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Two different reaction mechanisms of cinnamate side groups attached to the various polymer backbones

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Abstract

Cinnamate polymers are well known photoreactive polymers due to [2+2] cycloaddition reaction of cinnamate side group. In this work, we have found that the cinnamate side groups could be also reacted by thermal energy, and this reaction is presumed to attribute to the radical reaction of carbon double bond in the cinnamate groups. Contrary to the photocycloaddition reaction of the cinnamate side groups, the thermal reaction of cinnamate side group was closely related to the flexibility of polymer backbone. The difference of the mechanism between the photocycloaddition reaction and thermal crosslinking reaction was confirmed by ^{1}H NMR and ^{13}C NMR analysis of the model compound.

Keywords: Cinnamate; Polymer flexibility; Thermal crosslinking

1. Introduction

In recent years, the synthesis of polymers having a photocrosslinkable functional group has been an active field of research in polymer science because of their practical applications such as optical memory devices, holographic elements, and phase retarders for liquid crystal displays [1–6]. Since, the photocrosslinking is caused by the covalent bond formation from unsaturated chromophores, this kind of photosensitive polymers allow the modification of optical properties including refraction, birefringence, and the like, leading to the versatile photonics applications. The reaction of the 3, the emergence of anisotropic distribution of (2+2) photodimers and this could be utilized for the orientation of liquid crystal molecules [7–11]. This technique has been studied by many researchers for the practical application to the rubbing-free liquid crystal alignment layers, which are inevitable materials in the fabrication of liquid crystal display devices. For this purpose, photocrosslinkable polymers containing photodimerizable side groups such as cinnamate, coumarins [12,13], benzylidenephthalimidines [14], chalcones [15], and diphenylacetylenes [16] have been investigated.

In order to utilize the anisotropic distribution of photodimers of photocrosslinkable polymers for the molecular orientation film, the stable orientation of photodimers is required. However, the practical applications of photocrosslinkable polymers are quite restricted due to significant thermal relaxation of the photocrosslinkable polymers at high temperature, which causes the randomization of photodimers [17,18]. In order to enhance the thermal stability of molecular orientation of photocrosslinkable polymers, various methods were attempted such as blending of rigid polyimide [19], grafting of photodimerizable side groups onto the rigid polyimide backbone [20], and preparing the photoreactive liquid crystalline polymers [21].

Recently, we had found that the flexible polymer with cinnamate side groups irradiated by polarized UV preserved the liquid crystal orientation in spite of the thermal treatment at high temperature. This peculiar phenomenon was related to the additional crosslinking reaction of the unreacted cinnamate side groups by thermal energy [22]. From this result, we have suspected the possibility of thermal crosslinking reaction of photodimerizable cinnamate side groups attached to the flexible polymer backbone.

In this work, we studied the effect of the chain flexibility of polymer backbone on the reaction behavior of cinnamate side

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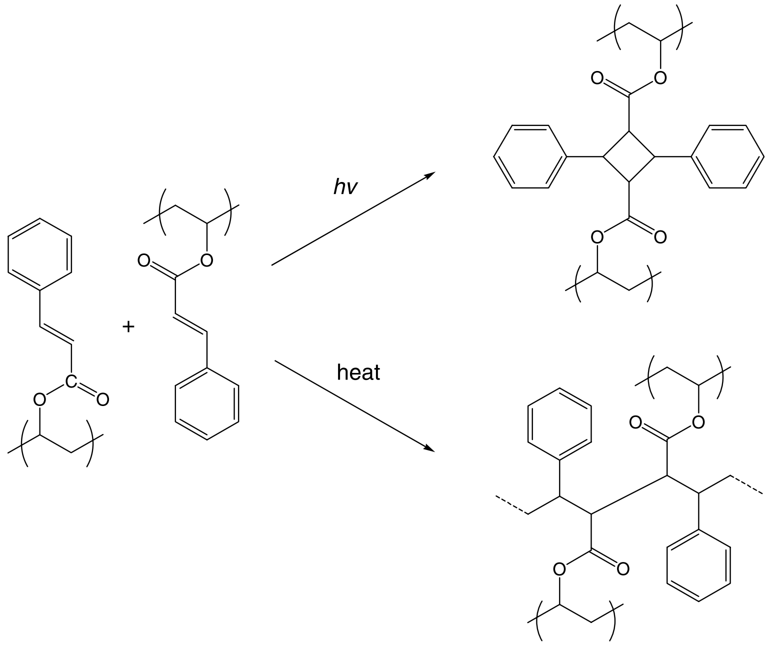

Fig. 1. Different mechanisms between photochemical and thermal reaction mechanisms of cinnamate side group.

groups induced by UV irradiation and heating. Three cinnamate polymers with different chain flexibility were prepared, and the photochemical and thermal reactions of these polymers were investigated by UV spectroscopy. In order to clarify the difference between the photocycloaddition and thermal crosslinking of the cinnamate side groups, we investigated the photochemical and thermal reaction mechanisms by taking ethyl cinnamate as a model compound. The photocycloaddition and thermal crosslinking reactions were supposed to be based on two different reaction mechanisms, pericyclic reacition and radical reaction (Fig. 1). Due to the radical mechanism of thermal crosslinking of cinnamate side groups, the chain flexibility of polymer backbone had considerable effect on the degree of thermal crosslinking reaction.

