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Polymer 40 (1999) 5857–5863

polymer

Orientation induced chromism in poly(methylhexysilane)

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Received 17 August 1998; received in revised form 20 October 1998; accepted 11 November 1998

Abstract

The orientation-induced conformational transition was studied on thin films of poly(methylhexylsilane) (PMHS). The orientation behavior of molecular chains was analyzed by the inclination-angle-dependence of the polarized UV spectrum and the FTIR reflection–absorption spectroscopy (RAS). The changes in conformation of PMHS chains were monitored with the UV absorption spectrum. It was shown that the structure of the spin-cast film depended upon the thickness of films. In thick film (408 nm), molecular chains are not oriented, and favor the disordered conformation, which shows absorption band at 300 nm. In contrast, extended conformation with trans-rich segments is produced in addition to the disordered conformation in thin spin-cast films (45–100 nm). The extended conformation gives rise to a sharp absorption band at 338 nm. The molecular chains with extended conformation are oriented parallel to the substrate surface. The uniaxially oriented films were prepared by drawing the film on supporting polymeric substrates and by crystallization on highly oriented polymer films. As the degree of orientation is increased, the 338 nm band increases in intensity relative to the 300 nm band. The 338 nm band dominated the UV spectrum of the highly oriented PMHS film instead of the 300 nm band. A conformational transition to the extended conformation from disordered state is induced by the molecular orientation, exhibiting a drastic spectral change in the UV spectrum.

Keywords: Orientation; Chromism; Polysilane

1. Introduction

Considerable attention has been focused on characterizing polysilanes, which exhibit unique electronic properties, such as electron conductivity, photoconductivity, thermochromism, photoresists, electroluminescence [1]. Polysilanes generally exhibit ultraviolet absorption bands, which originate from the exciton transition of the σ-electron system of silicone backbone. As the absorption arises from the silicon main-chains, the conformation of the main-chains strongly influences the peak position and the absorption intensity of the UV absorption spectrum. Therefore, the UV spectra of polysilanes are changed by the conformational transitions, which are induced by temperature [1–4], pressure [5,6], surface interaction [7–9], and solvent [10,11].

However, it is a matter of fact that the conformation of polymer chains is much affected by the orientation. For example, poly(vinylidene fluoride) undergoes a conformational transition from form II crystal with TGTG$'$ conformation to form I crystal with trans zigzag conformation by stretching of the polymer film [12]. In the case of poly(ethylene terephthalate) (PET), the conformation of the ethylene unit is affected by stretching. The infrared absorption bands originating from trans conformation of PET increase in intensity, whereas the intensity of the gauche bands decreases by the orientation development [13]. Poly-(butylene terephthalate) also shows a conformational transition under stress to β-form with extended trans conformation from α-form with gauche-rich conformation [14]. Recently Poly(dipentylsilane) (PDPS) has been dispersed in the ultrahigh molecular weight matrix as nano-sized domains and afterwards co-oriented by ultradrawing. The UV spectra showed that the all-trans segments were partially produced by ultradrawing of PDPS films in addition to the 7/3 helical conformation [15].

In contrast, it is not easy to prepare uniaxially oriented films of polysilane by stretching of a free standing film, because polysilane films are generally brittle and are easily fractured only at a small strain. In order to overcome the brittleness of polysilane films, hot drawing of polysilane was carried out on the supporting polymeric substrate [16,17]. The uniaxially oriented films of the poly(dimethylsilylene) (PDMS) were prepared by casting a film of PDMS on the polymeric substrate from α-chloronaphthalene

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PII: S0032-3861(98)00798-8

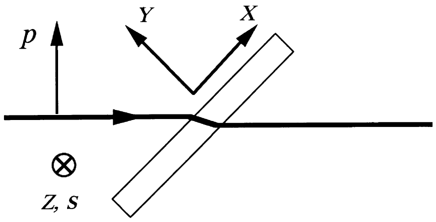

Fig. 1. Measurements of polarized UV spectrum with an inclined sample arrangement. *Z* and *s*-axes are vertical to the optical base and *X*, *Y* and *p*-axes are in the horizontal plane.

