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Photoinduced orientation in ionic-bonding photo-cross-linkable polymers

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ABSTRACT

Photosensitive polymer materials with photo-cross-linkable side chain group were prepared based on ionic self-assembly technology. The complex materials were constructed by the coupling of polyelectrolyte and cinnamate units with different spacer length (6 or 12 methylene units designated PCAM6 and PCAM12, respectively). Photochemical properties including photo-cross-linking and photoinduced alignment of such a complex materials with transparency in a visible region were investigated by irradiating with a polarized laser. Furthermore, a homogeneous and stable liquid crystals' alignment was achieved on the resultant anisotropic orientation film. This facile method to construct photosensitive polymers would be very attractive due to its practical applicability in versatile optical elements with birefringent characteristics.

1. Introduction

Functional polymers are crucial materials in modern chemistry because of their unique properties. The synthesis of different kinds of functional polymers has received much attention in recent years, such as temperature or pH sensitive polymer [1,2], electric active materials [3], photosensitive polymers [4,5] and so on. Conventional method to prepare these functional polymers is attaching the functional moieties to a polymer scaffold through covalent bond. However, covalent chemical synthesis of these functional polymers is usually complex, time-consuming and expensive because the synthetic processes involve many steps with low yield. Therefore, from a practical point of view, covalently linked polymers are not so attractive. It's still a challenging task to find a facile, environment-friendly and low-cost approach to obtain functional polymers with good properties.

Recently, the design of materials through noncovalent interactions (such as hydrogen bonding, coordination binding, acid–base interaction, electrostatic interaction and so on) has been identified in supramolecular chemistry [6–8]. Among them, ionic self-assembly (ISA), i.e., using the electrostatic interactions to bind the oppositely charged tectonic units together, is the most widely encountered noncovalent interaction, and these complex architectures can be tuned by the selection of tectonics according to the requirement of different applications. This technique is undoubtedly an indispensable guideline for researchers who are interested in the synthesis of different functional polymeric materials. Some works have already been reported in this area, with examples including the synthesis of liquid-crystalline polymers with long-range order [8–18], redox-active polymers with ordered mesomorphous structure [19], and other functional polymers showing switchable, luminescence and reversibly switchable conducting properties [20–23]. Unfortunately, few studies focused on the construct of photosensitive polymers using the ISA. The generation of anisotropy in films of photosensitive polymers is active focus of research because of its applications in information and optical technologies. We previously reported the synthesis of an azobenzene-containing photosensitive polymer obtained by the ionic self-assembly of poly(ionic liquid) and azobenzene dye, which exhibits lyotropic liquid crystal and photosensitive character [24]. Then we also successfully synthesized a series of thermotropic liquid-crystalline photosensitive polymers by ionic self-assembly of polyelectrolyte and functional unit azobenzene ionic liquid crystal, which show highly ordered liquid-crystalline structure with a lamellar morphology of different *d*-spacing and pronounced photoinduced orientation [25]. In comparison with those containing azobenzene groups, polymeric films comprised of cinnamoyl units should be more attractive for the photo-alignment of liquid crystals (LCs) and other optical applications because cinnamoyl units are transparent in a visible region. Here, we presented the design and synthesis of photosensitive polymer containing cinnamate groups in its side chain by ISA technology. The molecular structure and the basic properties of the complexes were characterized by nuclear magnetic resonance (NMR), Fourier-transform IR (FT-IR), thermogravimetric analysis (TGA). The photoinduced orientation

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behavior of the polymer film by irradiating with *s*-polarized laser was investigated using polarized UV–vis spectroscopy. LC alignment on the complex film was also studied, which indicates that these photosensitive ionic-bonding polymers have many potential optical applications, especially as photo-alignment layer of liquid crystal displays.

2. Experimental section

2.1. Materials and polymer synthesis

Methyl 4-hydroxycinnamate, potassium carbonate, 33 wt% trimethylamine alcoholic solution, 1,6-dibromohexane, 1,12-dibromododecane and organic solvents involved in this work were purchased from the Sinopharm Chemical Reagent Company and used without further purification. Poly(styrene sulfonic acid) sodium (PSS) was obtained from Alfa Aesar and reported to have a molar mass (M_w) 70,000 and used as received. The nematic liquid crystal 4-*n*-pentyl-4′-cyanbiphenyl (5CB) was obtained from Slichem LC Materials Company, Shijiazhuang, China. All reagents were of analytical grade. The water used was doubly distilled. Photo-cross-linkable tectonic unit and complexes were synthesized according to Scheme 1.