2. Experimental section

2.1. Polymer synthesis

All the materials were purchased from Aldrich and used as received. Poly(3-ethylene-*alt*-1 vinyl cinnamate) (PEVCi) was prepared by ring-opening metathesis polymerization [23]. Poly(vinyl cinnamate) (PVCi) was purchased from Aldrich. 4,4′-(Hexafluoroisopropylidene)diphthalic anhydride–3,3′-dihydroxy-4,4′-diaminobiphenyl (6FDA–HAB) was synthesized according to the synthesis scheme reported elsewhere [24] and the graft reaction of cinnamoyl chloride onto 6FDA–HAB was accomplished by using the reported method [20]. Poly(7-methacryloyloxy)coumarin (PMOC) was also synthesized by taking the procedure described in the previous report [13]. The chemical structures of the prepared polymers are shown in Fig. 2.

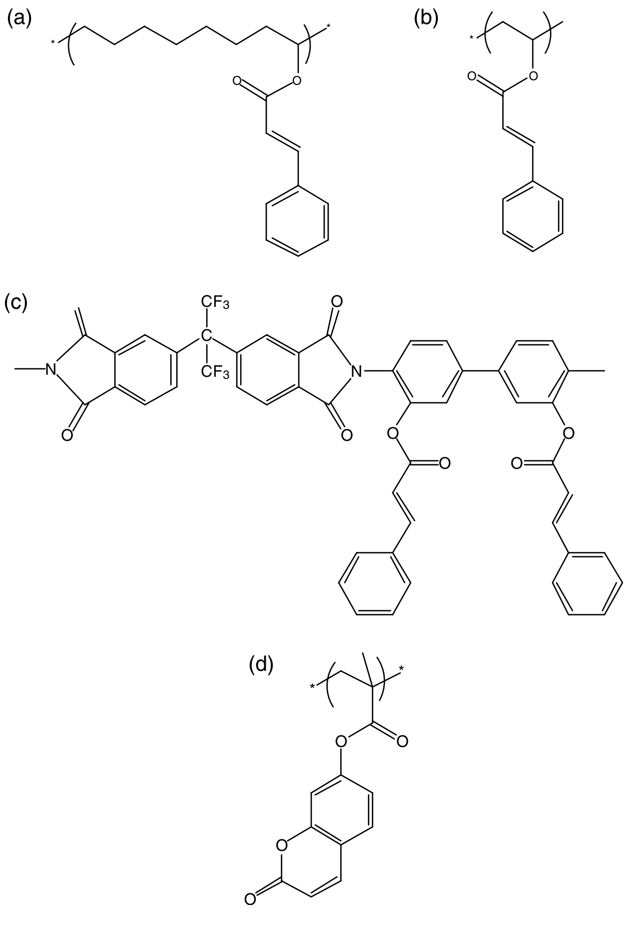

Fig. 2. Chemical structure of prepared polymers, (a) PEVCi, (b) PVCi, (c) 6FDA–HAB–Ci, (d) PMOC.

2.2. Characterization

The molecular weight was measured by a gel permeation chromatography (GPC, Waters 410 differential refractometer, Waters 600 pump) calibrated with polystyrene standards. Nuclear magnetic resonance (NMR) spectra were taken using Bruker AVANCE 400 spectrometer. Differential scanning calorimetry (DSC) experiment of the polymers was performed under a nitrogen atmosphere at a heating rate of 10 K/min with a TA Instruments 2010 analyzer. UV–Vis spectra were obtained with a Shimadzu UV-1601 spectrometer.

2.3. Photochemical and thermal reactions of polymers and model compound

Thin film of a polymer was prepared by spin-coating a polymer solution onto a quartz substrate. The film was irradiated by a 300 W high-pressure mercury arc lamp passed through UV filter (Oriel 59800). The intensity of the irradiated UV light measured using a UV detector (UIT-150, Ushio) was 20 mW cm^{-2} at 313 nm. The thermal reaction of polymer film was conducted by placing the polymer film on the hot plate (Cole Parmer, 04644 Digital Hot Plate) at 200 °C. The degree of reaction was monitored by the decrease in the peak intensity of –C=C– bond of the cinnamoyl group at 284 nm by UV–vis spectroscopy.

3. Results and discussion

3.1. Thermal properties of polymers

Characteristic properties of the prepared cinnamate polymers are summarized in Table 1. The glass transition temperature of the three cinnamate polymers is closely related to the chain flexibility of polymers. 6FDA–HAB grafted with cinnamate side groups (6FDA–HAB–Ci) showed higher glass transition temperature compared than the other two polymers and this would be attributed to the rigid polyimide backbone of 6FDA–HAB–Ci. In contrast, ethylene backbone of PEVCi can increase the chain flexibility of polymer and thus the glass transition temperature of PEVCi is found to be lowest among the three different cinnamate polymers.

