Light-Control Birefringence of Oriented Poly (vinyl cinnamate) by UV Irradiation

Xiaoming Dong, Jinbao Guo, Yang Jiao, Jie Wei

College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

ABSTRACT: The research focused on realizing the birefringence of light-control polymer films. The photoelastic birefringence exhibits when Poly (vinyl cinnamate) (PVCi) films are stretched below their glass transition temperature (T_g). The birefringence of PVCi decreases when the UV irradiation happens because the side chains of the PVCi photoreact when the oriented films are exposed to UV light. A method to quantify the birefringence ability of the polymer films is created and verified. Using this method, the decrease of the birefringence through the UV irradiation is quantified. The result shows the birefringence of PVCi can be controlled by altering the UV irradiation time. In addition, oriented PVCi films of different esterification degrees were prepared and irradiated at different time, and the birefringence of them was studied to clarify the birefringence mechanism of light-control polymer films. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 3367–3372, 2010

Key words: light-control polymer; poly (vinyl cinnamate); birefringence

INTRODUCTION

Polymer materials exhibit no birefringence when the polymer chains are randomly oriented, whereas the photoelastic birefringence exhibits when polymer films are stretched below their glass transition temperature (T_g). It is convinced that the side chains' orientation of the polymer molecules contributes to the photoelastic birefringence.[1] Optical birefringence is widely used for information recording, such as holographic recording.[2] As an external stimulus, light is a clean energy source that can be controlled remotely, instantly, and precisely; furthermore, using light as a stimulus no wires or connections are necessary. This enables easy fabrication of the devices and reduces the weight.[3,4] Thus, if light can be used to control the birefringence of polymers, it will not only be a promising method of information recording but also can lead to versatile applications to optical devices, such as optical switching, channel waveguide, waveguide lithography and so forth.

PVCi is the earliest synthetic photopolymer[5] and has played a leading role in the development of photopolymers.[6] The further advancement in polarization photochemistry of ultrathin films leaded to regulation of the orientation of liquid crystal molecules,[7–13] and these result in an enhanced interest in PVCi. The crosslinking of PVCi as shown in Scheme 1 is due to the [2 + 2] photocycloaddition.[14] Because carbonyl and phenyl groups provide favorable polarization to the double bond, the photoreaction of cinnamoyl groups takes place easily to form photocross-linking. In addition, cinnamate group can undergo rapid photodimerization without the addition of a photoinitiator. This ability is critically important in the context of the present investigation, as will become more apparent later.

In this paper, we are working to make use of this phenomenon to achieve light-control polymer birefringence. The PVCi film is stretched below its glass transition temperature (T_g) and photoelastic birefringence forms because of the orientation of the PVCi side chains. Then, the oriented film is exposed to UV light and the side chains of the PVCi photo reacts, so the birefringence decreases under the UV irradiation. In addition, how different esterification degrees of oriented PVCi films effects the birefringence ability was studied. The results can be obtained quantitatively by a measurement using polarization spectrometer. It can be widely used in information recording and optical devices.
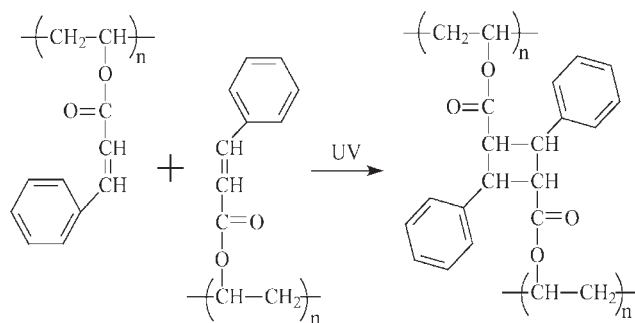
EXPERIMENTAL

Synthesis of PVCi

Polyvinyl alcohol was added to pyridine, refluxed at 100°C for 12 h, and then pyridine was added to the

Scheme 1 [2+2] Photodimerization of PVCi.

solution. Cinnamyl chloride in 2-butanone solution was dropped to polyvinyl alcohol–pyridine solution with stirring for 40 min at 50°C. After stirring at 60°C for 5 h, the reaction solution was put into water to precipitate. The precipitate was washed by ethanol and dried. IR(KBr): 3420 cm^{-1}(OH), 1750 cm^{-1}(C=O), 1620 cm^{-1}(C=C). UV–vis: 280 nm(C=C). FTIR was recorded with spectrometer (Nicolet 5700, Nicolet Company, simple measurement method). UV–vis transparence spectrum was recoded by using with a spectrophotometer (UV-3010, HITACHI Company).

