

Synthesis of Poly(cinnam-4'-yl methyl methacrylate) Derivatives and Their Thermal Stability as Photoalignment Layer

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Photocyclizable poly(cinnam-4'-yl methyl methacrylate) derivatives bearing methoxy benzene (PMCMMA), anthracene (PACMMA), and coumarin (PCCMMA) have been synthesized *via* Heck type reaction. Three different types of polymers are photoreactable using linearly polarized UV light and applicable as liquid crystal alignment layer. Anthracene and coumarin containing polymers (PACMMA, PCCMMA) have better thermal stability than PMCMMA. This observation may be attributed to the glass transition temperature elevation due to the bulky size and another photocrosslinking site provided by anthracene or coumarin group.

Keywords : Poly(cinnamate), Photoalignment, LCD, Thermal stability.

Introduction

Although conventional rubbing technique has been widely used for the liquid crystal (LC) alignment, it has several problems such as the dust and static charge due to the mechanical contact of rubbing cloth, causing mechanical damage of active display layer. Moreover, the general trend to achieve high performance for liquid crystal device (LCD) applications requires surface anchoring conditions that cannot be provided by a traditional rubbing method. For example, wide viewing angles can be achieved using multiple director orientations within a given pixel.¹⁻³ Among non-contact techniques to overcome the problems, photo-alignment method is natural.⁴ Polyvinylcinnamate (PVCi) derivatives are the most-well known materials which give liquid crystal alignment perpendicular to the polarization direction of the light.⁴⁻⁷ One of drawbacks of PVCi was found to be the lack of thermal stability due to low glass transition temperature. More recently, new types of photoalignment materials based on chalcone⁸ and coumarin⁹ structure are reported giving better thermal stability and both chalcone and coumarin structures give LC alignment parallel to the polarization plane of linearly polarized UV. For the photo-alignment mechanism, there exist some controversial debates: Schadt regarded the template effect of the dimerized species is responsible for the LC alignment¹⁰ whereas Ichimura *et al.* suggested that isomerization reaction is the real cause of photo-alignment.¹¹ Nevertheless, LC photoalignment method is one of the promising techniques for the future LCD applications.

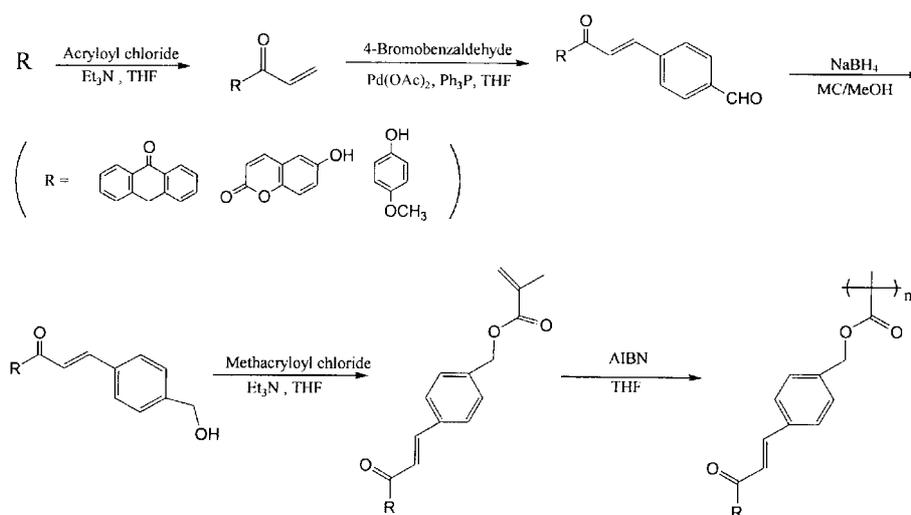
In this study, a series of poly(cinnam-4-yl methyl methacrylate) derivatives was synthesized and used as photo-induced alignment layer for liquid crystal. In our design, two different chromophores such as anthracene or coumarin were introduced in a given monomeric moiety. Their performances such as photoreactivity, thermal stability was compared.