3.2. Photochemical reaction of polymers

The chain flexibility of cinnamate polymers may influence on the photoreaction of the cinnamate side groups. The photoreaction of cinnamate polymers was investigated by observing the change of UV absorbance of cinnamoyl groups at 284 nm. Fig. 3 shows the change of UV absorption spectra of the three different cinnamate polymers with UV irradiation. All of the three cinnamate polymers showed the similar trend of the decrease of UV absorbance with irradiation energy in spite of the different chain flexibility from each other. Photochemical reaction of the cinnamate side group is the [2+2] cycloadditon reaction based on the pericyclic reaction mechanism and this reaction takes place easily in a single step by a cyclic

Table 1

Properties of polymers containing cinnamate side groups

Polymers	PEVCi	PVCi	6FDA–HAB–Ci	PMOC
Molecular weight (M_w)	103,000	200,000	35,000	32,000
Glass transition temperature (°C)	15	77	224	109

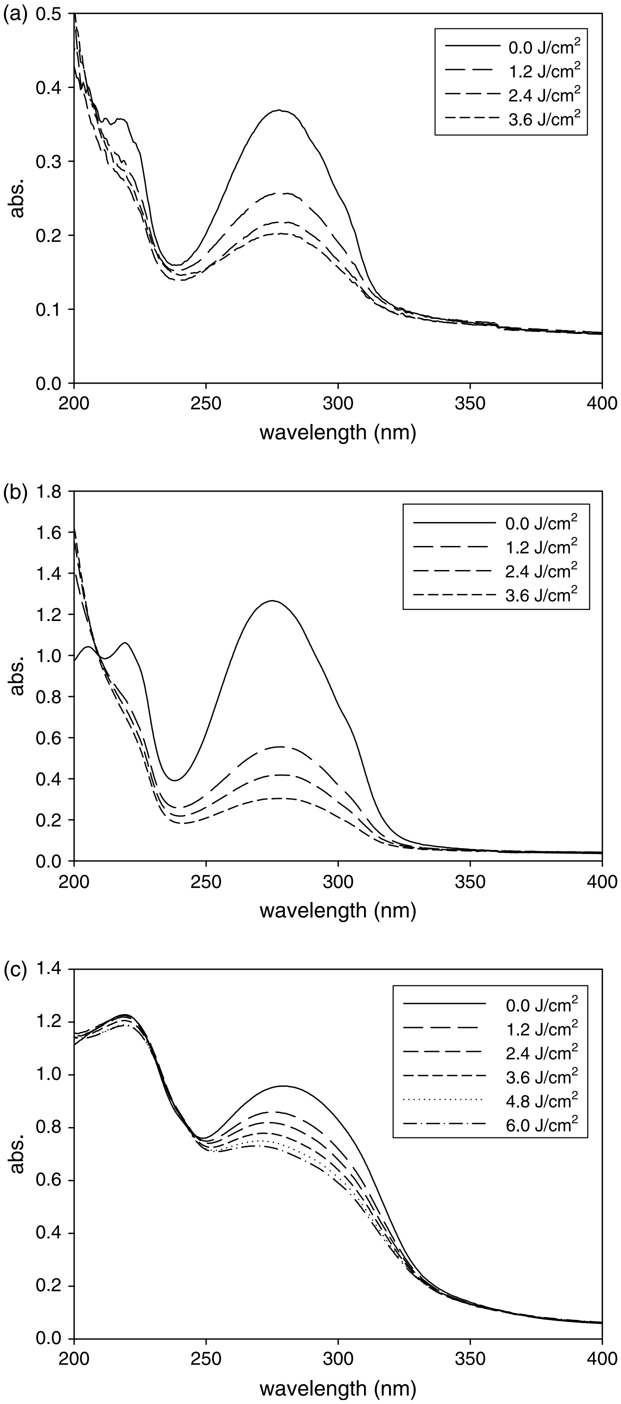

Fig. 3. The change of UV absorbance of polymer films with UV irradiation, (a) PEVCi, (b) PVCi, (c) 6FDA–HAB–Ci.

redistribution of bonding electrons [25]. It was reported that the [2+2] photocycloaddition of the cinnamate side groups attached to polymer backbone was possible in the case of the solid polymer films at room temperature [26]. For our cinnamate polymers, the photocycloaddition reaction of the cinnamate side groups was also observed for all the three cinnamate polymers and there was no clear relationship between the chain flexibility of polymer and the photocycloaddition reaction of cinnamate side groups.

3.3. Thermal reaction of polymers

The major chemical unit of the cinnamate groups related to photocycloaddition is the carbon double bond located between benzene ring and carbonyl group. The carbon double bond is excited by the UV irradiation and the cyclobutane ring is formed by the electron redistribution. Unlike the photocycloaddition, thermal cycloaddition reaction of the cinnamate groups does not occur due to the geometric constraints of molecular orbital [27]. However, the carbon double bond of cinnamate group might have the possibility of conventional radical reaction. In the case of radical reaction, the mobility of the carbon double bond might be an important factor for determining the behavior of reaction. Therefore, the radical reaction of the cinnamate side groups can be affected by the chain flexibility of polymers. We induced the thermal crosslinking reaction of the cinnamate polymers by heating the polymer film at 200 °C and the crosslinked film was not soluble in the common solvent such as NMP and cyclohexanone due to the crosslinking effect. We also investigated the degree of the thermal reaction of the cinnamate side groups. Fig. 4 shows the change of UV absorbance of the three different cinnamate polymers with heating time. It is found that there is a considerable difference in the thermal crosslinking reaction of the three cinnamate polymers. In the case of 6FDA–HAB–Ci, as is shown in Fig. 4(c), there is no change of UV absorbance after heating the polymer film for 60 min. However, as shown in Fig. 4(a) and (b), PEVCi and PVCi showed a clear change of UV absorbance after heating. PVCi showed a slight decrease of the UV absorbance and PEVCi showed a remarkable decrease of UV absorbance of the cinnamate side groups with irradiation time. In order to confirm the thermal crosslinking of the cinnamate polymers, the gelation phenomenon of polymer solution by heating at 200 °C for 20 h was also checked. PEVCi and PVCi exhibited the gelation of polymer solution and this result is in accord with the change of UV absorbance of the cinnamate polymers induced by heating, however, the gelation did not take place for 6FDA–HAB–Ci.