Film preparation

PVCi were dissolved in water. The PVCi solution was then spin-cast onto a glass slide and dried for 48 h at room temperature. The film was stretched to the extension ratio of 3.

Measurements of polarization character of photosensitive film

The stretched film was placed between the polarizer and the analyzer. The polarizer and the analyzer were always at parallel state. The polarizer and the analyzer were rotated simultaneously from 0° to 90°. The light intensity was measured by UV–vis spectrophotometer.

Film Photo-de-orientation and polarization character measurements

After the stretched film was exposed for 5 min, the film was placed between the polarizer and the analyzer. The polarizer and the analyzer were always at parallel state. The polarizer and the analyzer were rotated simultaneously from 0° to 90°. The light intensity was measured by UV–vis spectrophotometer. The light intensities were measured at the same states, after the film was exposed 10 min, 15 min, and 20 min.

RESULTS AND DISCUSSION

Photoreaction of PVCi

Because phenyl has influence on the conjugated system, the narrowest energy gap is not n orbital→π* orbital but π orbital→π* orbital. The strongest absorbency peak at 274 nm is corresponding to the vibration of C=C double bond, and the decreasing of the peak shows the reaction degree of photoreaction clearly. Figure 1 shows the photoreaction rate of the cinnamate decreases with UV irradiation. UV–vis absorption spectra is a convenient method to investigate the photoreaction of cinnamoyl moiety.[15,16] It allows an estimation of photoproduct distribution. Using absorbance at the maximal wavelength and an isosbestic point of the UV–vis spectra, the fraction of photoproducts can be calculated according to the following equations:

$$f_E = \varepsilon_E/(\varepsilon_E - \varepsilon_Z)[A/A^0 - (\varepsilon_Z/\varepsilon_E)(A_{iso}/A^0_{iso})] \quad (1)$$

$$f_Z = \varepsilon_E/(\varepsilon_E - \varepsilon_Z)[A_{iso}/A^0_{iso} - (A/A^0)] \quad (2)$$
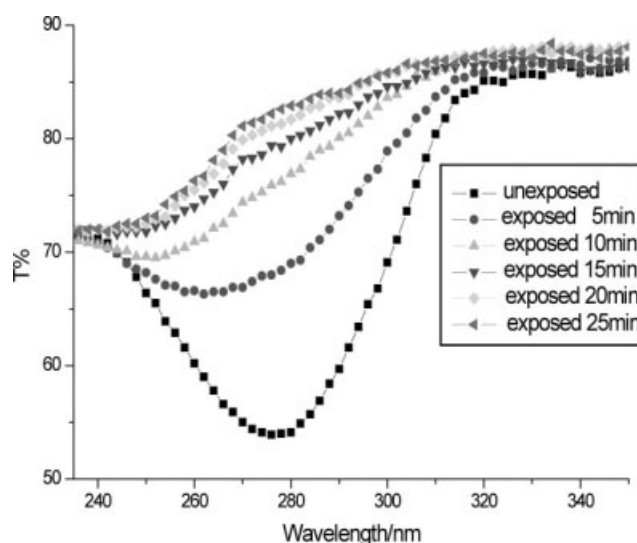
$$f_{Dimer} = 1 - A_{iso}/A^0_{iso} \quad (3)$$

A: absorbance at 274 nm for PVCi;
A^0: initial absorbance at 274 nm PVCi;
A_{iso}: absorbances at the isosbestic points (304 nm for PVCi);
A^0_{iso}: initial absorbances at the isosbestic points (304 nm for PVCi);
ε_E: molar extinction coefficients of the E-isomer (2.12*10^4 for PVCi);

