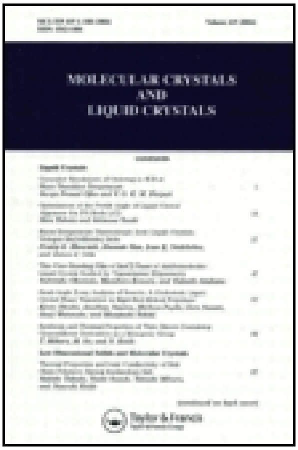

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Shusaku Nagano [a], Takahiro Seki [a] & Ichimura Kunihiro [a]

[a] Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 226-8503, Japan

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Conformational and Alignment Behavior of Polysilane Film Mixed with Liquid Crystal Molecule

SHUSAKU NAGANO, TAKAHIRO SEKI and ICHIMURA KUNIHIRO

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

Mixed films containing poly(dihexylsilane) (PDHS) and liquid crystal (LC) molecule were prepared onto a rubbed poly(vinyl alcohol) film by spin-casting. The conformational state and the alignment of the PDHS backbone were investigated by polarized UV-visible absorption spectroscopy. The absorption band ascribed to the crystalline state of PDHS in the mixed film showed a red shift from that of a pure PDHS film. The PDHS backbone in the mixed film was aligned parallel to the rubbing direction. The magnitude of the red shift and the alignment order of PDHS was enhanced by annealing at 60°C in the mixed film with some LC molecules.

Keywords: polysilane; nematic liquid crystal; conformation; in-plane anisotropy; mixed film; rubbed poly(vinyl alcohol)

INTRODUCTION

Polysilanes are a fascinating class of polymers that show unique optical and electronic properties due to the delocalization of σ-electrons along the Si-Si backbone.[1-4] The optical and electronic properties highly depend on the conformation and orientation of polymer backbone.[1-4]

Thus, it is important to develop controlling methods for conformation and orientation of the backbone in the basic studies and technological applications.

Recently, we reported that incorporation of calamitic LCs in the PDHS film leads to red shifts of the absorption band corresponding to the crystalline state.[5] It is proposed that the remarkable miscibility of LC molecule with PDHS was attained in the mixed film, and that insertion of rodlike molecules among the PDHS chains modifies the effective delocalization length of the σ-electron. In a relating study, we indicated that the co-spreading of PDHS and 4'-pentyl-4-cyanobiphenyl (5CB) onto water provides a monomolecularly extended state of PDHS assisted by the 5CB monolayer due to a high compatibility.[6]

The next target of this investigation would be to align PDHS backbone. In the LC technology, the uniaxial in-plane alignment of LC molecules is achieved by mechanical rubbing of polymer surface on the substrate. In this context, we attempted, in this study, to align the polymer backbone of PDHS by spin-casting a film on a rubbed surface. We will mainly report on the effects of the mixing of calamitic LC into the film on the orientation and conformation of the PDHS backbone.

EXPERIMENTAL

High molecular weight PDHS (PDHS-h) and low molecular weight PDHS (PDHS-l) were synthesized by the reductive condensation of dihexyldichlorosilane with metal sodium and were separated by fractional precipitation (PDHS-h: $M_w = 4.2 \times 10^5$, $M_w/M_n = 2.2$, PDHS-l: $M_w = 3.7 \times 10^4$, $M_w/M_n = 2.1$). Calamitic LC materials, DON-103, NPC-02 and RDP-60716 were gifts from DAINIPPON INK AND CHEMICALS, Inc and 5CB was donated by MERCK. They all exhibit the nematic phase at room temperature.

Thin films of pure PDHS and PDHS/LC mixtures were prepared by spin-casting onto a quartz substrate from hexane solutions. The molar ratio (R) defined as [LC molecule]/[PDHS unit] was 0.3. The substrates were beforehand coated with a poly(vinyl alcohol) (PVA) film by spin-casting from a 0.5% aqueous solution, and the film surface was rubbed once with paper wound around a glass tube. The thickness of the pure PDHS and PDHS/LC mixed films were ca. 130 - 150 nm.