The difference of thermal reaction behavior of the three cinnamate polymers would be related to the chain flexibility of polymer backbone. The heating temperature of the polymer films was selected to be 200 °C, which is below the glass transition temperature of 6FDA–HAB–Ci (224 °C). In the case of 6FDA–HAB–Ci, the mobility of the cinnamate side groups is restricted by the rigid polymer backbone and this would inhibit the radical reaction of carbon double bonds of the cinnamate side groups. On the other hand, the glass transition temperatures of PVCi and PEVCi are much lower than the heating temperature and the thermal crosslinking of the cinnamate side groups is expected feasible. The glass transition temperature of PEVCi is much lower than that of PVCi, indicating that the chain flexibility of PEVCi is considerably higher than that of PVCi. Therefore, the radical reaction of the cinnamate side groups of PEVCi is more feasible and thus the degree of thermal reaction of PEVCi is higher than that of PVCi.

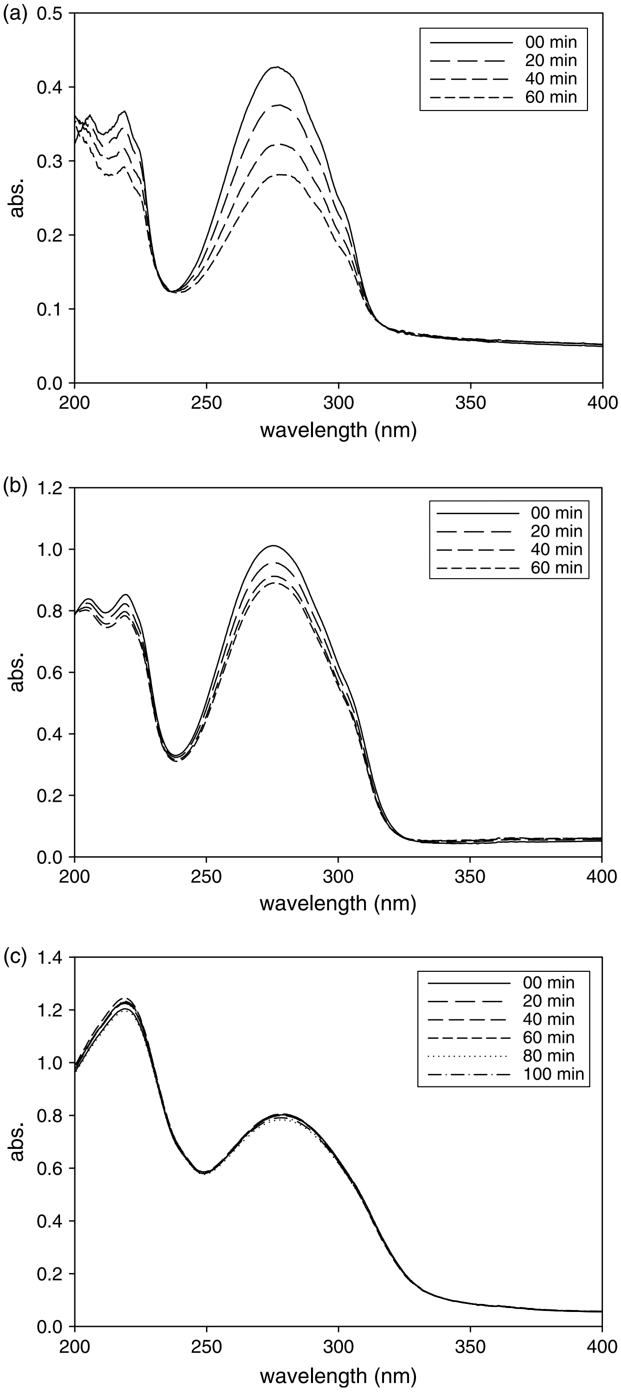

Fig. 4. The change of UV absorbance of polymer films with heating at 200 °C, (a) PEVCi, (b) PVCi, (c) 6FDA–HAB–Ci.

