an ability to catenate to form a stable long linear chain from single element, in a manner similar to the case of carbon. Chemists have dreamed of constructing a field of silicon chemistry in which carbon is substituted by silicon. A lot of compounds having Si–C and/or Si–Si bonds, which do not exist in nature, have been synthesized so far, and the organosilicon chemistry has developed as an important field of chemistry. It is an interesting theme to introduce Si atoms in polymer chains. A series of polysiloxanes are the most successful Si–based synthetic polymers in industry and the most famous inorganic polymers. Since their physical and chemical properties are very different from those of other polymers which consist of carbons in the main chain, they are used in various fields. Another Si–based polymer produced on an industrial scale at present is poly(dimethylsilylene) (PDMS), which is used as a raw material of silicon carbide (SiC) ceramics (preceramic polymer). PDMS is one of high–molecular–weight polysilanes, whose main chain is composed of only Si atoms. Yajima and his co–workers¹⁾ succeeded in obtaining β –SiC



by pyrolysis of a formable carbosilane which was obtained by low-temperature thermal conversion of PDMS. After their invention, polysilanes have been studied as preceramic polymers.

Nowadays, polysilanes get much attention as one of new materials. They exhibit characteristic electronic and optical behaviour like as polymers having π -conjugated carbon chains, though it is composed of Si-Si single bonds. This behavior originates from the electronic delocalization within the σ -bonded Si-Si framework, so-called " σ -conjugation". Many applications of polysilanes have been also examined. Their electrical conductivity²⁾, photoconductivity³⁾, charge transport⁴⁾, and non-linear optics⁵⁾ have been investigated. The photoreactivity of polysilanes enables the polymers to be used for photoinitiators of polymerization⁶⁾ and photoresists⁷⁾. Polymers composed of both Si and π -conjugated carbon linkages in the same skeletal chain are also hopeful materials for the electronic and optical usage.

The characteristic behavior due to the Si-Si linkage of polysilanes attracts a lot of scientific interests. We are also interested especially in the structure of polysilanes, because we here find a good example of polymers showing a close relationship between structure and physical properties. It is well known that the conformation of the polysilane affects the σ -conjugation character. The origin of σ -conjugation of the Si-Si chain and its dependence on the chain conformation are explained in terms of quantum chemical theory, as follows⁸⁻¹⁰⁾ (Figure 1-1). The resonance integral, β_{vic} between two sp^3 orbitals located on the adjacent silicon and pointing each other are responsible for the Si-Si σ -bond formation.

A less negative resonance integral β_{gem} between the two sp^3 hybrids located on the same silicon atom is responsible for the interaction between

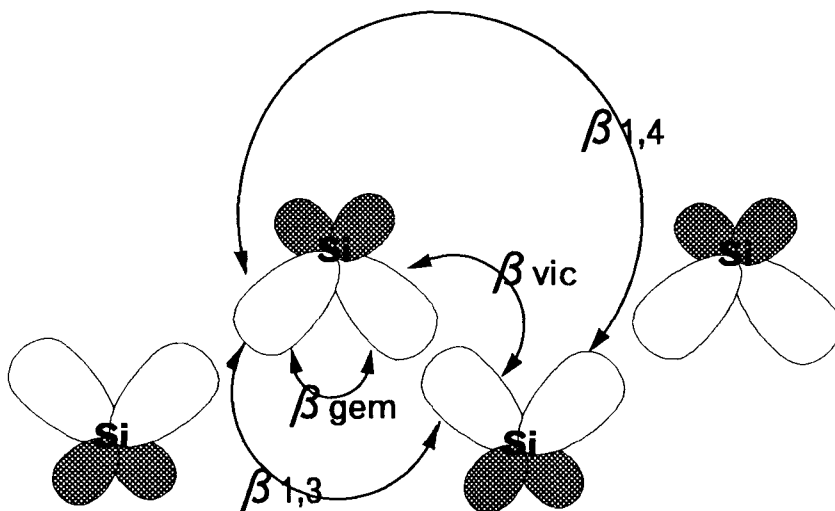
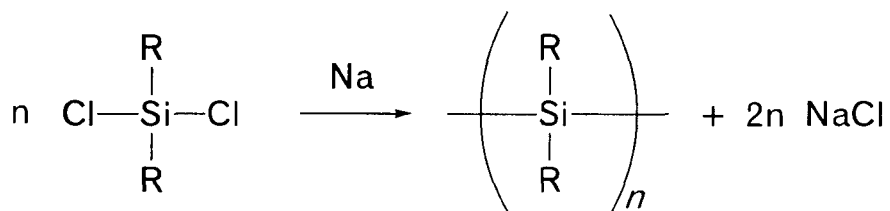


Figure 1-1. The resonance integrals between Si sp^3 orbitals in a polysilane.

localized orbitals carried by the same silicon. A linear combination of mutually interacting localized orbitals results, and the resultant molecular orbitals are delocalized throughout the whole silicon backbone. The orbital energies of polysilanes are very sensitive to molecular conformation. This sensitivity cannot be explained by the calculation that considers interactions beyond β_{vic} and β_{gem} , but it can be interpreted by the consideration of the resonance integrals, β_{14} between more distant hybrid orbitals⁸⁻¹⁰). The β_{14} value varies passing through zero during the change in the dihedral angle from 0 to 180°. The integral β_{14} , affected by a conformational change, is important for the σ -delocalization character.

The first report of the synthesis of polysilane was made by Kipping¹¹) who is called a father of organosilicon chemistry. In 1924 he prepared a polysilane through the condensation of diphenyldichlorosilane using sodium metal. Because the polymer obtained was insoluble, the molecular weight and chemical structure could not be clarified. (It was found afterward that "the polymer" is a low-molecular-weight cyclic compound.) More than 25 years had passed until the synthesis of the next polysilane was reported by Burkhard¹²). He prepared PDMS, which was the first linear high-molecular-weight polysilane, through the similar synthetic route as



Kipping. The polymer could not be well characterized due to its insolubility. Since polysilanes synthesized in early days were insoluble, all of high-molecular-weight polysilanes were believed for a long time to be intractable. The polysilane had been forgotten by researchers until

Yajima's process¹⁾ was discovered. Soluble polysilanes were independently prepared by three research groups in USA around 1980^{2, 13, 14)}. These discoveries of the soluble polysilanes indicated that high-molecular-weight polysilanes were not necessarily insoluble and intractable materials, and gave the chance to open the new age of the polysilane science. Thereafter, the explosive interest has arisen in the synthesis and the characterization of polysilanes, and it has continued until today.

At present, many varieties of soluble polysilanes have been synthesized. While, though poly(dimethylsilylene) having shortest side chains is insoluble in common solvents, it is important to study the structure and the properties of PDMS in order to understand the nature of the catenated Si atoms in polysilanes. The parent polysilane (a hydrogen substituted polysilane) cannot exist stably. Since PDMS is the simplest member among the really existing polysilanes, many computational and theoretical studies have been carried out^{10, 15, 16)}. However, detailed experimental studies of PDMS have been prevented by its lack of ability to be processed. As a model of highpolymers, physical properties of permethylated oligosilanes have been investigated¹⁷⁾. Recently, Lovinger *et al.*¹⁸⁾ prepared a PDMS film cast from a boiling α -chloronaphthalene solution and obtained an oriented film by stretching above 200°C. They also prepared the first single crystal of PDMS from an α -chloronaphthalene solution¹⁹⁾. They found that PDMS conformation is all-*trans* at ambient temperature. However, detailed structural analysis has not been made. Their oriented specimens were prepared in a quite complicated method and were limited to be used only for electron diffraction; in other words these samples were difficult to be employed for

other types of measurements such as electronic and vibrational spectroscopies. It is very important to measure the electronic properties of the oriented PDMS for understanding of the fundamental nature of polysilanes. We attempted to prepare highly oriented PDMS films, which is easily handled and whose structure and properties can be examined by various methods, and to perform the detailed structure analysis.

As stated above, preparation of oriented specimens is very important for the scientific research of structure and physical properties of the polymer. Since the polysilanes behave as one-dimensional semi-conductors, many researchers in the solid state physics are much interested in properties of polysilanes^{20, 21)}. If the "perfectly" oriented polysilane will be prepared, it will be very versatile for the investigation of low-dimensional semi-conductors as a simple model system. If vagueness arised from orientational disorders would be diminished, the information obtained from the oriented specimens should become clear. However, such highly oriented samples have not been prepared by methods already used. Moreover, control of the arrangement of polymeric chains enables the materials to have improved properties and to add anisotropy to the properties because the delocalization of electrons along the main chain is responsible for the unique electric properties of polysilanes, as mentioned before. For example, the third order non-linear optical susceptibility, $\chi^{(3)}$, was greatly improved by the molecular chain aligning of polysilanes²²⁾. More highly oriented polysilanes should have better properties for industrial usages. The already reported methods of preparing the oriented polysilanes may be classified as follows.

1) Stretching : The elongation is useful for the investigation of the properties and the structure of polysilanes^{23, 24, 25)}. As mentioned

before, the structural study of PDMS was performed by using the stretched film¹⁸⁾. However, as the stretching of polysilanes themselves is rather difficult, highly oriented samples cannot be obtained by this method. The elongation of its blends with normal polymers, such as polyethylene, was attempted²⁶⁾.

2) Rubbing method : It is interesting that the solution cast film of poly(di-*n*-hexylsilylene) (PDHS) can be oriented by a rubbing method^{27, 28)}. For usual polymers, only several nm surface can be oriented by the rubbing method, but a rather thick part below the surface of PDHS film can be oriented. Tachibana *et al.*^{27, 28)} investigated the anisotropy of electronic character of the polymer by using the oriented film prepared by rubbing. However, the method is not applicable to all polysilanes.

3) Langmuir–Blodgett (LB) method : LB technique is an elegant technique for control of the structure of the thin film in the molecular level.

The technique was tried to use for the preparation of the structure controlled polysilane film. However, since the ordinary polysilane has no hydrophilicity, it cannot be spread on the air–water interface. Thus researchers synthesized some new–type polysilanes, which bear bis(butoxyphenyl) substituents²⁹⁾, phenol groups^{30, 31)}, hydroxyalkyl groups, alkoxyalkyl groups³²⁾, or amphiphilic ammonium moieties³³⁾.

The Si backbone in these LB films tends to be aligned parallel to the dipping direction. This method requires to modify the chemical structure of polysilanes.

4) Vacuum deposition : The vacuum vapor deposition method was attempted to fabricate thin films of polysilanes^{34–36)}. Since the method needs not to pass any liquid phases, it is effective to prepare the film from

insoluble and infusible materials, PDMS. The deposited molecular chain was found to be aligned perpendicular to the face of the substrate on an appropriate condition³⁶⁾. However, the chain scission and some chemical changes in the molecule took place during the vacuum deposition³⁶⁾.

The orienting methods mentioned above have restrictions and weak points. A novel method has been desired, and we have noticed that the friction transfer method is a promising candidate.

Lately, much attention has been focused on the highly oriented poly(tetrafluoroethylene) (PTFE) film having the remarkable capacity of inducing oriented growth of a wide variety of materials, which has been investigated by Wittmann and his co-workers³⁷⁻⁴⁰⁾. The latest result showed that highly oriented films of soluble polysilanes were prepared by crystallization on the highly oriented PTFE film⁴¹⁾. They prepared the highly oriented film of PTFE by friction transfer. It is well established by workers in the field of polymer tribology that when PTFE is rubbed against a clean surface under appropriate conditions, a highly oriented thin film of PTFE is deposited onto the surface⁴²⁾. It is very interesting that a thin solid film is transferred onto the substrate directly from a solid polymer not via any liquid phases. Thus, it may be possible to prepare an oriented thin film from insoluble and infusible polymers such as PDMS by the friction transfer. Motamedi *et al.*³⁸⁾ investigated a lot of polymers as candidates for the formation of oriented films and found that only several polymers afforded oriented films. They confirmed that the formation of friction transferred film requires relatively weak interchain interactions and "smooth " molecular profiles. In this standpoint, PDMS should be a candidate for formation of a friction transferred film. A problem remained that the method requires the bulk polymer materials though PDMS can be

obtained only in a powder state. This was solved by using a polymer disk which is obtained by the compression of the powder. We successfully obtained an extraordinarily oriented PDMS film by the friction transfer technique.

While, it is interesting that the change in the chemical structure of substituents contributes to the change in the Si backbone conformation. In the di-*n*-hexyl, di-*n*-heptyl, and di-*n*-octyl substituted polysilanes, Si backbone adopts all-*trans* conformation under ambient conditions. These compounds undergo a reversible thermochromic transition to a conformation-disordered phase^{23, 24}). The conformational change induces a change in σ -conjugation and a shift of UV absorption from 374nm (ordered) to 317nm (disordered). The piezochromism (pressure-induced transition accompanied with a change of color) was also observed in PDHS^{43, 44}). The conformation of polysilanes with longer side chains, nonyl, decyl, and so on, were reported to be $\overline{\text{TGTG}}$ ⁴⁵). The structures of polysilanes with shorter substituents, di-*n*-butyl, and di-*n*-pentyl polysilanes (PDBS and PDPS), are more complex. They were found to adopt a 7/3 helical conformation under ambient conditions^{46, 47}). Their all-*trans* conformer is yielded by application of pressure of the order of 50–500 MPa^{48, 49}). Polysilanes with further shorter side chains, poly(di-*n*-propylsilylene) and poly(diethylsilylene) have all-*trans* conformation⁵⁰). Recently, soluble diaryl substituted polysilanes were synthesized and found to have rigid all-*trans* conformation because of their bulky side chains⁵¹). A di-aryl polysilane was found to undergo a thermochromic transition, which is very different from those of di-alkyl analogues⁵²). Alternating copolymers synthesized from masked disilenes have a thermochromism unlike random copolymers⁵³). A polysilane with

an optical active substituent was found to have a very rigid helical structure⁵⁴⁾. As shown above, the chemical structure of polysilanes much contributes to the solid state structure, and furthermore it affects the properties. Can one prepare highly oriented films by the friction transfer method from the polysilanes which have varieties of chemical structure and properties? If the friction transfer method may be use for various polysilanes, one will be able to investigate a relation between the chemical and the solid state structures and the physical properties of the various polysilanes.

This thesis describes the preparation of oriented films of Si-based polymers and the structural characterization of the films. Especially, excellently oriented films of PDMS and other polysilanes prepared by the friction transfer technique are described in detail. The optimum condition of preparing superior films is explored. The structure that the polysilane has inherently is investigated by using the oriented films. The higher-order structure of the transferred film is also studied. The problem is also discussed whether there is the difference in the properties between the extremely oriented ultrathin film and the bulk sample.

It is important to develop the methods to characterize such highly oriented ultrathin films of polysilanes. The electronic spectroscopy reveals electronic states of polysilanes. As the skeletal conformation affects the electronic state, the spectra can clarify structures of the Si main chain. The vibrational spectroscopy gives information for molecular structures, aggregation states of molecules, and orientations of particular chemical groups. Especially, structural information about alkyl side chains of polysilanes was obtained by the spectra. The reflection-absorption spectroscopy (RAS) is useful for the ultrathin film, and one can obtained

the information of orientation toward the film face. The diffraction methods display structures in the crystalline state and higher-order structures. It is difficult to characterize the ultrathin films by the conventional X-ray diffraction method because of the thinness. The electron diffraction is effective for the characterization of the ultrathin films.

Total reflection X-ray diffraction method^{55, 56)}, which uses the total reflection phenomenon of X-rays, is also available to characterize the ultrathin films.

The thesis is constructed with the following eight chapters.

Chapter 2 describes the preparation of highly oriented film of PDMS by the friction transfer. In order to find the most appropriate conditions, the relationship between the preparation conditions, especially substrate temperature, and properties of the film is investigated. The morphology is observed by using optical and electron microscopes. The electronic state and the structure of the main chain of the polysilane are monitored by UV absorption and fluorescence spectra. The polarized spectra is used for the estimation of orientation state of the film. The mechanism of the friction transfer is also discussed in this chapter.

Chapter 3 is concerned with the structure of the highly oriented PDMS film prepared by the friction transfer. The structure of the film is characterized by infrared spectroscopy and electron and X-ray diffraction methods. The molecular structure, the crystal packing of PDMS are analysed by using the oriented film. The higher-order structure in the PDMS film is investigated. It is examined whether there are any unusual properties and structure in the extremely oriented ultrathin film. The phase transition behavior of thin film and bulk sample is also investigated with UV and IR spectroscopies.

The structure and the properties of polysilanes vary by the effects of their substituents. In chapter 4, the friction transfer technique is applied to several polysilanes, such as poly(diethylsilylene) (PDES), poly(di-*n*-hexylsilylene) (PDHS), poly(di-*n*-butylsilylene) (PDBS), and poly(methylphenylsilylene) (PMPS). This chapter makes an issue of the difference among the polymers in the relation between the preparation temperature and the properties of the films. Thermochromic transition in the thin film of PDHS is also examined.

It is necessary for the investigation of thin films to develop characterization methods for thin films. Chapter 5 presents a new method, total reflection X-ray diffraction (TRXD) method^{55, 56)}, for the structural characterization of oriented thin films. The structure of the friction transferred film of PDBS is investigated by TRXD method. The molecular orientation in plane can be estimated by the method.

The characterization methods, which were used for the friction transferred films, were applied to the structure-controlled polysilane films prepared by another method, the LB method. Chapter 6 is devoted to the structural characterization of LB films of amphiphilic polysilanes. The molecular orientation is characterized by the UV and IR spectroscopies. The layer structure of the LB films is estimated by X-ray diffraction method.

Chapter 7 deals with the application of the friction transfer to another intractable polymer, poly(*p*-phenylene) (PPP), which has no Si atoms. Moreover, homoepitaxial polymerization of PPP on the friction transferred oriented film of PPP is also presented.

Chapter 8 summarizes main result and the conclusion of the present work.

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Chapter 2

Highly Oriented Film of Poly(dimethylsilylene)

Prepared by Friction Transfer

2-1. Introduction

Some specific electronic properties of polysilanes have been considered to be caused by delocalized σ -electrons in the Si-Si catenated backbone, so called " σ -conjugation". Therefore, preparation of well-oriented polysilane samples is important not only in the scientific research of anisotropy of electronic properties but also in industrial usage of these materials. Many researchers attempted to control the higher-ordered structure of polysilanes by various materialization techniques, such as elongation^{1, 2)}, rubbing⁵⁻⁹⁾, Langmuir-Blodgett technique⁵⁻⁹⁾, and vapor deposition¹⁰⁻¹²⁾.

Poly(dimethylsilylene) (PDMS) has the simplest chemical structure among polysilanes. Many computational studies of electronic structures and stable molecular conformation of PDMS were performed because of its simple chemical structure. However, it is insoluble and infusible, and then it has not been able to process for measurements of its properties and structure. Therefore, oriented specimen of PDMS has been desired.

Lovinger *et al.*¹³⁾ succeeded first in preparing PDMS samples in a form of oriented films. The oriented film was prepared by the following procedure.

They dissolved PDMS sample in boiling α -chloronaphthalene, and cast a film onto a fluorinated ethylene-propylene copolymer substrate. The oriented film of PDMS was prepared by uniaxial drawing of the cast film at *ca.* 200°C, after which the PDMS area was covered with a thick backing of

poly(acrylic acid) from an aqueous solution. After vacuum deposition of an ultrathin layer of amorphous carbon, the oriented film was removed with the poly(acrylic acid) from the substrate, followed by redissolution of the poly(acrylic acid) in water. They also prepared single crystals of PDMS, which was the first single crystal of polysilanes¹⁴⁾. They used these oriented samples for the structural study of PDMS by electron diffraction, and reported its skeletal conformation adopted the all-*trans* form at an ambient temperature. However, their samples were difficult to be handled manually and could not be used for other measurements. Other oriented specimen of PDMS has been needed, whose structure and properties can be measured with various methods.

The vacuum deposition of PDMS was carried out as another attempt to prepare films of the intractable Si-polymer¹⁰⁻¹²⁾. The deposited molecular chain was aligned perpendicular to the face of a fused silica substrate under an appropriate condition¹²⁾. However, the UV $\sigma - \sigma^*$ absorption of the vacuum deposited films was found to shift toward the shorter wavelength compared to that of the source polymer, suggesting that the chain scission took place during the process of vacuum deposition¹²⁾. The vacuum deposition induced also some chemical changes in the molecular chain¹²⁾.

We noted the friction deposition method. It is a newly developed orientation technique of polymer materials, and is well known by researchers in the field of polymer tribology¹⁵⁾. The friction transfer process is performed as follows. When a block of some polymer, such as poly(tetrafluoroethylene) (PTFE) or polyethylene (PE), is rubbed against a clean and flat face of a substrate, a highly oriented thin film is transferred onto the substrate. It is very interesting that a thin solid film can be

fabricated directly from a solid material without passing through any liquid phases. Recently, attention has been focused on the utility of the friction transferred films as proposed by Wittmann *et al.*¹⁶⁻¹⁹⁾ In addition, the surface of transferred PTFE film has an excellent ability of orienting other materials, such as liquid crystals, small organic compounds and polymers, when they were cast on it^{15, 18-23)}. Very recently, it was reported that soluble polysilanes were oriented on the friction transferred PTFE film²⁴⁾.

We attempted to orient intractable PDMS by applying the friction transfer technique.

This chapter is concerned with the investigation of conditions suitable for preparing highly oriented PDMS films. In particular, the effects of substrate temperature on the morphology and the molecular orientation of the resultant films are considered. The mechanism of the friction transfer of PDMS is also discussed in this chapter.

2-2. Experimental

2-2-1. Preparation of PDMS Oriented Films.

The powder sample of PDMS used for this study was obtained from Nippon Soda Co., Ltd. The powder was compressed into a disk at about 235 MPa under vacuum. As substrates optically flat quartz plates were used after dipping in *n*-hexane for washing the surfaces. Sliding the polymer disk on the smooth face of the substrate kept at a controlled temperature afforded an oriented film of PDMS on the surface, as shown in Figure 2-1. The pressure applied during the sliding was about 1 MPa. The friction transfer procedure was performed manually. (Afterward, an apparatus for the friction transfer has been designed and constructed, as seen in Chapter 5.)

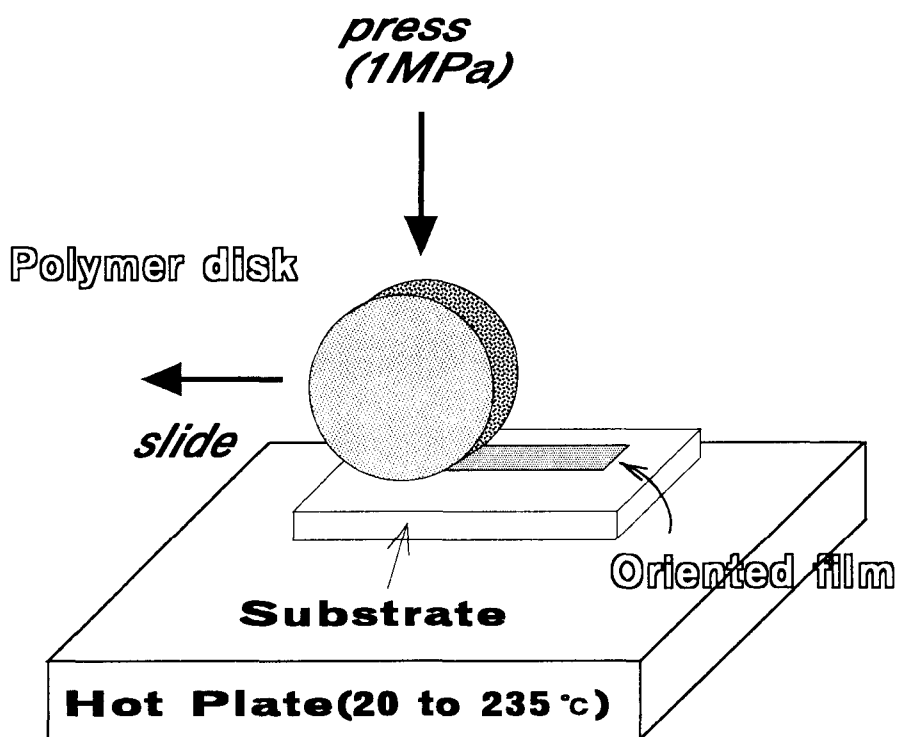


Figure 2-1. Schematic picture of friction transfer method.

2-2-2. Measurements

Differential scanning calorimetric (DSC) measurement of powder PDMS was carried out on a Perkin Elmer DSC7.

A Tencor Alpha-step 300 profiler was used for the characterization of surface roughness and the estimation of thickness of the films (the stylus method).

Transmission electron microscopic (TEM) observation was performed using a Zeiss CEM902. The specimen for TEM was covered with carbon for reinforcement, removed from the substrate onto a water surface, and scooped up onto an electron microscopic grid.

Ultraviolet (UV) spectra were measured using a Shimadzu MPS2000 spectrophotometer. The UV spectra of thin films deposited on the fused silica plates were obtained with a transmission mode. The fluorescecece spectroscopy was carried out with a JASCO FP-777 spectrophotometer, equipped with Glan-Thompson polarizing prisms for polarization measurements.

Infrared spectra of powder samples were measured with a Bio-rad FTS-60A/896 FT-IR spectrometer by KBr disk method.

2-3. Results and Discussion

2-3-1. Morphology of the Film

Through the friction transfer technique we could obtain oriented films of PDMS far easily compared with previously reported methods. The thin oriented films of PDMS on a quartz substrate could be obtained in the temperature range from 20 to 235°C. The over-all orientational state of transferred films was monitored with a polarized microscope. Under the

crossed Nicol condition, all areas of the film changed alternately between bright and dark for every 45° rotation. This was observed for all the films prepared. The temperature range was divided into four regions in terms of the uniformity of the resultant films. Around room temperature, the deposition occurred reproducibly. Significant ununiformity of the obtained films could be seen even by naked eyes. The polymer-free surface looked dark and the polymer film looked bright in the viewfield of polarized optical micrographs (Figures 2-2a). Below 150°C uniform deposition was rather difficult and the resultant film was very ununiform. It can be seen in Figure 2-2b that the polymer-free area is rather wide. At moderate temperatures, from 150°C to 210°C, the better films could be obtained than at lower temperatures. These films were found to be not so uniform by an optical microscope (Figures 2-2c, d). At higher temperatures, above 210°C uniform films of PDMS could be obtained (Figures 2-2e, f). The variation in uniformity of the transferred films seems to be related to the difference in the degree of orientation of the films, as will be mentioned latter.

The surface roughness and the thickness of the deposited films were checked by the stylus method. The film prepared at low temperature had many ridges and valleys. The height of the ridges was in the range from several tens of nm to a few hundreds nm. In contrast, such a roughness was not detected on the film prepared at high temperatures. Because the horizontal resolution of the stylus method is about 1 μm, the surface roughness of the film is considered to be smaller than 1 μm if any, we considered. The thickness of the deposited films was measured by infrared spectroscopy. The absorbance value of the 2949cm⁻¹ band measured for the films deposited on quartz plates was transformed to the

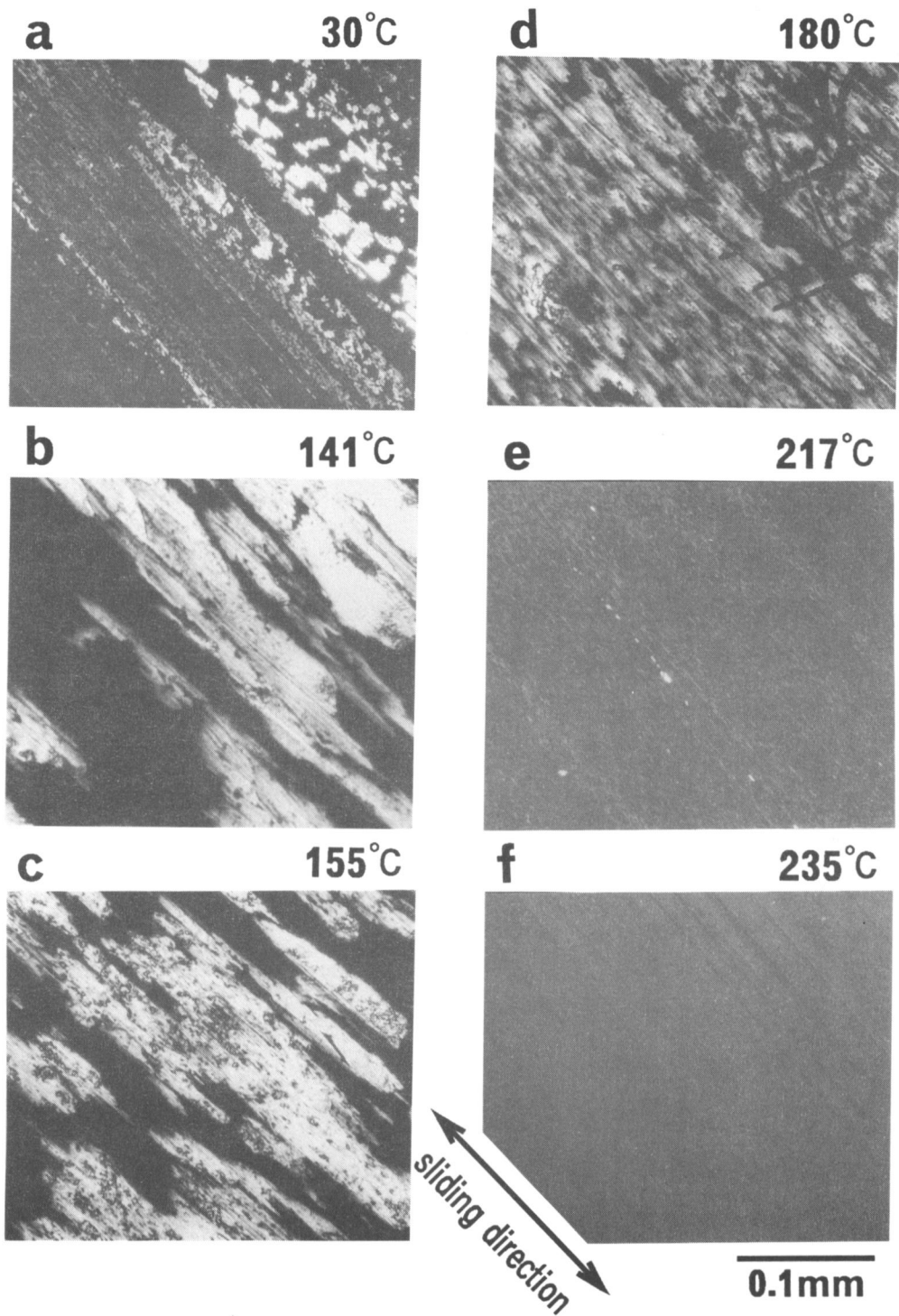


Figure 2-2. Polarized optical micrographs of PDMS thin films fraction transferred on quartz substrates at (a) 30°C, (b) 141°C, (c) 155°C, (d) 180°C, (e) 217°C, (f) 235°C. The arrow presents the slicing direction.

absolute scale on the reference to the absorbance of the standard sample prepared by the KBr disk method. (The orientational state of PDMS is considered to have a small influence on the absorbance of this band.) From the absolute values, the high temperature films were evaluated to be several nm thick.

Figure 2-3 shows a transmission electron micrograph of PDMS prepared at 205°C. The ridges (bright part) running in the sliding direction of the PDMS disk can be seen, whose widths range from several tens to 100nm. The dark part seems to be very thin layer of polymer.

2-3-2. UV Spectra

Tachibana *et al.*^{3, 4)} studied the anisotropy of the optical absorption of oriented poly(di-*n*-hexylsilylene), and concluded that the transition moment of the lowest singlet exciton associated with the $\sigma - \sigma^*$ band-gap lays along the *trans* planar Si-backbone chain. Therefore, we measured polarized ultraviolet absorption spectra of the oriented films on quartz substrates in order to evaluate the molecular orientation of the films. Polysilanes, including PDMS, have a UV absorption band at 300 to 350nm arising from the $\sigma - \sigma^*$ transition, and the polarized UV spectra have been used for evaluating the orientation degree of the samples^{1, 3-9, 12)}.

Figure 2-4 show the polarized UV spectra of the PDMS films, which were prepared on the substrates at various temperatures. Surprisingly, the PDMS films friction transferred at about 210°C on quartz substrates was found to be extremely oriented. In the UV spectra, a sharp and intense peak was observed at 345nm. This band is assigned to the exciton band with the $\sigma - \sigma^*$ transition. The film prepared at 217°C has a strong

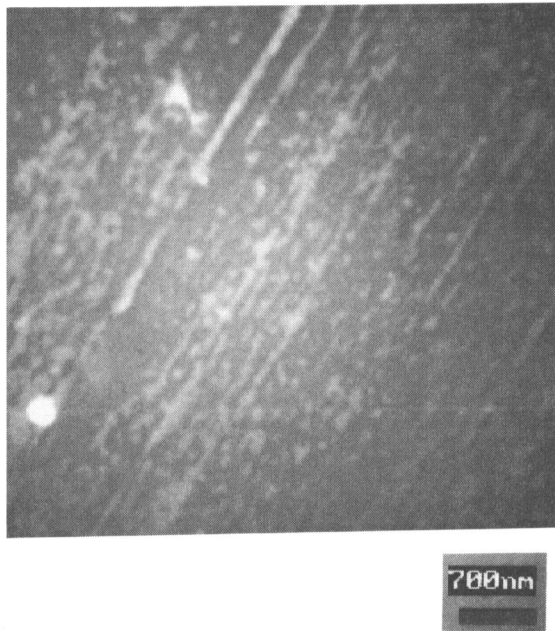


Figure 2–3. Transmission electron micrograph of a PDMS film deposited on quartz, prepared at 205°C .