solution and by subsequent drawing with the supporting film [17]. However, Wittmann and co-workers have recently proposed the mechanical deposition method, in which ultrathin oriented films are deposited onto the substrate by rubbing the polymer disk against the substrate [18,19]. They have reported that the mechanically deposited polytetrafluoroethylene (PTFE) film is able to orient other materials, which are cast on the substrate [18]. We have applied the mechanical deposition to prepare the uniaxially oriented films of PDMS, which is difficult to dissolve in most of the organic solvents, except for α-chloronaphthalene [20,21]. The highly oriented films of soluble polysilanes have been prepared by crystallization on the highly oriented PTFE [22–24] and PDMS [21,25] films, which were prepared by the mechanical deposition.

This work reports the orientation-induced conformational transition in poly(methylhexylsilane) (PMHS), in which the orientation of molecular chains induces a new absorption band in the UV spectrum. The structural organization in thin spin-cast films of PMHS was studied by polarized FTIR and UV spectroscopy. In addition, the uniaxially oriented films of PMHS were prepared by support-film drawing and by crystallization on highly oriented polymer films, and afterwards characterized with polarized UV spectroscopy.

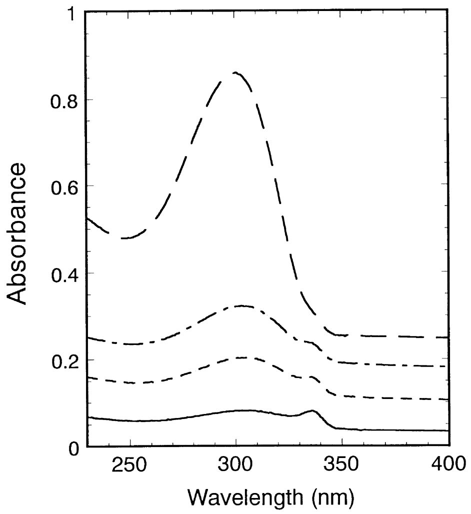

Fig. 2. Thickness dependence of UV spectra of spin cast films on quarts. –––: 408 nm, –---–: 100 nm, –-: 78 nm, — 45 nm.

2. Experimental section

2.1. Materials

PMHS was synthesized by the Wurtz coupling reaction of dichloromethylhexylsilane. Molecular weight of the product was measured with gel permeation chromatography calibrated with polystyrene standards. Higher molecular weight fraction ($M_w = 1\,800\,000$ and $M_w/M_n = 2.1$) was fractionated from the product by repeated fractional precipitation from hexane with 2-propanol.

PMHS films were spin-cast from hexane solution 1500 rpm. The film thickness is controlled by the concentration. As the surface of thin PMHS films was too soft to be probed, thickness was evaluated from the absorption intensity integrated in the spectral range of 250–360 nm, relative to the absorption intensity of the reference film with known thickness. The reference film 500 nm thick was spin-cast on a quartz plate with a size of 10 × 40 mm, and the weight of the film was carefully measured by a sensitive balance. The thickness of the reference film was calculated from the measured weight of the film, measured density of PMHS (0.86 g/cm^3) and the area.

The substrates used were quartz, aluminum, KBr, and highly oriented PDMS films, and PTFE films. The PDMS and PTFE films were prepared by the mechanical deposition method [18–21]. The films on quartz and aluminum were isotropic in any direction within the substrate plane, whereas those on the mechanically deposited films were oriented in the sliding direction.

PMHS films were stretched using polypropylene (PP) as a supporting film. PMHS films were cast from the hexane solution on the supporting polymer films. The polysilane films were co-oriented with the supporting polymer by stretching them at 45°C–135°C.