3.4. Effect of plasticization on the thermal reaction of cinnamate polymers

From the studies on the thermal crosslinking of the three different cinnamate polymers, it was found that the thermal reaction of the cinnamate side groups is closely related to the chain flexibility of polymer. In addition to this, the different backbone chemical structure of the three cinnamate polymers might also have some effects on the thermal reaction of the cinnamate side groups. In order to clarify the effect of the chain flexibility of polymer on the thermal reaction of cinnamate side groups, the systematic control of the chain flexibility of the cinnamate polymer was required. In many fields of polymer application, the chain flexibility of polymer is controlled by introducing small compatible molecules known as plasticizer [28]. In our work, we have increased the chain flexibility of PVCi by introducing dibutyl phthalate (DBP) as a plasticizer. We prepared the plasticized PVCi films by adding 50 wt% DBP based on PVCi to the polymer solution. The enhancement of the chain flexibility of PVCi was proved by the decrease in the glass transition temperature of the plasticized PVCi (T_g = 30 °C).

In order to investigate the thermal crosslinking of the plasticized PVCi, we also have measured the change of UV absorbance of the plasticized PVCi film with heating time (Fig. 5). The enhancement of the chain flexibility by using the plasticizer resulted in the increase of the degree of the thermal reaction of the cinnamate side groups and this is coincident with the previous result of the three cinnamate polymers. From these results, we could confirm that the thermal crosslinking of the cinnamate polymers is largely affected by the chain flexibility of polymers.

3.5. Model reaction of cinnamate group

In order to elucidate the mechanism of photochemical and thermal reactions of the cinnamate side groups, ethyl cinnamate was selected as a model compound and the photochemical and thermal reactions of the model compound were investigated. We checked the change of UV absorbance of ethyl cinnamate with UV irradiation or heating time (Fig. 6). The remarkable change of UV absorbance of ethyl cinnamate was observed for both cases of UV irradiation and heating at 200 °C. Compared with the cinnamate side groups attached to the polymer backbone, ethyl cinnamate has no hindrance on the mobility of the cinnamate groups for the thermal reaction. From the change of UV absorbance, the carbon double bond of ethyl cinnamate was found to react with UV irradiation as well as with thermal energy. This result provides an additional support on the effect of the chain flexibility on the thermal reaction of the cinnamate groups. However, from UV absorbance changes, we could not resolve each contribution from photochemical and thermal reactions. In order to clarify the mechanism of photochemical and thermal reactions of the cinnamate groups, we have investigated the change of chemical structure of ethyl cinnamate with UV irradiation or heating by ^{1}H NMR spectroscopy. Fig. 7 shows the change of ^{1}H NMR spectra of ethyl cinnamate with UV irradiation. In ^{1}H NMR spectra of ethyl cinnamate, the peaks around 7.5 ppm are due to the benzene ring and the peaks at 7.7 and 6.5 ppm arises from the carbon double bond of the cinnamate groups. The peaks at 4.2 ppm is assigned to methylene protons of ethyl cinnamate. As ethyl cinnamate was irradiated by UV, two

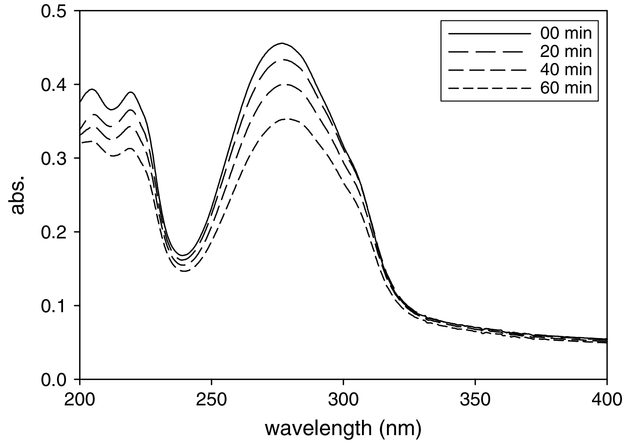

Fig. 5. The change of UV absorbance of plasticized PVCi films with heating at 200 °C.

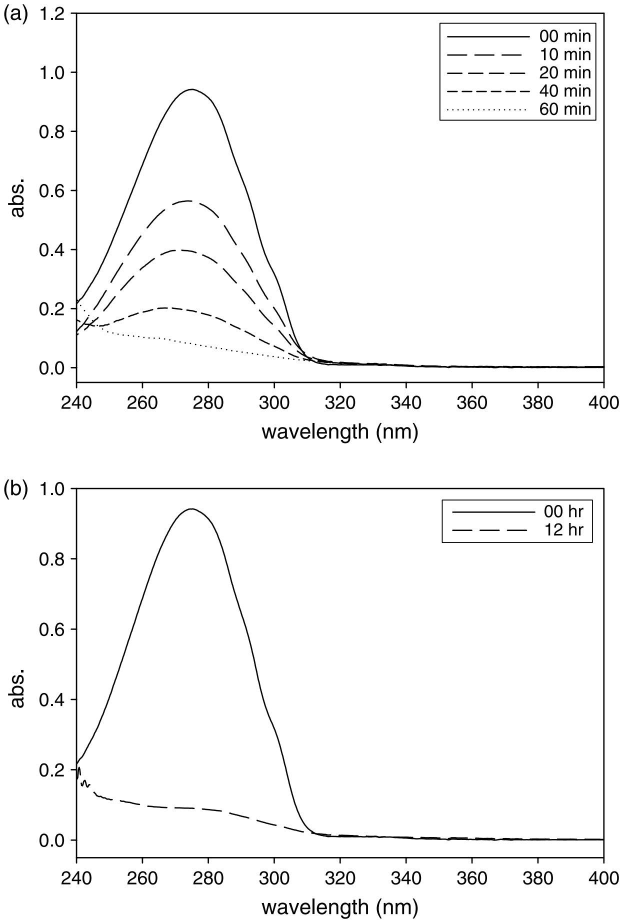

Fig. 6. The change of UV absorbance of ethyl cinnamate solutions (a) with UV irradiation, (b) with heating at 200 °C.