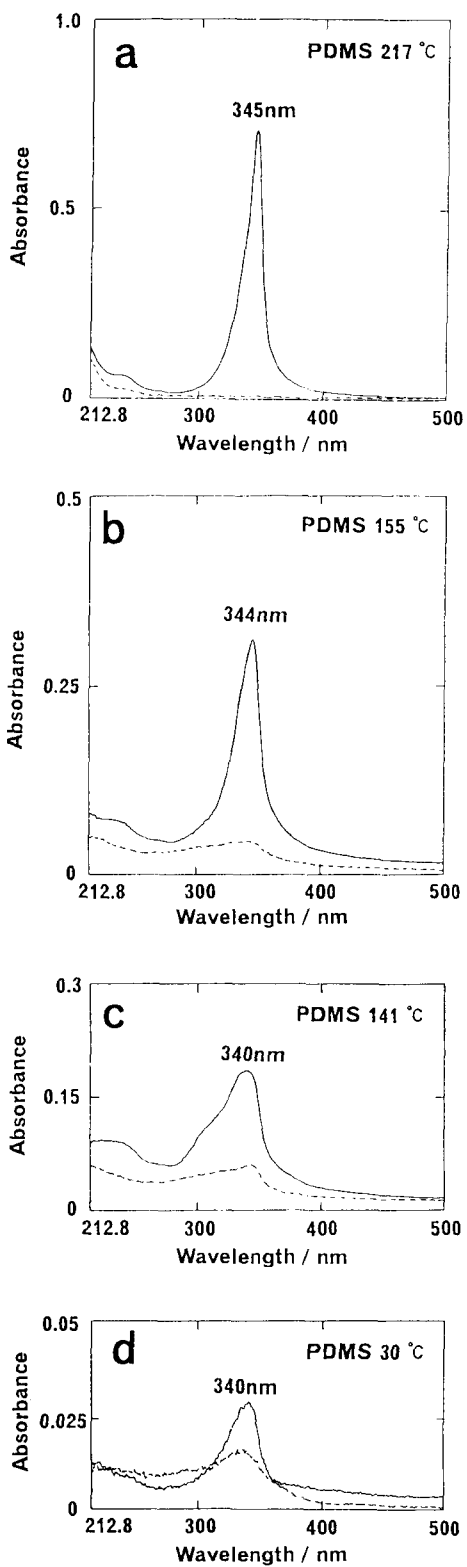


Figure 2-4. Polarized UV spectra of PDMS films on quartz substrates prepared at (a) 217°C, (b) 155°C, (c) 141°C, (d) 30°C. The spectra measured with the light parallel to the sliding direction (solid line) and perpendicular (broken line).

absorption for the electric vector of light polarized parallel to the sliding direction, but the absorption intensity is extremely low for the light polarized perpendicular to the sliding direction, resulting in the marked dichroism (Figure 2–4a). Therefore, the Si main chain is shown to be aligned in the sliding direction. Comparing these spectra, it is clear that the orientation state of the PDMS film was dependent on the substrate temperature during the friction transfer process.

The degree of orientation, F was calculated from the dichroic ratio of UV absorption, D by the following equation;

$$F = (1 - 1/D) / (1 + 2/D), \quad (2-1)$$

$$D = A_p / A_n, \quad (2-2)$$

where A_p and A_n are absorbance for the light polarized parallel and normal to the sliding direction, respectively. Assuming a uniaxial orientation, the F value is related to the second moment of orientation distribution function, $\langle \cos^2 \theta \rangle$:

$$F = \frac{3 \langle \cos^2 \theta \rangle - 1}{2}, \quad (2-3)$$

where the angle θ is defined to be spun between the transition moment of the absorption bond and the principal axis, namely the sliding direction. The F value varies from 1 (for the perfect orientation) to 0 (for the random). The degree of orientation F is plotted against the preparation temperature in Figure 2–5. It is seen that F scatters between 0 and 1 depending on the preparation temperature, but the orientation is almost perfect above 210°C. The degree of orientation increases with raising the preparation temperature except for neighborhood of room temperature.

In addition, the absorption maximum wavelength, which was related to the σ –conjugation length, varies in the range of 335–346nm with

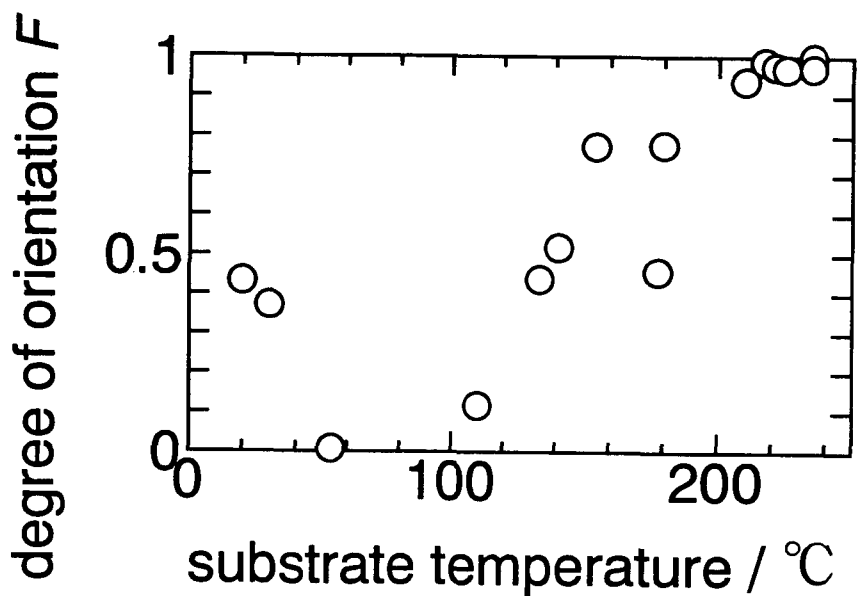


Figure 2-5. Preparation temperature variation of the degree of orientation from polarized UV spectra of PDMS friction transferred films.

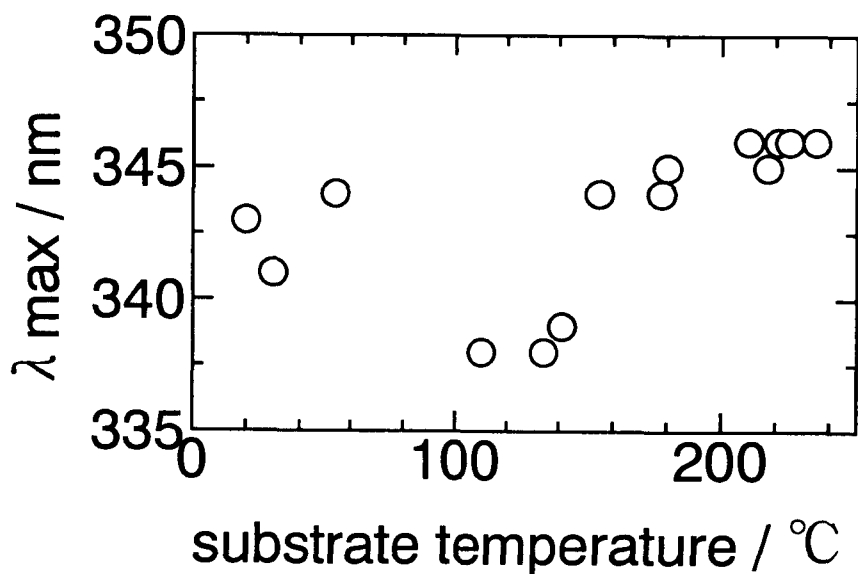


Figure 2-6. Preparation temperature dependence of the UV absorption maxima of PDMS friction transferred films.

substrate temperature as shown in Figure 2–6. It is known that UV absorption maximum shifts to longer wavelength when the σ –conjugation length is longer. The σ –conjugation character of the PDMS film is also depend on the preparation temperature. The absorption maximum is red–shifted with raising the preparation temperature except the neighborhood of room temperature. This change resembles to that of the orientation degree.

In the range of 50–120°C, it was difficult to prepare films. The deposition was not reproducible and the degree of orientation was low in this temperature range as seen in Figure 2–6. It took more time to deposit the film on the substrate in this temperature range compared to the other temperature ranges. Heat degradation readily occurred and caused a blue–shift of the UV absorption peak and a decrease in the orientation degree. The decomposition seemed to take place at a higher temperature range, also. However, because the exciton band had much larger absorption in the higher temperature range (Figure 2–7), the influence from the decomposition part, which had a shorter wavelength and a smaller dichroism, in UV spectra relatively decreased and could be ignored.

It can be also seen in Figure 2–5 and 6 that in the substrate temperature range of 150–210°C, the degree of orientation increases and the absorption maximum is red–shifted with raising a preparation temperature. At the same time, the spectrum becomes narrower.

In the highest temperature region (>210°C) the degree of orientation reached to nearly 1, *i. e.* an extremely highly oriented film was obtained. In the highest temperature region, the peak position was at the longest wavelength (345–346nm). The peak position corresponded to the σ – σ^* band–gap, which was related to the conformational order. The longer

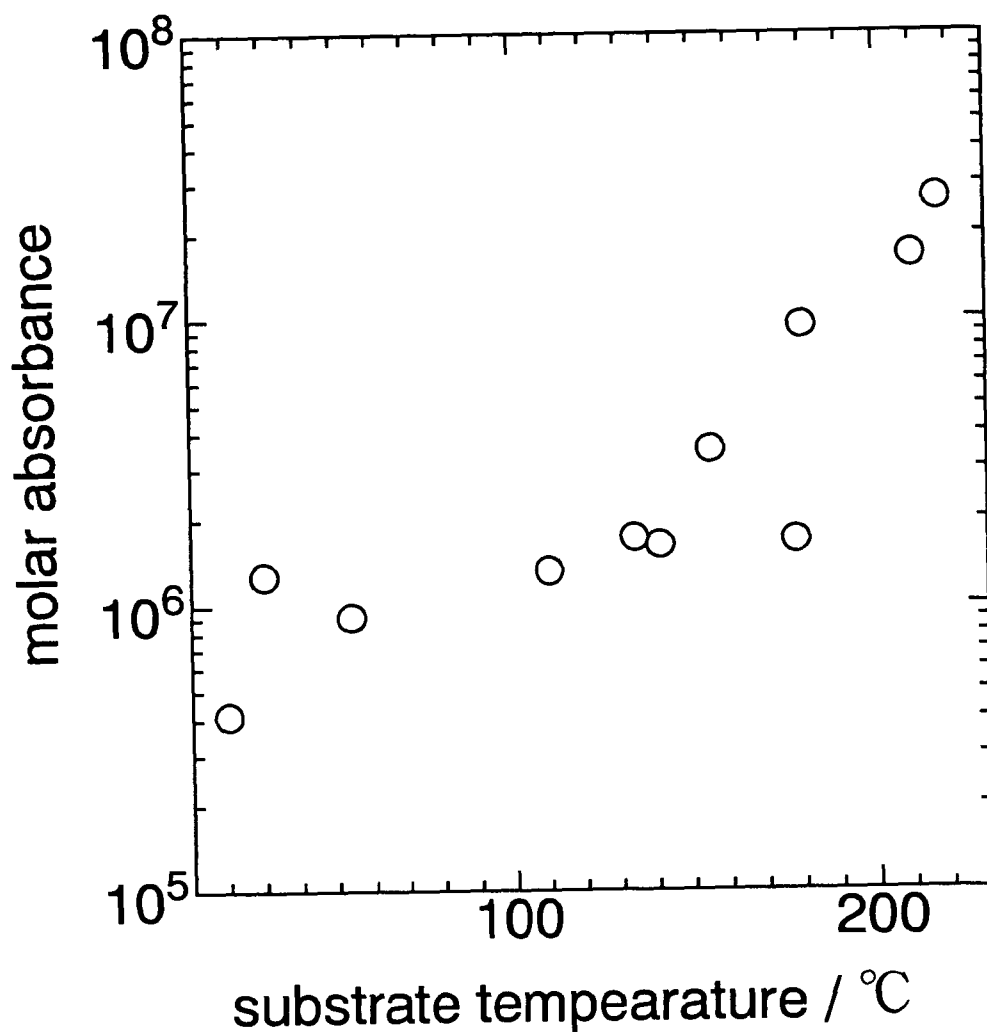


Figure 2-7. Preparation temperature dependence of the UV absorbance per Si atom of PDMS friction transferred film, which is normalized by the IR absorbance (2949cm^{-1}).

wavelength, *i. e.* the smaller band-gap suggested that the sequence of the all-*trans* conformation and the σ -conjugation system was longer.

The preparation temperatures, 150 and 210°C, at which the deposition behavior is changed, are near the phase transition temperature, 160 and 220°C, which is detected by the thermal analysis of the powder specimen. This will be mentioned later (in section 2-3-4).

Oriented film could be obtained on the substrate at room temperature, but the degree of orientation is relatively low. However, the degree of orientation is higher than those of the film transferred at the range of 50-150°C. This cannot be explained at present, but the deposition mechanism at room temperature appears to be different from that at other temperature ranges.

The peak width is considered to reflect the structural order. The calculation of a one-dimensional exciton model with lattice disorder revealed that the disorder caused the broadening of peak width of absorption²⁵⁾. In this case the one-dimensional lattice disorder means the conformational disordering. The peak narrowing suggests the ordering of the *trans*-planar chain. The film deposited at a high temperature has not only the highly ordered molecular alignment but also the highly ordered chain conformation.

Figure 2-7 shows the UV absorbance normalized by IR absorbance at 2949cm^{-1} plotted against the substrate temperature. (The orientational effect is considered to be small for the intensity of this IR band.) The IR absorbance is proportional to the amount of monomer units. Roughly speaking, the more highly oriented film seems to have much larger absorbance per Si unit. This peculiar phenomenon cannot be fully explained. It was reported for oligosilanes that the longer Si chain had the

larger absorbance per silicon unit, where the increase of UV absorbance was saturated when the number of silicon atoms exceeds $20^{26, 27}$. However, the experiment for the oligomers was performed in the solution state. It was considered that the saturation of absorbance was caused by the saturation of σ -conjugation length in solution. So the increase of absorbance in our experiment may be simply interpreted by the term of elongation of σ -conjugation for the condition with the fixed conformation. However, any theoretical consideration has not been proposed.

2-3-3. Fluorescence Spectra

Like the polarized UV absorption spectroscopy, the polarized fluorescence spectroscopy is known as a powerful method for evaluating the orientation of polysilane films²⁸. Therefore, we performed the fluorescence measurements using a geometry for the polarized fluorescence measurements shown in Figure 2-8. The incident excitation beam is 45° inclined from the film plane, and fluorescence is detected normal to the film plane. The polarization of the excitation beam is fixed perpendicular to the optical base. The principal axes of the sample films are labeled; the sliding direction (Z), the transverse direction (X), and the normal direction (Y). The intensity of fluorescence spectrum measured with a polarizer along the i -axis and an analyzer along the j -axis is denoted by I_{ij} ($i, j = X, Y, Z$). When the sliding direction is vertical to the optical base, the polarized fluorescence spectra, I_{ZZ} and I_{ZX} are measured. On the other hand, when the sliding direction is parallel to the optical base, the polarized spectra I_{XZ} and I_{XX} are obtained. Thus the four components of the polarized fluorescence spectra are measured by rotating the sample film and the polarization direction of the fluorescence beam.

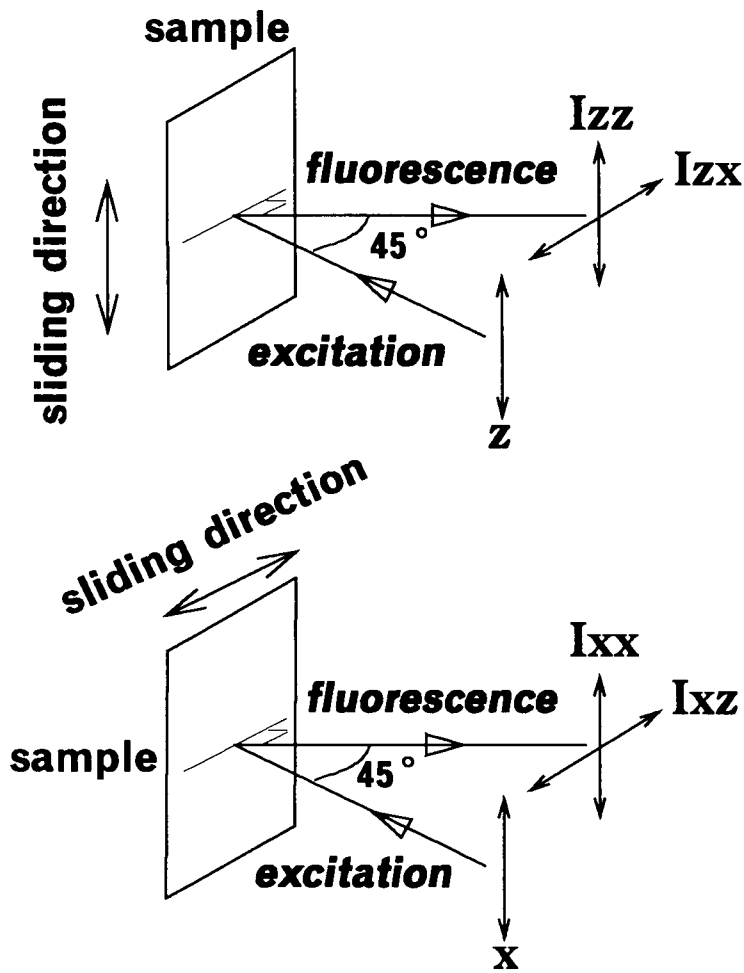


Figure 2-8. An optical system for polarized fluorescence measurements.

Figures 2–9 and 10 show the typical polarized fluorescence spectra and the excitation spectra, respectively, of the friction transferred PDMS film. The polarized component I_{zz} is much stronger than the other components. The polarized fluorescence spectra show that the molecular chains of PDMS is highly oriented to the sliding direction. If the transition moment angle of excited molecules is the same as that of the emitting molecules, the I_{xz} component coincides with the I_{zx} component. The observed fluorescence intensity I_{xz} was slightly higher than I_{zx} , suggesting that the transition moment of the emitting molecules was a little more highly oriented to the sliding direction than that of the excited molecules. It hints the existence of energy transfer. However, the present analysis regards that the I_{xz} and I_{zx} components are equivalent to each other, because their difference is small. The second and fourth moments of orientation distribution function are calculated from the four components of polarized fluorescence. The moments of orientation distribution are expressed as

$$\langle \cos^2 \theta \rangle = (I_{zz} + 2I_{zx}) / ((8/3)I_{xx} + 4I_{zx} + I_{zz}), \quad (2-4)$$

$$\langle \cos^4 \theta \rangle = I_{zz} / ((8/3)I_{xx} + 4I_{zx} + I_{zz}). \quad (2-5)$$

Here, the angle θ is spun between the direction of transition moments and the Z-axis (Figure 2–11). The values of $\langle \cos^2 \theta \rangle$ and $\langle \cos^4 \theta \rangle$ are plotted in Figure 2–12 against the preparation temperature. Both $\langle \cos^2 \theta \rangle$ and $\langle \cos^4 \theta \rangle$ increase with increasing substrate temperature.

The value of $\langle \cos^2 \theta \rangle$ for the film prepared above 210°C is almost 1, suggesting that extremely highly oriented film can be prepared at the temperature range. Furthermore, $\langle \cos^4 \theta \rangle$ of the PDMS film prepared at same temperature range is also near 1, suggesting that the film has a very narrow distribution of molecular chain orientation.

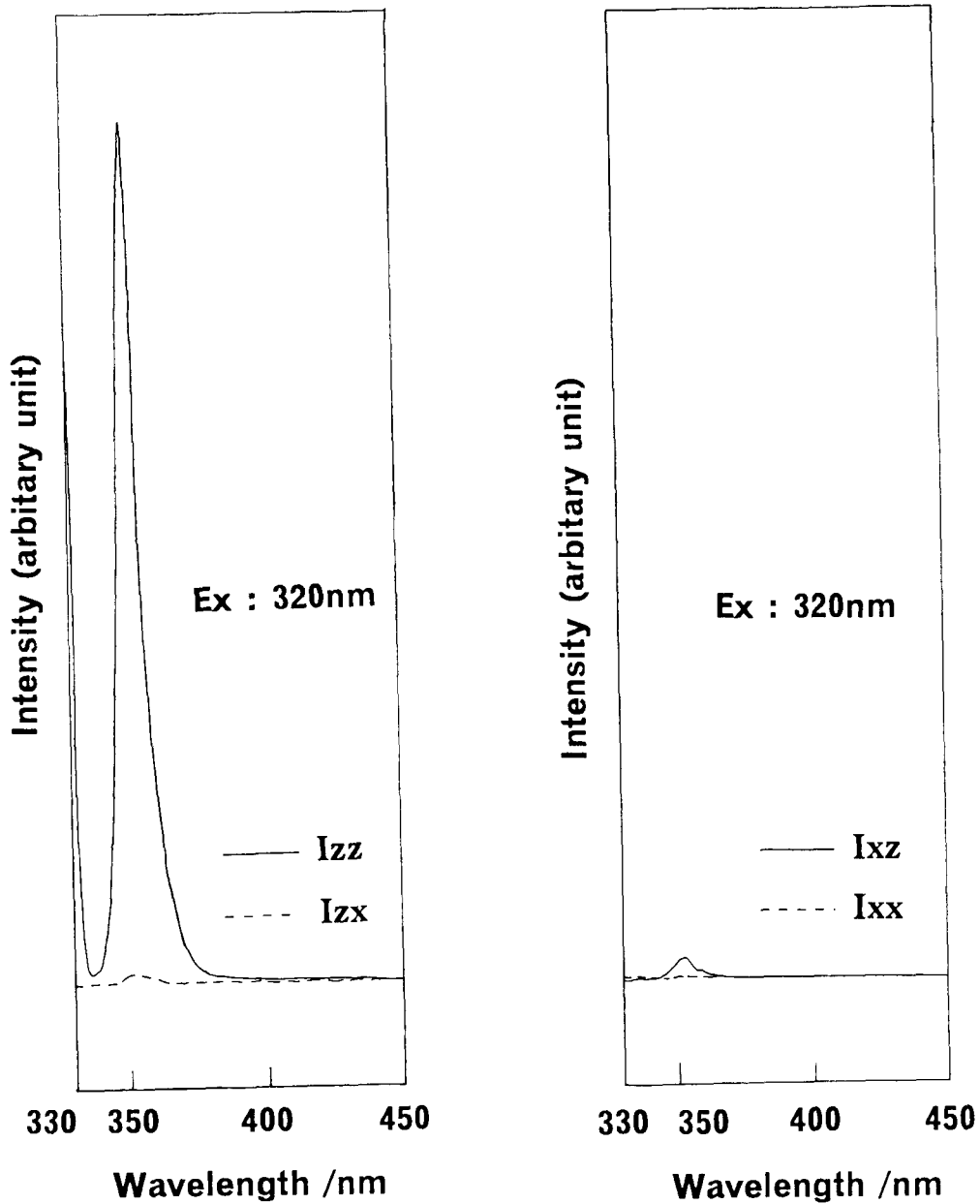


Figure 2-9. Polarized fluorescent emission spectra of a friction transferred PDMS on quartz, prepared at 235°C with excitation at 320nm.

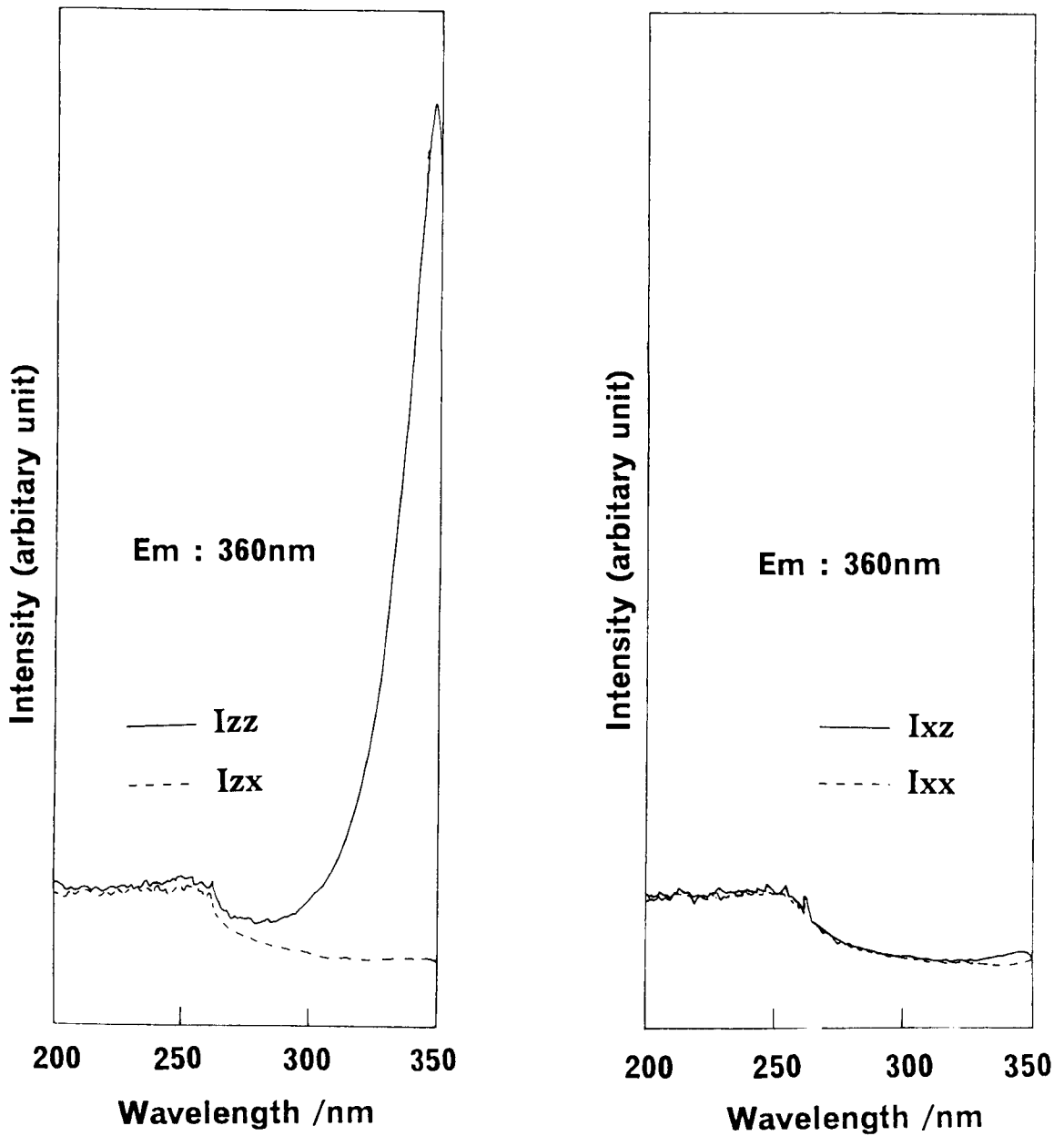


Figure 2-10. Polarized fluorescent excitation spectra measured at 360nm emission from a friction transferred PDMS on quartz, prepared at 235°C.

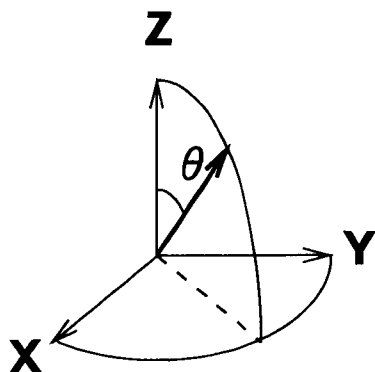


Figure 2-11. The coordinate system of the orientation measurements. Thick arrow is the direction of the transition moment.

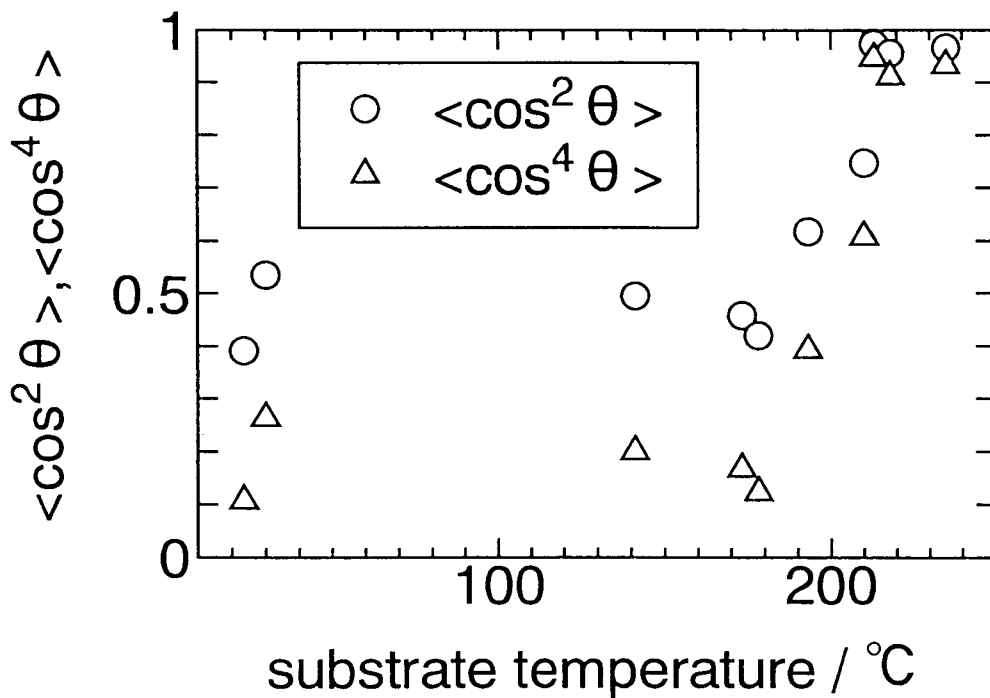


Figure 2-12. The second(circles) and fourth(triangles) moments of orientation distribution calculated from polarized fluorescence spectra. It is plotted against the preparation temperature of substrates.

2-3-4. Mechanism of Friction Transfer

The method preparing highly oriented films of polymers is useful for the structural investigation and some applications of polymers. With the friction transfer technique, we are able to prepare polymer films with extremely high orientation by selecting suitable conditions. However, application of this method is limited to some specific polymers. Motamedi *et al.*¹⁹⁾ investigated a lot of polymers as candidates for the formation of oriented films by friction transfer, and only a few polymers were found to give the oriented films. They are poly(tetrafluoroethylene) (PTFE), polyethylene (PE), an aromatic liquid crystalline copolyester of *p*-hydroxybenzoic acid and 2-hydroxy-6-naphthoic acid (Vectra®), and a perfluorinated copolymer of ethylene and propylene. We succeeded to prepare the highly oriented PDMS films. As a next step, we attempted to prepare the oriented films of the other polysilanes by friction transfer (in chapter 4). All the polysilanes examined afforded the highly oriented layers, but could not yield uniform films with except for PDMS and poly(diethylsilylene). Moreover, we could obtain the oriented ununiform films of poly(*p*-phenylene) by the method (chapter 7). What is the difference between the polymer group giving the highly oriented and uniform film and that not giving?

The significant preparation temperature dependence of the structure and properties of friction transferred PDMS films seems to be caused by the occurrence of the solid state phase transition. The DSC thermogram of PDMS powder exhibits two endothermic peaks at about 160 and 220°C (Figure 2-13). These transition temperatures are close to the preparation temperature at which the properties of the transferred film changes.

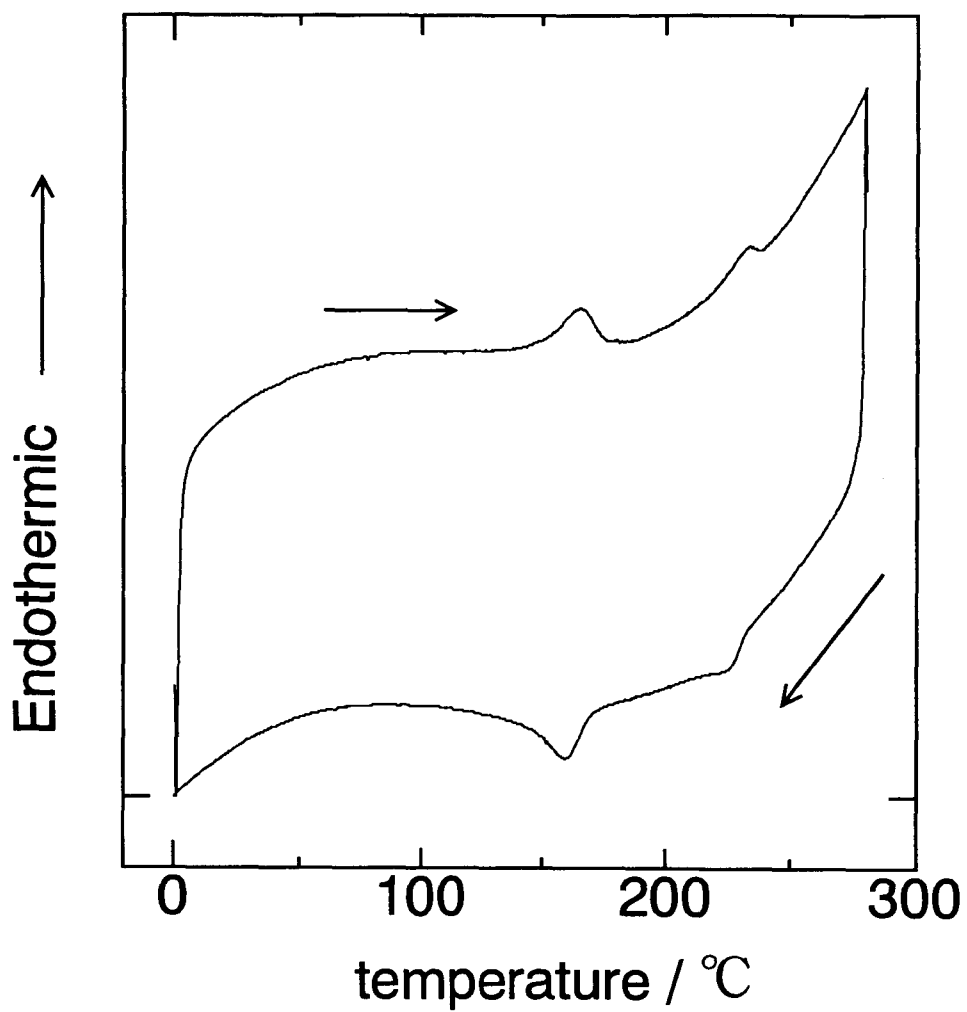


Figure 2-13. A DSC thermogram of PDMS powder sample.