2.2. Characterization

The Polarized UV spectra were measured with a Shimadzu MPS-2000 spectrophotometer and a Glan–Thompson polarizing prism. The measurements were carried out not only with the normal incidence of the UV beam to the surface, but also with the inclined sample arrangements, in which the sample film was inclined against the incident light beam with various angles (Fig. 1).

The polarized FTIR spectra were measured with a Bio-rad FTS-60A/896 FTIR spectrophotometer. The transmission FITR spectrum was measured for the PMHS films cast on KBr. The film on aluminum substrate was subjected to the reflection–absorption spectroscopy (RAS) measurements. The FTIR–RAS spectrum was measured at an 82° angle of incidence using a MCT detector and a wire-grid polarizer. A sufficient signal-to-noise ratio was achieved by accumulating the 256 and 1024 scans with 4 cm^{-1} nominal resolution, for the transmission and RAS measurements, respectively.

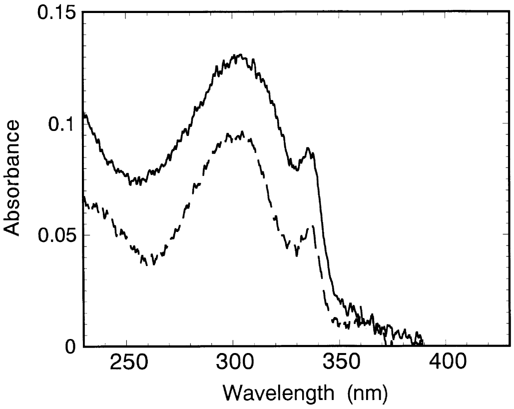

Fig. 3. Polarized UV spectra of a thin PMHS film (70 nm) measured at 45° inclination angle. —: *s*-polarization, – – –: *p*-polarization.

3. Results and discussion

3.1. Spectroscopic studies on PMHS films cast on quartz

Fig. 2 shows the thickness dependence of the UV spectra of spin-cast film on quartz. A thick film (408 nm) shows a broad absorption band around 300 nm. The UV absorption spectrum of the thick sample agrees with the spectrum reported by Yuan and West [26]. In the spectrum of the thinner films (100, 78 and 45 nm), however, a new absorption peak appears at 338 nm in addition to the main band at 300 nm. As the thickness of PMHS films is decreased, the new absorption peak increases in intensity, relative to the original band at 300 nm. In the PMHS film, discontinuous thermochromism was observed in the range of −10°C–40°C, and the 300 nm band is replaced by a new band around 330 nm at −40°C [26]. In solution, the absorption maximum continuously shifts to 330 nm as temperature is lowered [1]. The band at longer wavelength is considered to arise from the extended conformation with trans-rich segments [26]. It is reasonable to attribute the new band at 338 nm also to the extended conformation with trans-rich segment.

The thickness dependence of the UV spectrum has been studied for PDHS. [27–30]. As thickness is decreased, the longer-wavelength band (364 nm) decreases in intensity, whereas the shorter-wavelength band (315 nm) is intensified. The relative amount of extended all-trans conformers decreases with decreasing the thickness. The conformational change is induced by a change of thickness in the thin films of PDHS and PMPS, but the change in PMHS films is in the opposite direction to the change in PDHS films. As symmetrically-substituted PDHS is highly crystalline, the structural organization is dominated by the crystallization. In the very thin film (below 15 nm), the crystal growth starts at a surface and propagates one-dimensionally toward the middle of the thin film [30]. The one-dimensional growth is much slower than the three-dimensional growth in the bulk. The reduction in the rate of crystallization as well as decrease in crystallinity restricts the structural organization into trans conformation in the very thin films of PDHS.