2.1.1. The synthesis of methyl 4-(6-bromohexyloxy)cinnamate (A6)

A solution containing 10 g (0.056 mol) of methyl 4-hydroxycinnamate, 8.28 g (0.06 mol) of K_2CO_3 and a small amount of KI in 200 mL of acetone was refluxed for half an hour. Then 15.86 g (0.065 mol) of 1,6-dibromohexane was added, and the solution was refluxed for 24 h in a nitrogen atmosphere. The reaction mixture was filtered hot and the residue was washed with acetone. The acetone was removed under reduced pressure, and then petroleum ether (30–60 °C) was added to the concentrated organic extracts. The resultant solid was collected and dried. The crude product was recrystallized with hot filtration from ethanol. Yield: 9.55 g, 50%. ^{1}H NMR (400 MHz, DMSO-d_6, δ (ppm)), A6: 7.58–7.68, 6.92–6.98 (Ar**H**, 4H), 6.45–6.51 (Ar–**CH**═**CH**–, 2H), 3.98 (Br–C_5H_{10}–$\mathbf{CH_2}$–O–, 2H), 3.71 ($\mathbf{CH_3}$O, 3H), 3.24 (Br–$\mathbf{CH_2}$–, 2H), 1.80–1.63 (Br–CH_2–$\mathbf{CH_2}$–C_2H_4–$\mathbf{CH_2}$–CH_2–O–, 4H), 1.28 (Br–C_2H_4–$C_2\mathbf{H_4}$–C_2H_4–O–, 4H). Methyl 4-(12-bromohexyloxy)cinnamate (A12) was synthesized according to similar method stated above. ^{1}H NMR (400 MHz, DMSO-d_6, δ (ppm)), A12: 7.58–7.68, 6.92–6.98 (Ar**H**, 4H), 6.45–6.51 (Ar–**CH**═**CH**–, 2H), 4.00 (Br–$C_{11}H_{22}$–$\mathbf{CH_2}$–O–, 2H), 3.71 ($\mathbf{CH_3}$O, 3H), 3.26 (Br–$\mathbf{CH_2}$–, 2H), 1.75–1.60 (Br–CH_2–$\mathbf{CH_2}$–C_8H_{16}–$\mathbf{CH_2}$–CH_2–O–, 4H), 1.28 (Br–C_2H_4–$C_8\mathbf{H_{16}}$–C_2H_4–O–, 16H).

2.1.2. The synthesis of trimethylammonium functionalized methyl 4-(6-bromohexyloxy)cinnamate (CAM6)

8 g (0.023 mol) A6 was dissolved in 150 mL of absolute ethanol and the solution was refluxed for half an hour. Then 15 mL of trimethylamine alcoholic solution 33 wt% was added, and the solution was refluxed for 24 h under nitrogen protection. Ethanol was removed by evaporation. The crude product was purified by recrystallization from ethanol. ^{1}H NMR (400 MHz, DMSO-d_6, δ(ppm)), CAM6: 7.58–7.68, 6.92–6.98 (Ar**H**, 4H), 6.45–6.51 (Ar–**CH**═**CH**–, 2H), 3.98 (N–C_5H_{10}–$\mathbf{CH_2}$–O–, 2H), 3.71 ($\mathbf{CH_3}$O, 3H), 3.24 (N–$\mathbf{CH_2}$–, 2H), 3.03 (N($\mathbf{CH_3}$)$_3$, 9H), 1.80–1.63 (N–CH_2–$\mathbf{CH_2}$–C_2H_4–$\mathbf{CH_2}$–CH_2–O–, 4H), 1.28 (N–C_2H_4–$C_2\mathbf{H_4}$–C_2H_4–O–, 4H). Trimethylammonium functionalized methyl 4-(12-bromohexyloxy)-cinnamate (CAM12) was synthesized according to similar method stated above. CAM12: ^{1}H NMR (400 MHz, DMSO-d_6, δ (ppm)), CAM12: 7.58–7.68, 6.92–6.98 (Ar**H**, 4H), 6.45–6.51 (Ar–**CH**═**CH**–, 2H), 4.00 (N–$C_{11}H_{22}$–$\mathbf{CH_2}$–O–, 2H), 3.71 ($\mathbf{CH_3}$O, 3H), 3.26 (N–$\mathbf{CH_2}$–, 2H), 3.05 (N($\mathbf{CH_3}$)$_3$, 9H), 1.75–1.60 (N–CH_2–$\mathbf{CH_2}$–C_8H_{16}–$\mathbf{CH_2}$–CH_2–O–, 4H), 1.28 (N–C_2H_4–$C_8\mathbf{H_{16}}$–C_2H_4–O–, 16H).