Experimental Section

All chemicals were obtained from Aldrich. Solvents were purified before use. Polymer films on quartz plate were prepared using home-built spin-coater. 500Watts Mercury lamp (Altech, Korea) and UV-quality Glan-laser polarizer (Melles Griot, U.S.A.) were used as polarized UV light source. Glass transition temperature (T_g) and melting temperature (T_m) of the polymers were measured using differential scanning calorimetry (Perkin Elmer DSC7) and GPC (Waters 616LC) was used to determine the average molecular weight of polymers.

Synthesis. The overall synthesis procedure is summarized in Scheme 1. (9-Anthryl) acrylate, 4-methoxy phenyl acrylate, coumaryl acrylate were prepared by standard method. Starting reagents (0.025 mol of anthrone, 4-methoxy phenol, 7-hydroxy coumarine) and triethylamine (0.035 mol) were dissolved in 80 mL THF. Acryloyl chloride was added slowly at 0 °C under N₂ atmosphere. The resulting solution was allowed to stir for 2 h at room temperature and subsequently was poured into water. The aqueous layer was extracted with methylene chloride. The combined organic extracts were washed with brine, dried over anhydrous Na₂SO₄, and concentrated in vacuum. The acrylate derivatives were purified by flash column chromatography. The acrylate derivatives were converted to cinnam-4'-yl aldehyde form using Heck type reaction. Acrylate derivatives (0.03 mol), Pd(OAc)₂ (3 mmol) and PPh₃ (6 mmol) were dissolved in 100 mL tetrahydrofuran. Triethylamine (0.05 mol) and 4-bromobenzaldehyde (0.03 mol) was added at 0 °C. The resulting mixture was refluxed at 75 °C for 60h, poured into water. The aqueous layer was extracted with methylene chloride. The combined organic extracts were washed with brine, dried over anhydrous Na₂SO₄. After removing catalyst using Celite, the resulting product was purified by flash column chromatography. The cinnam-4'-yl aldehyde derivatives was converted into their alcohol derivatives using NaBH₄. The cinnam-4'-yl alcohol derivatives were further reacted with methacryloyl chloride and the monomeric

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forms of cinnam-4'-yl methacrylate were obtained. Radical polymerization of the monomeric compounds using AIBN as initiator yielded the corresponding polymers.

Measurements. In order to make thin polymer films, 2 wt% polymer solutions were prepared with CHCl_3 , filtered using $0.2 \mu\text{m}$ PTFE membrane filter (Gelman) and were spin-coated on $2.5 \text{ cm} \times 2.5 \text{ cm}$ quartz plate (ChemGlass). The resulting polymer films were exposed on polarized UV-source in order to induce photodimerization reactions with desired exposing times. The optical anisotropy of the prepared films was measured using UV-VIS spectrometer (Milton Roy 3000). In order to check the thermal stability of polymer films as photoalignment layer, a simple LCD cell was made using $25 \mu\text{m}$ gap tape. 5CB (Merck) as liquid crystal and methyl violet as probing dye were used. In order to eliminate capillary effect, 5CB/methyl violet solution was heated to 60°C above isotropic temperature and filled into LCD cell. 545 nm peak of methyl violet was utilized to check the dichroic ratio of prepared LCD cells.

Results and Discussion

Poly(4-methoxy phenyl cinnam-4'-yl methyl methacrylate) (PMCMMA), poly(9-anthryl cinnam-4'-yl methyl methacrylate) (PACMMA), and poly(coumaryl cinnam-4'-yl methyl methacrylate) (PCCMMA) were successfully synthesized according to Scheme 1. In the case of PCCMMA, the second step reaction had side-reaction due to the acidic hydrolysis of coumarin group and gave 20% yield. Currently, we are developing new synthesis method for this specific case.