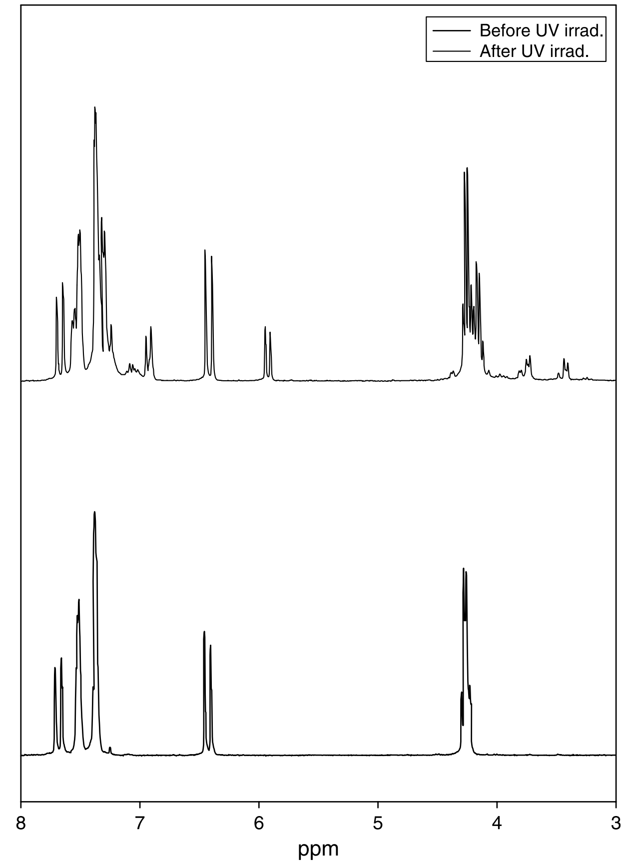

Fig. 7. ^{1}H NMR spectra of ethyl cinnamate before and after UV irradiation for 20 h.

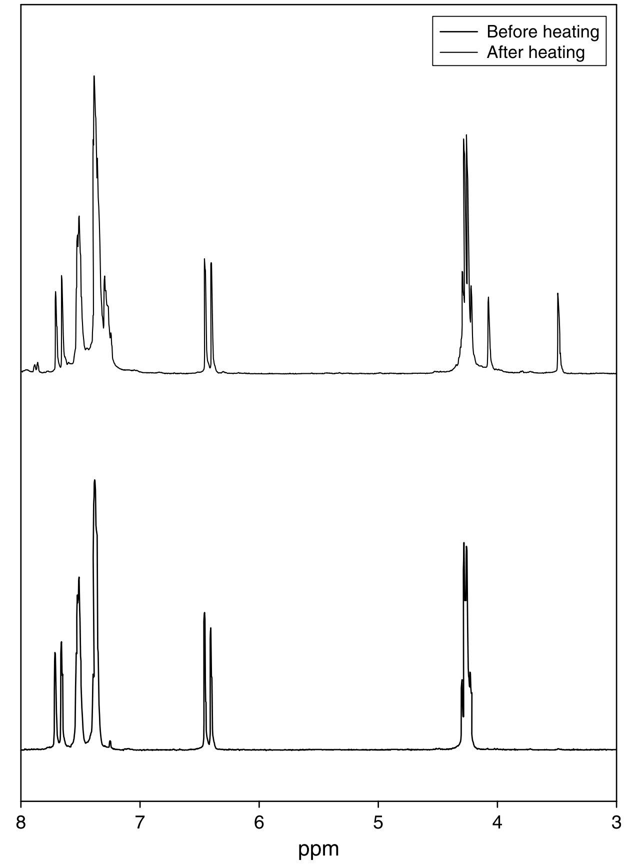

Fig. 8. ^{1}H NMR spectra of ethyl cinnamate before and after heating at 200 °C for 20 h.

groups of new peaks appeared. The first one was located at 6 and 7 ppm and the second one was at 3.3 and 3.8 ppm. Two different groups of new peaks correspond to the products of two different photochemical reactions of ethyl cinnamate, photoisomerization and photodimerization. The new peaks at 6 and 7 ppm are due to the protons of carbon double bond of ethyl cinnamate in cis conformation. The peaks at 3.3 and 3.8 ppm are generated from the protons of cyclobutane ring formed by the photodimerization of ethyl cinnamate and the peaks showed AA′BB′ pattern, the characteristics of cyclobutane ring [29]. From this result, it is found that the products of photochemical reaction of ethyl cinnamate are composed of *cis*-ethyl cinnamate and photodimer of ethyl cinnamate. This is in good agreement with the conventional photochemical reaction mechanism of cinnamate groups.