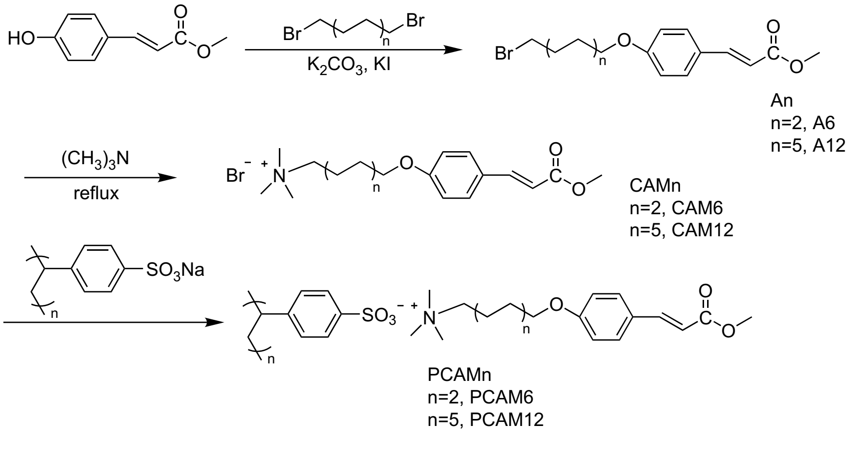
2.2. The preparation of ISA complexes

1 g CAM6 (0.0025 mol) and 0.5150 g PSS were dissolved in doubly distilled water, respectively. Then PSS aqueous solution was added dropwise to CAM6 aqueous solution in a 1:1 molar charge ratio. The precipitated complex PCAM6 was filtrated and washed several times with doubly distilled water to remove residual salts and possible noncomplexed precursors, then dried in vacuum at 50 °C for 12 h. The complex PCAM12 was synthesized according to similar method stated above.

2.3. Photoreaction

The PCAM*n* films were prepared by spin-coating a chloroform/ethanol (v:v, 9:1) solution of complexes (30 mg/mL) onto quartz plates, silica substrates and glass slides (speed: 2000 rpm, time: 20 s, room temperature: *ca.* 25 °C). The thickness of the resultant film was approximately 200–300 nm measured according to ellipsometer.

An *s*-polarized Nd:YAG laser (355 nm), with pulse duration of 5 ns and repetition rate of 10 Hz, was used as light source. The polymer film was fixed on an *X*–*Y* platform and moving speeds were 0.1 and 5 mm/s in *X* and *Y* directions, respectively. The incident angle θ was fixed at 15° with respect to the film normal. The PCAM*n* films were irradiated at room temperature (*ca.* 25 °C) with different exposure fluence. The degree of the photoreaction of the



Scheme 1. Synthetic pathway of PCAM*n*.

film was estimated using UV spectroscopy to monitor the decrease in absorbance at 311 nm (λ_{max}) for PCAM6 and 288 nm (λ_{max}) for PCAM12.

2.4. *Instruments and characterization*

Fourier-Transform IR spectra were recorded on a Perkin–Elmer Paragon 1000 FT-IR spectrometer on pressed thin transparent disks of the samples mixed with KBr. Nuclear magnetic resonance (NMR) studies were carried out with a Varian Mercury Plus 400 MHz spectrometer in DMSO-d_6 solvent at room temperature (*ca.* 25 °C). The chemical shifts were referenced relative to tetramethylsilane. Thermogravimetric analysis (TGA) was performed using a Perkin–Elmer model 7 instrument. Samples were heated at 20 °C/min from room temperature to 600 °C in a flowing nitrogen atmosphere. UV–vis spectra of the PCAM*n* films were recorded using a Perkin–Elmer lamda 20 UV–vis spectrophotometer. The polarized UV–vis spectra were measured using the same device equipped with a Glan–Taylor prism.

The dichroism (DR) of the photoinduced optical anisotropy of a film is calculated as Eq. (1).

$$\mathrm{DR} = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + A_{\perp}} \tag{1}$$

Here polarized UV–vis spectroscopies of the film were employed, where $A_{\parallel}$ and $A_{\perp}$ are the absorbance at λ_{max} parallel and perpendicular to laser polarization direction (E), respectively.

2.5. *LC alignment*

A LC cell was fabricated by sandwiching nematic LC (5CB) between a PCAM12-coated substrate and a counter buffing polyimide (PI) substrate. The two surfaces were separated by 10 µm spacers and held together using epoxy resin. A nematic LC 5CB was heated up to 45 °C to get isotropic phase, and then injected to the cell by capillary force. Optical measurements were carried out by placing LC cell between crossed polarisers and measuring the transmittance from a He–Ne laser at 628 nm using a detector coupled to an oscillograph.

3. Results and discussion

3.1. *The synthesis and thermal properties of ISA complexes*

The ISA complexes PCAM*n* were synthesized according to Scheme 1. The obtained CAM*n* have excellent solubility in water. The ISA complex as precipitates was obtained by 1:1 charge ratio mixing of two aqueous solutions of CAM*n* and PSS. The resultant complexes no longer dissolve in water, ethanol, THF, acetone or nonpolar solvents but can dissolve in chloroform/ethanol (v:v, 9/1), DMSO, DMF. The reason should be due to the high polarity of the PCAM*n* complex.