Below 150°C the friction transfer of PDMS is not reproducible, and above the temperature the transferred film is easily obtained. For bulk sample spectral changes were observed a little below the transition temperature, 160°C (see in Chapter 3, section 3-3-4). Some part of PDMS may change to the phase II at 150°C. It seems that the friction transfer of PDMS requires the high temperature phases. Moreover, it is noteworthy that the almost perfectly oriented and very uniform film was obtained on the substrate kept over 210°C, which is a little lower than the second transition temperature (220°C). In the friction transfer process, parts of the polymer contacting the substrate may locally go across the transition temperature. Lovinger *et al.* proposed that PDMS undergoes a primary transition from a pseudo-orthorhombic packing of all-*trans* molecular chains (phase I) to a metrically hexagonal packing (phase II) above 160°C, while the all-*trans* conformation is preserved. The second transition at 220°C includes the disordering of the chain conformation along with the lattice transition to the hexagonal packing (phase III)^{13, 29}, which is a mesophase, a liquid crystal like solid phase. It is considered that the PDMS molecule may be more mobile in the high temperature phases with hexagonal packing than in the low temperature phase with pseudo-orthorhombic packing. The mobile solid phase seems to be related to the mechanism of friction transferring the oriented film. For the case of PTFE and PE, mobile phases similarly exist in the high-temperature and/or the high-pressure condition. The PTFE crystallite was disordered in the high-temperature phase. The PE high-pressure phase (so called as rotator phase) is a very disordered phase. The polymer chains in these phases are considered to be mobile because of a decrease in the inter chain forces. In addition, the extended

chain single crystals of polymers are known to be crystallized from such hexagonal phases³⁰⁾. The molecular chain mobility in the longitudinal direction causes it. It may be possible that the plastic character of the disordered and mobile solid phase plays an important role in the friction transfer phenomenon in a general case, containing PDMS.

2- 4. Conclusion

PDMS could afford a highly oriented film on a smooth substrate by friction transfer method. Especially, an extremely oriented, uniform and ultrathin film was prepared above 210°C. The molecular chain was found to be aligned in the sliding direction. The technique is much more convenient and gives more highly oriented films than the previous methods. The highly oriented ultrathin film will be useful for the scientific investigation of structure and properties and the industrial application in the field of electronics and photonics.

The highly oriented PDMS film prepared at high temperature also had a high conformational order. The highly oriented thin film had a larger absorbance of exciton band per Si unit than the poorly oriented films.

The preparation temperature dependence of the properties of the friction transferred films suggests that the transfer of films may take place via the mobile phase (high temperature phases, phase II and III).

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Chapter 3

Structure of the Oriented Thin Film of Poly(dimethylsilylene)

3-1. Introduction

The electronic properties of polysilanes are considered to be caused by the delocalized σ -electrons in the Si-Si backbone, so called " σ -conjugation". The σ -conjugation character is known to be affected by the conformation of the main chain¹⁾. Many studies have been carried out about the solid state structure of polysilanes having various side chains. Especially, symmetrically dialkyl substituted polysilanes were investigated intensively. It is known that the side chain largely affects the structure in not only molecular packing but also conformation of the main chain.

Poly(dimethylsilylene) (PDMS) is the second earliest synthesized polysilane²⁾ and has the shortest side chains, methyl groups. It is very important to study structure and properties of PDMS in order to understand the nature of the catenated Si chain in polysilanes because it is least influenced by the effects of the substituents. Many theoretical and computational studies on the electronic structure and the conformation of PDMS were carried out because of its simple chemical structure. This material is produced industrially for the precursor of silicon carbide by Yajima's method³⁾. However, its insolubility has prevented its detailed investigation of structure, properties and other applications. Wesson and Williams investigated various properties of PDMS 30 years later from the first synthesis⁴⁾. It cost moreover 10 years that a film and an oriented specimen were prepared first by Lovinger *et al.*⁵⁾. They performed structural study of PDMS by use of the oriented film and a single crystal⁶⁾.

The conformation of PDMS adopts all-*trans* form at an ambient temperature. The crystal lattice was reported to be a monoclinic unit cell with the dimensions, $a=1.218\text{nm}$, $b=0.800\text{nm}$, $c=0.388$ and $\gamma=91^\circ$. The polymer undergoes two phase transitions at *ca.* 160 and 220°C. At the first transition, the molecular packing was proposed to change from a pseudo-orthorhombic lattice (phase I) to a metrical hexagonal one (phase II) but the all-*trans* chain conformation is preserved. The second transition includes disordering of the chain conformation, and the lattice changes to a hexagonal lattice (phase III). However, the chain packing in the phase I has not been finally determined yet. The crystal energy was calculated by Patnaik and Farmer⁷⁾. They presented several models for the three solid phases. Furukawa *et al.*⁸⁾ proposed a crystal structure model of phase I having a monoclinic unit cell, which was different from Lovingers' one and had a single chain in it, on the basis of the powder X-ray diffraction data. Leites *et al.*⁹⁾ investigated the molecular structure of PDMS by vibrational and electronic spectroscopies. Recently, as model compounds of PDMS, several oligomeric permethylsilanes were synthesized, whose structure and properties were investigated in details¹⁰⁾.

The preceding chapter dealt with the new method of preparing the highly oriented thin film of PDMS, that is the friction transfer technique. In this chapter, the structure of the friction transferred PDMS was characterized by spectroscopic and diffraction methods. We discuss whether friction transferred films differ in the condensed state and the molecular structure from bulk samples. The phase transition behavior of PDMS in the ultrathin film and bulk sample is also discussed.

3-2. Experimental

3-2-1. Preparation of PDMS Oriented Films.

The friction transferred PDMS film was prepared according to the method described in the previous chapter. A glass slide, a fused silica (quartz) plate, a silicon wafer (Si(111)), and an aluminum plate were used as the substrates. A polycrystalline disk, an optical flat single crystal and a freshly cleaved single crystal of potassium bromide (KBr) were also used.

3-2-2. Electron Diffraction

Electron diffraction (ED) measurements were performed with a JEOL JEX2000FX II with an acceleration voltage of 100kV. The specimen for ED was covered with carbon for reinforcement, separated from the KBr substrate on a water surface and scooped up onto an electron microscopic grid.

3-2-3. X-ray Diffraction

CuK α radiation monochromatized by a pyrolyzed graphite was used (Rigaku RU300, 40KV and 200mA) for X-ray diffraction measurements. The diffraction profiles were recorded by the reflection mode of $\theta - 2\theta$ scan (RAD-C system).

3-2-4. Infrared Spectroscopy

Infrared spectra were measured with a Perkin-Elmer 1800 FT-IR spectrometer and a Bio-rad FTS-60A/896 FT-IR spectrometer equipped with a wire-grid polarizer. The transmission spectra were measured by using the fused silica, the KBr crystal or the silicon wafer as substrates. The IR reflection-absorption spectrum (RAS) was measured on thin films

deposited on the flat surface of aluminum plate. Spectra at variable temperature were recorded by an IR-microscope Bio-rad UMA-500 with a Mettler hot-stage FP900.

3-2-5. Ultraviolet Spectroscopy

The ultraviolet (UV) spectra were measured with a Shimadzu MPS2000 spectrophotometer equipped with Glan-Thompson polarizing prisms. The UV spectra of thin film deposited on the fused silica plates were obtained with a transmission mode. The UV spectra as a function of temperature were recorded by using a heating cell.

3-3. Results and Discussion

3-3-1. Electron Diffraction and X-ray Diffraction

An electron diffraction (ED) pattern of a friction transferred film of PDMS (prepared at 213°C) is shown in Figure 3-1. It shows a single-crystal like pattern. The orientation and the crystallinity are comparable to those of the friction transferred PTFE^{1,1)} and the gel-drawn fiber of high-molecular-weight polyethylene^{1,2)}. The ED pattern of the friction transferred film shows that the film has much higher orientation than that prepared by Lovinger *et al.*⁵⁾ The reflections could be indexed by the pseudo-orthorhombic unit cell reported by Lovinger *et al.*⁵⁾ The meridional reflections can be indexed as 002 and 004 reflections, respectively. The fiber period calculated from the 002 and 004 reflections and the layer line position is 0.39nm, suggesting that the PDMS molecule in the friction transferred film assumes the all-*trans* conformation as the case of the stretched PDMS thin film⁵⁾, which was believed to be uniaxially oriented.

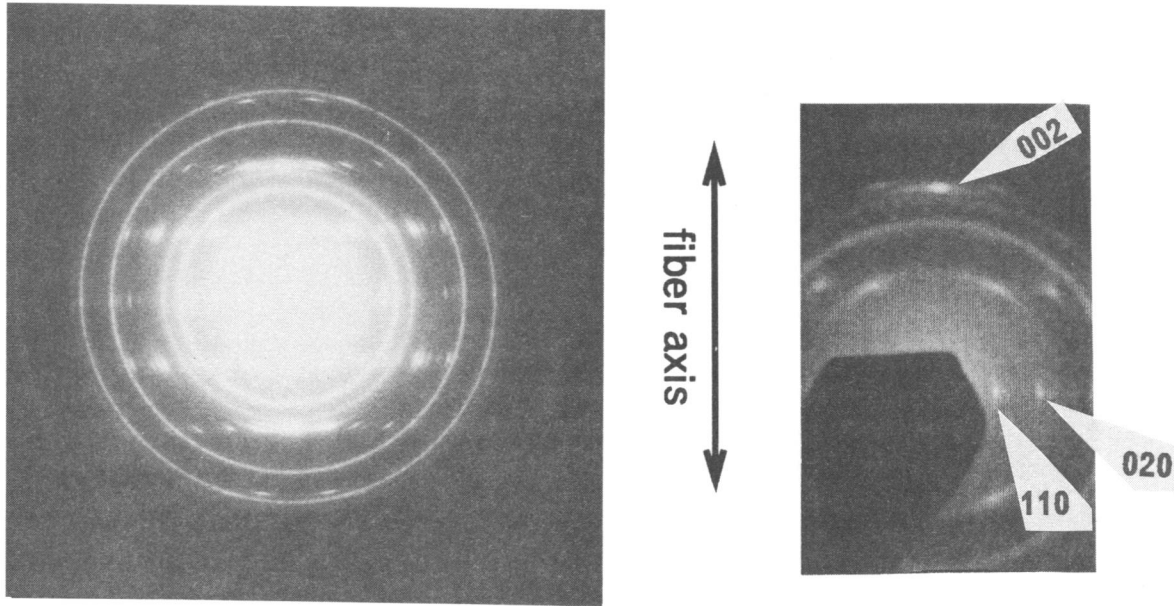


Figure 3–1. An electron diffraction pattern of PDMS friction transferred at 213°C. The small picture shows the central part of the large one, which cannot be seen in the large one. Some ring patterns in the pictures came from gold, which was used for the calibration of the camera length.

In the electron diffraction of the friction transferred film, the 200 reflection is too weak to be detectable (Figure 3-1), although the reflection was relatively strong in the previously reported pattern of the stretched film sample⁵⁾. Moreover, Figure 3-1 also shows a strong 020 reflection, which is weaker than the 200 reflection in the ED pattern of a uniaxially oriented sample. The difference between the ED patterns of the uniaxially oriented film and ultrathin film in this study suggests that the PDMS crystallite in ultrathin film sample may not be uniaxially oriented but doubly oriented. The detailed discussion about the double orientation will be offered in section 3-3-3.

An X-ray diffraction pattern (reflection mode) of the friction transferred PDMS on glass is compared with the powder pattern of as-received PDMS in Figure 3-2. The two reflections observed at $2\theta = 13^\circ$ and 14° can be indexed as the $110+\overline{110}$ and 200 reflections by using Lovingers' lattice parameters, respectively. The diffraction angles of the $110+\overline{110}$ and 200 reflections are similar to the powder pattern. The other diffraction seen in the powder pattern could not be observed, which are weaker than the two reflections, because the film was very thin. In the powder diffraction pattern, the $110+\overline{110}$ reflection is the strongest. However, the $110+\overline{110}$ reflection is weaker than the 200 reflection in the diffraction pattern of the transferred film. This also supports the possibility that the PDMS crystallite in the deposited film may have some orientation toward the substrate surface.

3-3-2. Infrared Spectra

Fused silica, a KBr and an Si wafer (111) were employed as the substrates for the IR transmission measurements. No difference was

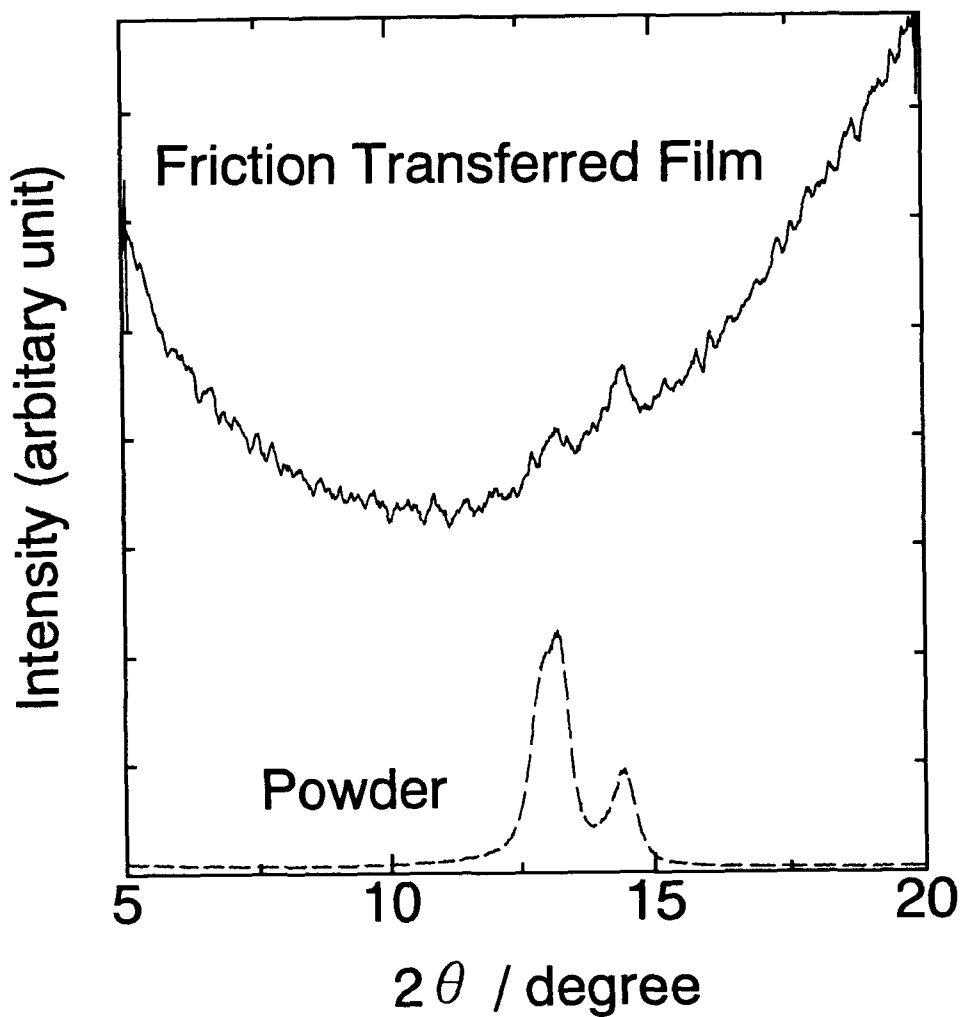


Figure 3-2. X-ray diffraction patterns of PDMS measured on reflection mode; solid line represents that of the friction transferred film on glass at 235°C , and dotted line represents that of the powder sample.

found among the spectra of thin films on three substrates. It was found that the preparation temperature affected only the degree of orientation, but did not affect frequencies of all vibrational bands. The frequencies and the assignment of the IR bands measured on the thin film samples on various substrates at room temperature are listed in Table 3-1 along with the frequencies measured on a powder sample (KBr disk) at three temperatures. The assignment of the IR band has been made referring to the previous study by Leites *et al.*⁹⁾ The frequency shifts with temperature seen for a few bands of the powder are due to the two phase transitions located at 160 and 220°C, respectively (see section 3-3-4). The wavenumbers of all band were observed closely to those of powder specimen at room temperature. Therefore, the friction transferred film of PDMS was reconfirmed to be in phase I, the lowest temperature phase, at room temperature.

Figure 3-3 is the polarized IR spectra of the PDMS film on an optically flat KBr single crystal. This is the first success in getting the highly polarized IR spectra of PDMS film.

Leites *et al.*⁹⁾ made the normal mode analysis for the skeletal chain of PDMS without hydrogen atoms. We checked the assignments of the IR bands in terms of the dichroism of the spectra and the factor analysis of the whole molecule. The skeletal conformation of PDMS is *trans*-planar. Assuming that methyl groups have rotational symmetry along the Si-C bond axis, or that they are at staggered conformation, the whole PDMS molecule is also isomorphous with the point group D_{2h} . The result of the factor group analysis of a PDMS molecule is listed in Table 3-2. The coordinate in the PDMS molecule is shown in Figure 3-4. The normal modes of the PDMS molecule are classified into 8 symmetry species:

Table 3– 1. Frequencies and Assignments of IR bands of PDMS

at 25°C	frequency / cm ⁻¹					assignment
	powder		KBr	film		
	180°C	250°C		Si	quartz	
2949	2949	2949	2950	2950	2953	C– H stretching(as)
2894	2893	2892	2895	2895	2891	C– H stretching(s)
1413	1410	–	1418	–	–	CH ₃ deformation(as)
1401	1403	1402	1399	–	–	CH ₃ deformation(as)
1247	1246	1246	1248	1247	–	CH ₃ deformation(s)
832	833	833	832	833	–	CH ₃ rocking
743	748	751	743	743	–	CH ₃ rocking
731	730	–	731	732	–	CH ₃ rocking
690	690	689	690	–	–	Si– C stretching
629	627	–	630	632	–	Si– C stretching

s : symmetric as : asymmetric

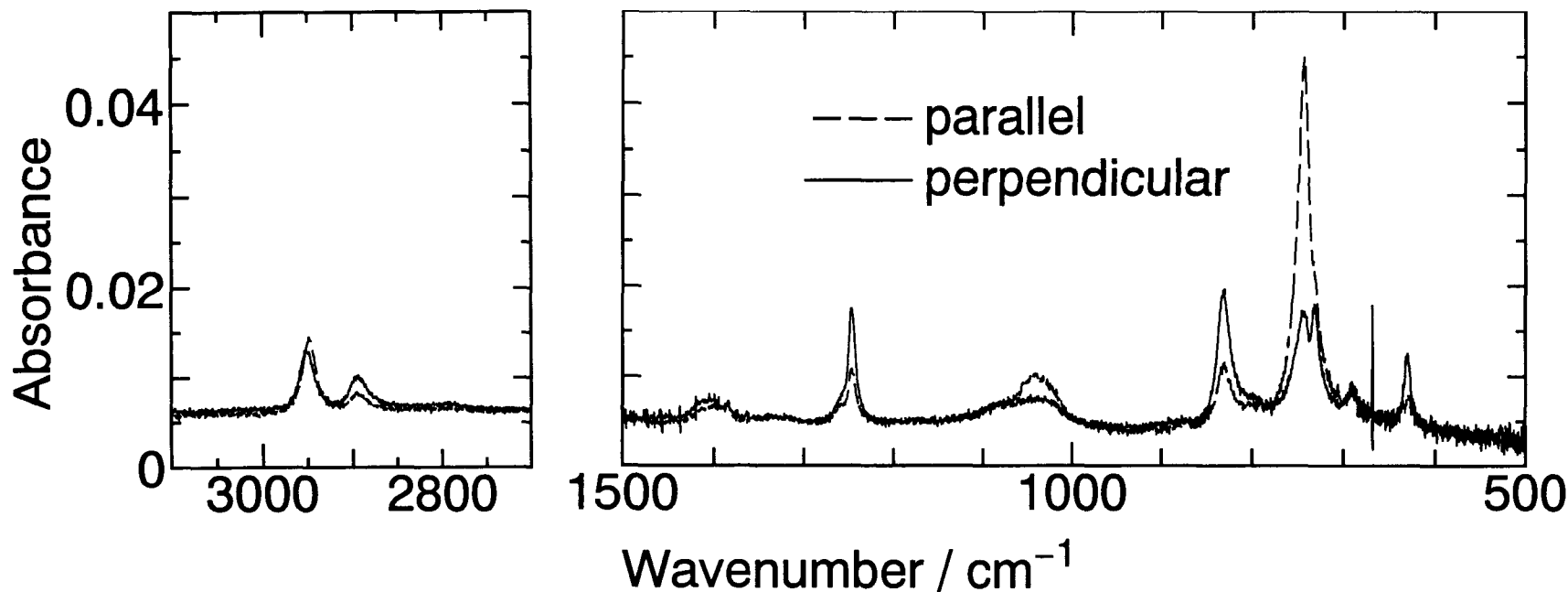


Figure 3-3. The polarized IR spectra of PDMS film on the KBr crystal substrate deposited at 215°C measured with the electric vector of incident IR perpendicular to the sliding direction (solid line); parallel (broken line). The broad band at about 1050cm⁻¹ arises from the Si-O bond which originated from the thermal decomposition.

Table 3-2. Factor group analysis of PDMS molecule

<i>D</i> 2 <i>h</i>	E	C2(x)	C2(y)	C2s(z)	i	σ g(yz)	σ (zx)	σ (xy)	n	IR	Raman
A1g	1	1	1	1	1	1	1	1	8	inactive	active
B1g	1	1	-1	-1	1	1	-1	-1	5	inactive	active
B2g	1	-1	1	-1	1	-1	1	-1	6	inactive	active
B3g	1	-1	-1	1	1	-1	-1	1	7	inactive	active
Au	1	1	1	1	-1	-1	-1	-1	5	inactive	inactive
B1u	1	1	-1	-1	-1	-1	1	1	7	active(\perp)	inactive
B2u	1	-1	1	-1	-1	1	-1	1	7	active(\perp)	inactive
B3u	1	-1	-1	1	-1	1	1	-1	5	active(\parallel)	inactive
N	18	2	0	0	0	0	2	10			
(+1+2cos ϕ)	3	-1	-1	-1	-3	1	1	1			
χ(R)	54	-2	0	0	0	0	2	10			

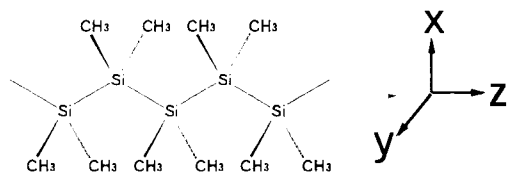


Figure 3-4. The coordinate in a PDMS molecular for the factor analysis

$$\Gamma = 8A_g + 5A_u + 7B_{1u} + 5B_{1g} + 7B_{2u} + 6B_{2g} + 5B_{3u} + 7B_{3g}.$$

All the "*gerade*" species are active only in the Raman spectrum, and the "*ungerade*" species are IR active except the A_u which is inactive both in IR and Raman. The band assignments of the vibrational spectra of PDMS are summarized in Table 3-3, based on the factor group analysis.

The bands in the region around 2900cm^{-1} are attributable to C-H stretching vibrations of the methyl group. The band at 2894cm^{-1} is assigned to the C-H symmetric stretching vibration and is polarized perpendicularly to the sliding direction. The C-H asymmetric stretching vibration was found to split into two bands, at 2951cm^{-1} and 2948cm^{-1} . The former shows parallel polarization, while the latter shows perpendicular one (Figure 3-3).

It is considered that the IR-active three CH_3 rocking modes have different directions of transition moment (each belongs to the B_{1u} , B_{2u} , and B_{3u} species, respectively). One component has the polarization parallel to the chain direction, and the rest two have the perpendicular polarization. The very strong IR band at 743cm^{-1} was assigned to the CH_3 rocking with parallel polarization (B_{3u}). The intense band at 832cm^{-1} is attributed to the perpendicular components. The band at 731cm^{-1} has not been assigned yet. This band has perpendicular polarization, and may be assigned to the CH_3 rocking vibration. It is seen in Table 3-1 that the parallel band of CH_3 rocking at 743cm^{-1} is very sensitive to the temperature change. Indeed the frequency of this band was largely sifted to the higher frequency side with an increase in temperature. The frequency 743cm^{-1} at 25°C suggests that the thin film PDMS is in phase I at room temperature.

The Si-C stretching band is very important for the investigation of

Table 3–3. Assignments of IR Bands of PDMS

frequency / cm^{-1}	species(polarization)	assignments
2952	$B_{1u} + B_{2u}(\perp)$	C–H stretching(as)
2948	$B_{3u}(\parallel)$	C–H stretching(as)
2895	$B_{1u} + B_{2u}(\perp)$	C–H stretching(s)
1418	B_{1u} or B_{2u} or $B_{3u}(\?)$	CH_3 deformation(as)
1399	B_{1u} or B_{2u} or $B_{3u}(\?)$	CH_3 deformation(as)
1248	$B_{1u} + B_{2u}(\perp)$	CH_3 deformation(s)
832	B_{1u} or $B_{2u}(\perp)$	CH_3 rocking
743	$B_{3u}(\parallel)$	CH_3 rocking
731	B_{1u} or $B_{2u}(\perp)$	CH_3 rocking
690	$B_{2u}(\perp)$	Si–C stretching(as)
630	$B_{1u}(\perp)$	Si–C stretching(s)
–	$B_{1u}(\perp)$	C–Si–C deformation
–	$B_{3u}(\parallel)$	C–Si–C wagging
–	$B_{2u}(\perp)$	C–Si–C rocking

s : symmetric as : asymmetric

the molecular orientation of polysilanes. The two bands at 690cm^{-1} and 630cm^{-1} have been assigned to the Si-C stretching. The former may be antisymmetric (B_{2u}) and another symmetric (B_{1u}). Both of them have the same polarization perpendicular to the sliding direction, *i. e.* the chain direction.

The IR-RA spectra of the friction transferred PDMS film were measured in order to investigate the molecular orientation relative to the substrate surface. In the IR-RAS, the band with the transition moment perpendicular to the surface is enhanced. Figure 3-5 shows the IR-RAS of the PDMS on the aluminum substrate. It was found that all absorption peaks are very sharp and intenser than the transmission spectra. The CH_3 deformation band at 1247cm^{-1} , the CH_3 rocking bands at 832 and 731cm^{-1} and the Si-C stretching bands at 690 and 630cm^{-1} could be observed strongly. They are also seen clearly in the transmission spectra with the polarization perpendicular to the sliding direction (see Figure 3-3). The RAS and the transmission spectrum measured with the perpendicularly polarized light have essentially the same polarization character. However, all bands with parallel polarization to the chain direction are much weaker in the RA spectra than in the transmission spectra with perpendicular polarization. This suggests that the deviation of the chain orientation from the sliding direction is larger in the film plane than out of it.

3-3-3. Structure of PDMS in the Friction Transferred Film

The polarized UV spectra, the polarized fluorescence spectra (in former chapter combined together), the electron diffraction, and the polarized IR spectra suggested that the molecular chains in the friction

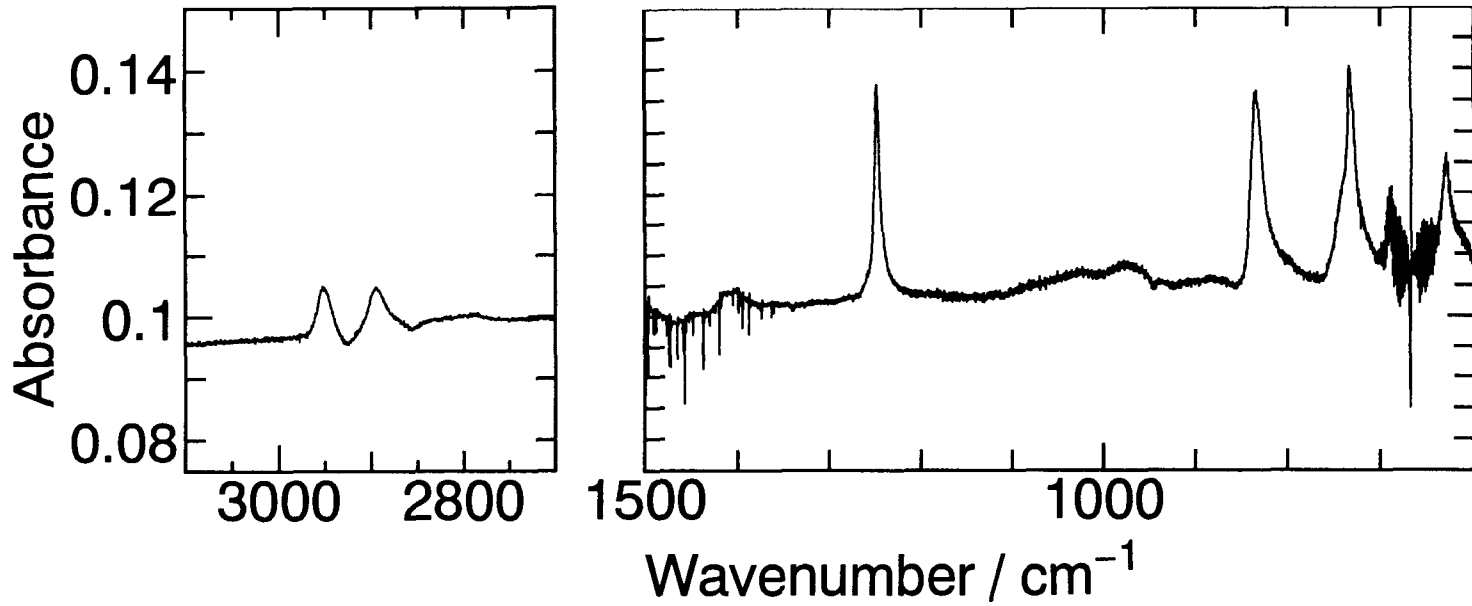


Figure 3-5. IR-RA spectrum of PDMS friction transferred on Al substrate at 235°C.

transferred PDMS film are aligned in the sliding direction. This is in agreement with the previous observation that friction transferred molecular chains are also aligned in the sliding direction for PTFE, polyethylene and so on^{1,3)}.

The electron diffraction pattern revealed the chain conformation of PDMS is all-*trans*. The absorption at about 345nm caused by the $\sigma - \sigma^*$ transition is explained by the all-*trans* conformation, and the fluorescence at 355nm confirmed it.

The X-ray and the electron diffraction patterns of the friction transferred film coincided with those of the powder specimen^{4, 8)} and the uniaxially stretched film⁵⁾ observed at room temperature. The IR spectra of the friction transferred film were essentially similar to that of the powder specimen measured at a room temperature. Therefore, the crystal structure of the friction transferred PDMS is similar to that of the bulk samples. The friction transferred film of PDMS is formed from the mobile phase, phase II and III (chapter 2) and recrystallization process to phase I is considered to follow it.

The crystal structure of PDMS has not been clearly determined. Furukawa *et al.*⁸⁾ proposed a crystal structure of PDMS with the monoclinic packing on the basis of the X-ray diffraction of the powder specimen. Patnaik and Farmer⁷⁾ investigated the crystal structure of PDMS by energy calculations and proposed two models for phase I and models for two high temperature phases. For phase I, one is the model with the orthorhombic unit cell reported by Lovinger *et al.* and another is that with the monoclinic unit cell, which seems to be virtually similar to the model of Furukawa *et al.* However, an electron diffraction pattern of PDMS single crystal⁶⁾ cannot be fully interpreted by their monoclinic unit

cell. If the single crystal does not have a specific structure at room temperature, the pseudo-orthorhombic unit cell proposed by Lovinger *et al.* seems to be adaptable.

It was reported that the friction transferred PTFE and high-density-polyethylene (HDPE) are doubly oriented. The X-ray diffraction study showed that (010) plane of PTFE was parallel to the substrate surface¹⁴⁾. The electron diffraction pattern of the HDPE indicated a double orientation¹⁵⁾. The friction transferred PDMS is considered also to have a higher-order structure, possibly of double orientation type. In the electron diffraction pattern of the friction transferred PDMS, the 200 reflection cannot be observed, but the 020 reflection appears strongly (Figure 3-1). Moreover, the X-ray diffraction pattern of the PDMS film measured by reflection mode showed that the $110 + \overline{110}$ reflection is weakened and the 200 reflection is strengthened in comparison with unoriented specimen (These indices are based on the unit cell by Lovinger *et al.*⁵⁾) (Figure 3-2). The result indicates that the (200) plane is arranged nearly parallel to the substrate surface. In other words, the *a* axis stands vertically on the substrate face in the thin film.

Comparison between the IR-RA and transmission spectra enables us to discuss the molecular alignment to the substrate surface. The RA spectrum polarized normal to the substrate face (therefore, normal also to the sliding direction within the face) is nearly the same as the transmission spectrum taken with the light polarized normal to the sliding direction and parallel to the substrate face. This provides two possibilities in the molecular alignment: (1) the friction transferred film is uniaxially oriented around the sliding direction without any preferred orientation to the substrate surface, or (2) the PDMS crystallite is doubly oriented but

molecular packing in the unit cell compensates the IR dichroism. The X-ray and the electron diffraction data suggest the double orientation of the crystal lattice. So, the latter alignment seems to be the case. Two models are proposed on the basis of the experimental results. Figures 3–6a and b represent possible models respectively with an orthorhombic unit cell and a monoclinic unit cell. The molecular packing proposed by Patnaik and Farmer⁷⁾ is used. For the monoclinic cell (Figure 3–6b), the 110 reflection corresponds to the 200 reflection for the orthorhombic packing. There are two types of molecular chain plane orientation in the orthorhombic cell (Figure 3–6a). In a crystallite, two types of chains cancel out each other. In this model, any distinct difference does not appear between the RA spectrum and the transmission spectrum with perpendicular polarization. No splitting of IR band arising from intermolecular forces in the crystal was observed, which would be a proof for the orthorhombic unit cell if it had been observed. Assuming the monoclinic packing with one molecular chain in the unit cell, it is difficult to interpret the resemblance of the dichroism between the RA spectrum and the transmission spectrum with parallel polarization. For the unit cell with a single chain, it is considered to be a rare case having the molecular orientation so that a transition moment of a vibrational mode in the all-*trans* zigzag plane (or in that normal to it) has the same size of components in the substrate plane direction and in the vertical direction. The favorable model is the one with the (pseudo)orthorhombic packing (Figure 3–6a).