We also investigated the change of ^{1}H NMR spectra of ethyl cinnamate after heating (Fig. 8). The change of ^{1}H NMR spectra generated with heating was different from the result obtained with the UV irradiation. There was only one group of new peaks at 3.5 and 4 ppm and these correspond to the new protons generated by breaking the carbon double bond of ethyl cinnamate. Contrary to the proton peaks of cyclobutane ring of photodimer, the new peaks generated by thermal reaction did not show the AA′BB′ pattern. In order to conform those two mechanisms, we also have investigated the change of chemical structure of ethyl cinnamate with UV irradiation or heating by ^{13}C NMR spectroscopy. Fig. 9 shows the change of ^{13}C NMR spectroscopy of ethyl cinnamate with UV irradiation. The peaks at 45 and 47 ppm are generated from the carbon of cyclobutane ring formed by the photodimerization of ethyl cinnamate. We also investigated the change of ^{13}C NMR spectroscopy of ethyl cinnamate after heating (Fig. 10). New peaks at 35 and 40 ppm correspond to the new linear carbon in ^{13}C NMR spectroscopy. The reacted carbon peak after thermal reaction appeared in the upfield, comparing with the reacted

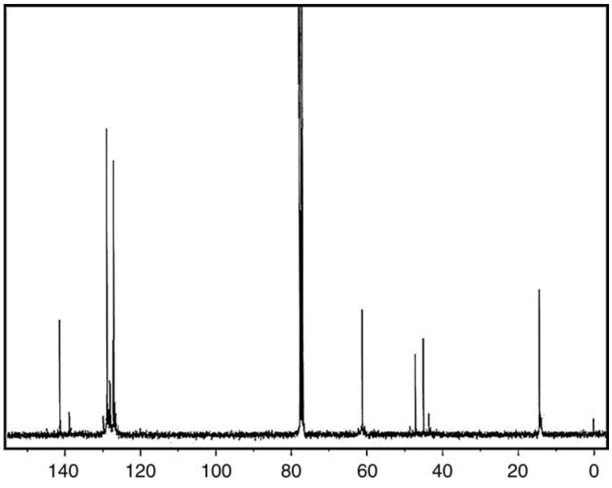

Fig. 9. ^{13}C NMR spectra of ethyl cinnamate after UV irradiation for 20 h.

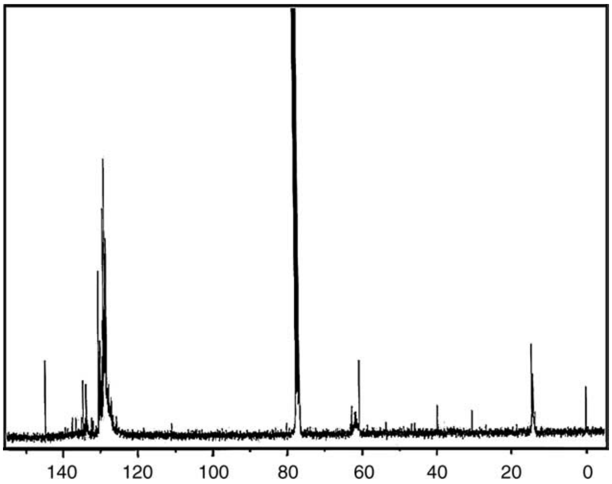

Fig. 10. ^{13}C NMR spectra of ethyl cinnamate after heating at 200 °C for 20 h.

carbon peak after UV-irradiation, due to the low density in cyclo compound.

From this result, we could presume that the new structure generated by thermal reaction of ethyl cinnamate is the linearly linked structure of carbon double bonds of ethyl cinnamate by radical mechanism.

3.6. The electron delocalization of photo-dimerizable groups and radical reaction

The [2+2] cycloaddition reaction generally occurs by photochemical process and the thermal process is known to be incongruent by the Woodward Hoffman rule [27]. In spite of that, the thermal crosslinking reaction of the flexible cinnamate polymers was also observed in this study and this is assumed to attribute to the radical reaction of the cinnamate side groups. Photodimerizable groups generally contain the carbon double bond participating in photocycloaddition and this also has the possibility of radical reaction. The degree of radical reaction is known to be related to the electron delocalization of carbon double bond. In order to investigate the effect of electron delocalization on the thermal reaction of photodimerizable group, we have checked with the thermal reaction of PMOC. Coumarin group is another representative photodimerizable molecules and its photochemical reaction was reported by many other researchers [12,13,16,30]. Compared with the resonance structure of cinnamate groups, the pi electrons of carbon double bond of the coumarin group would be delocalized more efficiently and the possibility of its radical reaction will be much lower than that of the cinnamate groups. In order to confirm the difference of thermal reaction between cinnamate and coumarin groups, we have investigated the change of UV absorbance of PMOC with heating (Fig. 11). In spite of heating for 60 min, there was no change of UV absorbance for PMOC. The glass transition temperature of the coumarin polymer was about 108 °C and this is much lower than the heating temperature 200 °C. Therefore, the carbon double bond of coumarin will have the sufficient mobility for the radical reaction. However, due to the strong electron delocalization of coumarin groups, the radical reaction of carbon double bond becomes more difficult and thus the thermal crosslinking of coumarin polymer was not observed. The resonance structure of photodimerizable group is also considered an important factor for determining the possibility of additional thermal crosslinking reaction of photodimerizable groups.