However, the crystalline texture does not form at room temperature in the bulk of PMHS having asymmetric substituents. It is expected that the structural organization in the thin films of PMHS is closely related to the alignment of molecular chains. If the molecular chains align with each other, an ordered conformation is of advantage to decrease the inter-chain repulsive interaction. Although the PMHS films cast on quartz are isotropic in any directions in the film plane, the molecular chains of PMHS are possibly oriented either standing-up or lying-down on the substrate surface. It has been shown by the *X*-ray diffraction studies that the molecular chains in the spin-cast poly(hexylpentylsilane) films are oriented parallel to the film surface [31]. In this work, the orientation of PMHS molecular chains was studied with the inclination-angle-dependence of polarized UV spectrum and the polarized FTIR spectroscopy.

The polarization measurements with the inclined film arrangement are schematically shown in Fig. 1. If the transition moments are distributed parallel in the film plane, the transition moments interact strongly with the electric field vector of the light polarized along the *s*-axis in Fig. 1, whereas their interaction with the electric field vector is reduced for the polarization along the *p*-axis. Therefore, the plane orientation of the transition moment is expected to induce a large dichroism in the polarized spectrum measured with the inclined arrangement.

In this work, the substrate plane is defined by the X–Z plane, the Z-axis is perpendicular to the optical base, and the normal of substrate is set parallel to the Y-axis. Three components of absorbance A_x, A_y, and A_z are defined as the absorbances for the radiation polarized along the X-, Y-, and Z-axes, respectively. The dichroic ratio, D, was calculated as the ratio of absorption intensity, A_s to A_p. The dichroic ratio, which is measured by inclining the normal of substrate from incident UV beam, can be expressed by the three components of the absorbance,

$$D(\theta) = A_s(\theta)/A_p(\theta) = A_z/(A_x \cos^2\theta + A_y \sin^2\theta), \qquad (1)$$

where θ is the angle between the electric field vector of the radiation (p-axis) and the X-axis. In the case of the film cast on quartz, A_z equals to A_x, and then Eq. (1) leads to

$$D(\theta) = 1/(\cos^2\theta + (A_y/A_x)\sin^2\theta). \qquad (2)$$

If the transition moments are oriented parallel to the substrate surface, $A_y/A_x < 1$ and the value of $D(\theta)$ is expected to increase with increasing inclination angle. Fig. 3 shows the polarized UV spectra of a thin PMHS film (78 nm), measured at a 45° inclination angle. The absorbance A_s is higher than A_p in the wavelength region of 250–360 nm, and the dichroic ratio of the 338 nm band is higher than that of the 300 nm band. The dichroic ratio versus inclination angle is shown in Fig. 4. As the dichroic

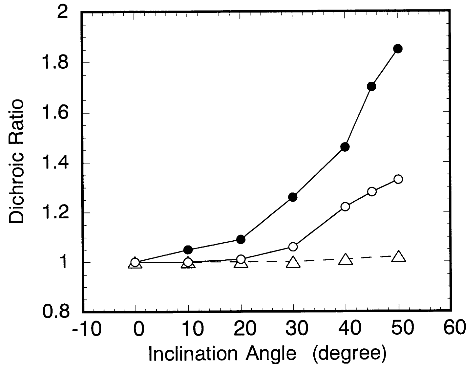

Fig. 4. Dichroic ratio of spin-cast PMHS films on quartz as a function of inclination angle. △: 300 nm band, thickness = 408 nm, ○: 300 nm band, thickness = 70 nm, ●: 338 nm band, thickness = 70 nm.

ratio for the thick film (408 nm) is constant against the inclination angles, the molecular chains are not oriented as a whole in the thick film. However, the dichroic ratio for the thin films increases with increasing the inclination angle, indicating that the molecular chains are oriented parallel to the substrate plane ($A_y/A_x < 1$). The molecular chains with trans-rich conformation are oriented in the plane more highly than those with disordered conformation. In the thin spin-cast films, the in-plane orientation of the molecular chains induces a conformational transition to the extended conformation with higher amount of trans segments.