3–3–4. Phase Transition Behavior

The PDMS bulk sample undergoes two solid–solid phase transition

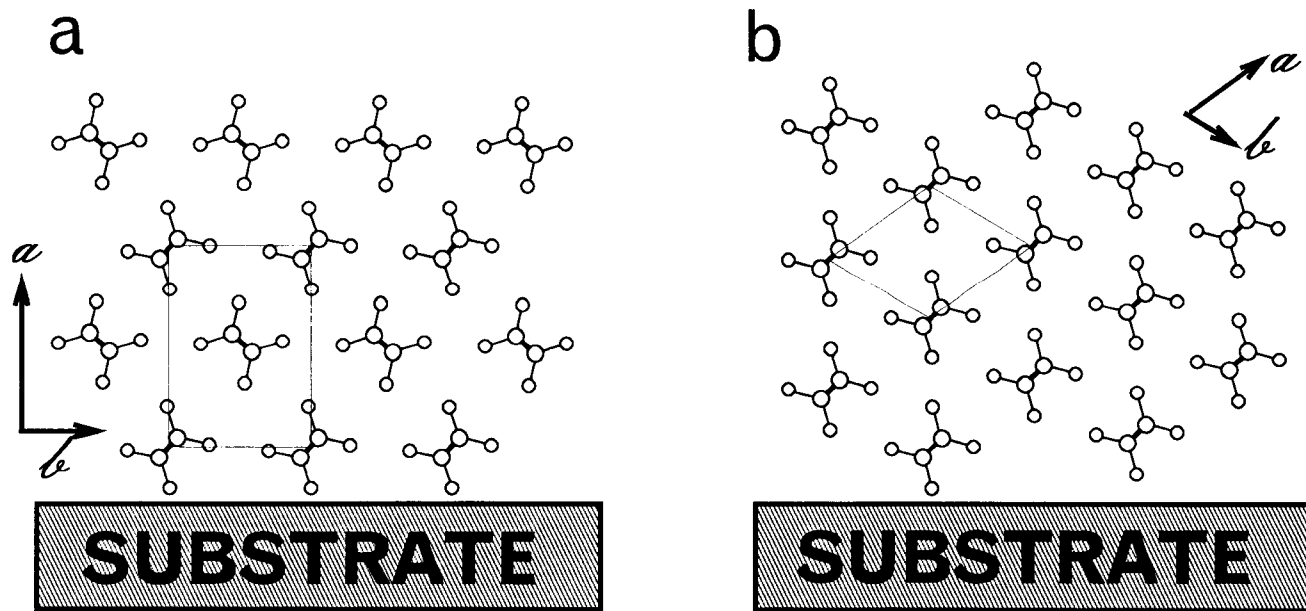


Figure 3-6. The models of arrangement of the PDMS unit cell to the substrate surface. The sliding direction is normal to the plane of the paper. The cell dimension and molecular packing of the model were based on the report by Patnaik and Farmer⁷ for orthorhombic lattice (a) and monoclinic (b).

at 160 and 220°C. The phase transition behavior of PDMS thin film was investigated by UV and IR spectroscopies. Figure 3–7 shows temperature dependent UV spectra of PDMS thin film. The spectra change continuously across the two phase transition temperatures. Figure 3–8 shows the polarized UV spectra measured at various temperatures, which encompass the two phase transition temperatures for the bulk sample. The band polarization behavior is preserved at all temperatures. It has been already reported that PDMS has not a distinct thermochromic property unlike PDHS^{16, 17}). For the bulk sample the UV absorption maxima, λ_{max} , slightly shifted to shorter wavelength side when PDMS undergoes an order–disorder phase transition. For the friction transferred film, the λ_{max} also shifted to shorter wavelength with the increase in the temperature. Figure 3–9a shows the λ_{max} plotted against the temperature. The λ_{max} is closely related the σ –conjugation character. The shortening of wavelength means the shortening of the conjugated length, caused by disordering of the all–*trans* skeletal conformation. However, the blue–shift was relatively smaller than that in the other thermochromic polysilanes, such as PDHS. This suggests that the phase transition does not accompanies no large disordering of the all–*trans* main chain, but slight distortion of the conformation. A blue–shift of several nm could be observed in thermal transition of the bulk sample^{5, 9}), which was same level of the thin film. We also measured temperature dependent UV spectra of the PDMS powder sample. For the powder sample, the blue–shift was found to start at 130°C and to finish at 160°C, which is the first phase transition temperature. For the friction transferred film, the phase transition seems to occur at 140°C (Figure 3–9a). This is considered to be caused by the thinness of the film. The second phase

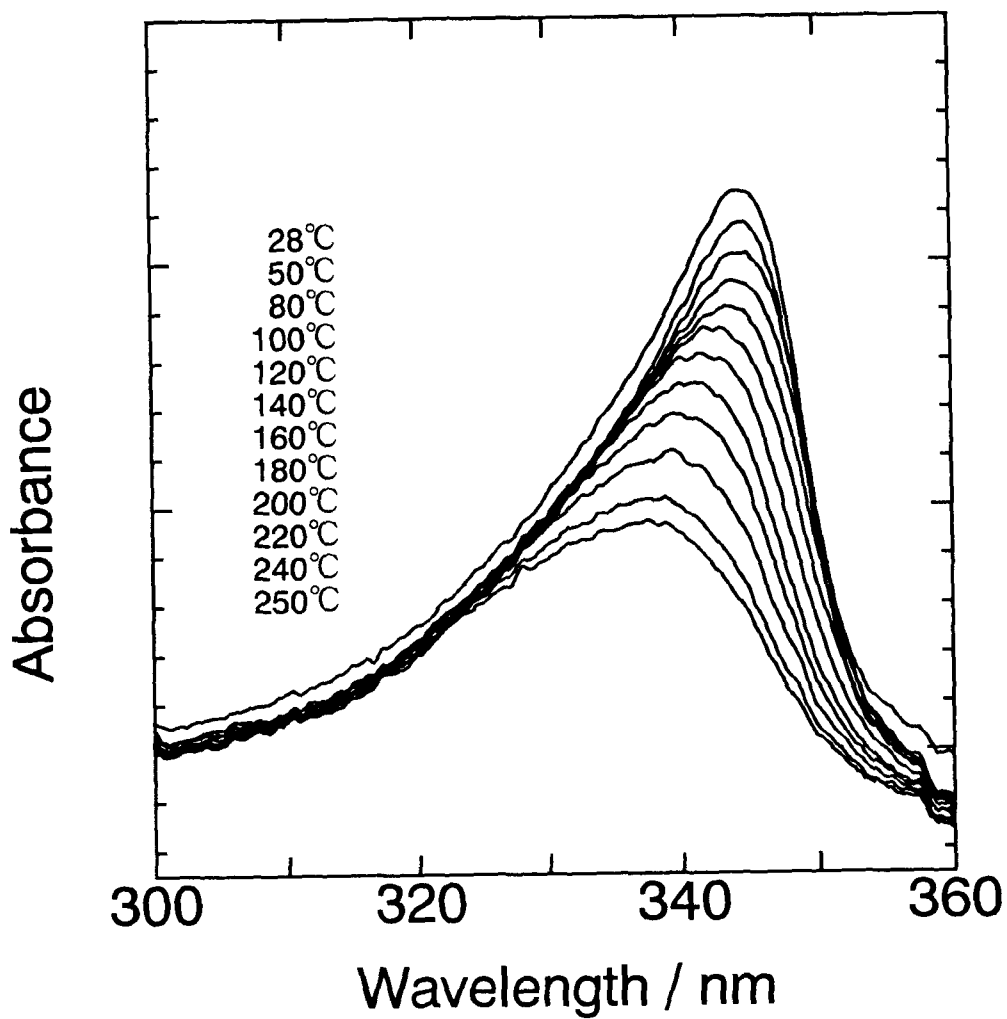


Figure 3-7. Temperature dependence of UV spectra of PDMS film which was transferred on quartz substrate kept at 218°C .

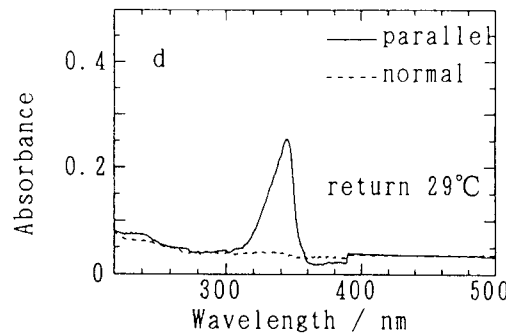
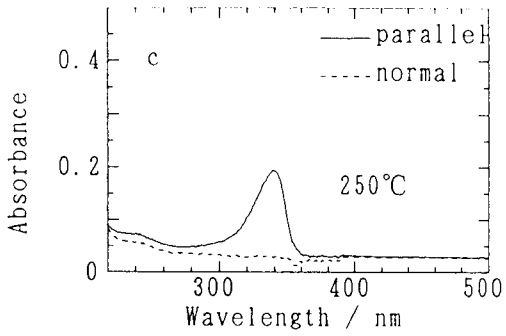
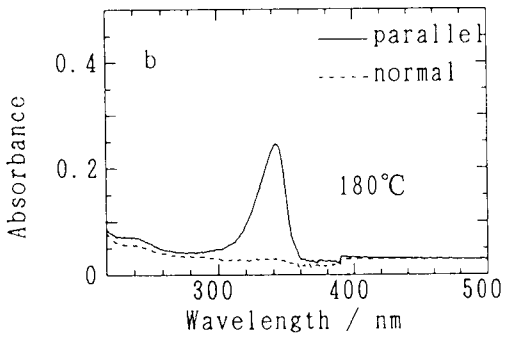
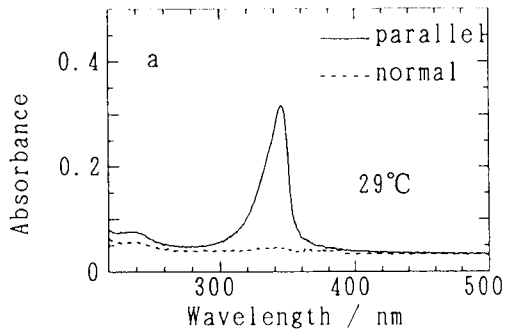


Figure 3-8. The polarized UV spectra of PDMS at various temperatures (a)29°C, (b)180°C, (c)250°C, and (d)cool down to 29°C. The PDMS were deposited on a quartz substrate at 218°C.

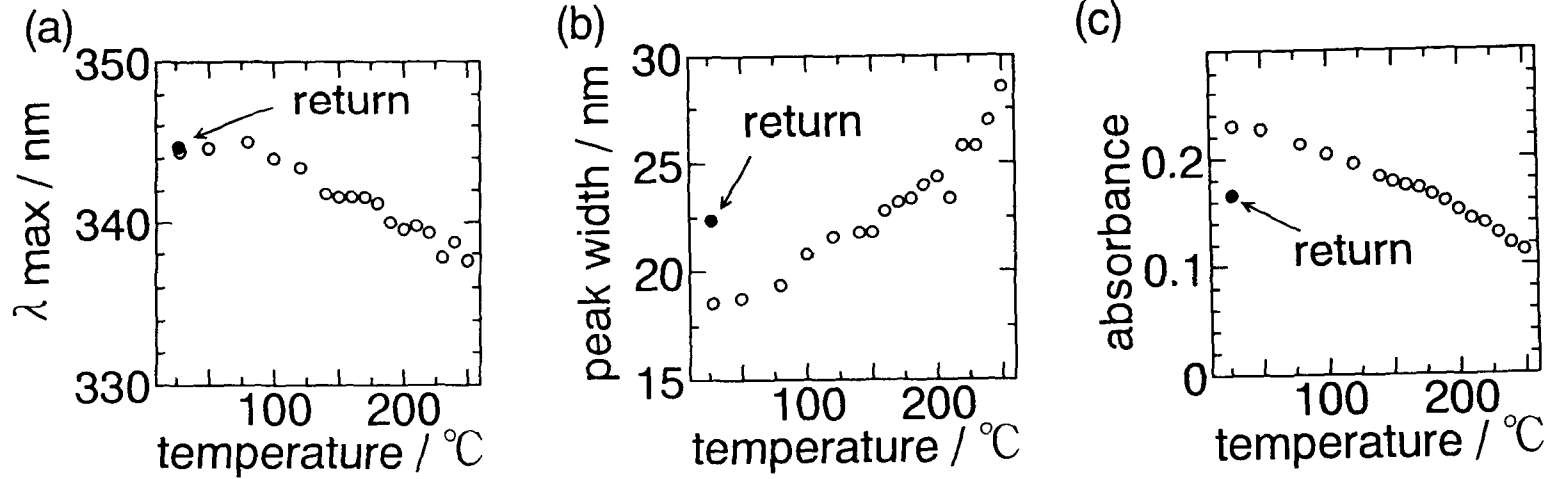


Figure 3-9. The temperature dependence of absorption maxima (a), peak width (b), and absorbance at the maximum (c) of UV spectra of the PDMS film prepared at 218°C.

transition could not be seen for the powder sample because decomposition occurred below the second transition temperature. For the film the second transition seems to occur at about 200°C.

Figures 3-9b and c show that the band width and absorbance also change with the temperature raised. The band width increases when the temperature is raised. The absorbance becomes smaller with the higher temperature. The spectral shape was also changed. At low temperatures, a very steep edge of the absorption peak was observed on the long wavelength side, but at high temperatures the absorption peak became symmetric. These changes seem to be also caused by the disordering. The UV spectra of Figure 3-8(d) shows that the friction transferred PDMS film undergoes a reversible change. A small broadening of the peak and a small decrease in the absorbance on the second run are considered to be caused by a small decomposition in the air. In the stretched film the deterioration of orientation accompanied with the transition at 220°C was reported⁵⁾. However, no such worsening of orientation was observed in the friction transferred film. This seems to come from the influence of the substrate. Another possible reason is considered as follows. Less decomposition appears to occur in the friction transferred film than the stretched film. Because the thermal decomposition may cause the deterioration of orientation, the orientation of the stretched film is worsened more largely than that of the friction transferred one.

The phase transition behavior was also observed by IR spectroscopy. For the powder sample, the intensest band assigned to the CH₃ rocking vibration (B_{3u}) was very sensitive to temperature variation (see 3-3-2). This band, which was observed at 742cm⁻¹ at 27°C, moved to the higher frequency with elevated temperature. A shift over 10cm⁻¹ was observed

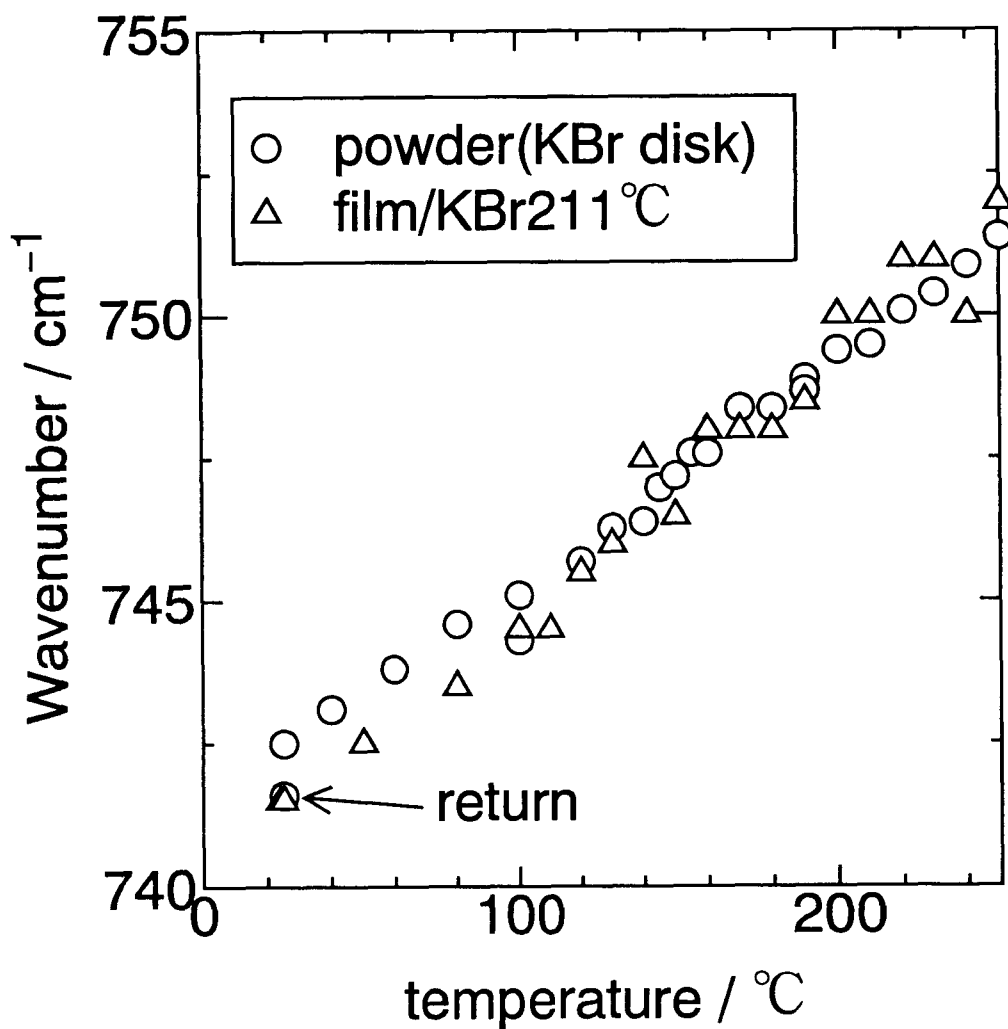


Figure 3-10. The temperature dependence of IR frequencies for CH_3 rocking band (B_{3u}) of a friction transferred thin film on KBr and powder sample (in KBr).

at phase III (250°C). The same band shift was also observed for the friction transferred film. In Figure 3-10 the IR band shift of the transferred film plotted against the measuring temperature is compared with that of the powder specimen. The shift is essentially the same for the both samples. This change in IR spectra was reversible like as UV spectra. The polarization character of this parallel band of the CH₃ rocking vibration was preserved with raising the temperature. For IR spectra, we could not detect the obvious difference between the temperature dependent behavior of the powder and the film sample.

3-4. Conclusion

The molecular chain in the friction transferred film aligned in the sliding direction. The molecular conformation of PDMS was found to be highly ordered all-*trans* and the film was highly crystalline. The crystallite was doubly oriented in the transferred film. That is an achievement of the three-dimensional molecular arrangement by friction transfer. The transferred film of PDMS underwent the reversible solid state transition keeping the orientation state, substantially unchanged. The phase transition temperature of the thin film was lower than that of the powder sample.

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Chapter 4

Friction Transfer of Dialkyl Substituted Polysilanes and Poly(methylphenylsilylene)

4- 1. Introduction

Polysilanes are composed of Si-catenated main chains and two alkyl or aryl substituents connected with all Si atoms. Their unusual electric and optical properties are considered to be caused by the delocalization of σ -electron along the Si backbone¹⁾ (σ -conjugation). The σ -conjugation character is strongly dependent on the conformation of Si backbone. Polysilanes widely vary in structure and properties with their side chains. The solid state structure of di-alkyl substituted polysilanes has been extensively studied. The all-*trans* conformation was observed in dimethyl²⁾, diethyl, di-*n*-propyl³⁾, di-*n*-hexyl, di-*n*-heptyl, and di-*n*-octyl polysilanes⁴⁾. The 7/3 helix was found in di-*n*-butyl and di-*n*-pentyl polysilanes⁵⁾. The TGTG conformation was found in di-*n*-nonyl, di-*n*-decyl and longer alkyl substituted polysilanes⁶⁾. Most of polysilanes are known to undergo some solid state phase transitions caused by changes of temperature or pressure.

Aligning the Si main chain of polysilanes is very important for the scientific investigation and industrial usage of the physical properties. A lot of methods were attempted to fabricate oriented specimens of polysilanes. On the other hand, a new method of preparing oriented films of polymers such as poly(tetrafluoroethylene) (PTFE) was reported, in which dragging the polymer against the clean smooth surface of a substrate afforded the highly oriented film on the substrate⁷⁻⁹⁾. The technique is

called as mechanical deposition, friction deposition, or friction transfer. The highly oriented film of poly(dimethylsilylene) could be prepared by the method (chapters 2 and 3).

In this chapter, it is examined whether it is possible to apply the friction transfer technique for preparing the oriented films to various polysilanes, such as poly(diethylsilylene) (PDES), poly(di-*n*-butylsilylene) (PDBS), poly(di-*n*-hexylsilylene) (PDHS) and poly(methylphenylsilylene) PMPS. PDES is a polysilane with the longer side chain by one methylene unit than PDMS. It was reported that PDES has all-*trans* skeleton and that it undergoes solid state transition with conformation preserved like as PDMS¹⁰⁾. PDHS is the most widely studied polysilane. Its thermochromism^{4, 11, 12)} and piezochromism^{13, 14)} attracted many interests for researchers. On the other hand, PDBS is a helical polymer in the contrary to the former polymers⁵⁾. It was found that application of a pressure changes the conformation from 7/3 helix to all-*trans*^{13, 15)}. Which conformation should be adopted in a friction-transferred film of PDBS? PMPS is an asymmetrical substituted polysilane and is thought to be not crystalline but amorphous. It is a polysilane whose industrial usages has been most widely studied. The difference in the friction transfer phenomena among the polysilanes, which have various side chains, is discussed.

4-2. Experimental

4-2-1. Materials

The polymers were synthesized by Wultz-type condensation with sodium from the corresponding dichlorosilanes. Weight averaged molecular weights, \overline{Mw} were 2.0×10^6 , 4.6×10^5 and 9.0×10^3 ,

respectively of PDBS, PDHS, PMPS, which were measured by gel permeation chromatography (Waters GPC 150C) with the polystyrene standards. Because PDES was insoluble in common organic solvents, its \overline{Mw} could not be determined.

Oriented films of polysilanes were prepared as follow. The polymer, as synthesized, was compressed into a disk with about 235 MPa pressure.

The polysilane disk so prepared was slid onto the smooth substrate, whose temperature was controlled while applying a pressure. The temperature of the substrate during deposition was varied from 11 to 235°C.

A fused silica (quartz), a glass slide, and a KBr crystal were used for the substrates.

4-2-2. Measurements

The friction transferred films of the polysilanes were characterized by polarized UV and IR spectroscopies and electron and X-ray diffraction methods. These measurements have been already mentioned (Chapter 3).

4-3. Results and Discussion

We obtained oriented films of all polysilanes by the friction transfer technique. The polarized UV spectra showed the Si backbone of the polysilanes in the transferred film was aligned in the sliding direction. As mentioned in the previous chapter, the quality of the transferred film of PDMS depended on the substrate temperature during the preparation. This is more or less true for the other polysilanes. The following describes the behavior of each polysilane.

4-3-1. Poly(diethylsilylene)

The film of PDES was deposited on the substrate at higher temperature, it was more highly oriented and more uniform like as PDMS.

The uniform film was obtained when it was prepared at temperature higher than 200°C. The polarized UV spectra of PDES film are shown in Figure 4-1. Like as PDMS, the dichroic ratio of the spectra increases with the increase in preparation temperature. Moreover, the peak position of the spectrum shifts from 342nm to 371nm with increasing preparation temperature. Figure 4-2 shows the variation of UV spectra with the preparation temperature. This red-shift was also observed in the PDMS film, which was considered to be caused by improvement on conformational regularity of all-*trans* Si backbone. However, the red-shift of PDES is found to be larger than that of PDMS. The friction transferred film of PDES prepared at the high temperature is considered to have a highly ordered structure, both in the conformation and the higher-order structure.

PDES has three solid state phases. The lowest temperature phase (phase I) and the middle temperature phase (phase II) were the ordered crystalline phases, and the highest phase was the disordered one (phase III) by X-ray diffraction study. The phase transitions were observed at about 40°C and 200°C by differential scanning calorimetry. These transitions can be also detected by vibrational spectroscopy¹⁰⁾. Many IR bands of PDES in phase I were found to be split by intermolecular forces in the crystal for powder specimen. The IR spectra of the friction transferred film measured at room temperature was similar to those of bulk sample in phase I. Thus, at room temperature, the friction transferred film was found in the lowest temperature phase. Figure 4-3 shows the polarized IR spectra of friction transferred film, which indicates the friction

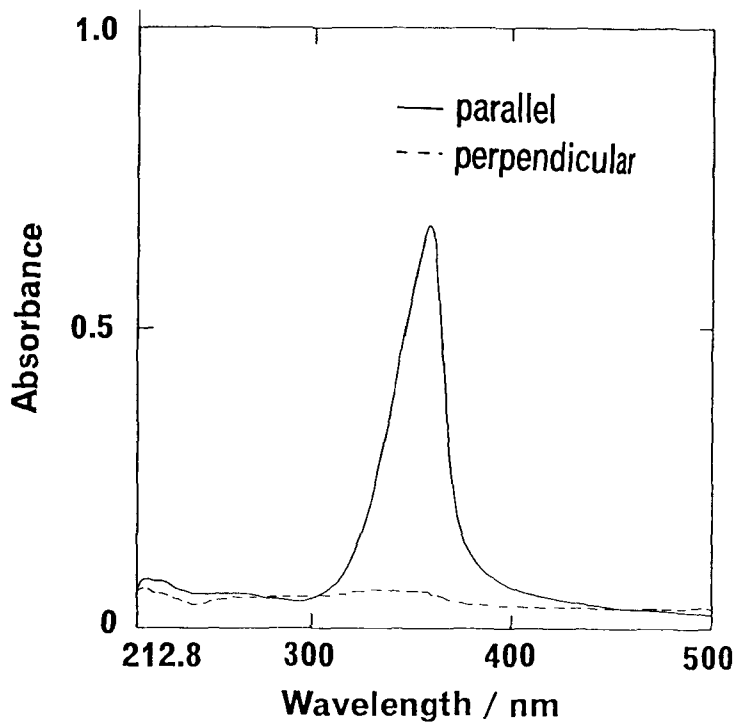


Figure 4-1. Polarized UV spectra of PDES friction transferred on quartz at 180°C.

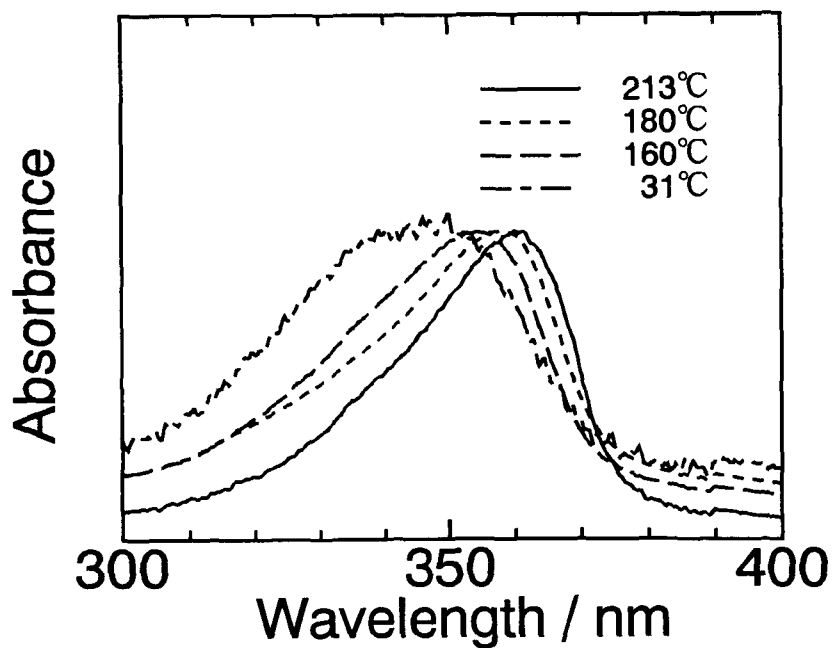


Figure 4-2. Preparation temperature dependence of the UV spectra of PDES film.

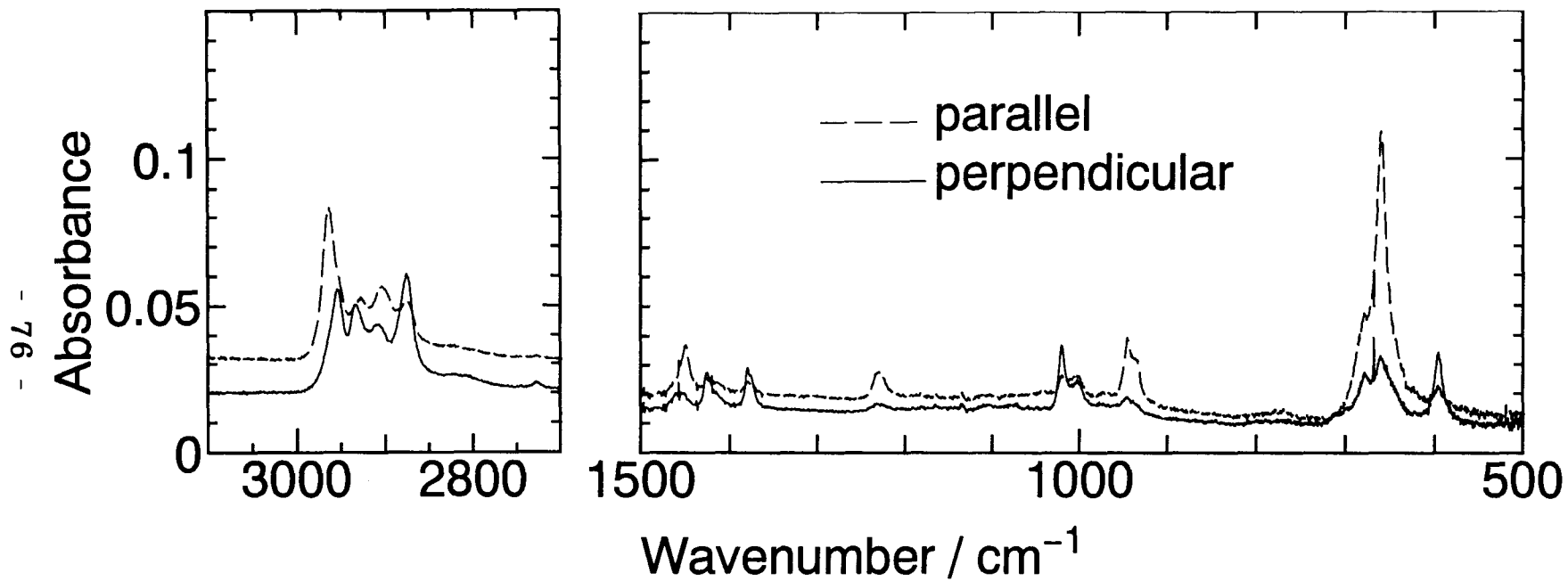


Figure 4-3. Polarized IR spectra of PDES friction transferred on an optical flat face of KBr single crystal at 184°C.

transferred film is highly oriented.

4-3-2. Poly(*di-n-hexylsilylene*)

No uniform films of PDHS could be obtained even at high substrate temperature, but the ununiform PDHS film was found to be oriented. Figure 4-4 shows an electron diffraction pattern of PDHS. It revealed that the film is highly oriented and crystalline. The crystal packing of thin film appeared to be essentially similar to the bulk sample. Figure 4-5 shows polarized IR spectra of the PDHS friction transferred film. It also shows that PDHS is highly oriented. The polarized spectra resemble the previously reported those of oriented film prepared by casting on a highly oriented PTFE substrate¹⁶⁾. Two vibrational bands with very intense absorption are observed at 2920cm^{-1} and 660cm^{-1} in the spectra with the parallel polarization to the sliding direction. The band at 2920cm^{-1} can be assigned to the CH_2 antisymmetric stretching vibration. Its polarization character can be interpreted by assuming that the zigzag plane of *n*-hexyl chain is normal to the main chain direction. This model does not completely agree with the crystal structure determined by X-ray analysis¹⁷⁾. In the crystal structure model, the zigzag planes of alkyl chain attached to Si atom is not completely normal to the main chain direction. While, the 660cm^{-1} band, which was previously assigned to the Si-C stretching vibration^{4, 16)}, has a parallel polarization, which seems to be contradictory. The Si-C stretching vibration must have a transition moment perpendicular to the main chain direction. As the main chain direction coincides with the sliding direction, the Si-C stretching band should be perpendicular band. Therefore we consider that 660cm^{-1} band is assigned not to the Si-C stretching but the (Si-)CH₂ rocking band.

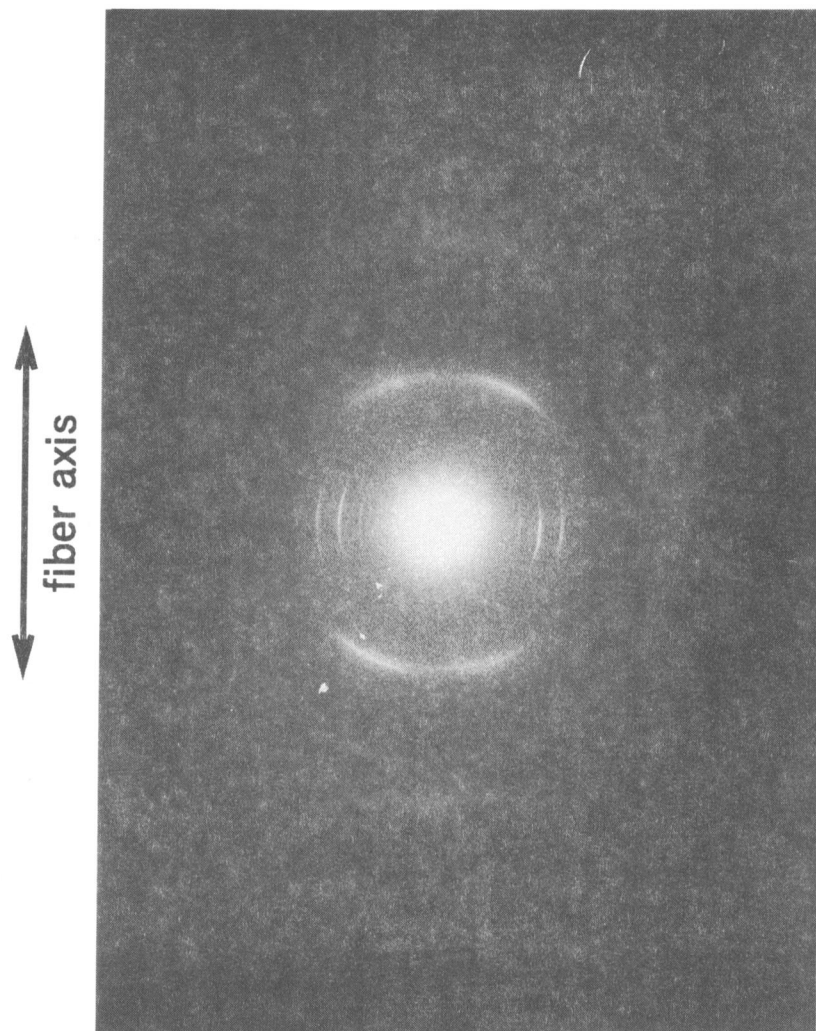


Figure 4-4. Electron diffraction of PDHS film prepared at 100°C.