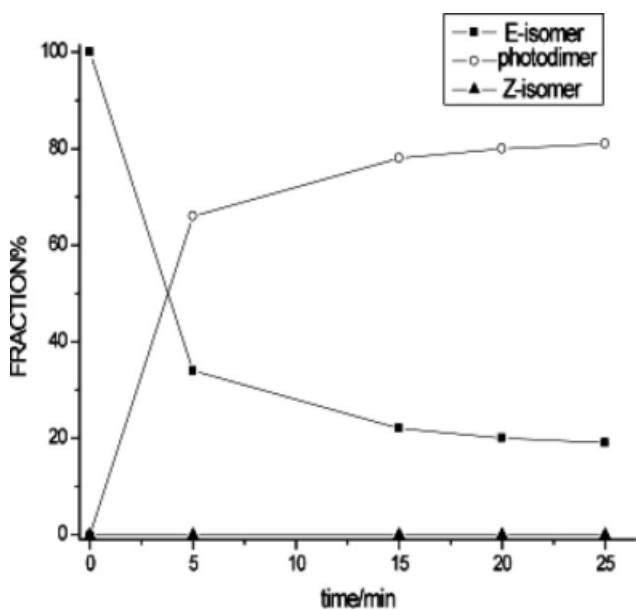**Figure 1** Cinnamate transmittance at different UV irradiation time.

Figure 2 The fraction of photoprodcts.

Figure 3 Schematic of the incident linearly polarized light vibration decompose.

ε_Z: molar extinction coefficients of the Z-isomer ($1.20*10^4$ for PVCi).

The distribution of the photoproducts of both geometrical E- and Z-isomers and photodimers of the cinnamoyl moieties in the stretched PVCi film (esterification degree 3%) is shown in Figure 2. Cinnamoyl side chains of PVCi film produced the photodimerized formation after the UV irradiation. Because the orientation of the side chains of the polymer molecules is believed to make a major contribution to photoelastic birefringence, the birefringence of the film should decrease followed by the photoreaction.

As we mentioned earlier, the orientation of the side chains of the polymer molecules is believed to make a major contribution to photoelastic birefringence; so,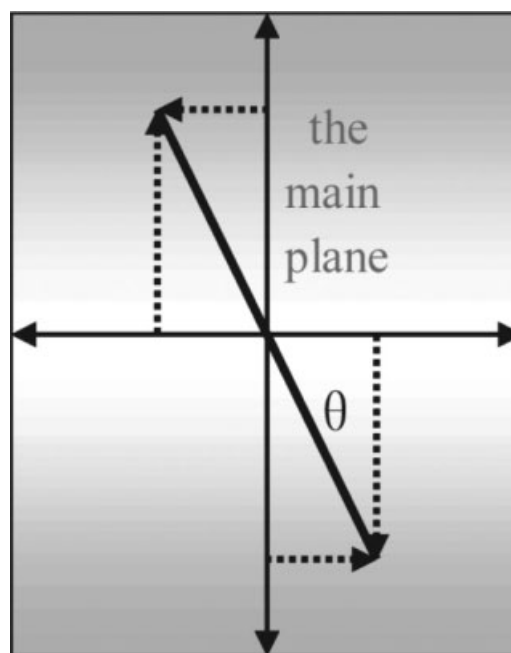 if the orientated side chains photoreact and the orientation structure is destroyed, the birefringence of stretched film should decrease. Because of lacking a method to quantify the birefringence ability of polymer film, establishing the method is essential. So, we could identify the effects of the photoreaction of the orientated side chains.