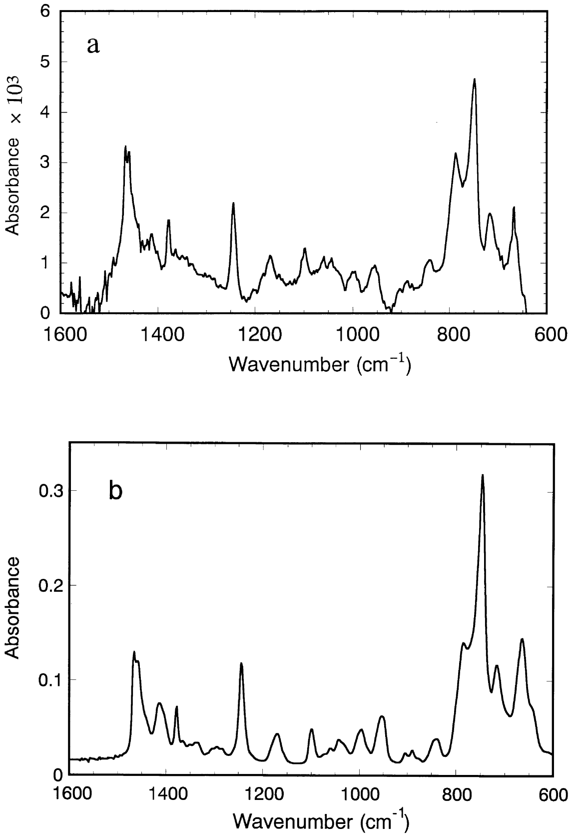

Fig. 5. FTIR spectra of PMHS films. (a) reflection–absorption spectrum (b) transmission spectrum.

Table 1
Vibrational assignment of poly(methylhexylsilane)

Frequency, cm [−1]	Assignment	Polarization
1466 m	CH_2 deformation in hexyl group	
1412 w	CH_3 asymmetric deformation in hexyl and Si–CH_3 groups	∥ & ⊥
1377 w	CH_2 symmetric deformation in hexyl group	
1244 m	CH_3 symmetric deformation in Si–CH_3 group	⊥
785 m	CH_3 rocking in Si–CH_3 groups	⊥
746 s	CH_3 rocking in Si–CH_3 groups	∥
716 m	CH_2 rocking in hexyl group	

The FTIR–RAS spectrum of PMHS on aluminum is shown in Fig. 5. Together with the transmission spectrum of PMHS on KBr substrate. The film for the transmission spectrum was cast on KBr from 0.2% hexane solution without spinning, and that for the FTIR–RAS spectroscopy was spin-cast from 0.02% solution at a spinning speed of 1500 rpm. The thickness of the sample for transmission spectrum is about 9 μm and that for the FTIR–RAS is estimated to be an order of ten nanometers. The thick film is considered to be isotropic as a whole from the results of the polarized UV spectra. The orientation of the very thin film cast on the metallic substrate can be evaluated by comparing the relative band intensities in the FTIR–RAS spectrum with those in the transmission FTIR spectrum of the isotropic sample.

A lot of absorption bands are observed in the wavenumber region of 1600–600 cm^{-1}. Some of the IR bands can be assigned either to the *n*-hexyl and methyl groups, in reference to the spectral assignments of PDHS [29,32] and PDMS [33,34]. The assignment of vibrational bands is shown in Table 1 together with the polarization characteristics. We have recently studied the spectral assignment of methyl rocking vibration of PDMS, and poly(methylethylsilane) (PMES) [34]. In analogy with the assignment of PMES, the 746 cm^{-1} band is assigned to the methyl rocking vibration, whose transition moment is parallel to the molecular chain axis, whereas the 785 cm^{-1} band is the other methyl rocking vibration having transition moment perpendicular to the chain axis. The 1412 and 1244 cm^{-1} bands are the asymmetric and symmetric CH_3 bending vibrations, respectively, of the Si–CH_3 group. The transition moment of the symmetric CH_3 bending vibration is perpendicular to the molecular chain axis, whereas that for the degenerated asymmetric CH_3 bending vibration contains both components of transition moment. Although the detailed assignment of the absorption bands in the region of 1200–800 cm^{-1} is not established, they are possibly assigned to the CH_2 wagging, CH_2 twisting, and CC stretching vibrations of the hexyl side chains.