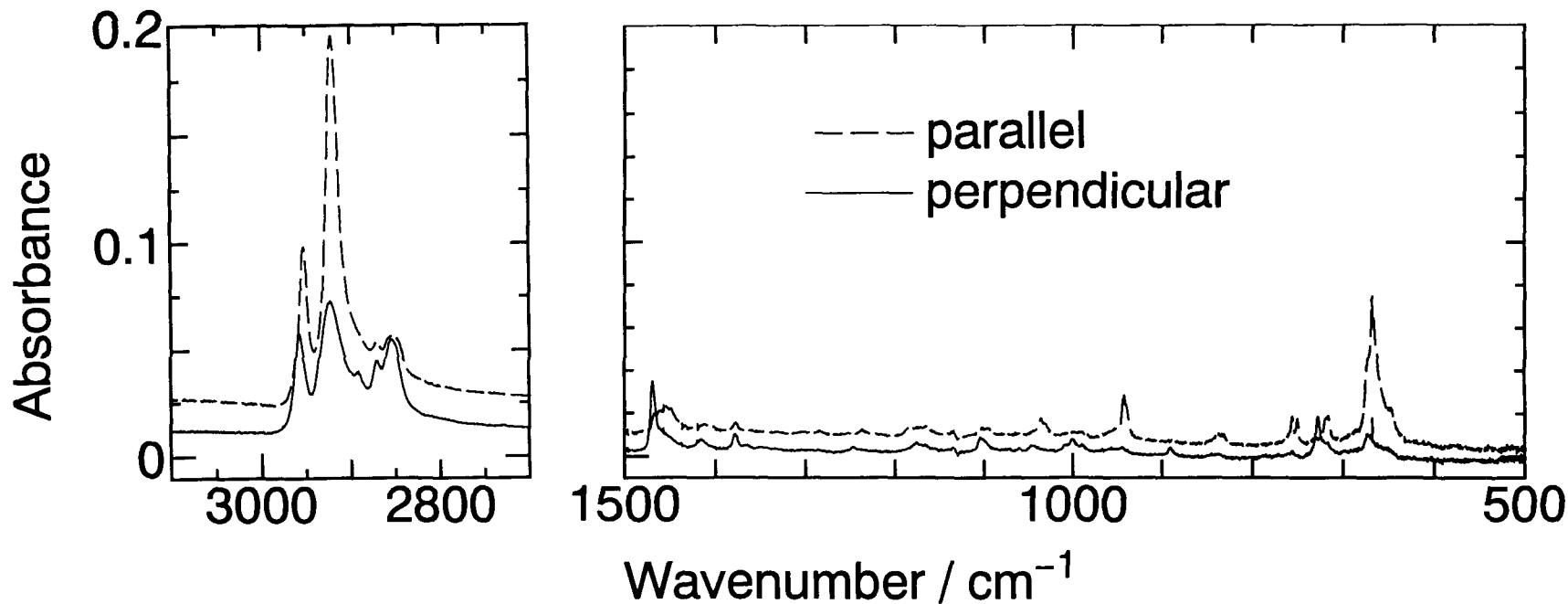


Figure 4-5. Polarized IR spectra of PDHS film friction transferred on KBr single crystal at 100°C.

The IR spectra in the wavenumber region higher than 600cm^{-1} exhibit mainly vibrational band from alkyl side chains. These large dichroic character of the 660cm^{-1} band suggests that not only the main chain but the side chain are oriented. This is considered to be caused by crystallization of the side chains.

Figure 4-6 shows the polarized UV spectra of the friction transferred films of PDHS prepared at various temperature. PDHS is well known to show reversible thermochromism in the solid state, which originates from the first order transition at 42°C ^{4, 11, 12}). At ambient temperature, two solid state phases co-exist in a PDHS solution cast film^{4, 11, 12}). There are two peaks in the UV spectra of the PDHS films transferred at various temperature and measured at room temperature. It suggests that the friction transferred PDHS film is also composed of two solid state phases. The peak with the longer wavelength corresponds to the low temperature phase (phase I), having all-*trans* conformation and the shorter wavelength peak corresponds to the high temperature phase (phase II). The proportion of the two phases depends on the preparation temperature. In the film deposited below the phase transition temperature, phase I is dominant (Figure 4-6a). When the film was prepared around the phase transition temperature ($35-45^\circ\text{C}$), the proportion of phase II and phase I are seen to be comparable and the degree of orientation of the film is small (Figure 4-6b). Unexpectedly, phase II decreased when the film was deposited at the much higher temperature than the phase transition temperature (Figure 4-6c). So recrystallization seemed to be occurred during the friction transfer. For all of the samples prepared at various temperature, the dichroic ratio of absorption spectra of phase I was larger than that from phase II. The

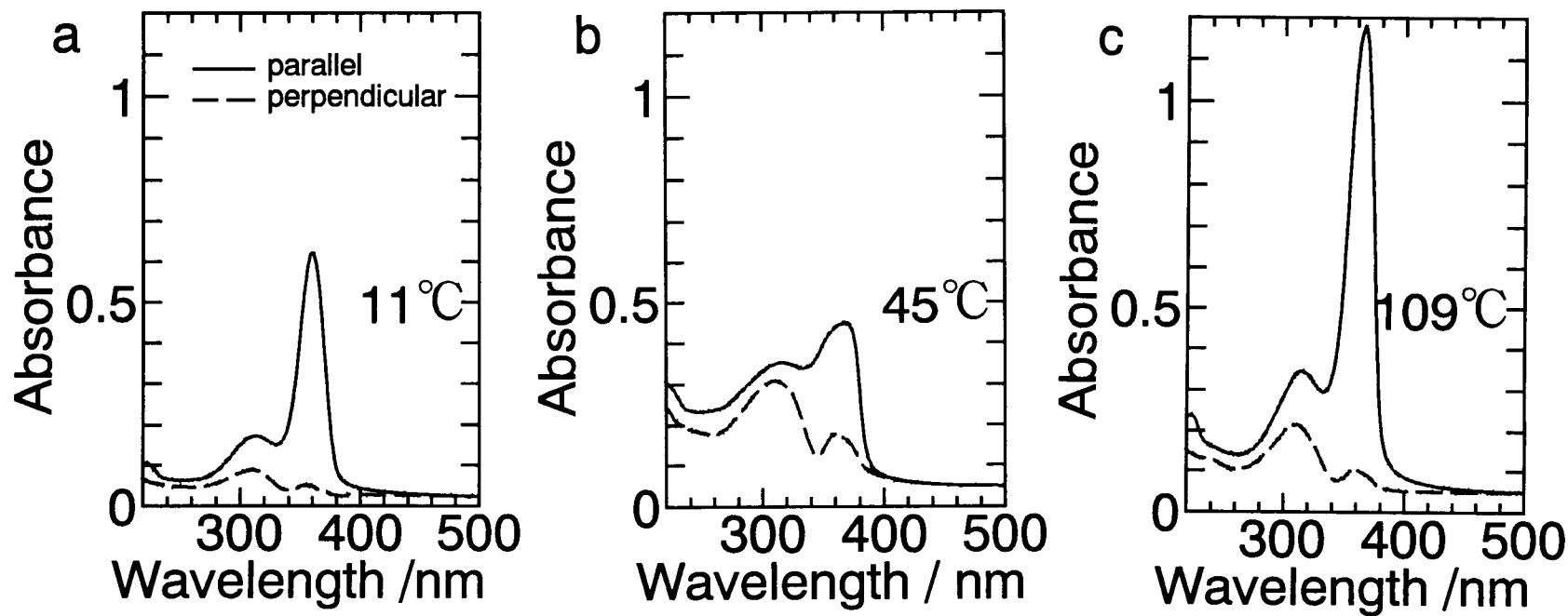


Figure 4-6. The polarized UV spectra of friction transferred PDHS film prepared at 11°C (a), 45°C (b) and 109°C.

same phenomenon could be observed in the polarized IR spectra. The IR bands arisen from phase II (*gauche* band) had smaller dichroic ratios than those from phase I. The smaller orientation degree of phase II revealed that it was more difficult to align for the molecular chains in the part of the disordered phase, phase II. While the molecular chain is ready to align in phase I, an ordered crystalline phase.

The temperature evolution of the UV measurement was carried out in order to confirm whether the friction transferred film has thermochromic transition as the bulk sample. Figure 4–7 shows the polarized UV spectra measured at various temperature. As shown in Figure 4–8, the friction transferred film undergoes a reversible thermochromic transition (Figure 4–8). Passing through the phase transition, the orientation state was almost preserved. However, orientation degree decreased slightly and the population of phase I increased slightly when the temperature returned to the room temperature. The annealing effect on the friction transferred film was smaller than that on the cast film. The phase transition temperature of the thin film was similar to the bulk sample.

4–3–3. Poly(*di-n-butylsilylene*)

The oriented film of PDBS could be obtained by friction transfer method, but it was not uniform at all the temperatures examined like as PDHS. The uniformity and the orientation degree of the transferred film was found to be independent of the substrate temperature. The conformation of PDBS in the bulk solid was known to be 7/3 helix⁵⁾, unlike the polysilanes mentioned before. However, an applying a pressure changes PDBS skeletal conformation to the all-*trans* state, and the pressure-induced state is relatively stable at an ambient pressure^{13, 15)}.

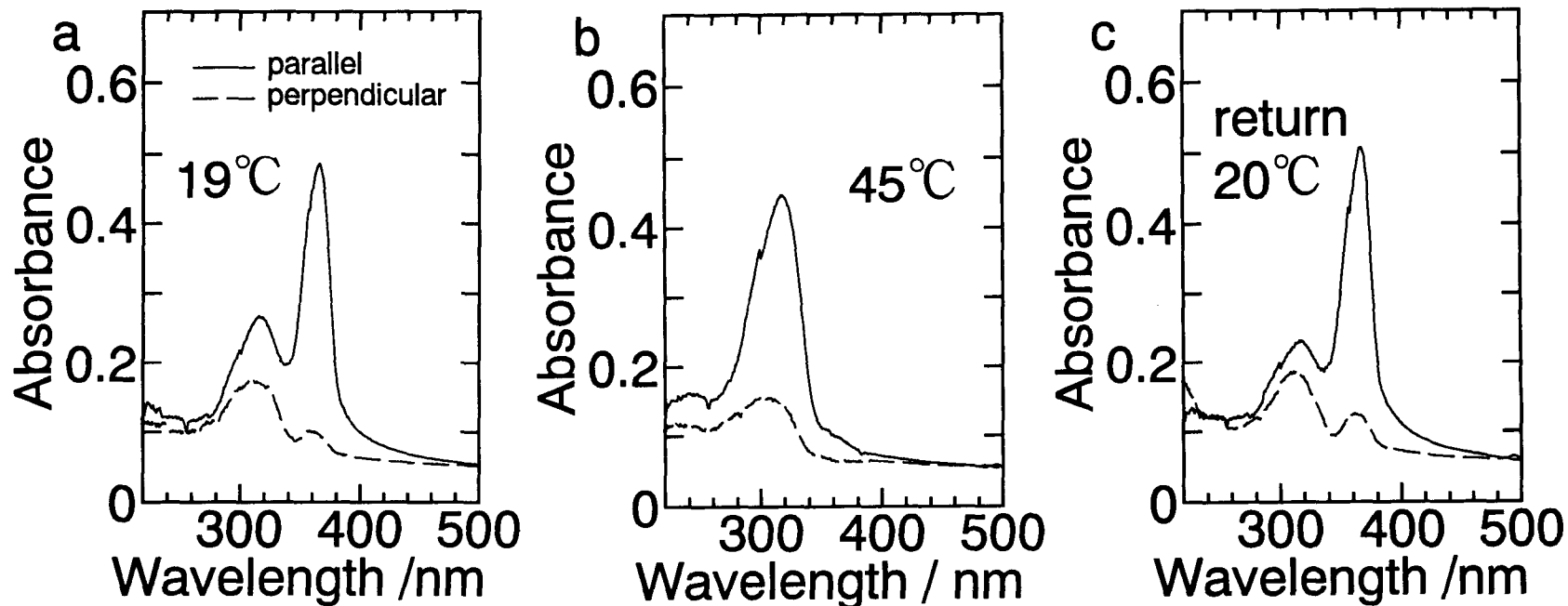


Figure 4-7. Temperature dependent polarized UV spectra of PDHS friction transferred at 19°C; measured at 19°C (a), 45°C (b) and return to 20°C (c).

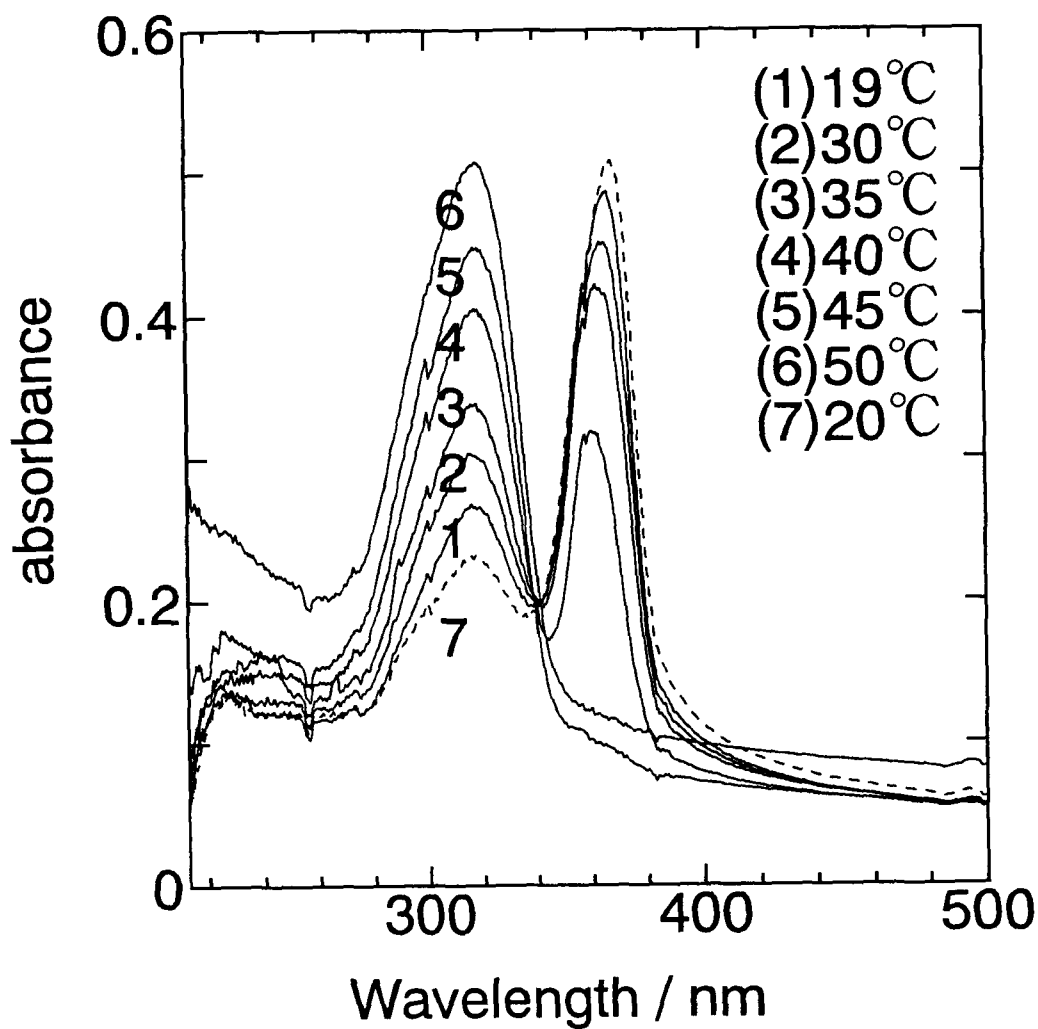


Figure 4-8. Temperature evolution UV spectra of PDHS film, polarized parallel to the sliding direction. Measured at 19°C, 30°C, 35°C, 40°C, 45°C, 50°C, and return to 20°C (dotted line).

The helical polysilane has an absorption at about 310nm and the all- *trans* one absorbs at about 370nm. Which conformation is adopted to the friction transferred film of PDBS? The pressure applied during the friction transfer ranged from 1 to 5 MPa, which is too small to change the conformation. However, it was expected that there would exist some effect of pressing under a very large shear different from that of simple hydrostatic pressure. Figure 4-9 shows the polarized UV spectra of PDBS. The UV spectra have absorption maxima was found near 310nm, suggesting the conformation of the friction transferred PDBS is also 7/3 helix. An electron diffraction pattern (Figure 4-10) shows a fiber diagram with the fiber axis being parallel to the sliding direction, and the fiber diagram also confirms the friction transferred PDBS has a helical structure.

Thus we see that this helical polysilane can be oriented by the friction transfer technique and the molecules in the transferred film keep the helical conformation.

4-3-4. *Poly(methylphenylsilylene)*

The oriented film of an asymmetrically substituted polysilane, PMPS could be also prepared by the friction transfer technique. The oriented films so prepared were very ununiform. The polarized UV spectra of PMPS is shown in Figure 4-11. The absorption at 340nm polarized parallel to the sliding direction arises from the $\sigma - \sigma^*$ transition. The preparation temperature dependence of PMPS films was different from the films of the other polysilanes which were mentioned before. When the temperature was lower than 150°C, the higher degree of orientation was observed in the film prepared at higher substrate temperature. However, a very small orientation was observed in the film deposited above 150°C.

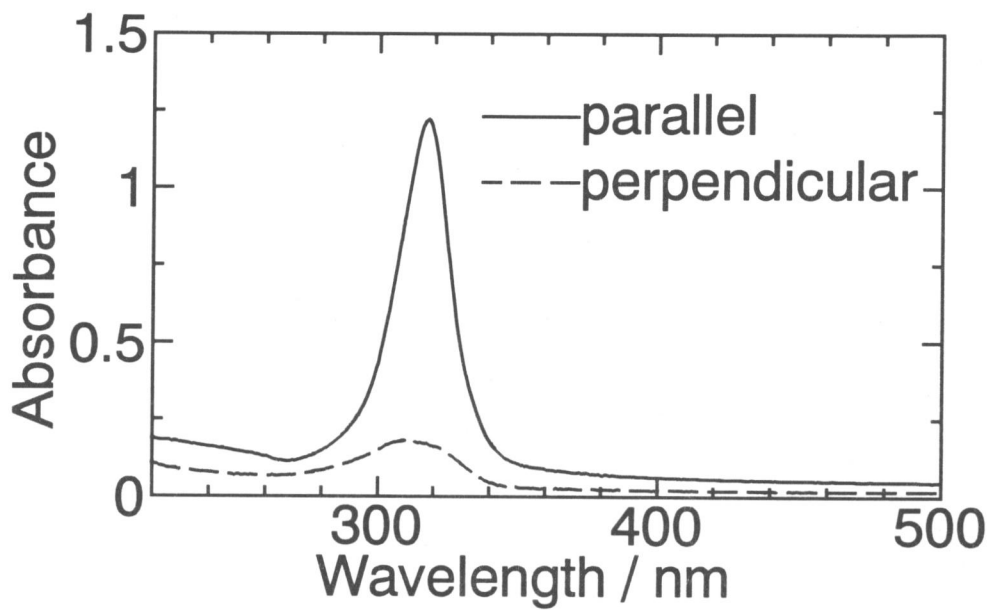


Figure 4-9. Polarized UV spectra of PDBS friction transferred at 100°C.

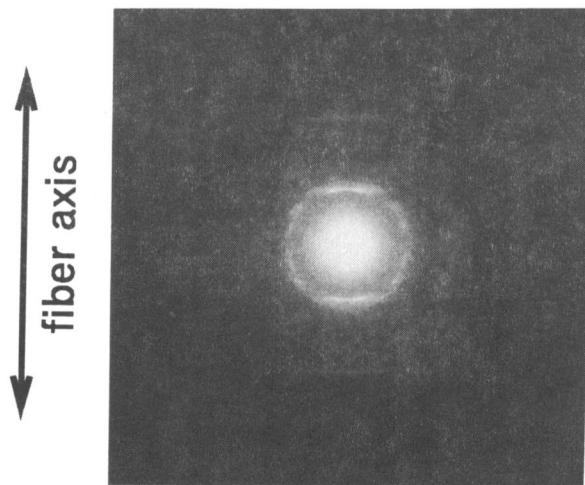


Figure 4-10. Electron diffraction of PDBS film prepared at 100°C.

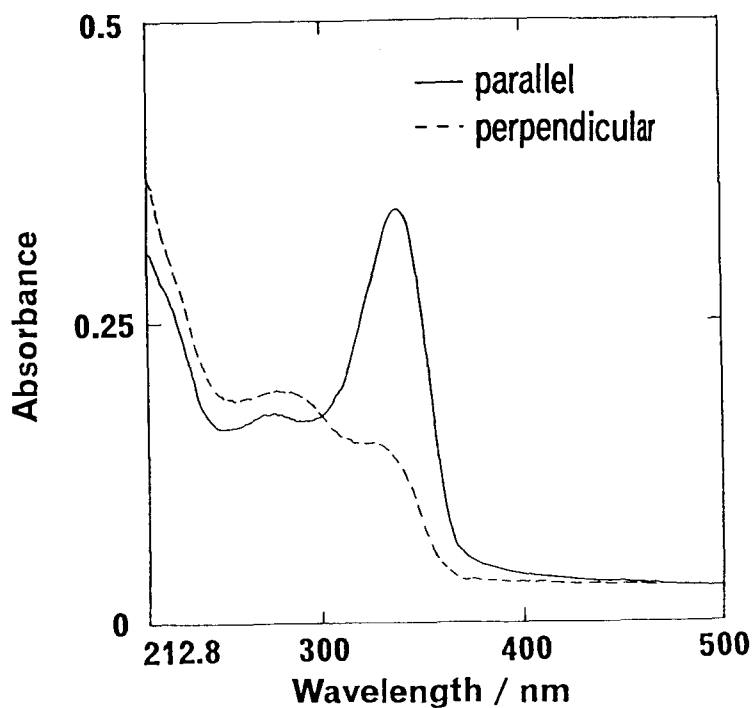


Figure 4-11. Polarized UV spectra of PMPS friction transferred at 120°C.

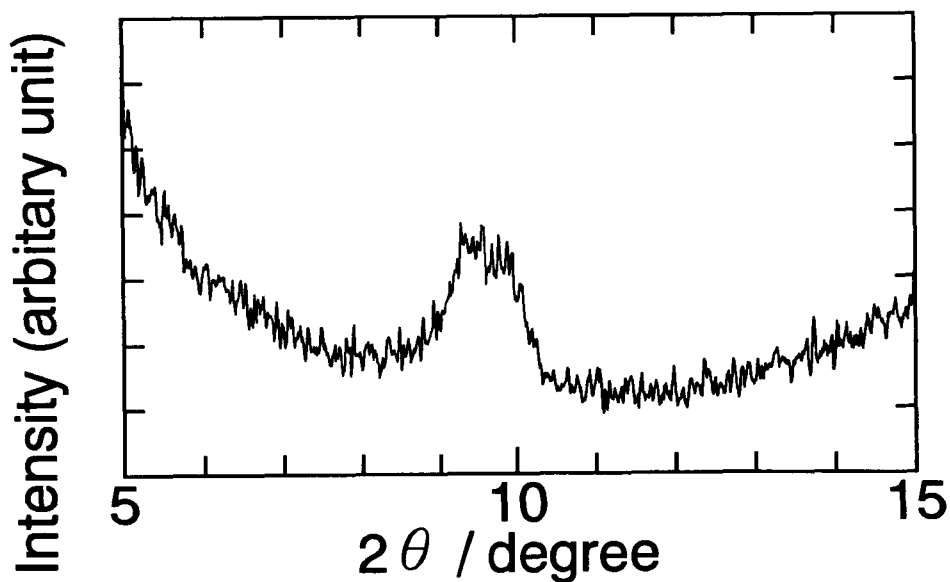


Figure 4-12. X-ray diffraction pattern of PMPS friction transferred on glass slide.

A possible origin of the phenomenon is considered to be related to the glass transition of PMPS. The glass transition temperature is thought to be around 150°C. (For the other polysilanes glass transition temperature is considered to be much lower than room temperature.)

PMPS has been considered to be amorphous in solid state. However, the stretched film of PMPS showed a fiber diagram¹⁸⁾. Figure 4-12 shows the X-ray diffraction of the friction transferred film of PMPS. Two peaks were observed in the diffractogram, suggesting that it was crystalline. PMPS seems to be crystallized by orienting. The detail solid state structure has not been investigated yet.

4-4. Conclusion

We obtained highly oriented films of several polysilanes such as PDMS, PDES, PDBS, PDHS, and PMPS. The polarized UV absorption spectra suggested that the chain axes of friction transferred polysilanes were aligned parallel to the sliding direction. Uniform films were obtained only for PDMS and PDES.

From these experiments we may say that this method can be applied to prepare the oriented films of any polysilane derivatives, enabling for one to investigate the relationship between properties and structure of the polysilanes.

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Chapter 5

Total Reflection X-ray Diffractometry of the Polysilane Thin Film

5-1. Introduction

Thin film is a very suitable form for the use as functional materials. Arrangement of molecules in films is one of important factors on application of the function of the organic thin films. Many researchers have investigated preparation of organic thin films and controlling molecular arrangements in them. The author also studied on the preparation of highly oriented thin film of polysilanes on smooth substrates by friction transfer method (in Chapter 2, 3 and 4).

The evaluation of molecular arrangements in thin films is essentially important for the investigation of organic thin films. Especially, diffraction method is very effective for evaluation of molecular arrangements. The electron diffraction method (reflection high-energy electron diffraction, RHEED, and low-energy electron diffraction, LEED) have been used for characterization of thin films. However, these methods are sometimes accompanied with a damaging of organic thin films, and they have a restriction that they have to be measured under high-vacuum. X-ray diffraction method is also suitable for characterization of molecular arrangements. However, it is difficult to apply the conventional X-ray diffraction method to organic thin films because of small volume and small scattering factors of organic thin films. In order to circumvent this difficulty, the total reflection X-ray diffraction (TRXD) method has been developed for characterization of thin films¹⁻¹⁰⁾ In the TRXD method, X-rays irradiated at a very shallow glancing angle are totally reflected at

the boundary between the film sample and the substrate. Therefore, the X-rays diffracted by the film can be observed with eliminating the scattering by the substrate. In the TRXD method, it is possible to measure not only the structure with the reciprocal vector normal to the substrate (vertical-type), but in-plane structure (parallel-type) of the sample.

This chapter describes the molecular arrangement of a friction transferred film evaluated by the TRXD method. Especially, the molecular orientation and its distribution in the substrate plane are examined. Poly(di-*n*-butylsilylene) (PDBS) was employed as the material in this study.

5-2. Experimental

5-2-1. Sample

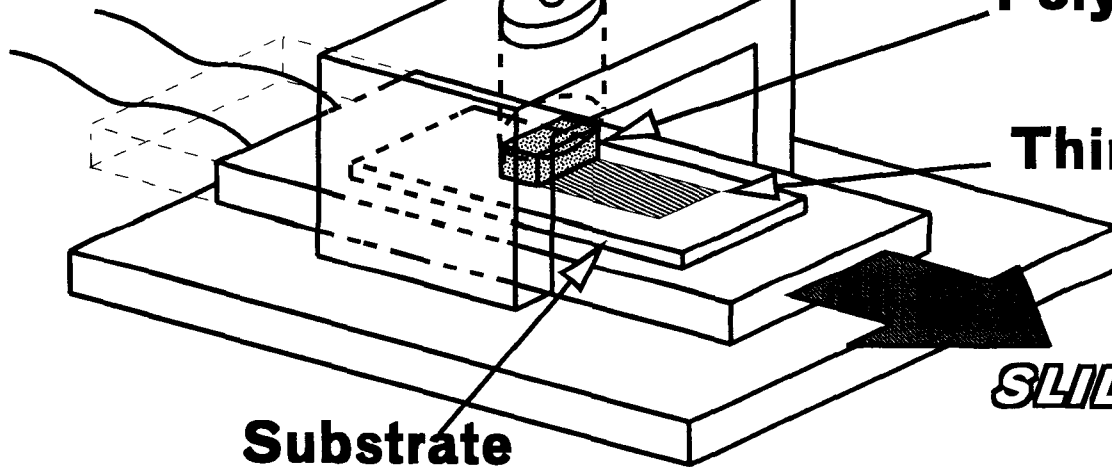
PDBS was synthesized as described in chapter 4. The friction transferred PDBS film was prepared as following. The polymer block was made by press with about 235MPa under vacuum. Figure 5-1 is a schematic drawing of an apparatus for the friction transfer. The polymer was put on the substrates under a pressure by some weight, and the substrate was slid in one direction. Typically, the weight was 3200g and the contact area of the polymer with the substrate was 0.665mm^2 , resulting the pressure of about 5 MPa. The temperature of the substrate was kept at 100°C during the procedure. The fused silica (quartz) and glass slide were used for substrate and they were used after dipping in *n*-hexane for washing the face.

5-2-2. Energy-Dispersive Total Reflection X-ray Diffraction

PRESS



Temp.Control



Polymer

Thin Film

SLIDE

Substrate

Figure 5-1. Schematic diagram of the equipment used for the friction transfer.

The principal of total X-ray diffractometry is briefly described^{3, 6)}. Figure 5-2 shows a schematic picture of incident and reflected X-rays from a thin film on a substrate. When the glancing angle of the incident X-rays, α , is very small, the X-rays should be totally reflected at the surface of materials. The critical X-ray energies for total reflections at interfaces between vacuum and organic thin films, and between thin films and substrates, $E_{c.v.o}$ and $E_{c.o.s}$, can be expressed, respectively, by

$$E_{c.v.o} = \frac{hc}{a} \sqrt{\frac{e^2}{mc^2} \cdot \frac{n_{org}}{\pi}} \quad (5-1)$$

$$E_{c.o.s} = \frac{hc}{a} \sqrt{\frac{e^2}{mc^2} \cdot \frac{n_{sub} - n_{org}}{\pi}} \quad (5-2)$$

where e and m are the electronic charge and mass of the electron, c is the velocity of light in vacuum, h is Planck's constant and n_{org} and n_{sub} are the number densities of electrons in thin films and substrate, respectively.

When $E_{c.o.s}$ is larger than $E_{c.v.o}$, the incident X-rays with energy E , which is in the range of $E_{c.v.o} < E < E_{c.o.s}$ pass through the organic layer and then are totally reflected at the surface of the substrate.

White X-rays *i. e.* non-monochromatized X-rays are used. With the fixed diffraction angle, the diffracted X-rays were recorded as an energy spectrum instead of scanning the diffraction angle. From the Bragg's equation, the relation between the lattice spacing of hkl reflection, d_{hkl} and the energy of diffracted X-ray, E_{hkl} can be represented as following:

$$E_{hkl} = hcn / 2d_{hkl} \sin \theta, \quad (5-3)$$

where n is the order of reflection and θ is the Bragg angle. If the energies of the diffracted X-rays E_{hkl} are selected the value to be

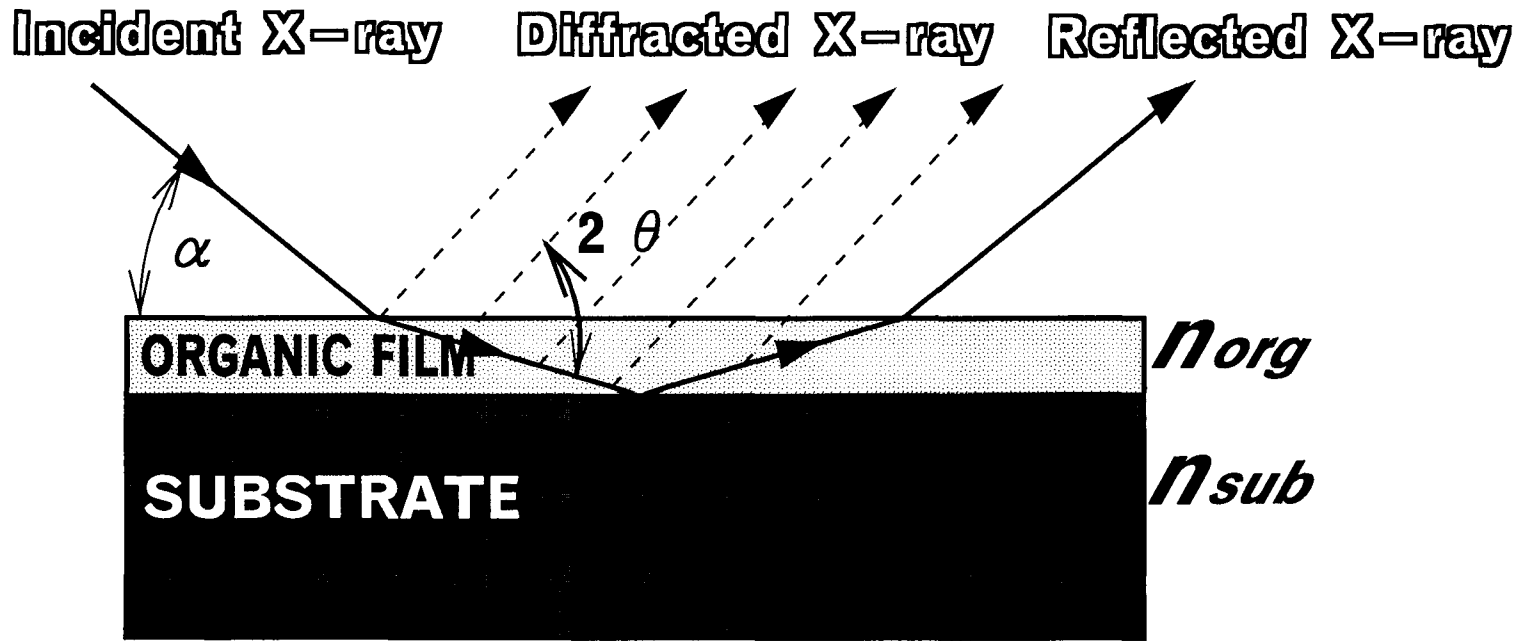


Figure 5-2. Principal of total reflection on the boundary of thin film and substrate

between $E_{c. \nu o}$ and $E_{c. o s}$, only a diffraction profile of the thin film can be obtained without the obstructing X-rays scattered by the substrate.