The formation of ISA complexes from CAM*n* and PSS can be testified by FT-IR. Fig. 1(a) shows the FT-IR spectra of CAM12, PSS and their complex PCAM12. The absorption band of PCAM12 at 1710 cm^{-1} corresponds to the characteristic peak of carbonyl stretching vibration from CAM12, while the absorption bands at 1200 cm^{-1}, 1032 cm^{-1} in the complex correspond to the asymmetric and symmetric stretching vibrations of the sulfonic groups from PSS. Similar to the assembly of phosphate or alkylcarboxylic acid and polyelectrolyte [10,14], we observe the significant shifts from 1040 cm^{-1} to 1032 cm^{-1} in the symmetric stretching vibrations of the sulfonic groups due to binding. Similar phenomenon was also clearly observed for PCAM6 as shown in Fig. 1(b).

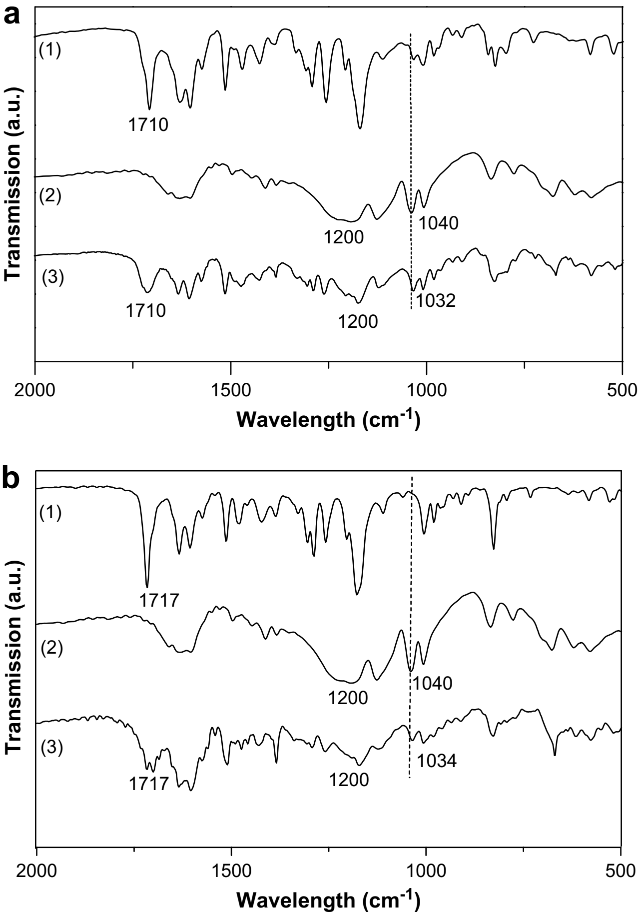


Fig. 1. (a) FT-IR of (1) CAM12, (2) PSS, (3) PCAM12. (b) FT-IR of (1) CAM6, (2) PSS, (3) PCAM6.

^{1}H NMR spectra of PCAM12 complex and CAM12 in DMSO-d_6 were also provided, as shown in Fig. 2. All proton signals belonging to PCAM12 and CAM12 are confirmed. The chemical shifts of 7.52–7.64 and 6.86–6.94 ppm in PCAM12 come from the proton signals of phenyl-moiety of CAM12 and styrene sulfonic-moiety of PSS. The CAM12 motif signals of the complex PCAM12 have slightly shifted to upfield compared to those of the resource CAM12, especially the peak of proton 1 (from 3.05 to 2.96), which resulted from the influence of the opposite negative charge unit. Furthermore, compared to the signals of small molecule CAM12, there is a new peak with a chemical shift of 1.56 ppm in PCAM12 which is corresponded to the proton signals of alkyl parts of PSS. In complex, the proton signals of side-chain moiety undergo obviously broadening compared to the resolved resonances of small molecule CAM12 due to its attachment to PSS.

The obtained powder material was subjected to thermal analysis to determine its stability, as shown in Fig. 3. Thermogravimetric analysis shows the degradation of ISA complexes took place in one step except the 5% weight loss of H_2O at about 100 °C. The complexes are stable up to at last 230 °C and their thermal stability increases slightly with increasing of their spacer length.