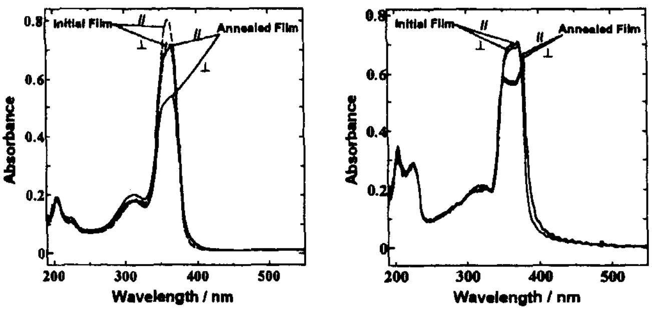
The conformation and the orientation of a polymer backbone were evaluated by polarized UV-visible spectra taken on a Hewlett-Packard diode array spectrometer (8452A) equipped with a polarizer. The annealing of samples were carried out in a drying oven at 60 °C.

RESULTS AND DISCUSSION

Conformation and Orientation of PDHS-l film on Rubbed PVA Surface

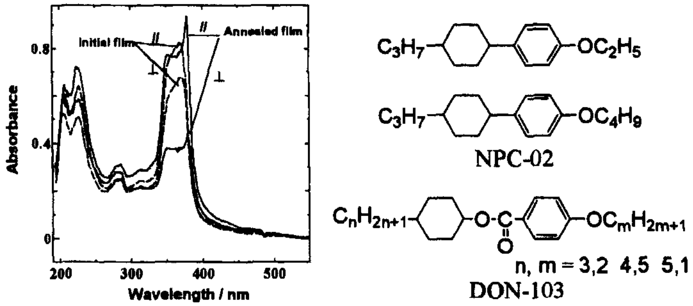
FIGURE 1 depicts polarized UV-visible absorption spectra of pure PDHS-l (a), PDHS-l/NPC-02 (b), and PDHS-l/DON-103 (c) films at R = 0.3 at the initial state and after annealing. These films were prepared on a rubbed PVA surface. In the pure PDHS-l film (a), the sharp σ-σ^* band attributed to the crystalline state of PDHS was observed at 362 nm, and band due to the disordered conformation of the backbone or non-crystalline phase was seen at 315 nm as a minor band. As shown, the absorbance along the rubbing direction of PVA (//) was larger than that in perpendicular one ($\perp$). Thus the PDHS backbone aligned to the rubbing direction. The in-plane dichroism was a relatively small in the initial state. The annealed film at 60 °C for 1 h exhibited some improvement of the dichroism, and a slight red shift to 365 nm of the band for the crystalline phase was observed.

In both cases of PDHS/LC mixed films (b and c), the red shift of



a) "pure" PDHS-l film

b) PDHS-l/NPC-02 film



c) PDHS-l/DON-103 film

FIGURE 1. Polarized UV-visible absorption spectra of "pure" PDHS-l (a) and PDHS/LC molecules, PDHS-l/NPC-02 (b) and PDHS-l/DON-103 (c) mixed films at R = 0.3 for initial state and annealed film.

the bands attributed to the PDHS crystalline phase was observed at 373 nm. The absorbance at this wavelength was in consistent with that observed for the extended all-trans-zigzag conformation promoted by mixing LC molecules shown in our previous study.[5] Upon annealing, the band peak showed a further shift to 378 nm in both mixed films. Plasticization by mixing of LC molecules and heating both should increase the film viscosity. In the course of the nematic ordering in such a fluidized state, the column length can be extended in the hexagonal columnar phase of PDHS. Consequently, annealing induced the further extension of the trans-zigzag conformation of the

PDHS backbone.

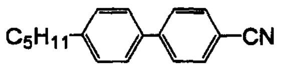
As shown in FIGURE 1, the two kinds of LC affected the orientational behavior of PDHS in quite different ways. In the case of PDHS-l/NPC-02 mixed film (b), the anisotropy of a PDHS backbone was hardly admitted and annealing did not improve the orientational order. In contrast, in the case of PDHS-l/DON-103 mixed film (c), a relatively large dichroism was already observed at the initial stage, and the orientational order was markedly improved upon annealing at 60 °C. It is supposed that the difference in the N-I transition temperature of the two LC materials is attributable to the discrepancy in the alignment behavior.

The above-mentioned assumption was confirmed by further examinations with other LC materials. TABLE 1 shows the order parameter (S) and absorption peak wavelength of PDHS-l for the crystalline phase of the films mixed with four kinds of LC materials.