The method to quantify the birefringence ability of polymer film

Birefringence is mainly occurred when the polymer is oriented by stretching. In theory, when a linearly polarized light irradiates the perfectly oriented film,
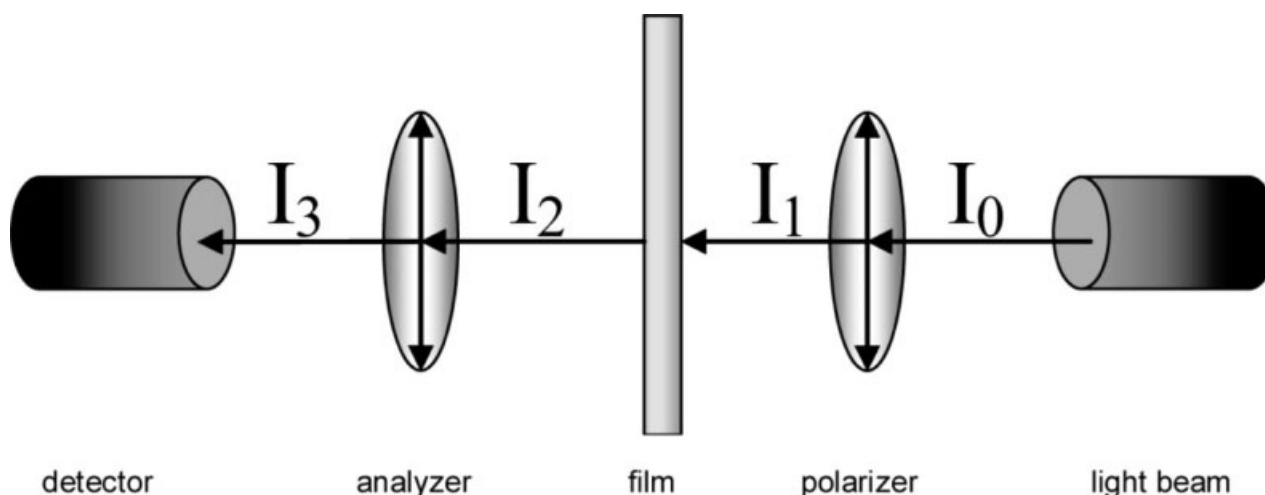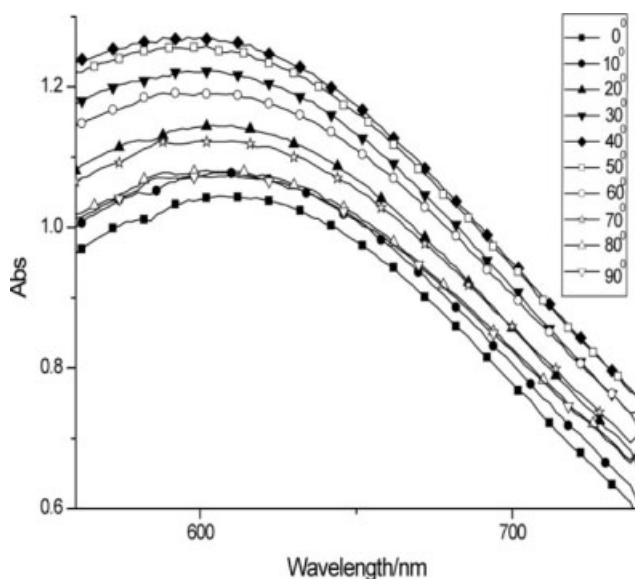

Figure 4 Schematic setup of the polarization character spectrometer.

Figure 5 The film absorbencies measured in different angles.

all of the incident linearly polarized lights will decompose into two kinds of vibrations. Some vibrate in a plane paralleled with the main plane and others vibrate in a plane perpendicularly to the main plane (Fig. 3). In fact, only parts of incident light will decompose into these two vibration planes, and the rest will remain the original state and transmit through the photoelastomer. The decomposing incident light will increase, in pace with the increasing of the birefringence ability of the polymers (Usually the birefringence ability of the polymer film is proportional to the extension ratio of the film.). In other word, light remain the original state decreases. Therefore, the ratio of the decomposing light intensity to the total incident light intensity can characterize the birefringence ability of the polymer. Sign η is used to stand for the ratio.

The birefringence ability can be quantified by the polarization spectrometer. The optical setup of the

TABLE I
Contrast Between the Theoretic Absorbency and the Practical Absorbency

α	Absorbency of polarizer and the analyzer	The theoretic absorbency	The practical absorbency
0°	0.931	0.9812	0.980
10°	0.932	1.0104	1.010
20°	0.934	1.0678	1.068
30°	0.937	1.1330	1.133
40°	0.942	1.1732	1.174
50°	0.948	1.1633	1.162
60°	0.952	1.1117	1.111
70°	0.956	1.0541	1.054
80°	0.959	1.0164	1.018
90°	0.961	1.0112	1.012

polarization spectrometer is schematically depicted in Figure 4. First, the incident light beam was linearly polarized. The measurement of the polarization character of the photosensitive film is shown in experimental part.

We assume the angle between the vibration plane of the incident light and the main plane is θ. When the polarizer and the analyzer are rotated α at the same time, the angle between the vibration plane of the incident light and the main plane is $\alpha+\theta$. The η is used to stand for birefringence ratio. The transmittance of polarizer is K (the transmittance of analyzer is obviously the same); the transmittance of the film is k; $T\%$ is the final detected intensity, the equation is:

$$T\% = I_3/I_O = K^2 k[1 - \eta \sin^2(2\alpha + 2\theta)/2]/2 \quad (4)$$

The numerical values of K and k can be tested easily. The polarizer and the analyzer at parallel polarizer state were both rotated α_1, and then they were rotated α_2, the numerical values of η and θ can be worked out.