3.2. *The photoreaction of ISA complexes*

Fig. 4 shows the UV–vis absorption spectrum of the synthesized ISA complex PCAM12 in solution and film. The maximal absorptions of the PCAM12 in solution and in film are at 311 nm and

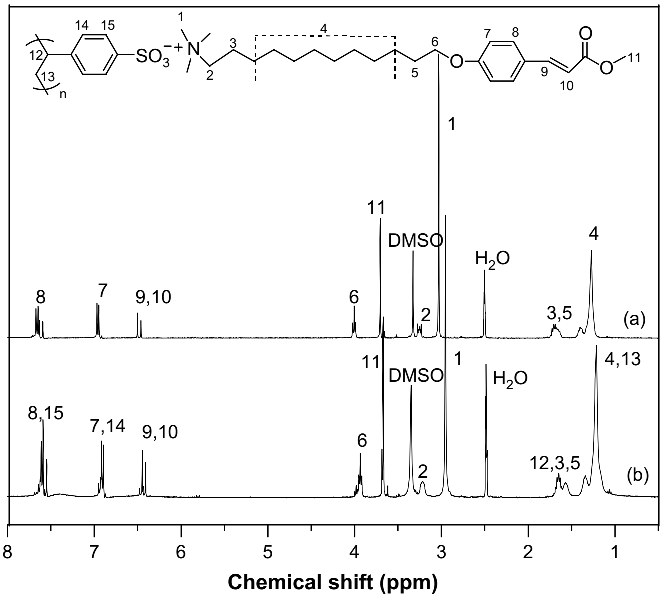


Fig. 2. ^{1}H NMR of CAM12 (a) and PCAM12 (b) in DMSO.

288 nm, while at 312 nm and 311 nm for PCAM6, respectively. The dramatic blue-shift of the maximal absorption of the cinnamic acid chromophores in film compared with that in solution indicates that aggregation occurs in the ISA complex films and the aggregation of the PCAM12 film is more obvious than that of the PCAM6 film.

Fig. 5(a) shows the changes in the absorption spectrum of a PCAM12 film upon irradiating with polarized laser. It reveals that the absorption at 288 nm gradually decreases with increasing exposure energy. The photoreaction of the PCAM12 includes a [2 + 2] photo-dimerization reaction and photo-isomerization of the cinnamic acid [26–28]. The photoreaction of a PCAM12 film was further elucidated by FT-IR spectroscopy. Fig. 5(b) shows the changes in the FT-IR spectrum of a PCAM12 film before and after irradiating with polarized laser. Here, the absorption band at 1126 cm^{-1} in the FT-IR spectra of the PCAM12 film, corresponds to the vibration of C–C framework, was chosen as the reference because its intensity kept stable before and after irradiating with polarized laser. The absorption band of the FT-IR spectrum at 1713 cm^{-1} corresponds to carbonyl stretching vibration, 1635 cm^{-1}

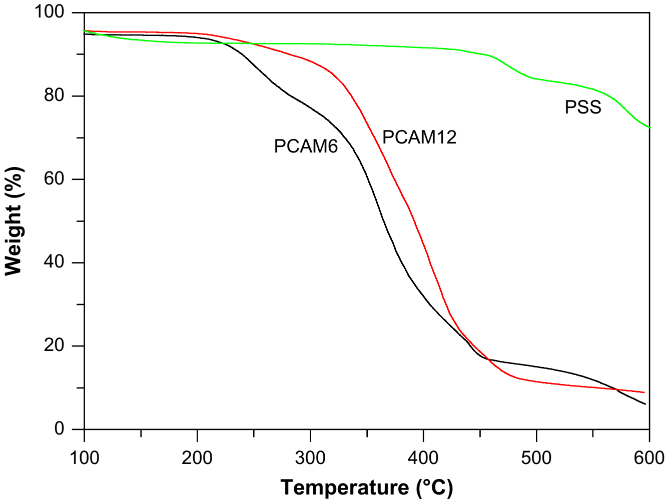


Fig. 3. TGA curves of PCAM6, PCAM12 and PSS.

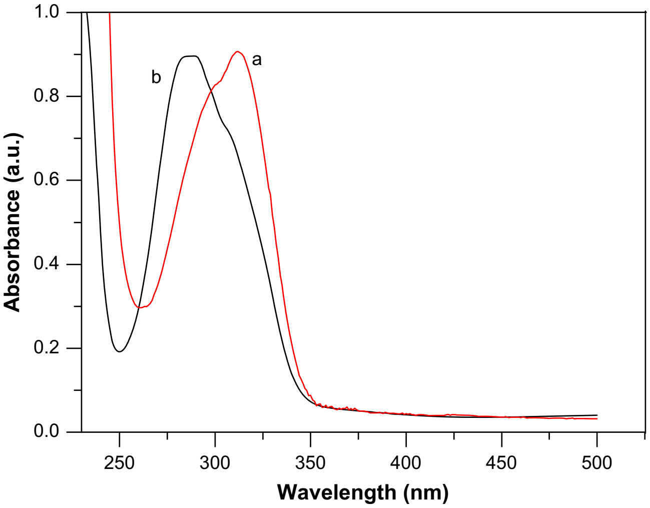


Fig. 4. Normalized UV–vis absorption spectrum of (a) PCAM12 in chloroform/ethanol (v:v, 9/1) and (b) PCAM12 film.