The TRXD system was designed on the basis of the previous instruments developed by Matsushige's group^{3, 5, 6)}, and was constructed by Rigaku Co. Ltd. Figure 5-3 shows a photograph of the TRXD system used here. The white X-rays generated by a molybdenum (Mo) target was used as incident X-rays. Typically, incident X-rays were set up at a glancing angle of about 0.1° . The incident X-rays were collimated by a Soller slit with a divergent angle of 0.2° . The diffracted X-rays passed through a Soller slit with a divergent angle of 0.2° and detected by a pure germanium (Ge) solid state detector (SSD) (Canberra 7935-2/S), which is an energy dispersive detector. The signals detected by the SSD were converted to the energy spectra through a multichannel-analyzer (Rigaku MCA2), and then the digital data of spectra were stored and analyzed on a workstation (Hewlett-Packard Apollo 9000) with RINT 2000 system (Rigaku).

The schematic diagram of TRXD geometry is illustrated in Figure 5-4. In order to carry out the both of vertical- and parallel-type measurements, the SSD can be moved in the two directions so that the diffraction angle can be changed. In the vertical-type measurements, one can detect the reflection with a scattering vector normal to the plane of the substrate, *i. e.* the layer structure. In the parallel-type measurements, the reflection with a scattering vector in the plane of substrate can be observed. On the parallel-type measurements, the orientation and its distribution of the in-plane structure can be analyzed by azimuthal rotation of the sample.

In unique performance of this TRXD system, the comparison

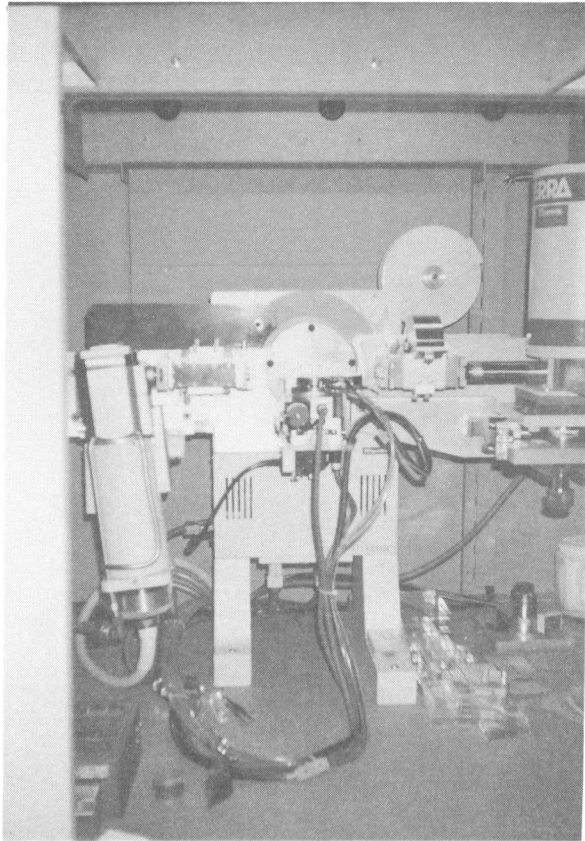


Figure 5-3. A Photograph of the TRXD system.

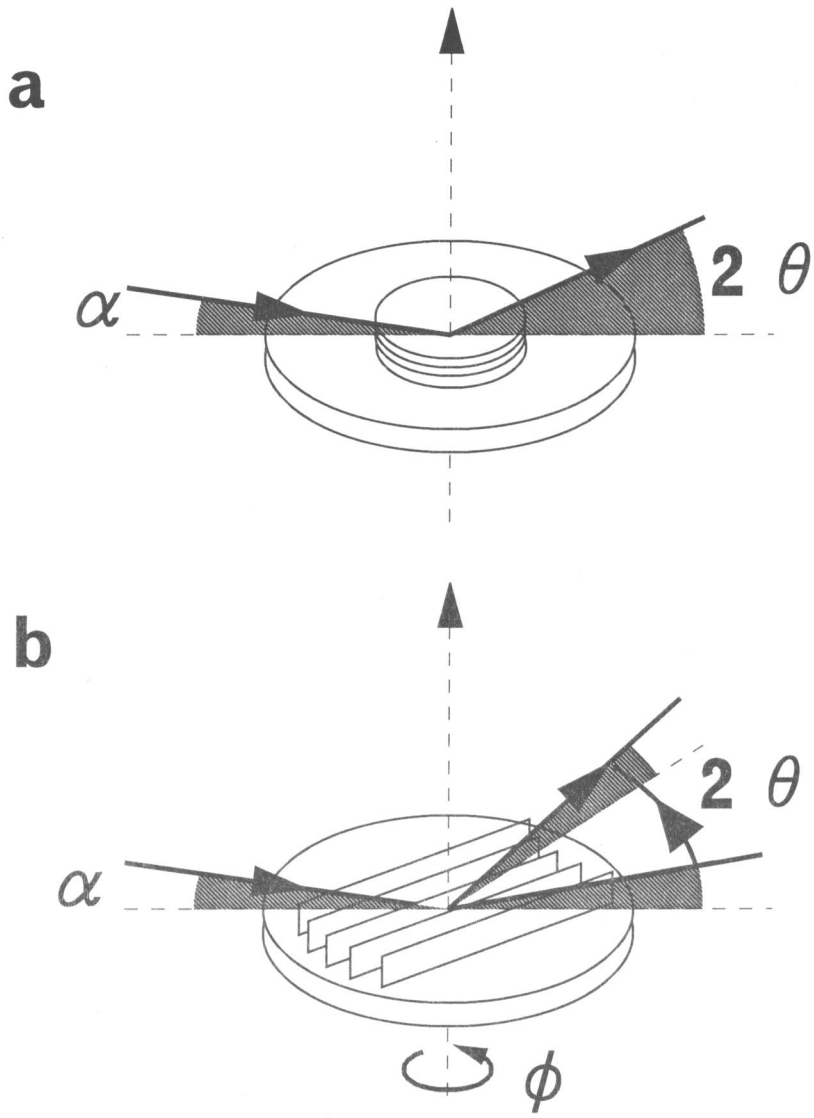


Figure 5-4. Two geometries of TRXD system for (a) vertical-type and (b) parallel-type.

between the diffraction patterns in vertical and parallel-type geometries reveals the orientation of crystals relative to the film plane. The parallel-type measurements enable us to easily evaluate the orientation in the film plane. It is difficult to obtain the information by the ordinary X-ray diffraction.

5-3. Results and Discussion

It was reported that PDBS was crystallized in an orthorhombic (orthohexagonal) unit cell with dimensions, $a = 1.284\text{nm}$, $b = 2.224\text{nm}$ and c (fiber axis) $= 1.39\text{nm}$ ⁹⁾. Figure 5-5 shows the vertical-type and parallel-type TRXD profiles of the PDBS film. A peak at 13.7keV can be seen in the profile, which is considered to be a diffraction peak from the PDBS sample. This diffraction peak is shown to correspond to a lattice spacing of 1.08nm, as calculated from the equation (5-3) with the diffraction angle, $2\theta = 4.8^\circ$. It can be indexed to the 110 reflection of PDBS, which is the strongest reflection in the diffraction pattern from the powder specimen. This equatorial reflection, the 110, can be observed in both geometries. This suggests that PDBS molecules lay down parallel on the substrate plane. This is consistent with the UV spectroscopic study revealed that PDBS molecular chains aligned in the sliding direction in chapter 4.

It seems that the diffraction patterns in both geometries are essentially similar to each other. This suggests that the film has a uniaxial orientation. The conformation of PDBS backbone was reported to be 7/3 helix^{9, 10)}, and the shape of PDBS molecule can be regarded as a cylinder. Therefore, it is reasonable to consider that PDBS in the film should readily have a uniaxial oriented, neither 2 nor 3-dimensional one. This

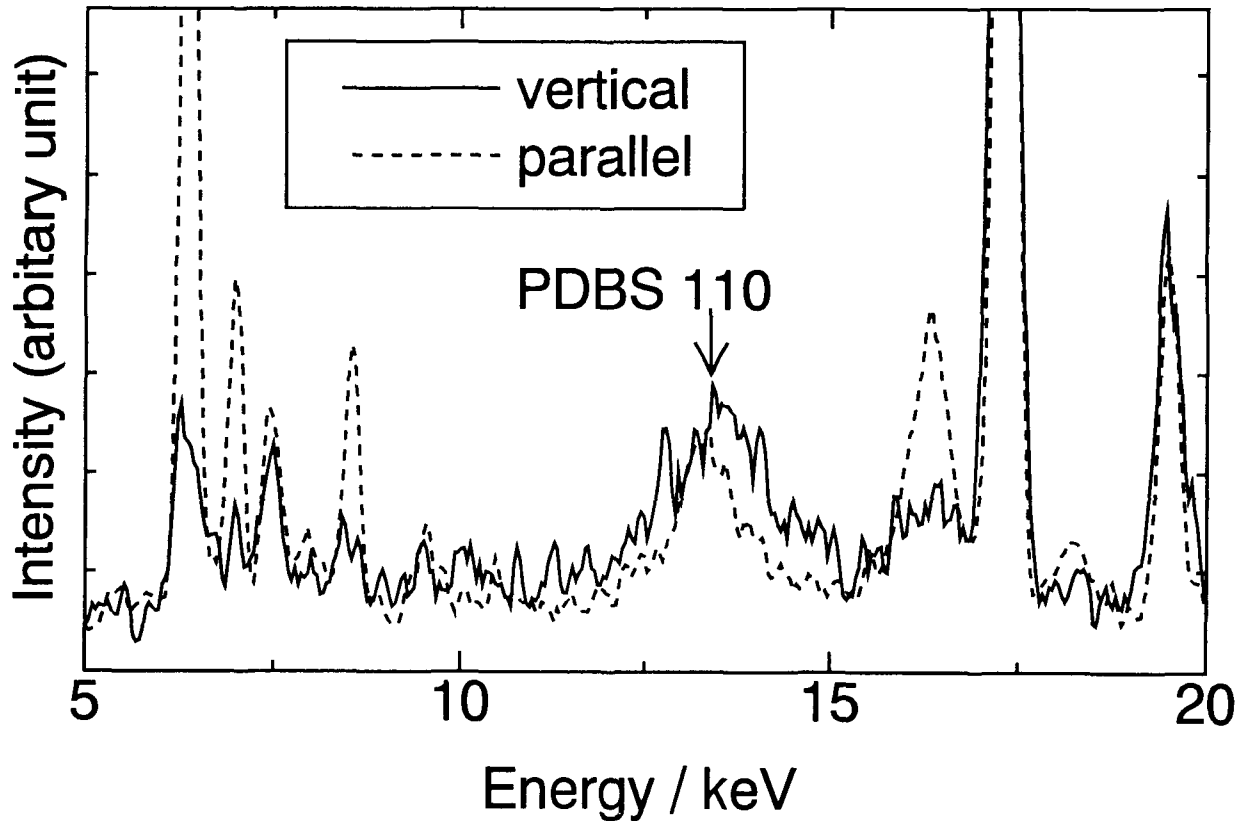


Figure 5-5. X-ray diffraction patterns of PDBS film on glass substrate measured by the parallel-type TRXD system and vertical-type one. Some peaks in the range of 15-20 keV are assigned to MoK radiation and their Compton scattering. Some peaks below 10keV came from fluorescences of metal elements of the slit system.

uniaxial orientation was confirmed by a comparison between the powder diffraction and the symmetrical reflection X-ray diffraction of the film of PDBS.

In order to estimate the in-plane orientation, X-ray diffraction measurements were carried out with varying azimuthal angles. The azimuthal rotation angle was set to zero when the diffracting plane was normal to the sliding direction. Figure 5-6 shows a series of the TRXD profiles of the PDBS film observed at different azimuthal rotation angles (ϕ) (Figure 5-4). The intensity of the 110 reflection of PDBS depends on the rotation angle. Figure 5-7 shows the azimuthal rotation angular dependence of intensity of the 110 reflection. When the azimuthal rotation angle ϕ deviates, the intensity of the reflection decreases rapidly. This suggests that the fiber axis of PDBS crystallite is in the direction parallel to the sliding direction. The half width of distribution is found to be about 18° .

Alternatively, it is frequent to use the second and forth moment of the orientation distribution, which can be calculated from the angular dependent intensity of diffraction:

$$\langle \cos^2 \phi \rangle = \frac{\int_0^{\pi/2} I(\phi) \cos^2 \phi \sin \phi d\phi}{\int_0^{\pi/2} I(\phi) \sin \phi d\phi} \quad (5-4)$$

$$\langle \cos^4 \phi \rangle = \frac{\int_0^{\pi/2} I(\phi) \cos^4 \phi \sin \phi d\phi}{\int_0^{\pi/2} I(\phi) \sin \phi d\phi} \quad (5-5)$$

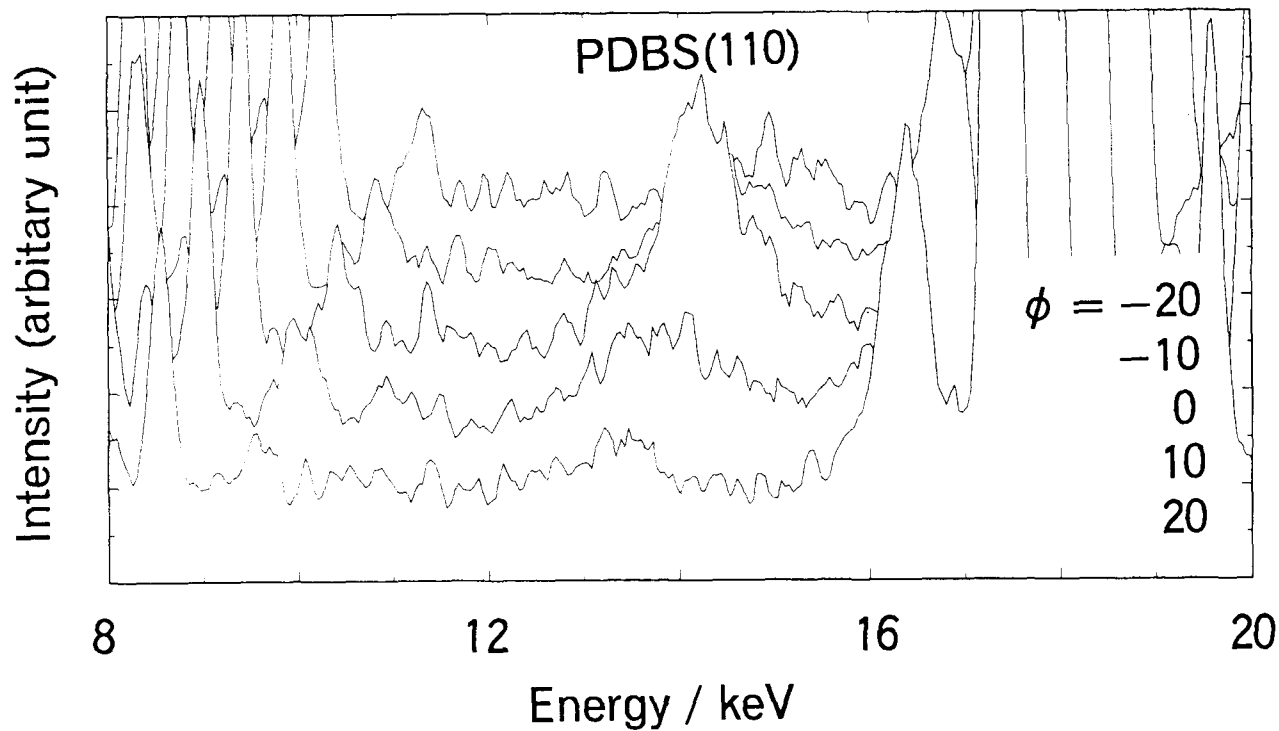


Figure 5-6. Diffraction patterns of PDBS observed at different azimuthal rotational angles.

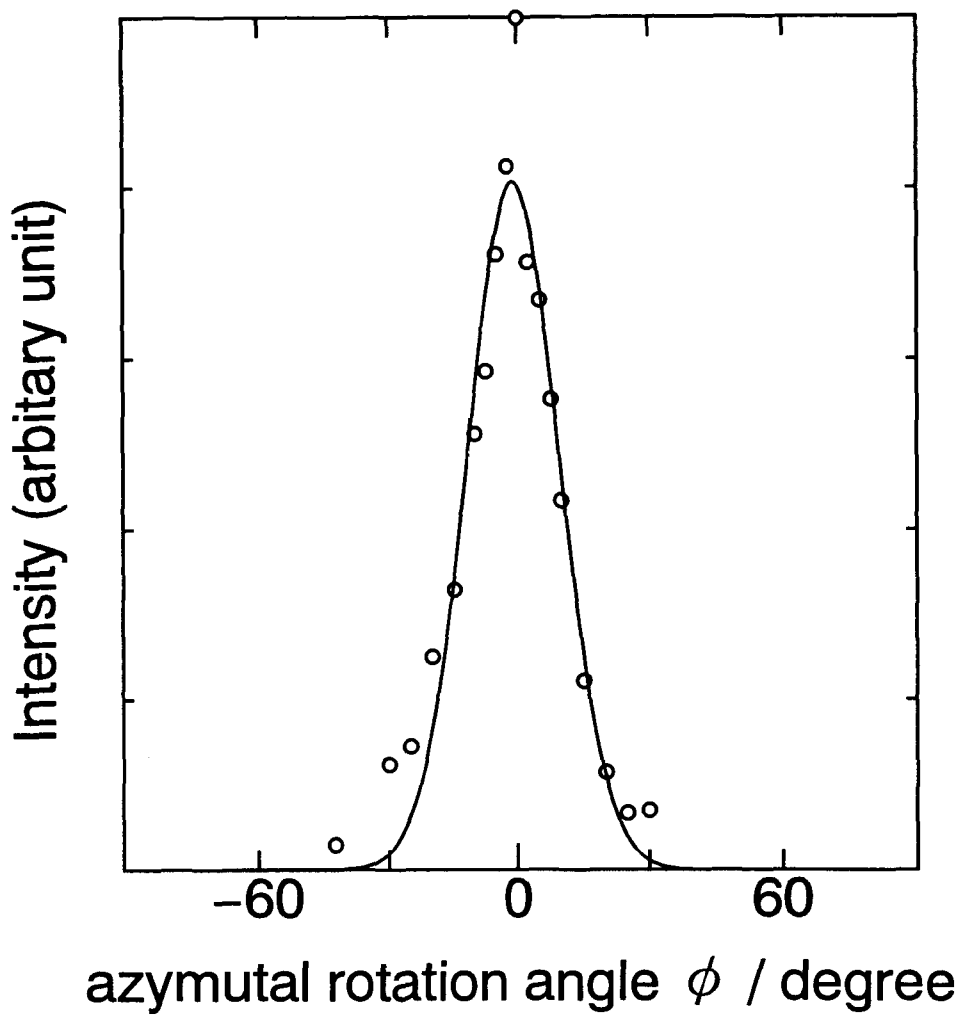


Figure 5-7. Azimuthal rotational angular variation in intensity of PDBS 110 reflection.

where $I(\phi)$ presents the intensity of the reflection at the azimuthal angle ϕ .

These values may be compared with those obtained by other measurements, *e. g.* the polarized fluorescence spectroscopy. Because the $\sigma - \sigma^*$ transition responsible for the fluorescence is considered to be parallel to the helical axis of PDBS, the orientation can be evaluated by the polarized fluorescence. Figure 5-8 shows the polarized fluorescence spectra of the friction transferred PDBS film, for which X-ray diffraction was measured, with the optical geometry of fluorescence measurements shown. The intensity of fluorescence spectrum measured with a polarizer along the i -axis and an analyzer along the j -axis is denoted by I_{ij} ($i, j = X, Y, Z$). The second and fourth moment of orientation distribution can be calculated by:

$$\langle \cos^2 \phi \rangle = (I_{zz} + 2I_{zx}) / ((8/3)I_{xx} + 4I_{zx} + I_{zz}), \quad (5-5)$$

$$\langle \cos^4 \phi \rangle = I_{zz} / ((8/3)I_{xx} + 4I_{zx} + I_{zz}). \quad (5-6)$$

The estimated moments of orientation distribution are listed in Table 5-1.

The moments calculated from the fluorescence are smaller than those from the TRXD measurements. It may be probable that the orientation state was not so properly evaluated from the fluorescence because any energy transfer in the photoluminescence would lower the moments. On the other hand, because X-ray diffraction detects only the orientation state of crystalline parts of the sample, the degree of orientation would be overestimated.

5-4. Conclusion

The oriented thin film of PDBS friction transferred was characterized by the TRXD method. The PDBS film was found to be uniaxially oriented.

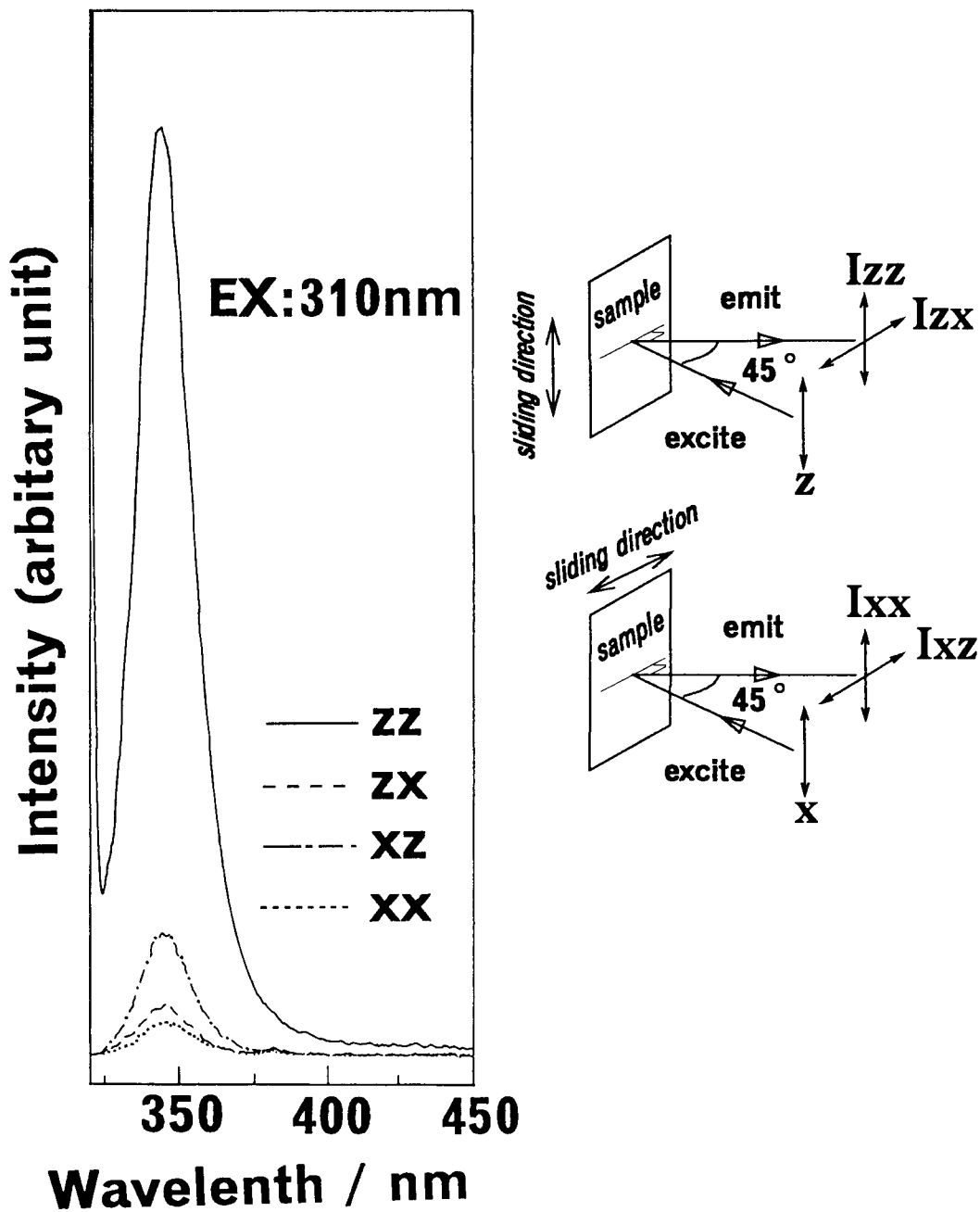


Figure 5-8. Polarized fluorescence spectra of PDBS thin films with excitation at 310nm and its experimental geometry.

Table 5-1. The second and fourth moment of orientation

method	$\langle \cos^2 \phi \rangle$	$\langle \cos^4 \phi \rangle$
TRXD	0.906	0.828
fluorescence	0.804	0.668

The orientation distribution was evaluated by the TRXD method and its width of distribution was found to be about 18° . It has been confirmed that the TRXD method is very effective for the characterization of the friction transferred thin films polysilanes.

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Chapter 6

Structural Characterization of Langmuir–Blodgett Films of Amphiphilic Polysilanes

6– 1. Introduction

In the general introduction, we pointed out the availability of Langmuir–Blodgett (LB) technique to prepare the highly ordered thin films of polysilanes in addition to the friction transfer method. In this chapter, we applied the characterization methods, which were confirmed to be useful for the friction transferred films, to the structure–controlled polysilane film prepared by the LB method.

Generally speaking, however, the LB investigation of ordinary alkyl– and aryl–substituted polysilanes is difficult due to lack of hydrophilicity for interaction with water surface. The following research groups have circumvented their difficulty by using chemically functionalized polysilanes.

Embs *et al.*¹⁾ first reported LB work on polysilanes having bis(butyloxyphenyl) substituents that generate stiff backbones to form a rodlike structure. With their polysilanes, the ether linkage was found to be essential for spreading as a monolayer on the water subphase. Due to the stiffness of these material, highly oriented LB films were generated with their backbone aligned parallel to the dipping direction. Neher *et al.*²⁾ have described the evaluation of non–linear optical properties (third harmonic generation) of these highly oriented LB multilayers.

Hayase's group^{3, 4)} synthesized polysilanes bearing a phenol group in the substituent that are well suited for LB film preparation. Introduction of the phenol moiety was achieved by protection with a

trialkylsilyl group during the Wurtz-type condensation polymerization. Some of their polysilanes were found to form highly in-plane oriented LB films, and the orientational order was discussed on the basis of the polarized fluorescence data⁵⁾. More recently, hydroxyalkyl- and alkoxyalkyl-substituted polysilanes have been exploited⁶⁾, and the anisotropy of the thermochromism with regard to the dipping direction was observed in the LB films of a poly[bis(alkoxylalkyl)silane].

Seki *et al.*⁷⁻⁹⁾ have focused their efforts onto LB investigation using ionic polysilanes which bear ammonium substituents. Their experiments have revealed that the polysilanes with a long alkyl ammonium moiety can form a stable monolayer on water that is readily transferred onto a solid substrate by the LB method. Moreover, they found a UV absorption spectral shift of a monolayer on water subphase as a function of the area in the monolayer per Si unit⁷⁾. The $\sigma - \sigma^*$ absorption band around 300nm exhibited the clear continuous blue-shift as the monolayer area was reduced. It was explained in term of the destruction of σ -conjugation by the bidimensional pressure. Another type of polysilane LB films was prepared by Seki *et al.* from a water-soluble polysilane when ion-complexed with an arachidic acid monolayer at the air-water interface¹⁰⁾. Thus it is interesting to examine the structure of film transferred from an air-water interface by the LB technique.

In this chapter, the structure of the LB films of the polysilanes bearing the amphiphilic ammonium group was characterized by UV and IR spectroscopy and X-ray diffraction. The UV and IR spectroscopies reveal the main chain structure and the side chains, respectively, and X-ray diffraction gives the layer structure.

6-2. Experimental

6-2-1. Amphiphilic Polysilanes and its LB Films

The molecular structure of the amphiphilic polysilanes used in this study is shown in Scheme 6-1. These polysilanes were synthesized by Dr. Seki⁷⁻⁹). The starting polysilanes were synthesized by the conventional Wurtz-type coupling. The functionalization process is shown in Scheme 6-2.

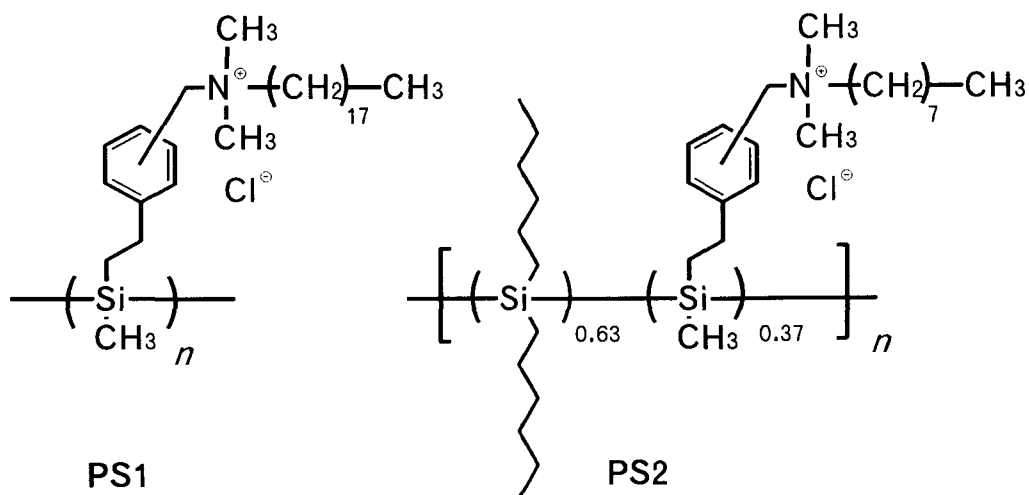
The LB films of the amphiphilic polysilanes were prepared by Dr. Seki. The amphiphilic polysilanes were spread from chloroform solution (ca. 1×10^{-3} unit mol dm⁻³) on Lauda MGW film balance filled distilled water under dim red light. For the LB deposition, the monolayer compressed at a given surface pressure was transferred onto the glass slide by the vertical dipping technique in the Y mode. (The depositions occurs in both dipping procedure, up and down.)

6-2-2. Characterization

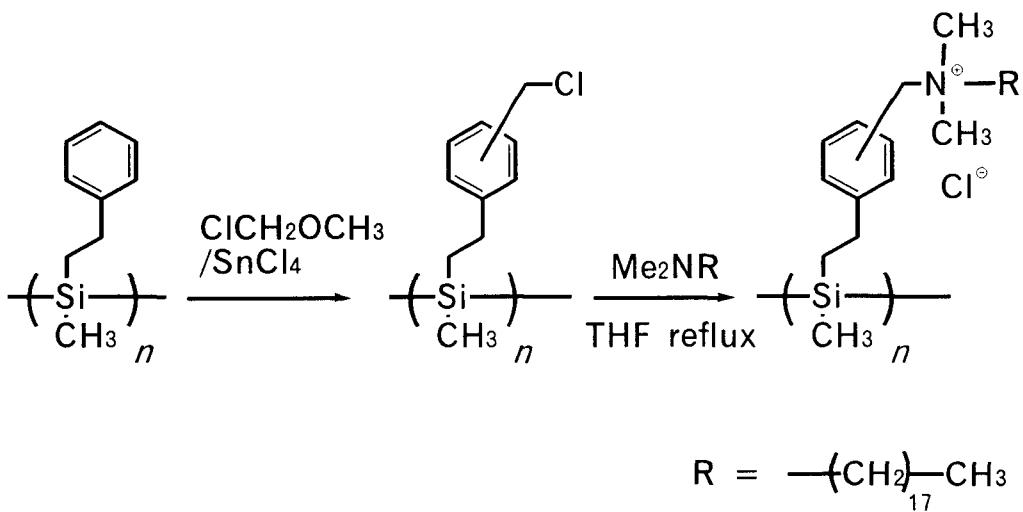
UV absorption and dichroism experiments of LB films were carried out on a JASCO HSSP-3 spectrophotometer equipped with a polarizer.

Transmission IR experiments were performed with a Perkin-Elmer 1800 instrument at room temperature. Twenty scans at the resolution of 2.0cm⁻¹ were collected and averaged. For the out-of-plane hydrocarbon orientation, an angle-dependent absorption spectrum was measured with a tilting apparatus attachment. The tilting angles were corrected by refractive index of the films.

X-ray diffractometry was performed with a Rigaku RU-300 at room temperature. The specimens were scanned at 0.2° 2θ/min in the reflection geometry using CuKα radiation monochromatized by a



Scheme 6-1



Scheme 6-2

pyrolyzed graphite.

6-3. Results and Discussion

6-3-1. UV Spectroscopy

The transition moment of the first $\sigma - \sigma^*$ band around 300nm is parallel to the Si chain direction¹¹⁾. Therefore, the Si chain orientation is readily estimated by the polarized UV absorption spectroscopy. Figure 6-1 displays polarized UV absorption spectra of LB films of (a) nine-layered PS1 and (b) twenty one-layered PS2 deposited from the surface of NaClO₄ solution at 25 mN m⁻¹. The electric vector of polarized light in normal incidence was set parallel (solid curve) and perpendicular (dotted curve) to the dipping direction. The absorptivity of the $\sigma - \sigma^*$ band for both samples is larger when the polarization plane is parallel to the dipping direction, indicating that the polymer backbone preferentially aligns parallel to the dipping direction.

Figure 6-2 presents the dichroic ratio of the LB films as a function of the number of transferred layers. For both polymers, the in-plane dichroic ratio increased with the number of deposition up to *ca.* twenty layers and then saturated. From the dependence on the deposition number, the Si main chain is seemingly aligned by the flow orientation on the water surface as a consequence of the successive deposition process rather than the force field at the meniscus on the substrate¹²⁾. Agreement of the UV spectra of the monolayer on the water subphase and those transferred onto the solid substrate⁷⁾ further supports this interpretation.

The dichroic ratio obtained is rather small for PS1 (*ca.* 1.1); however, it is improved with PS2 (>1.5 for the sufficiently large deposition number).