Figure 1, 2 and 3 show UV spectra and dichroic ratio of PMCMMA and PACMMA, PCCMMA, respectively. In the case of PMCMMA, the dichroic ratio reaches the maximum at 700s whereas it requires 1500s for PACMMA. For PCCMMA, its photoreactivity is similar to that of PMCMMA. This indicates that bulky anthracene group hinders the photocyclization reaction of cinnamic moiety. Since we did not control the wavelength of polarized UV light in these cases, we cannot exclude the possibility of cross photocycloaddi-

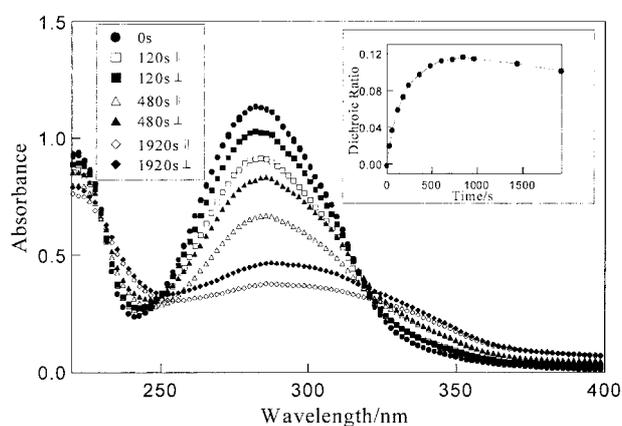


Figure 1. UV spectra and dichroic ratio of poly((4-methoxy phenyl cinnam-4'-yl methyl methacrylate)(PMCMMA). The number after symbol denotes the exposure time and polarization angle (|| means parallel direction, and \perp means perpendicular direction). The inset shows its dichroic ratio with the exposure time.

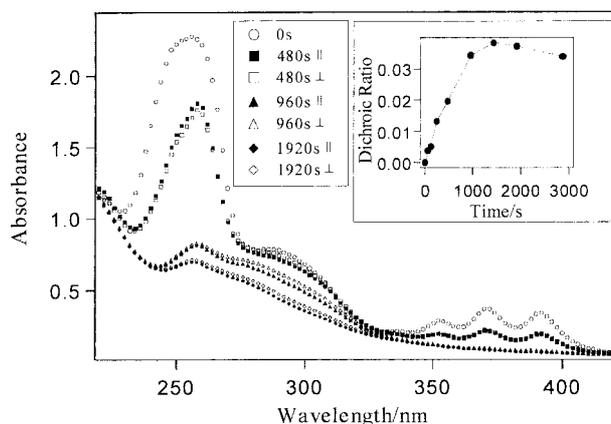


Figure 2. UV spectra and dichroic ratio of poly((9-anthryl cinnam-4'-yl methyl methacrylate) (PACMMA). The number after symbol denotes the exposure time and polarization angle. The inset shows its dichroic ratio with the exposure time.

tion reaction between cinnamic and anthryl groups. With 350 nm cutoff filter, photodimerization or/and photooxida-

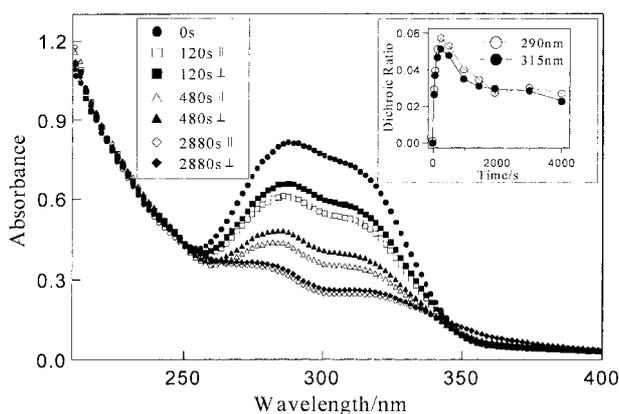


Figure 3. UV spectra and dichroic ratio of poly (coumaryl cinnam-4'-yl methyl methacrylate) (PCCMMA). The number after symbol denotes the exposure time and polarization angle. The inset shows its dichroic ratio with the exposure time. The absorbances at 290 nm, 315 nm come from cinnamic and coumarin group, respectively.

tion of anthryl group can be selectively induced but it did not show any optical anisotropy. Hence, anthracene itself cannot induce any optical anisotropy.