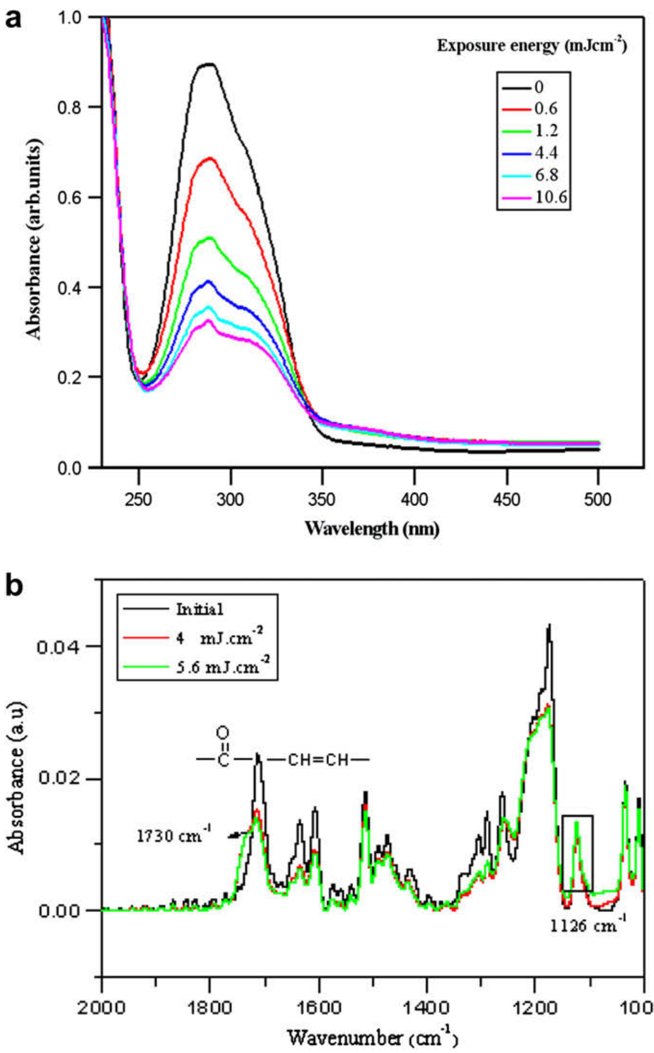


Fig. 5. (a) Changes in UV–vis absorption spectrum and (b) changes in FT-IR spectrum of a PCAM12 film upon irradiating with polarized laser.

corresponds to –CH=CH– stretching vibration, 1607 cm^{-1} corresponds to the stretching vibration of phenyl. All the bands mentioned above decrease with increasing exposure energy as a result of the [2 + 2] photo-dimerization reaction. Besides, a new band at 1730 cm^{-1} appears which corresponds to the carbonyl stretching vibration of the [2 + 2] photo-cross-linked groups.

Fig. 6 shows the degree of the photoreaction as a function of exposure energy, which is calculated by monitoring the decrease in absorbance at 288 nm for PCAM12 and 311 nm for PCAM6 using UV spectroscopy, respectively. It reveals that the PCAM6 and PCAM12 films exhibit similar photoreactivities. The degree of the photoreaction of the PCAM6 is larger than that of the PCAM12 at the same exposure energy, indicating that the length of spacer with 6 methylene units makes all cinnamate groups to easily close up with each other in complex polymer and further makes photo-cross-linking reaction to easily occur under irradiation. Besides, it should be noted that the conversion of the photoreaction is hard to achieve 100% even though the exposure energy is increased. That is to say, there is still a considerable amount of unreacted cinnamate groups at the late stage of the photoreaction because the network formed by photoreaction causes the solidification of the cinnamate groups and the mobility of unreacted cinnamate groups decreases dramatically.

3.3. Photoinduced optical anisotropy of ISA complexes

The optical anisotropy of the irradiated PCAM*n* film was confirmed by anisotropic absorption of the film in polarized UV–vis spectra as shown in Fig. 7. The PCAM12 film exposed to polarized laser, whose exposure energy was approximately 5.4 mJ/cm^2, exhibited large anisotropic absorption in polarized spectroscopy. It shows that the absorbance in the direction parallel to the polarization of the laser beam is remarkably smaller than that in the direction perpendicular to the polarization of the laser beam, and a negative DR is generated. These results demonstrated that the axis-selective photoreaction of the cinnamate groups occurred in the procedure of laser irradiation.

The comparison of the photoinduced DR of a PCAM12 film at 288 nm and a PCAM6 at 311 nm is presented in Fig. 8. The absolute value of DR increases with increasing exposure energy, and reaches a maximum (0.035 for PCAM6 and 0.095 for PCAM12) when the exposure energy is approximately 4–6 mJ/cm^2. Further irradiation leads to the decrease of the absolute DR value. Furthermore, we found that the absolute DR value for PCAM12 is larger than that of PCAM6 under the same exposure energy.