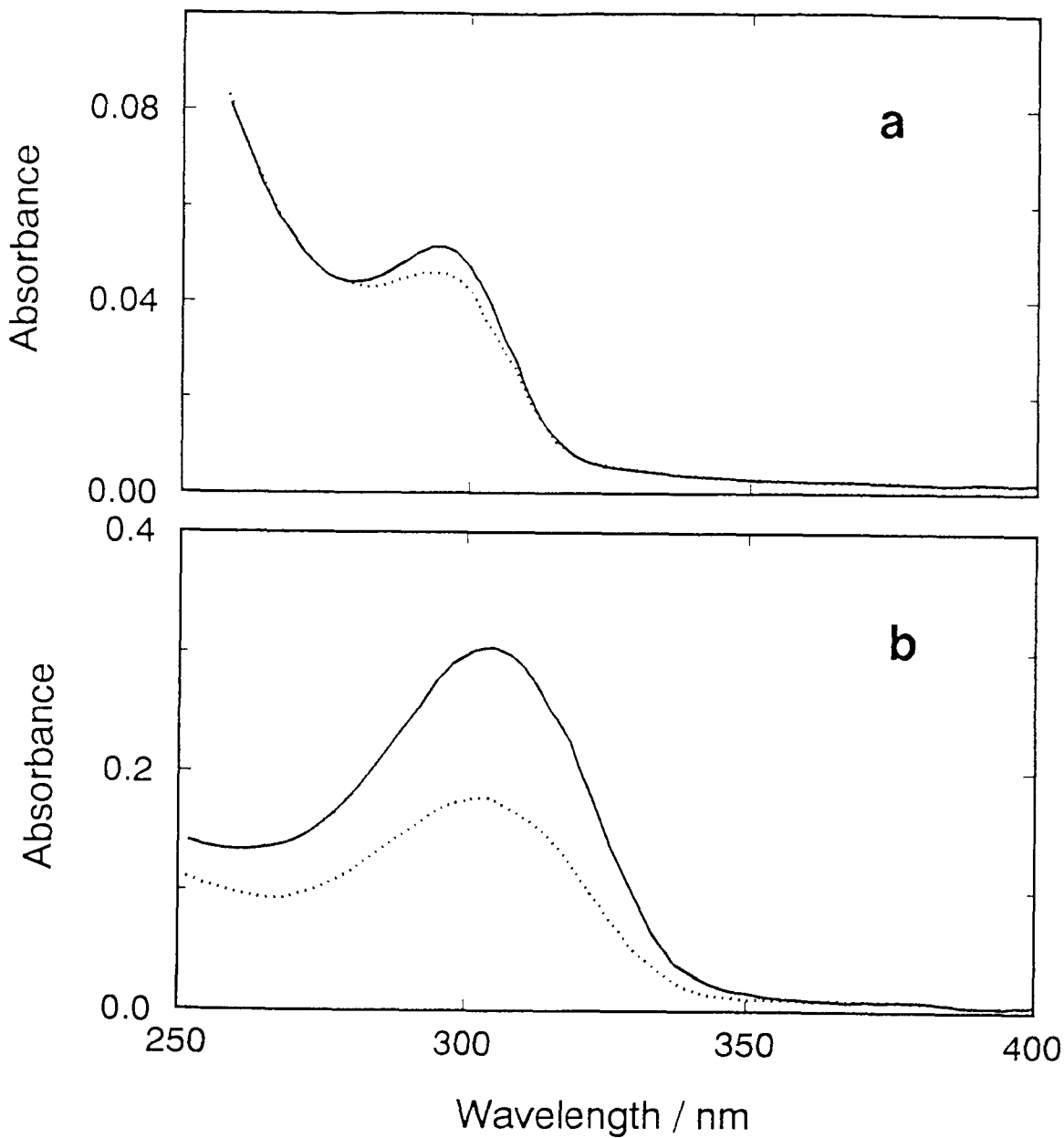


Figure 6-1. Polarized UV absorption spectra of LB films of nine-layered PS1 (a) and twenty one-layered PS2 (b) on both sides of quartz plate. Absorption spectra were taken in normal incidence with the linearly polarized light set parallel (solid line) and orthogonal (dotted line) to the dipping direction.

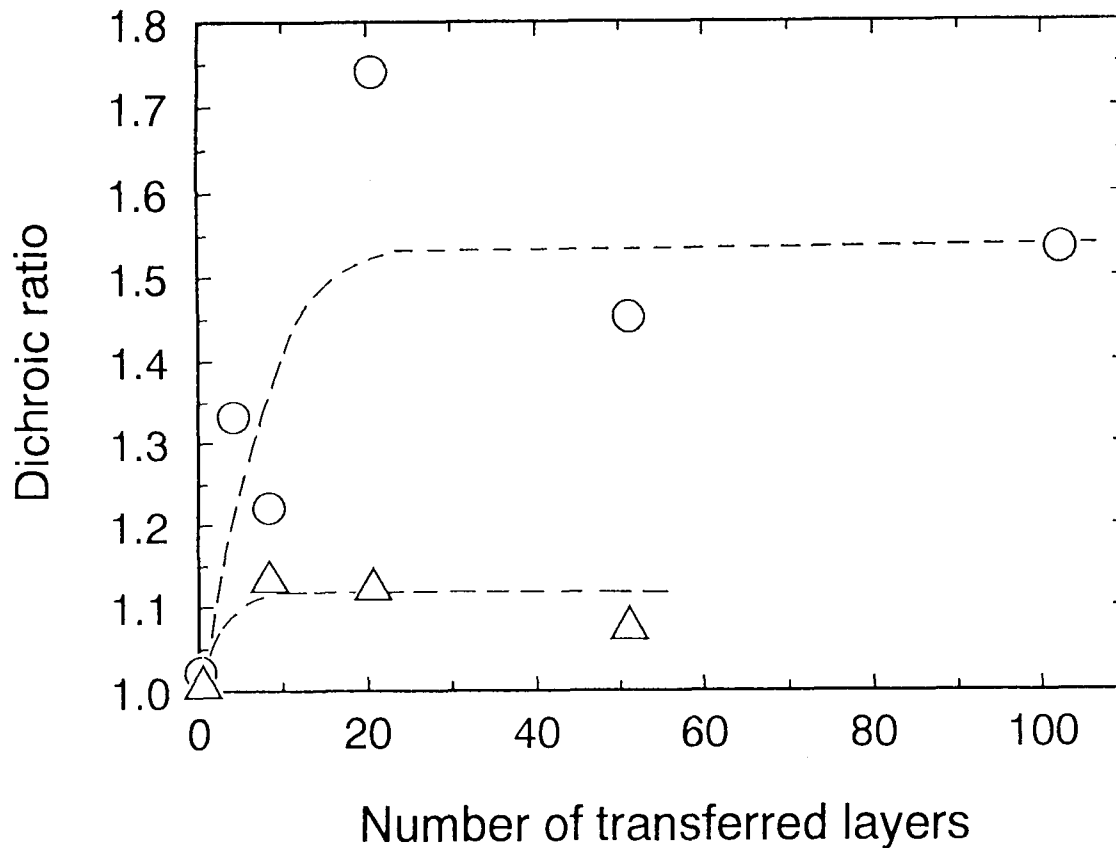


Figure 6-2. Dichroic ratios of the LB films due to the backbone orientation along the dipping direction as a function of the number of transferred layers. Triangles and circles are data for PS1 and PS2, respectively.

On the other hand, some of the other polysilane LB films reported by both Embs *et al.*¹⁾ and Kani *et al.*⁴⁻⁶⁾ are highly oriented in the dipping direction. Such LB films have a dichroic ratio of more than 3. It is assumed that high flexibility and lack of stereoregularity for these polysilanes are responsible for the rather poor orientation. The di-*n*-hexyl component introduced in PS2, which presumably increased the chain rigidity, improved the orientational order, but a clear explanation for it cannot be presented at the moment. It seems difficult to deduce definitive orienting factor from the molecular structure alone. In fact, Kani *et al.*⁴⁾ have demonstrated that a very subtle change in the substituent structure influences the orientational order of the materials in a crucial manner.

6-3-2. IR Spectroscopy

UV absorption measurements provide information only about the Si backbone. Structural information about the hydrocarbon side chain of the polymer can be obtained by IR spectroscopy.

Figure 6-3 shows a typical transmission IR spectra of CH₂ stretching bands of a forty three-layered LB film on glass slide of PS1. The intense bands at 2853cm⁻¹ and 2922cm⁻¹ are assigned to the CH₂ symmetric and antisymmetric stretching modes of the *n*-octadecyl hydrocarbon chain. It is known that the frequencies of the CH₂ stretching bands are sensitive to the conformation of the hydrocarbon chain¹³⁾; the low frequencies (2920 and 2850cm⁻¹) of this bands are characteristic of the highly ordered (*trans*-zigzag) alkyl chain, while their shifts to higher frequencies are indicative of increase in conformational disorder containing *gauche* conformers¹³⁾. Judging from the position of the observed CH₂

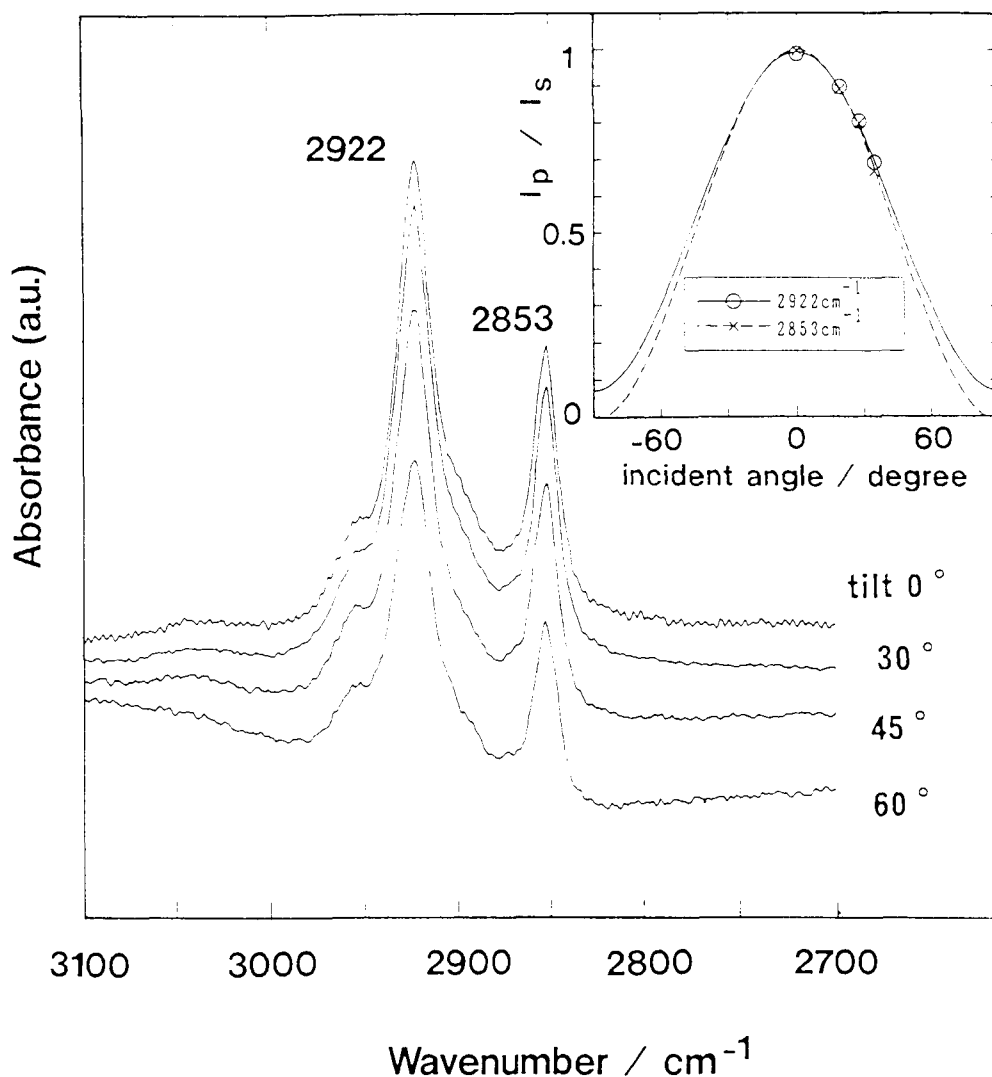


Figure 6-3. IR spectra in the region of CH₂ stretching bands of forty-three layered PS1. Out-of-plane tilt angles of the specimen are indicated in the spectra. The inset presents the relative band intensity observed at the four tilt angles. In the ordinate, the band intensity observed with *p*-polarized light (I_p) is divided by that with *s*-polarized light (I_s) for correction of observing area changes resulted from tilt arrangement. Note that the deviation of tilt angle in inset figure from the observing the spectrum stems from the correction using refractive indices of the polysilane.

symmetric band, 2853cm^{-1} , the hydrocarbon chain in the PS1 LB film is not ordered in perfectly *trans*-zigzag but contains considerable amounts of *gauche* conformers. The frequency value of this LB film is comparable to that of hydrocarbon chains in a lipid bilayer membrane in the fluid liquid crystalline state above the thermal phase transition temperature¹³⁾.

With regard to the out-of-plane orientation, measurements were made varying the tilt angles ranging from 0 to 60° from the surface normal. The larger tilt angle gave the smaller absorbance, indicating that the hydrocarbon side chain orients statistically perpendicular to the substrate plane. The inset of the Figure 6-3 depicts the relative absorption intensity against the tilt angle corrected for the refractive index of the polysilane for the 2922 and 2853cm^{-1} bands. The solid and dashed lines indicate cosine curves fitted to the four experimental points for the two bands respectively assuming the ideal normal orientation of the hydrocarbon chain. The hydrocarbon side chains form an aggregation state with only orientational order, like as a mesophase.

Measurements of polarized transmission IR were undertaken to evaluate the in-plane anisotropy of the hydrocarbon chain. However, practically no difference in the absorbance of the CH_2 stretching band was observed for the measurements at various in-plane angles. Thus, it is found that the in-plane orientation of the Si main chain as proved by the polarized UV absorption measurements is not reflected in the orientation of the side hydrocarbon chain.

6-3-3. X-ray Reflection

The structures of the LB layers of PS1 and PS2 were investigated by small angle X-ray diffraction in reflection geometry. The X-ray

reflection profile of both films exhibited two characteristic features, a periodical modulation of the reflectivity, the so-called Kiessig fringes and one Bragg peak. Typical profiles are shown in Figure 6-4 for the PS1 and PS2. The Kiessig fringes give the overall thickness of the films (l) and the Bragg peak provides the long spacing (d) of the layer structure. In this study, these parameters are calculated by simply applying the Bragg's law:

$$2d \sin \theta_{\text{Bragg}} = n_B \lambda \quad (6-1)$$

$$2l \sin \theta_{\text{Kiessig}} = n_K \lambda, \quad (6-2)$$

where θ_{Bragg} and θ_{Kiessig} are the diffraction angle for the Bragg peak and Kiessig fringes, respectively, n_B and n_K are the orders of reflection and λ is the wavelength of X-rays. The structural data obtained by this experiment are summarized in Table 6-1. The X-ray reflections at the wide angle range were also taken. However, no obvious structure except for the higher order reflection from layer spacing was observed in the profile, indicating that no appreciable crystalline structure exists within the LB films. Thus, the LB films are regarded as to be comprised of amorphous and homogeneous layers.

The layer spacing, d , should correspond to that of the double layer length because the LB films are constantly transferred in the Y mode and the number of the Kiessig fringes should be half the deposition number. The double layered structure is also confirmed by the following consideration. When the whole thickness of the film is divided by the layer spacing, the layer number will be obtained. This number agrees with half the deposition number.

The layer spacing, d is too large for a single layer structure and should indicate the length of the bilayer. If the side chain moiety of PS1 is

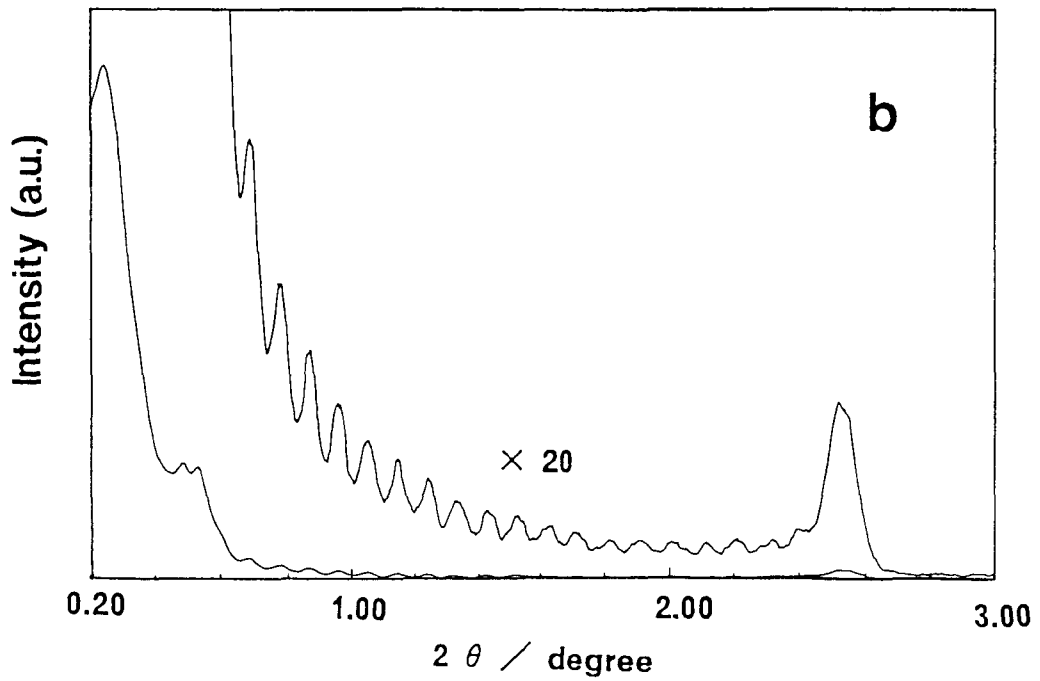
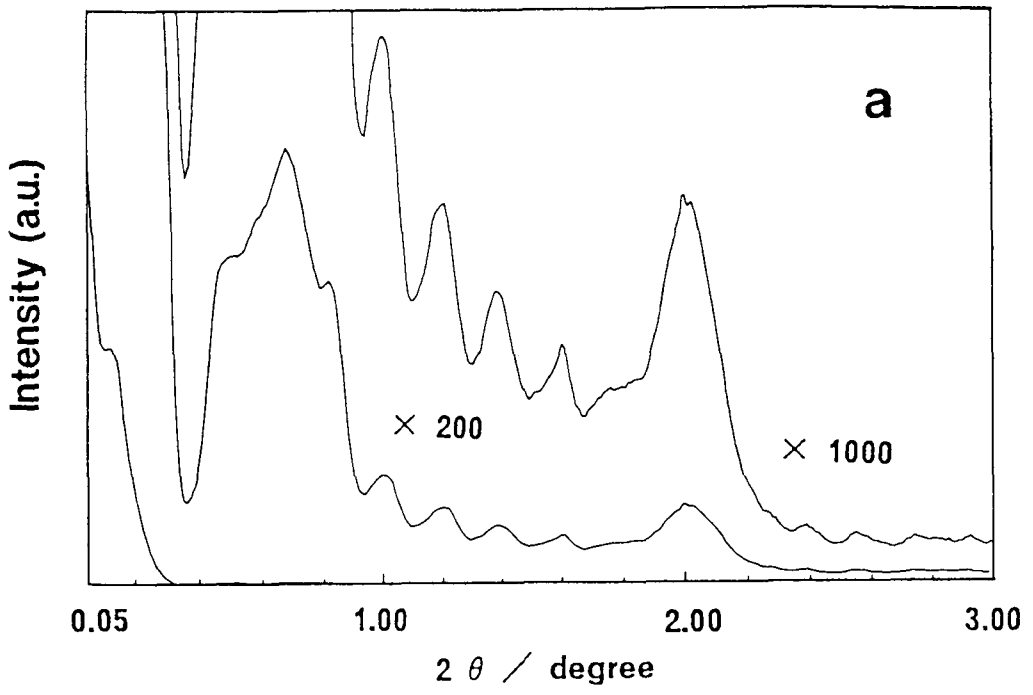


Figure 6-4. Small angle X-ray reflection from a twenty-one layered PS1 film (a) and a fifty-one layered PS2 LB films (b).

Table 6– 1. Layer structure evaluated by X– ray reflectivity.

polysilane	no. of layers	layer spacing spacing ^a / nm	film thickness ^b / nm
PS1	21	4.42	51.1
	43	4.31	90.4
PS2	51	3.50	92.0

Key; a: determined by Bragg peak, b: determined by Kiessig fringes.

assumed to be extended as *trans* zigzag conformers, the length from the skeletal silicon atom to the terminal methyl group of the hydrocarbon chain is *ca.* 3.5nm, giving the bilayer spacing of *ca.* 7nm. On the other hand, the length measured from the ammonium nitrogen to the terminal methyl group is *ca.* 2.5nm distance, giving the bilayer spacing of *ca.* 7nm. Considering a fairly perpendicular orientation of the side hydrocarbon chain to the substrate plane without tilting as indicated by the IR experiments, the observed spacing, $d = 4.3\text{--}4.4\text{nm}$, is a good agreement with the latter model (5nm). The shortening of the d value might result from involvement of *gauche* conformers and interdigitating of the hydrocarbon chains in a same layer. Thus, a picture can be presented in which the ammonium moieties are positioned at the interface of the double layers and the Si main chain is located at the middle. A plausible illustration for the double-layered structure of the PS1 LB film is drawn in Figure 6–5.

The long spacing of PS2, $d = 3.5\text{nm}$, is approximately 20% smaller than that of PS1, possibly due to the shorter chain length of the alkyl side chain. A quantitative argument for the layer length would be expected because there exists ambiguity in the main chain structure which is possibly composed of blockly segments.

6–4. Conclusion

This chapter has shown that the characterization techniques, which were used for the friction transferred films of polysilanes, can be applied also to the polysilane LB films.

It has been confirmed that the LB technique, as well as the friction transfer technique, can give also the method to orient the polysilanes in a definite manner. It provides quite homogeneous and defined

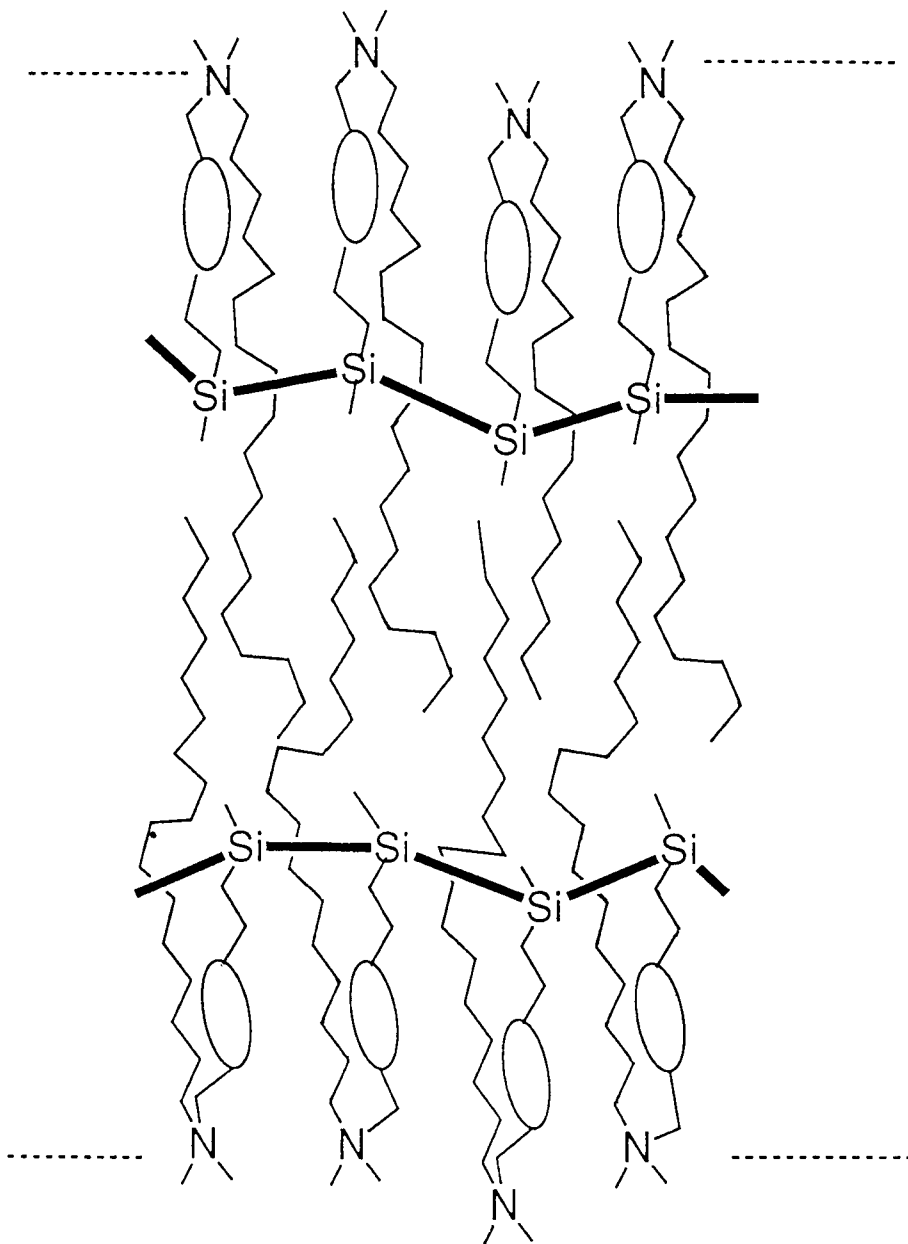


Figure 6–5. Schematic illustration of a plausible double layered structure of PS1 in the multilayered LB film.

layer-structured thin films of polysilanes. The ordered but amorphous structure can be called a kind of mesophase. The well-defined and non-crystalline film is expected to have different properties and different usages from the crystalline films for electronics and optics.

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Chapter 7

Friction Transferred Oriented Films of Poly(*p*-phenylene) and Homoepitaxially Polymerized Films on It

7-1. Introduction

It is very difficult to prepare functional films for such as polyacetylene, polyphenylene, polythiophene and polypyrrole having electrical and/or optical properties because of their insolubility. Such properties can be improved by aligning the main chains. For example, a stretched polyacetylene film shows an electric conductivity by 100 times higher than the unoriented one¹⁾. The chemical modification would make the polymers soluble to several solvents. However, most of modified polymers have lower performance than the parent polymers.

Recently, a sophisticated technique has been reported by Wittmann and Smith²⁾, in which a highly oriented film of poly(tetrafluoroethylene) has been mechanically transferred onto a smooth counterface by dragging the polymer. It is very interesting that a thin solid film is transferred onto the substrate directly from a solid polymer not via any liquid phase. Thus, it may be possible to prepare films from insoluble and infusible polymers by the technique. We have applied the friction transfer technique to a so-called intractable powder polymer, such as poly(dimethylsilylene) (chapter 2 and 3).

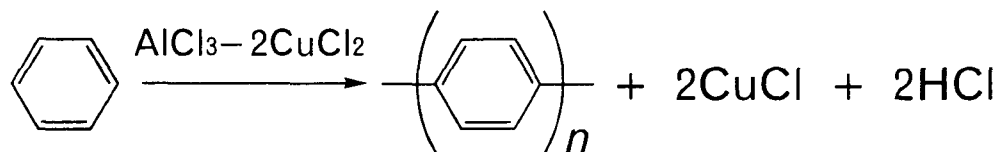
Although poly(*p*-phenylene) (PPP) is famous as an electric conducting polymer, it remains the difficulty in processing for further application. It has been obtained by chemical oxidation in the powder state, and by electro-oxidation in the film. There are a few reports on

the oriented PPP film. Tieke, *et al.* prepared an oriented film of PPP by applying the shearing stress while polymerization³⁾. Now, we attempted to prepare an oriented film of PPP by the friction transfer. However, the obtained film was very thin and ununiform. In order to increase the thickness and the uniformity of the film, PPP was newly polymerized on the friction transferred film.

7-2. Experimental

7-2-1. Materials

PPP was synthesized from benzene, aluminum chloride and copper (II) chloride by the method of Kovacic and Kyriakis⁴⁾. Elemental analysis showed that 3.7% of hydrogen had been substituted by chlorine.



7-2-2. Friction Transfer

The brown powder of PPP was compressed into a black-purple disk at about 235MPa. Sliding the PPP disk on the smooth counterface such as a quartz plate at a controlled temperature (160–235°C) afforded an oriented layer of the polymer on the surface.

7-2-3. Oriented Growth in Polymerization

The friction transferred PPP film on a substrate was put into the mixture of benzene, aluminum chloride and copper(II) chloride, and then polymerization was started by heating under nitrogen. When the substrate was picked up, a red-brown PPP film covered on the friction transferred

film. The polymerized film was dipped in benzene, boiling hydrochloric acid, and water, in that order, for washing off the catalysts and also the unoriented PPP.

7-2-4. Measurements

Transmission electron micrographs were taken by a Hitachi H-9000 with an acceleration voltage of 300 kV. The specimen for TEM was covered with carbon for reinforcement, separated from the substrate on water surface, and scooped up onto an electron microscopic grid.

A Tencor Alpha-step 300 profiler was used for the characterization of surface roughness and the estimation of thickness of the films (the stylus method).

UV, fluorescence and IR spectroscopic measurements were performed as the same manner described before (in Chapters 2 and 3).

The specimen transferred on a polycrystalline KBr disk substrate was used for IR measurements, and quartz substrates were used for UV and fluorescence spectroscopy.

The electronic conductivity was measured by two-electrode method with vacuum vapor deposited silver electrodes. The doping of PPP film on quartz substrate with antimony pentafluoride (SbF_5) and measurement were carried out under vacuum. Figure 7-1 illustrates the deposited Ag electrodes on the PPP film for the measurement of anisotropy in the electric conductivity.

7-3. Results and Discussion

7-3-1. Friction Transferred Film of PPP

When PPP disk was slid on the smooth substrates, such as quartz

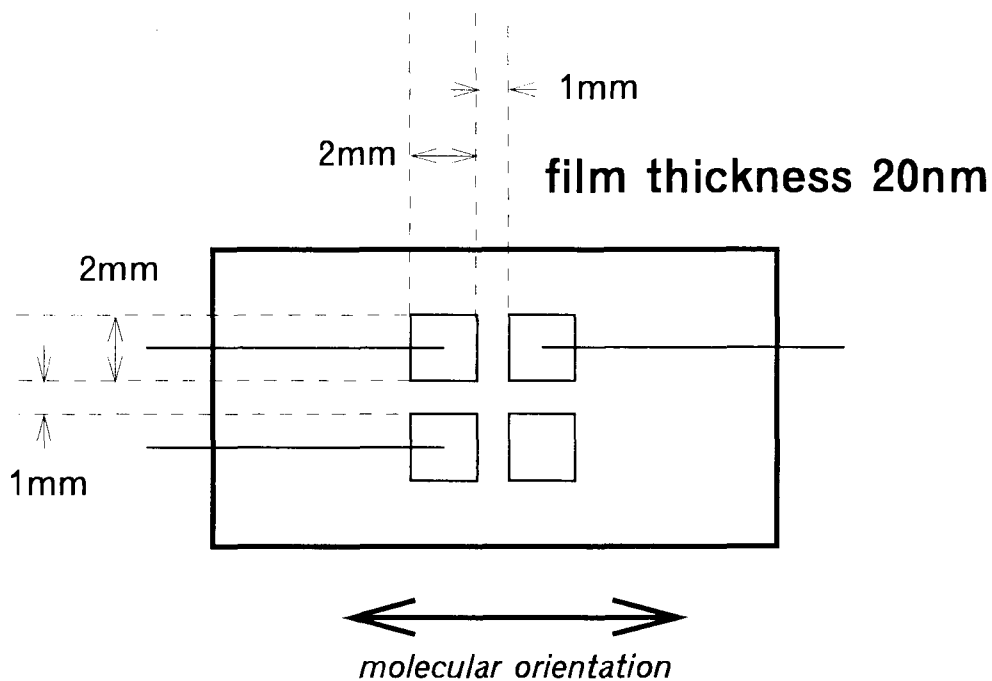


Figure 7-1. The arrangement of Ag electrodes deposited on the PPP film for measurements of anisotropy in the electric conduction.

plate, highly oriented layer was obtained on the surface of the substrates. The polymer layer could be transferred when the substrate temperature was higher than 160°C. A polarized light micrograph shows that the film of PPP is not uniform (Figure 7-2). The thickness of the film estimated by a stylus method was widespread between 10nm and 1 μm. The transmission electron micrograph also reveals the discontinuity of the film and very anisotropic morphology (Figure 7-3a). The electron diffraction pattern shows a fiber pattern (Figure 7-3b), suggesting that the film consists of oriented crystallites.

In order to evaluate the orientation of the friction transferred film, polarized UV spectra and IR spectra were measured. The PPP film has a broad peak at 389nm in the UV spectrum. The polarized spectra represents a large dichroism (Figure 7-4). The film absorbs only the parallel polarized light to the sliding direction. The polarized IR spectra also shows a dichroism for absorption bands at 1481, 1000, and 806cm⁻¹ (Figure 7-5). The bands are assigned to the C=C stretching, the C-H in-plane bending and the C-H out-of-plane bending, respectively. The bands at 1481 and 1000cm⁻¹ are found to be parallel and 806cm⁻¹ is perpendicular to the sliding direction. Therefore, PPP molecules are considered to be aligned in the sliding direction. Unlike the PDMS film, the degree of orientation of the PPP films was not found to depend upon the preparation temperature above 160°C.