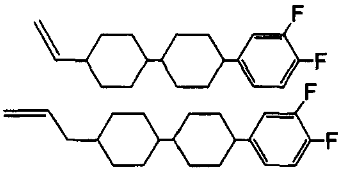
TABLE 1. Order parameters (S) estimated at 370 nm and absorption maxima of PDHS-l / LC molecules mixed fims.

additive LC	T_{N-I} a) / °C	λ_{max} b)/ nm	Order parameter (S)	
			initial	annealed
none	-	364-366	0.03	0.10
5CB	35	372	0.00	0.00
NPC-02	35	378	0.01	0.01
DON-103	73	378	0.07	0.27
RDP-60716	117.5	378	0.12	0.21

a) The temperature of the nematic-isotropic transition of "pure" liquid crystall molecules. b) after annealing



5CB



RDP-60716

Here, the order parameter (S) is defined as,

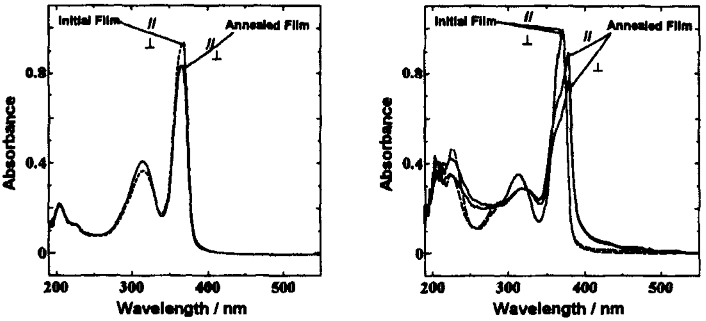
$$S = (A_{//} - A_{\perp})/(A_{//} + 2A_{\perp}),$$

where $A_{//}$ and $A_{\perp}$ are absorbances observed in the parallel and perpendicular direction of the rubbing, respectively. The mixed films with 5CB and NPC-02 whose nematic-isotropic transition ($T_{N\text{-}I}$) is low as 35 °C did not exhibit the appreciable in-plane dichroism. Also, the improvement of the backbone orientation by annealing was negligible. On the other hand, the mixed film with DON-103 and RDP-60715 gave the larger dichroism in the mixed film compared with the pure film. As expected, with these LC materials having high $T_{N\text{-}I}$ temperatures, considerable enhancement in the orientational order was observed upon annealing by a factor of 2 - 3.

Annealing at low temperatures (35-40 °C) for 2 - 3 h scarcely changed the dichroism for the all mixed films. The enhancement of the orientation required the annealing above 40 °C also for the pure PDHS film. Above this temperature the hexyl side chains of PDHS melt, and the polymer chain adopts hexagonal mesophase.[1] It is likely that, for enhancement of the orientational order of the backbone, the LC materials should take the nematic phase at temperatures above 40 °C. In this state, the doped LC molecule in the nematic phase may facilitate the enhancement of the orientational order of the hexagonal packed mesophasic polymer assembly. DON-103 and RDP-60715 out of the four LC materials fulfill these conditions.

Conformation and Orientation of PDHS-h film on Rubbed PVA Surface

FIGURE 2 indicates polarized UV-visible absorption spectra of pure PDHS-h film (a) and PDHS-h/DON-103 (b) mixed at R = 0.3 in the initial state and after annealing. The pure film did not exhibit the in-plane anisotropy, and moreover, the annealing affected no change (a).



a) "pure" PDHS-h film

b) PDHS-h/DON-103 film

FIGURE 2. Polarized UV-visible absorption spectra of "pure" PDHS-h (a) and PDHS/DON-103 (b) mixed films at R = 0.3 for initial state and annealed films.

Only the PDHS-h/DON-103 mixed film indicated a slight dichroism at the initial stage, and a small enhancement in the orientation was observed by annealing. Concurrently, annealing induced a further red shift from 370 nm to 378 nm in this mixed film. In this way, the induction of the in-plane anisotropy of PDHS was achieved only in the presence of LC having a relatively high T_{N-I}.

CONCLUSION

We found in this work that LC molecule facilitate the conformational induction and enhancement of in-plane orientation of PDHS film spincast on a rubbed PVA surface. Annealing effect is pronounced when the doped LC material adopts the nematic phase above 40 °C.

Embs et al.[2] have reported that the improvement in the orientation of a polysilane LB multilayer was observed by annealing. Very recently, we have shown a similar phenomenon of the orientational order enhancement for the spin-cast ultrathin film of

PDHS on the photochromic alignment monolayer.[7] During annealing process, reduction of the free volume should occur in the packed rod polymers. It is reasonable to suppose that this exclusion of the free volume taking place in a somewhat aligned rodlike polymer array causes the improvement of the orientation. When the LC molecule in the nematic phase is present, the orientation of the rodlike polymer chain was enhanced to more extents probably by "anisotropic plasticization."

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