As we all know that the photoinduced anisotropy of cinnamate-containing materials was due to the axis-selective photoreaction of cinnamate groups. The main photoinduced reaction of cinnamate-containing materials includes photo-dimerization and E/Z photo-isomerization. Compared with photo-dimerization, E/Z isomerization was a fast process and mainly occurred when the light intensity was small than a certain value, in other word, at the initial stage of light irradiation [29,30]. Prolonging irradiation often leads to the reduction of the content of unsaturated double bond of the cinnamate groups and the further progress the photo-dimerization, which plays a minor role in the occurrence of the anisotropic property of the irradiated film. Ichimura et al. previously investigated the photoreaction of photo-cross-linkable polymer films containing cinnamate groups irradiating with LPUV light and concluded that the photoinduced anisotropy was mainly resulted from the polarization photo-isomerization of cinnamate group [27,31]. In our work, PCAM12 has a longer aliphatic spacer, which shows smaller degree of the photo-dimerization compared with PCAM6. On the other hand, long aliphatic spacer also

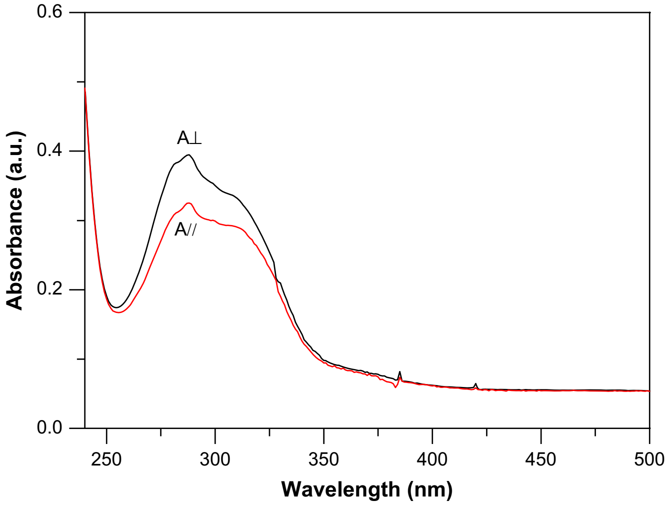


Fig. 7. Changes of polarized absorbance spectra in a film of the PCAM12 polymer under irradiation with pulsed UV laser at laser fluence of 5.4 mJ/cm^2.

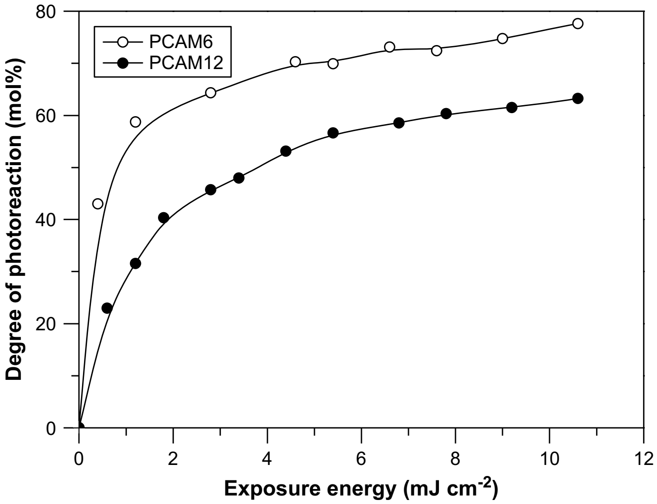


Fig. 6. Degree of the photoreaction of PCAM12 (closed circles) and PCAM6 (open circles) films as a function of exposure energy.

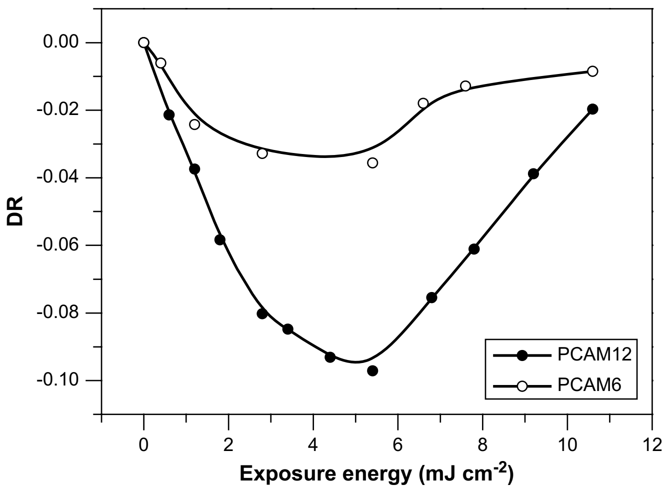


Fig. 8. Photoinduced DR values of PCAM12 film (closed circles) at 288 nm and PCAM6 film (open circles) at 311 nm as functions of exposure energy, respectively.