The feasibility of quantifying the birefringence ability of the polymer film

Figure 5 shows the absorbencies of the stretched film. Take wave 650 nm light for example, $k = 89.42\%$, $K^2/2 = 11.64\%$. From Figure 4, when $\alpha = 20°$, $T\% = 8.551\%$, $\eta\sin^2(2\theta+40°) = 0.3569$; when $\alpha = 30°$, $T\% = 7.362\%$ $\eta\sin^2(2\theta+60°) = 0.5756$.

$$\text{Through} \begin{cases} \eta \sin^2(2\theta+40°)=0.3569 \\ \eta \sin^2(2\theta+60°)=0.5756 \end{cases}$$
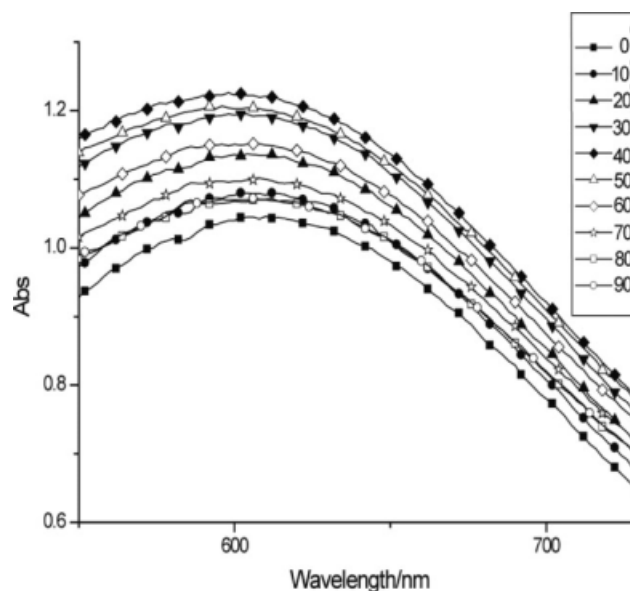
Figure 6 The film absorbencies measured in different angles after exposed 5 min.

TABLE II
Contrast Between the Theoretic Absorbency and the Practical Absorbency after Exposed 5 min

| α	Absorbency of the polarizer and the analyzer	The theoretic absorbency	The practical absorbency
0°	0.931	0.9833	0.981
10°	0.932	1.0127	1.012
20°	0.934	1.0620	1.061
30°	0.937	1.1114	1.108
40°	0.942	1.1362	1.137
50°	0.948	1.1225	1.122
60°	0.952	1.0800	1.077
70°	0.956	1.0367	1.034
80°	0.959	1.0113	1.009
90°	0.961	1.0133	1.010

We work out that $\theta = 3°$, $\eta = 0.69$.

$$T\% = K^2 k[1 - \eta \sin^2(2\alpha + 2\theta)/2]/2$$
$$= K^2 k[1 - 0.69 \sin^2(2\alpha + 6°)/2]/2 \quad (5)$$

Then, we send $\alpha = 0°$, $10°$, $20°$, $30°$, $40°$, $50°$, $60°$, $70°$, $80°$, and $90°$ to eq. (5), and the theoretic absorbency can be worked out. Table I shows the contrast between the theoretic absorbency and the practical absorbency.

After the film was exposed for 5 min, the absorbencies of the exposed film were measured in the same way. According to Figure 6, we work out that $\eta = 0.57$, so the theoretic absorbency can be worked out. Table II shows the contrast between the theoretic absorbency and the practical absorbency. Therefore, this method to quantify the birefringence ability of the film is feasible.
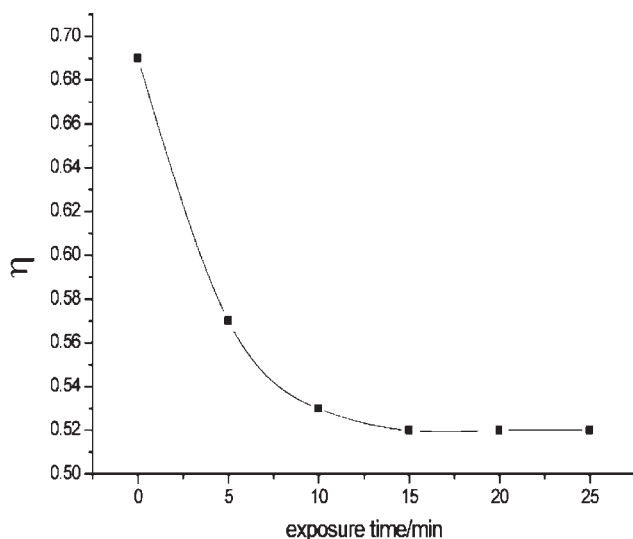
Figure 7 Birefringence ratio at different UV irradiation time.