The polarized fluorescence spectra of the friction transferred PPP is shown in Figure 7-6. Highly polarized light was emitted by the oriented PPP film, like as PDMS. It was reported that fluorescence of PPP powder synthesized by Kovacic's method is composed of two different bands, which is dominated by a broad structureless band at around 700nm and structured

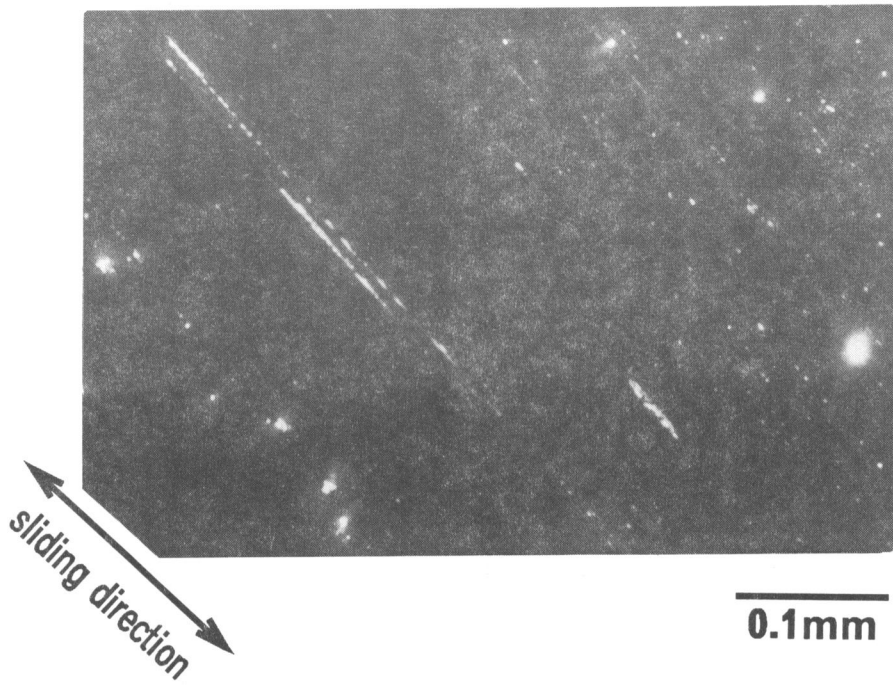


Figure 7-2. An optical micrograph of friction transferred PPP on quartz substrate prepared at 170°C with crossed polarizers.

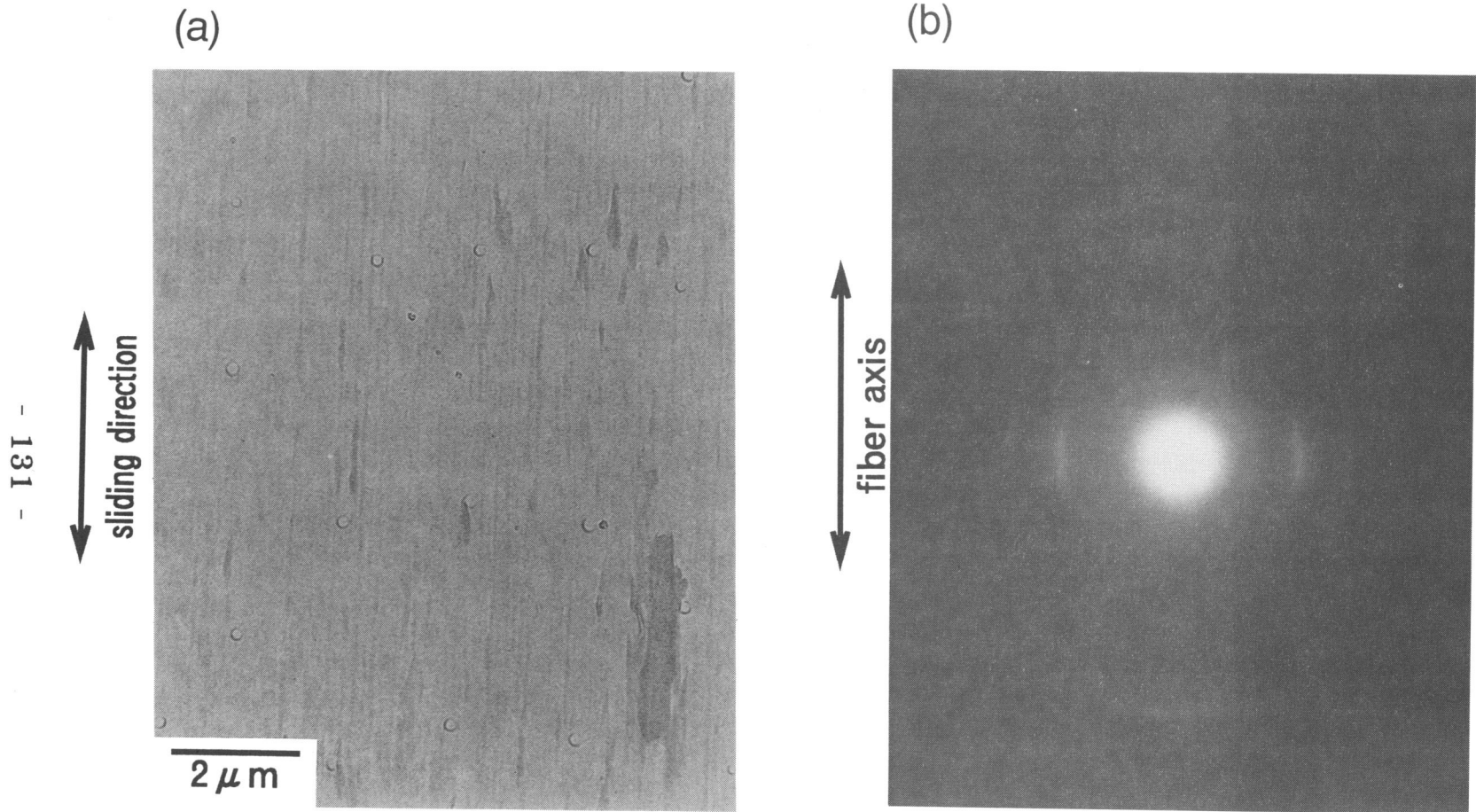


Figure 7-3. (a) An electron micrograph and (b) an electron diffraction pattern of friction transferred PPP on quartz

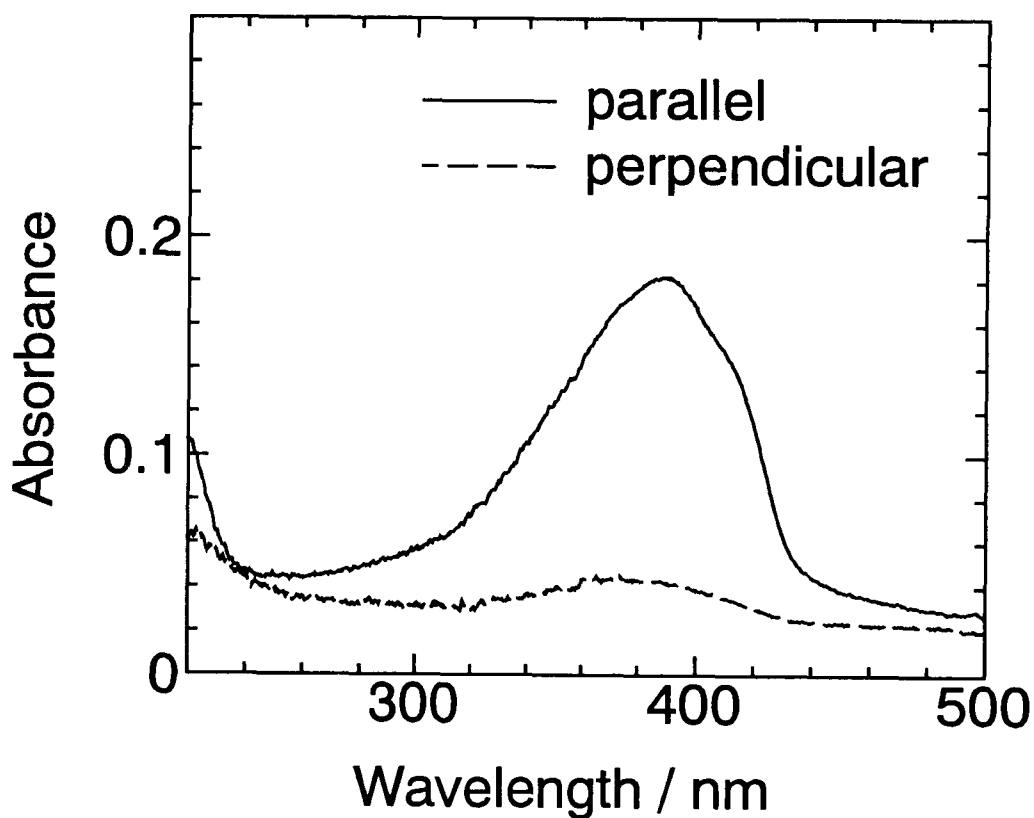


Figure 7-4. Polarized UV spectra of PPP film friction transferred. The solid and dashed lines represent the polarization perpendicular and parallel to the sliding direction, respectively.

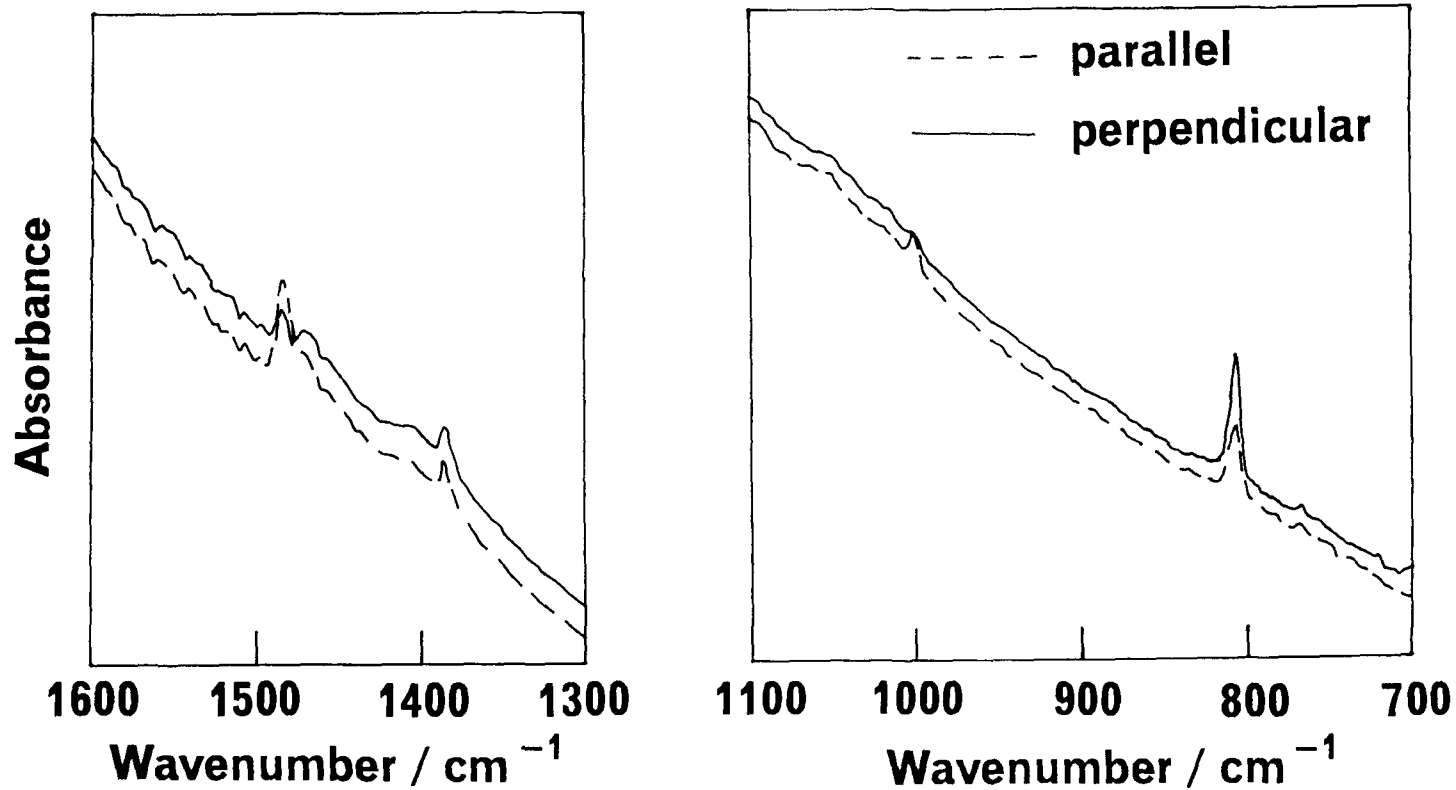


Figure 7-5. Polarized IR spectra of friction transferred film on KBr disk prepared at 179°C. The solid and dashed lines represent the polarization perpendicular and parallel to the sliding direction, respectively

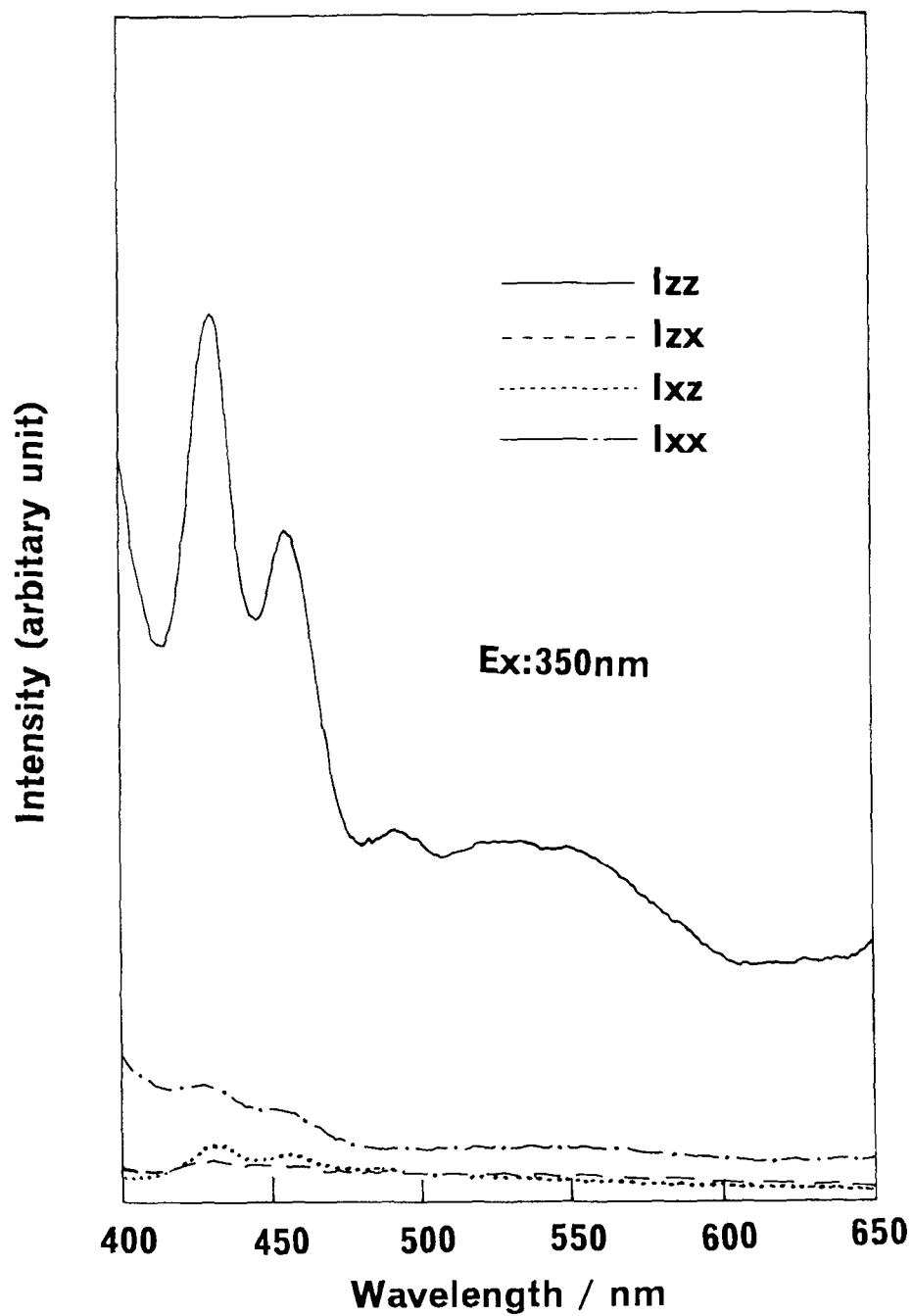


Figure 7-6. Polarized fluorescence spectra of friction transferred PPP film.

bands in the range of 400 to 500nm⁵⁾. The fluorescence spectra emitted from the film is composed of the same components previously reported. For all bands, the I_{zz} component of fluorescence is much stronger than the other components. Even when a non-polarized light excited the PPP film, it emitted a highly polarized light, whose electric vector was parallel to the sliding direction.

7-3-2. Oriented Growth in Polymerization

Several authors⁶⁾ reported that monomers epitaxially aligned on substrates were polymerized to highly ordered polymers. Recently, Sano *et al.*⁷⁻¹⁰⁾ obtained bidimensional crystalline monolayers of polymers epitaxially grown on the graphite substrates during polymerization. Wittmann and Smith²⁾ reported oriented polymerization of poly(*p*-xylylene) on friction transferred poly(tetrafluoroethylene). Now, we attempted homoepitaxial growth of PPP in polymerization. When the friction transferred PPP film was immersed into the reaction mixture, PPP was newly deposited on the friction transferred PPP substrate in polymerization. This film is more uniform than the friction transferred one as shown in Figure 7-7. The thickness of the polymerized film was ranging between 20nm and 5 μ m detected by the stylus method. The polarized UV spectra of the polymerized film is shown in Figure 7-8, comparing with the original spectra of the friction transferred film, which was used for the orienting substrate. It shows that the polymerized film is oriented. The degree of orientation of the polymerized film is lower than that of the original friction transferred film. However, the distinct dichroism of UV spectra remains even though the original spectra of the friction transferred film would be subtracted from the spectra of the

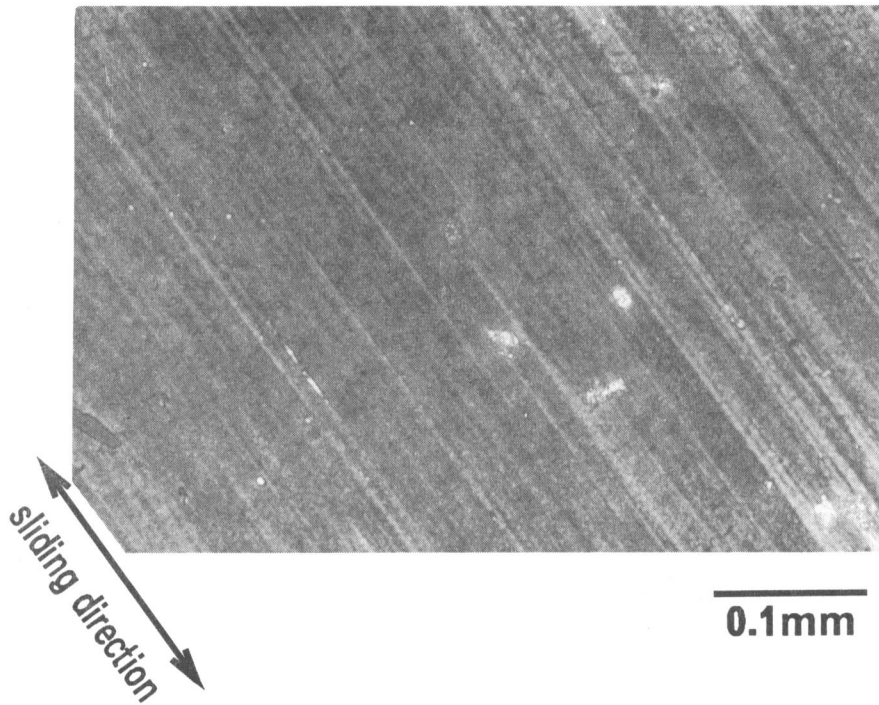


Figure 7-7. An optical micrograph of polymerized PPP film on friction transferred PPP with crossed polarizers.

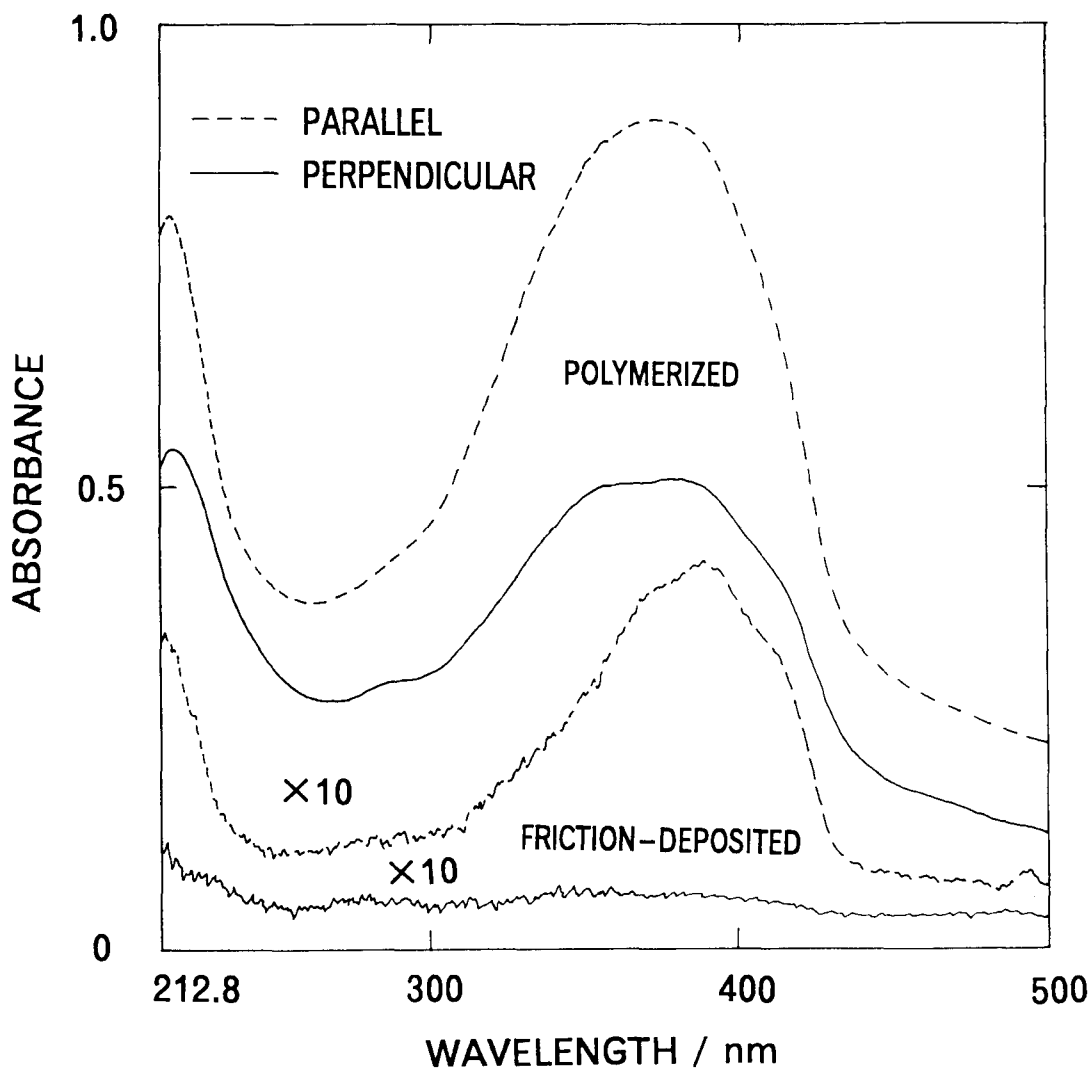


Figure 7-8. Polarized UV spectra of PPP film; friction transferred (lower $\times 10$) and oriented growing in polymerization (upper). The solid and dashed lines represent the polarization perpendicular and parallel to the sliding direction, respectively.

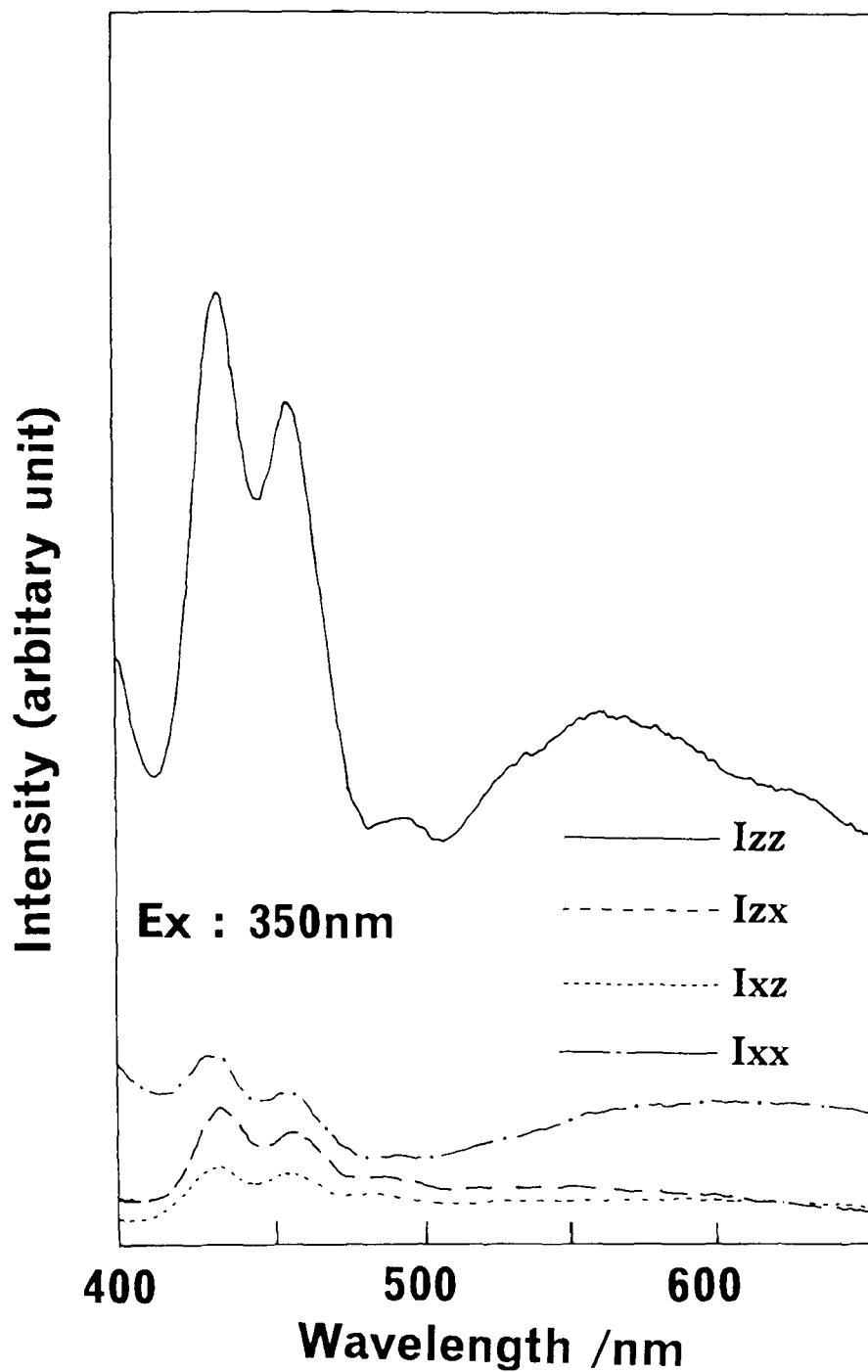


Figure 7-9. Polarized fluorescence spectra of the polymerized PPP film.

polymerized film. Therefore, the film newly deposited during polymerization is obviously oriented. As an absorption peak is blue-shifted, it is expected that the polymerized film has a smaller degree of polymerization than the powder specimen (Figure 7–8).

The polymerized film also showed a polarized photoluminescent character. The polarized fluorescence spectra are shown in Figure 7–9. The I_{zz} component of the fluorescence is stronger than the other components, like as the friction transferred film. Moreover, the polymerized film had an anisotropic electric conductivity when it was doped with SbF_5 . Along the direction of molecular chain, its conductivity was measured to be 5 Scm^{-1} . However, in the perpendicular direction, its conductivity was 0.005 Scm^{-1} .

7–4. Conclusion

The friction transfer technique has been found to be useful for preparation of the highly oriented PPP films. There is no dependence of the properties of films on preparation temperature. The film was not uniform but highly oriented so that the PPP molecules were parallel to the sliding direction. The benzene was homoepitaxially polymerized to the oriented and uniform PPP film on the friction transferred film. The oriented polymerized film had anisotropies in the optical and electric properties.

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Chapter 8

Summary and Conclusion

This thesis has dealt with the following subjects:

- 1) The preparation of highly oriented films of poly(dimethylsilylene) (PDMS) and other polysilanes by friction transfer. The technique was applied to also another intractable polymer, poly(*p*-phenylene).
- 2) Dependence of the structure and the surface morphology of films on the substrate temperature which is essentially important condition to prepare these thin films.
- 3) The molecular structure and the crystal structure of PDMS.
- 4) The higher-order structure of the oriented films of the polysilanes, which contain the friction transferred films and the Langmuir-Blodgett films.
- 5) Thermal phase transition behavior of the oriented thin films of PDMS and PDHS.

The main results and conclusions obtained are summarized as follows:

Chapter 2

PDMS could afford highly oriented films by friction transfer method. The molecular chain was found to be aligned along the sliding direction of the pellet sample. Uniformity and molecular orientation in the friction transferred film of PDMS strongly depended on the substrate temperature during deposition. As the substrate temperature increased in the range from 150 to 235°C, the more highly oriented films with uniform surface

were obtained. An extremely oriented and uniform film could be prepared by sliding the bulk sample on the substrate maintained above 210°C. The narrow molecular orientation distribution in the film deposited within these temperature ranges was confirmed. The film prepared at the higher temperature range also exhibited a higher conformational order. The highly oriented thin film had a larger absorbance of exciton band per Si unit than the poorly ordered films. The transferred films emitted the highly polarized fluorescence at 355nm with the electric vector of the light parallel to the sliding direction. The mechanism of the friction transfer of PDMS was found to relate well with the appearance the mobile phase (high temperature phase, phases II and III).

Chapter 3

The main chains in the friction transferred films of PDMS oriented along the sliding direction of sample. The molecular conformation of PDMS was found to be all-*trans*, and the crystal structure at ambient temperature was similar to that of the bulk sample in phase I. The crystallites were doubly oriented in the transferred film. The PDMS with (pseudo)orthorhombic crystal lattice was arranged so that the *a* axis should be vertical to the substrate face. The reversible solid state transition was also observed in the transferred film of PDMS like as the bulk sample. The orientation state in the transferred film was found to be perfectly preserved passing through the phase transition. It was resulted that the PDMS with all-*trans* conformation was not largely changed during the phase transition.

Chapter 4

Highly oriented films of several polysilanes such as PDMS, poly(diethylsilylene) (PDES), poly(di-*n*-butylsilylene) (PDBS), poly(di-*n*-hexylsilylene) (PDHS), and poly(methylphenylsilylene) (PMPS) could be obtained. The friction transfer method may be used for preparation of any of polysilanes. The polarized UV absorption spectra suggested that the chain axes of these friction transferred polysilanes were also aligned parallel to the sliding direction. Uniform films were obtained only for PDMS and PDES. Dependence of PDES films on the substrate temperature was analogous to the PDMS films. The deposition mechanism of PDMS and PDES might differ from that of PDBS, PDHS and PMPS. Like as the bulk sample, the reversible thermochromic transition was observed in the friction transferred film of PDHS with the orientation state almost kept. It was found that the highly oriented PDBS film can be obtained with preserving the helical conformation even after the friction transfer. In the case of PMPS, which had been believed to be amorphous, the crystallization induced by orienting was observed in the friction transferred film.

Chapter 5

It was established that total reflection X-ray diffraction (TRXD) method is very effective for the structural characterization of the oriented thin films of friction transferred polysilanes. The friction transferred PDBS film was found to be uniaxially oriented in the film. The orientation distribution in the substrate plane was evaluated by the TRXD method and its width of distribution was found to be about 18° , which was narrower than that estimated by polarized fluorescence spectroscopy.

Chapter 6

The characterization techniques, which were used for the friction transferred films of polysilanes, could be applied to the polysilane LB films.

When amphiphilic polysilanes bearing an ammonium moiety in side substituents were spread on air–water interface and transferred on the solid substrate, the LB films could be fabricated. The Si backbone was found to be preferentially oriented along the dipping direction possibly due to the flow orientation on the water surface. The hydrocarbon side chain oriented statistically along the direction perpendicular to the substrate plane, but randomly in the lateral direction of the plane. The side chain might not be crystallized in the LB films. The LB films were found to be composed of periodical double–layeres having a homogeneous and amorphous character.

Chapter 7

The friction transfer technique could be also applied to an insoluble polymer, poly(*p*-phenylene) (PPP), giving a highly oriented but ununiform film. There is no dependence of the properties of films on the preparation temperature. The PPP molecules were found to be aligned to the sliding direction. Moreover, the benzene could be homoepitaxially polymerized to form the oriented and uniform PPP film on the friction transferred film. The oriented polymerized film exhibited anisotropies in the optical and electric properties.

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This thesis shows that friction transfer technique is very effective for

preparing the highly oriented polysilane thin films which cannot be attained by any other method. This method is superior in terms of not only giving the excellently oriented film but also being applicable to many polysilanes.

Structural investigations of the polysilanes, especially intractable PDMS were performed by using these highly oriented specimens. We believe the highly oriented ultrathin films of the polysilanes prepared by using the friction transfer technique may be quite useful not only for the precise structural analysis but also for getting the information of the physical properties of the polysilanes.

List of Publications

The contents of this thesis have been and will be published in the following papers.

- 1) Highly Oriented Films of Poly(dimethylsilylene) by friction deposition.
N. Tanigaki, K. Yase, A. Kaito and K. Ueno, *Polymer*, **36**, 2477 (1995).
- 2) Oriented Films of Poly(*p*-phenylene) by Friction–Deposition and Oriented Growth in Polymerization.
N. Tanigaki, K. Yase and A. Kaito, *Mol. Cryst. Liq. Cryst.*, **267**, 335 (1995).
- 3) Langmuir–Blodgett Films of Amphiphilic Polysilanes Bearing a Pendant Ammonium Moiety.
T. Seki, N. Tanigaki, K. Yase, A. Kaito, T. Tamaki, K. Ueno and Y. Tanaka, *Macromolecules*, **28**, 5609 (1995).
- 4) Oriented Films of Polysilanes Prepared by Friction–Deposition.
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- 7) Oriented Films of Insoluble Polymer by Friction.

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7) Molecular Orientation and Periodical Structure of Vacuum– Deposited
Long– Chain Molecules.

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8) Direct Measurements of Organic Molecular Beams by Q– mass.

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