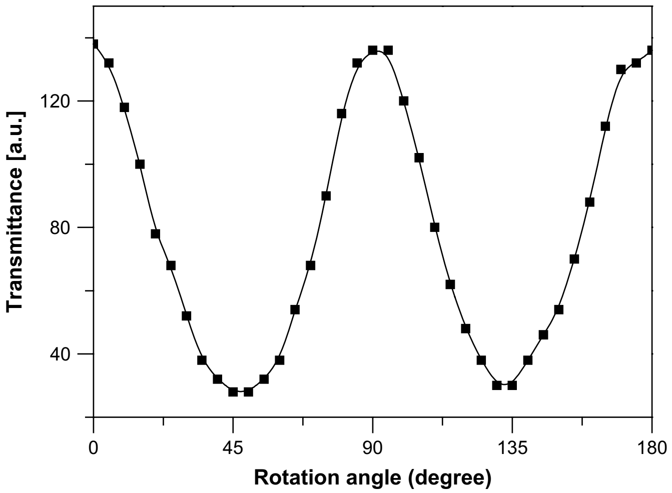


Fig. 9. Optical transmittance of LC cell as a function of the rotation angle of the cell between crossed polarisers. The cell was assembled by a PCAM12 substrate irradiated with pulsed laser at a fluence 5.6 mJ/cm^2 and a counter buffing polyimide substrate.

enhances the mobility of the cinnamate group. These characters make the degree of the photo-isomerization of cinnamate group in PCAM12 larger than that in PCAM6. So we think the anisotropy caused by photo-dimerization is relatively weaker than that from photo-isomerization in our experiment.

Another thing we deserve to pay close attention is the actual value of photoinduced anisotropy. Generally, the photo-cross-linkable polymer films containing cinnamate groups often generate a small photoinduced optical anisotropy irradiating with LPUV light, mostly at the level of or less than 0.04 [32–34]. Here, the DR values for PCAM12 can reach 0.095, which would be very useful for its practical application as versatile optical elements with large birefringent character.

3.4. LC alignment on PCAM12 film

In order to prove the potential application of this novel photo-cross-linkable material, preliminary optical investigations in the field of LC alignment were performed. It is well known that the alignment of LC molecules can be controlled by anisotropic surface of alignment layer, either by its topography or by oriented molecular chain. In order to investigate the LC alignment on the complex surface after being irradiated by polarized laser, a LC cell was fabricated using a PCAM12 film irradiating with the exposure energy of 5.6 mJ/cm^2 and a polyimide counter substrate rubbed in the direction parallel to the laser polarization dealing with PCAM12 substrate. The cell was examined by placing LC cell between two crossed polarisers and measuring the transmittance from a He–Ne laser at 628 nm using a detector coupled to an oscillograph. For a cell with uniform LC alignment between crossed polarisers, the transmittance changes with the rotation of LC cell with respect to the normal line of the substrate can be calculated according to the following formula: [35]

$$T = \sin^2(2\theta)\sin^2(\pi\Delta nd/\lambda)$$

where T is the transmittance of the light through the LC cell, θ is the rotation angle of the LC cell, d is the thickness of the cell, Δn is the refractive index of the filled LC molecules and λ is the wavelength of the detected laser. For a given cell, the terms except θ are fixed and the transmittance is only related to the rotation angle θ. In the experiment, the initial position of LC cell was set to be 0° when the buffing direction of the reference substrate was parallel to either polarization direction of the polarisers. The transmittance of He–Ne laser through LC cells is presented in Fig. 9. The LC cell exhibits maximum transmittance at the initial position, indicating that the directions of LC alignment on the two substrates were perpendicular to each other (twist-mode LC cell), we can conclude that the direction of LC alignment on the irradiated PCAM12 film was perpendicular to polarization of laser. The dependence of optical transmittance on the rotation angle of LC cell between crossed polarisers with a period of 90° demonstrated that the homogeneous LC alignment was achieved on the PCAM12 film.

4. Conclusions

A new kind of photosensitive polymer which contains cinnamate groups in the side chain was synthesized by ionic self-assembly of the cinnamate derivatives and poly(styrene sulfonic acid). The axis-selective photoreaction of the cinnamate groups irradiating with an *s*-polarized laser generates the optical anisotropy. The orientation behavior of the complex films is estimated by polarized UV spectroscopy, and the results show that the conversion of the photoreaction of the PCAM6 is larger than that of the PCAM12 under the same exposure energy, while the absolute negative dichroism values for PCAM12 are much larger than that of PCAM6 because of their different aliphatic spacers. Maximum of the absolute dichroism value of a PCAM12 film is about 0.095 when the exposure energy is 5.6 mJ/cm^2, which is a large value because photo-cross-linkable polymer films containing cinnamoyl groups often generate a small photoinduced optical anisotropy irradiating with LPUV light. Furthermore, a homogeneous and stable LC alignment on irradiated PCAM12 film was achieved.

Acknowledgments

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