In the FTIR–RAS experiment, the molecular vibrations

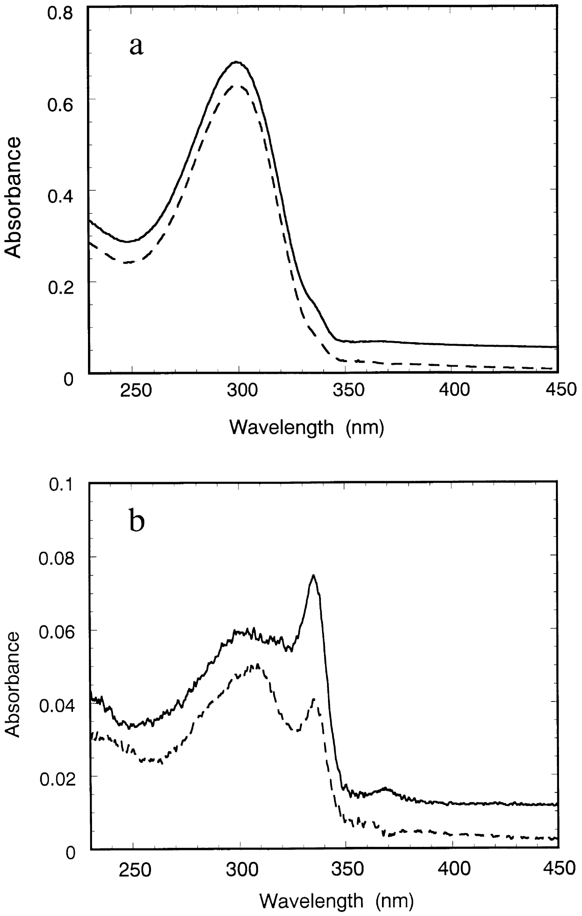

Fig. 6. Polarized UV spectra of PMHS cast on highly oriented PTFE substrate. (a) 408 nm (b) 42 nm, —: parallel polarization, – – –: perpendicular polarization.

having the component of transition moment normal to the metallic surface are expected to appear with enhanced intensity, whereas the component of transition moment parallel to the surface does not interact with the IR radiation. The intensities of the 746 and 1412 cm^{-1} bands are decreased more than those of the 1244 and 785 cm^{-1} bands in the FTIR–RAS spectrum of the thin PMHS film, relative to their absorption intensities in the transmission spectrum of isotropic films. The relative absorption intensities in the reflection–absorption and transmission spectra confirms that the molecular chains of PMHS are oriented parallel to the substrate surface in the very thin films.

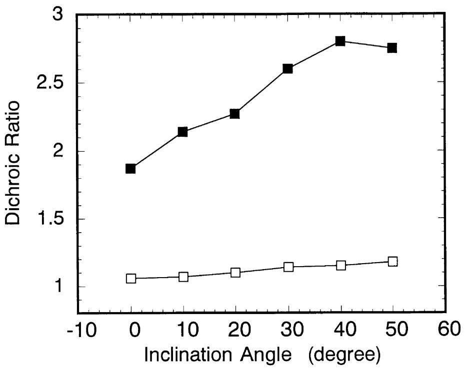

Fig. 7. Dichroic ratio of spin cast PMHS films (59 nm) on highly oriented PTFE substrate as a function of inclination angle. □: 300 nm band, ■: 338 nm band.