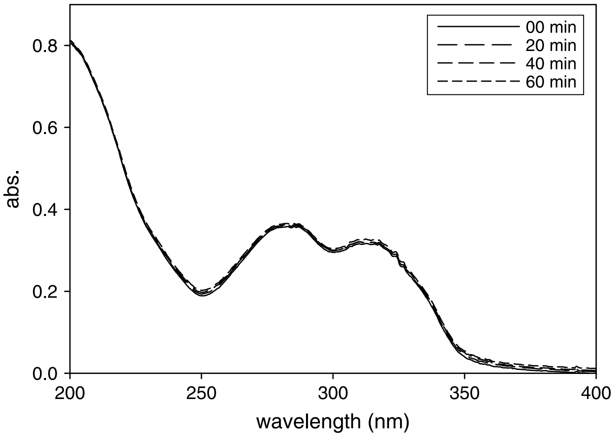

Fig. 11. The change of UV absorbance of poly(7-methacryloyloxy)coumarin film with heating at 200 °C.

4. Conclusions

In summary, the cinnamate side groups attached to polymer backbone are expected to undergo two possible chemical reactions, photocycloaddition and thermal crosslinking. The photocycloaddition is based on the [2+2] cycloaddition reaction mechanism and the thermal crosslinking is supposed to be based on the radical reaction mechanism. Due to the radical mechanism of thermal crosslinking reaction of the cinnamate side groups, the flexibility of polymer has the considerable effect on the thermal crosslinking of cinnamate polymers. The increase of the chain flexibility of the cinnamate polymer enhanced the thermal crosslinking reaction of the cinnamate side groups. The difference between the photocycloaddition and thermal crosslinking of the cinnamate side groups was confirmed by the ^{1}H NMR and ^{13}C NMR analysis of the photochemical and thermal reaction of model compound. The possibility of the radical reaction of photodimerizable molecule was also closely related to the electron delocalization state of carbon double bond.

Acknowledgements

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References

[1] Shibaev VP. Polymers as electroactive and photooptical media. Springer: Berlin; 1996.

[2] MacArdle CB. Applied photochromic polymer systems. New York: Blackie; 1991.

[3] Anderle K, Birenheide R, Eich M, Wendrorff JH. Makromol Chem Rapid Commun 1989;10:477.
[4] Benecke C, Seiberle H, Schadt M. Jpn J Appl Phys 2000;39:525.
[5] Ichimura K. Chem Rev 2000;100:1847.
[6] O'Neil M, Kelly SM. J Phys D: Appl Phys 2000;33:R67.
[7] Schadt M, Schmitt K, Kozinkov V, Chigrinov V. Jpn J Appl Phys 1992;7: 2155.
[8] Iimura Y, Satoh T, Kobayashi S. J Photopolym Sci Technol 1995;8:257.
[9] Ichimura K, Akita Y, Akiyama H, Hayashi Y, Kudo K. Macromolecules 1997;30:903.
[10] Obi M, Morino S, Ichimura K. Jpn J Appl Phys 1999;38:L145.
[11] Schadt M, Seiberle H, Schuster A. Nature 1996;381:212.
[12] Obi M, Morino S, Ichimura K. Macromol Rapid Commun 1998;19:643.
[13] Jackson PO, O'Neil M. Chem Mater 2001;13:694.
[14] Suh DH, Kudo K, Ichimura K. Macromol Chem Phys 1998;199:375.
[15] Makita Y, Natsui T, Kimura S, Nataka S, Kimura M, Matsuki Y, et al. J Photopolym Sci Technol 1998;11:187.
[16] Obi M, Mirono S, Ichimura K. Chem Mater 1999;11:656.
[17] Kawatsuki N, Kawakami T, Yamamoto T. Adv Mater 2001;13:1337.
[18] Kawatsuki N, Matsuyoshi K, Hayashi M, Takatsuka H, Yamamoto T. Chem Mater 2000;12:1549.
[19] Kim HT, Lee JW, Sung SJ, Park JK. Liq Cryst 2000;27:1343.
[20] Kim HT, Lee JW, Sung SJ, Park JK. Mol Cryst Liq Cryst 2000;338: 99.
[21] Oriol L, Pinol M, Serrano JL, Tejedor RM. J Photochem Photobiol, A 2003;37:45.
[22] Sung SJ, Cho KY, Yoo JH, Kim WS, Chang HS, Cho I, et al. Chem Phys Lett 2004;394:243.
[23] Yoo JH, Sung S-J, Jo S-Y, Pyun G-S, Cho I, Kim S-Y. In preparation.
[24] Lee SW, Chang T, Ree M. Macromol Rapid Commun 2001;22:941.
[25] McMurry J. Organic chemistry. Belmont: Brooks/Cole; 2004.
[26] Lin AA, Reiser A. Macromolecules 1989;22:3898.
[27] Woodward RB, Hoffmann R. J Amer Chem Soc 1965;87:395.
[28] Salamone JC. Polymeric materials encyclopedia. Boca Raton: CRC Press; 1996.
[29] Cibin FR, Bello ND, Doddi G, Fares V, Mencarelli P, Ullucci E. Tetrahedron 2003;59:9971.
[30] Kawatsuki N, Goto K, Yamamoto T. Liq Cryst 2001;28:1171.