TABLE III
The Birefringence Ratio of Different esterification Degree Through the UV

Time/s	0	5	10	15	20
Esterification degree					
0%	0.69	0.69	0.69	0.69	0.69
1%	0.69	0.69	0.69	0.69	0.69
3%	0.69	0.61	0.58	0.58	0.58
5%	0.69	0.57	0.53	0.52	0.52
10%	0.69	0.53	0.50	0.50	0.50

Birefringence of light-control polymer film

Figure 7 shows the oriented PVCi film's ratio of the decomposing light intensity to the total incident light intensity under the UV irradiation. The ratio decreases when the UV irradiation lasts. It means that the birefringence of the polymer film can be controlled by handling the time of UV irradiation. Through photoreaction, cinnamoyl side chains of PVCi film produced the photodimerized formation of cinnamoyl moieties. Because the orientation of the side chains of the polymer molecules makes a major contribution to photoelastic birefringence, the birefringence of the film decreases.

Table III shows the ratios of the decomposing light intensity to the total incident light intensity of different esterification degree PVCi films. When the esterification degree is low, the ratio does not change though the UV irradiation time increases. This is because the consistency of photosensitive group in the oriented film is very low, so the orientation structure could not be destroyed through photoreaction. As the esterification degree increases, the orientation structure could be destroyed through the reaction and the ratio decreases through the UV irradiation.

CONCLUSIONS

In this study, a feasible method to quantify the birefringence ability of the polymer film is verified. The orientation structure of the PVCi films can be destroyed more efficiently through UV irradiation when the esterification degrees are higher. For one PVCi film, the birefringence ability changes while the UV irradiation time is altered. Therefore, the birefringence of the oriented PVCi film can be light controlled by altering the UV exposing time. This is a promising method for information recording and can be applied in optical devices with light external stimulus.

References

1. Ohkita, H.; Ishibashi, K.; Tanaka, R.; Tagaya, A.; Koike, Y. Jpn J Appl Phys 2005, 44, 3975.

2. Barachensky, V. A. J Photopolym Sci Technol 1991, 4, 177.
3. Yu, Y.; Ikeda, T. Macromol Chem Phys 2005, 206, 1705.
4. Yu, Y.; Maeda, T.; Mamiya, J.; Ikeda, T. Angew Chem Int Ed 2007, 46, 881.
5. Reiser, A. Photoreactive Polymers; Wiley Interscience: New York, 1989; p 11.
6. Minsk, L. M.; Smith, J. G.; Deusen, W. P. V.; Wright, J. F. J Appl Polym Sci 1959, 2, 302.
7. Gibbons, W. M.; Shannon, P. J.; Sun, S. T.; Swetlin, B. J. Nature (London) 1991, 351, 49.
8. Gibbons, W. M.; Shannon, P. J.; Sun, S. T. Mol Cryst Liq Cryst 1994, 251, 191.
9. Shannon, P. J.; Gibbons, W. M.; Sun, S. T. Nature (London) 1994, 368, 532.
10. Iimura, Y.; Kusano, J.; Kobayaashi, S.; Aoyagi, T. T. S. Jpn J Appl Phys 1993, 32, L93.
11. Kawanishi, Y.; Tamaki, T.; Sakuragi, M.; Seki, T.; Suzuki, Y.; Ichimura, K. Langmuir 1992, 8, 2601.
12. Kawanishi, Y.; Tamaki, T.; Sakuragi, M.; Seki, T.; Ichimura, K. Mol Cryst Liq Cryst 1992, 218, 153.
13. Ichimura, K.; Hayashi, Y.; Akiyama, H.; Ikeda, T.; Ishizuki, N. Appl Phys Lett 1993, 63, 449.
14. Egerton, P. L.; Pitts, E.; Reiser, A. Macromolecules 1981, 14, 95.
15. Ichimura, K.; Akita, Y.; Akiyama, H.; Kudo, K.; Hayashi, Y. Macromolecules 1997, 30, 903.
16. Chae, B.; Lee, S. W.; Ree, M.; Jung, Y. M.; Kim, S. B. Langmuir 2003, 19, 687.