3.2. Spectroscopic studies on PMHS films crystallized on highly oriented polymer substrate

Fig. 6 shows the polarized UV absorption spectra of PMHS crystallized on highly oriented PTFE substrate. The film thickness strongly influences the polarized UV spectra. The film 408 nm thick is isotropic as a whole and the 338 nm band appears only as a shoulder on the tail of the 300 nm band. In the thin film (42 nm), the 338 nm band is clearly observed in addition to the 300 nm band. The dichroic ratio for the 338 nm band is higher than that for the 300 nm band. As the film thickness is decreased, the degree of orientation increases and the 338 nm band is intensified relative to the 300 nm band. Although a small peak was observed around 370 nm, the appearance of the peak is not reproducible. This is probably the artifact, because the background spectrum in the polarization measurements is curved because of the large polarization-characteristics of the spectrometer in this range.

Fig. 7 shows the inclination angle dependence of the dichroic ratio of thin PMHS film (59 nm) which is crystallized on the highly oriented PTFE substrate. The polarized spectra were measured with the arrangement shown in Fig. 1. The *Z*-axis is set to be the orientation direction of the substrate polymers. The *X*- and *Y*-axes are the transverse direction and the normal direction respectively, of the substrate. The dichroic ratio of the 300 nm band increases only slightly with inclination angle, and lies in the range of 1.05–1.20, suggesting the low degree of orientation. The dichroic ratio of the 338 nm band shows a marked increase with inclination angle. The trans-rich segments are aligned in the substrate plane and preferentially oriented in the orientation direction of the substrate polymer; $A_z > A_x > A_y$.

Fig. 8 shows the polarized UV absorption spectra of PMHS film (43 nm) crystallized on highly oriented PDMS substrate. The absorption spectrum of PDMS is subtracted from the observed spectra, and the difference spectra are shown in Fig. 8. The molecular chains of PMHS films are shown to be oriented in the orientation direction of PDMS. The UV spectra of the annealed sample are dominated by the intense 338 nm band with a large dichroism, instead of the 300 nm band, suggesting that the trans-rich segments are highly oriented in the very thin film annealed on the oriented PDMS. The annealing on highly oriented PDMS is effective on orienting PMHS and on inducing a conformational transition.

3.3. Spectroscopic studies on PMHS films stretched on supporting polymers

Fig. 9 shows the polarized UV spectra of PMHS film stretched on PP at 130°C. The stretching of the PMHS

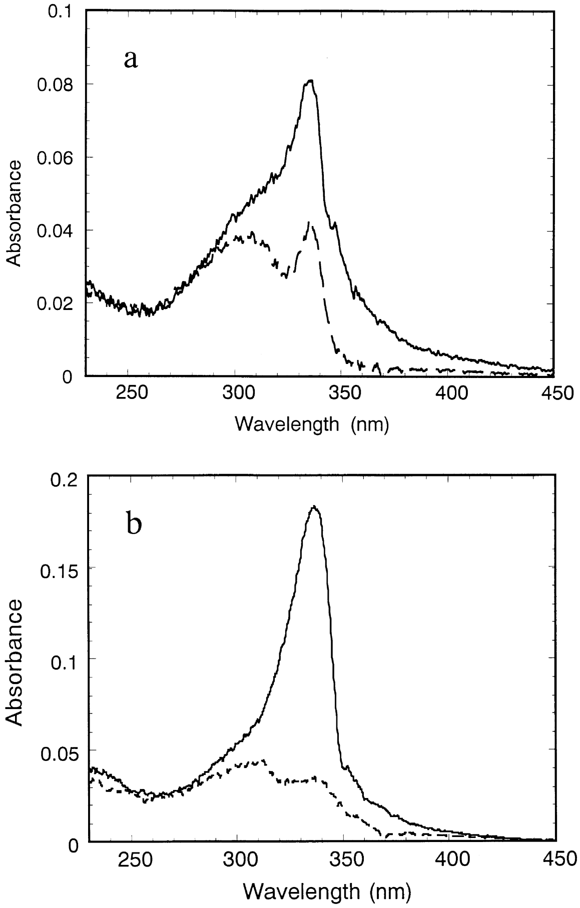

Fig. 8. Polarized UV spectra of PMHS (43 nm) cast on highly oriented PDMS substrate. (a) As-cast (b) Annealed, —: parallel polarization, ---: perpendicular polarization.

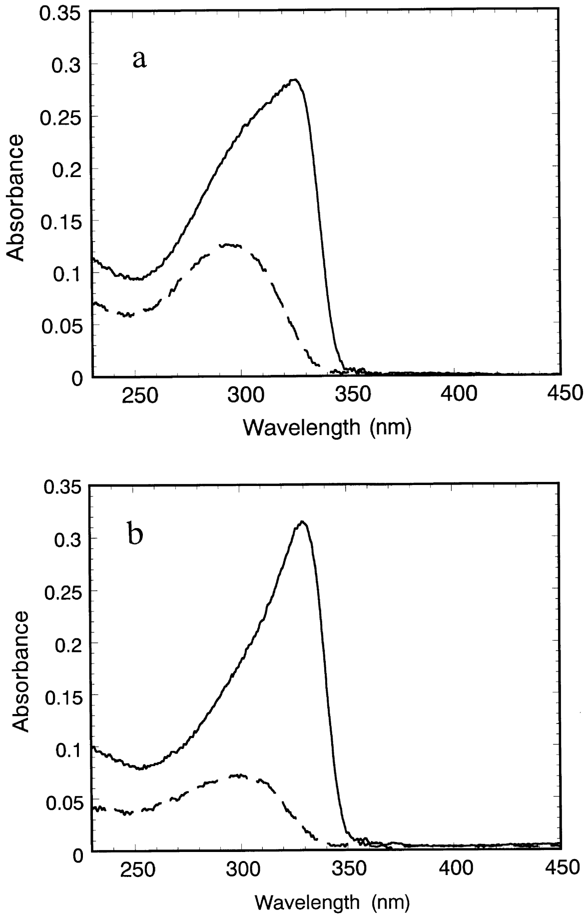

Fig. 9. Polarized UV spectra of PMHS film drawn on PP at 130°C. (a) draw ratio = 9.6 (b) draw ratio = 13, —: parallel polarization, ---: perpendicular polarization.

film on the supporting film is effective on inducing a chromic transition. The absorption maximum is observed around 300 nm in the spectrum measured with the perpendicular polarization, whereas the 300 nm band is replaced by the 330 nm band in the spectrum with parallel polarization. The extended conformation with trans-rich segments is highly oriented in the stretching direction, in contrast to the low degree of orientation of the disordered conformation. The degree of orientation increases and the conformational transition is facilitated with increasing draw ratio.

4. Conclusions

The UV absorption spectrum in the thin films of PMHS was studied in relation to the orientation-induced conformational transition from the disordered conformation to the extended conformation with higher amounts of trans-rich segments. The UV spectrum of a thick isotropic film shows only a broad absorption band arising from the disordered conformation around 300 nm. In the thin spin-cast film, however, the conformational change into the extended trans-rich conformation gives rise to a new UV absorption band at 338 nm. The conformational change in the very thin film is induced by the parallel alignment of molecular chains in the substrate plane. The conformational change in the thin PMHS film is in contrast to that in the PDHS film [27–30], in which amount of trans conformation decreases as a result of the suppression of the crystallization in very thin films.

The uniaxially oriented films of PMHS were prepared by drawing the film on supporting polymer substrates and by crystallization on highly oriented polymer substrates. The uniaxial orientation induces a drastic change in the UV absorption spectrum, in which the broad absorption band at 300 nm is replaced by the 338 nm band with a large dichroism. The orientation of molecular chains is closely correlated with the conformations of molecular chains. As the degree of orientation is increased, the molecular chains favor the extended conformation with trans-rich segments. Thus, the orientation of the molecular chains induces a conformational transition to the extended conformation with higher amount of trans-rich segments.

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