The LCD cell was constructed with two polymer-coated glass plates after UV-exposure. In order to monitor LC alignment, 5CB/methyl violet solution was prepared and inserted into the gap by capillary action. The polar plot of 545 nm methyl violet absorbance with PCCMMA film was obtained with polarized visible light after 10 min thermal annealing treatment successively at a given temperature, given in Figure 4. LCD cell with PCCMMA started to deteriorate above 80 °C and did not seem to have a good thermal stability. Whereas PACMMA and PCCMMA gave very good thermal stability up to 120 °C, as shown in Figure 5 and Figure 6, respectively. The better thermal stability may come from the fact that anthracene and coumarin group are bulkier than 4-methoxy phenyl group so that the the glass transition temperatures of PACMMA and PCCMMA is higher and consequently these polymers have better charac-

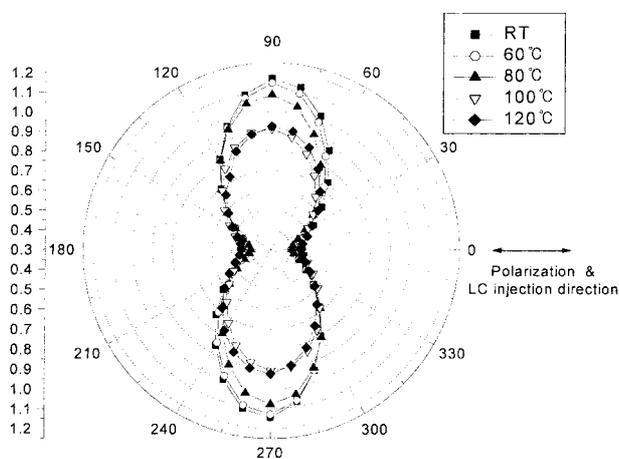


Figure 4. Polar plot of methyl violet absorbance in LCD cell with PCCMMA photoalignment layer.

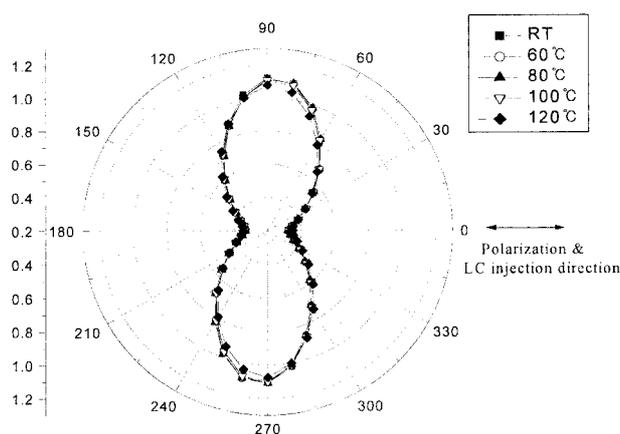


Figure 5. Polar plot of methyl violet absorbance in LCD cell with PACMMA photoalignment layer.

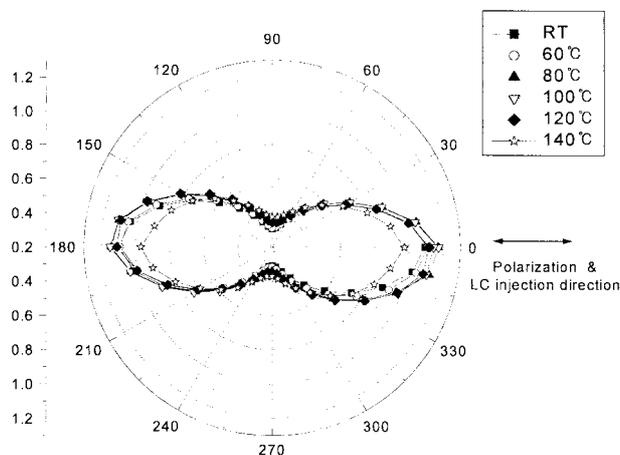


Figure 6. Polar plot of methyl violet absorbance in LCD cell with PCCMMA photoalignment layer. PCCMMA film was exposed on polarized UV for 700s before LCD cell assembly.

teristics. In fact, T_g of PACMMA and PCCMMA are 163 °C and 140 °C respectively, whereas T_g of PCCMMA is 89 °C. Another possible reason may be due to the fact that both PACMMA and PCCMMA have two cycloaddition sites. This can be another photocrosslinking site to increase the physical and chemical stability of these films. Neither a copolymer of MCMMA and ACMMA or a mixture of PCCMMA and PACMMA did not improve thermal stability as a photoalignment layer.

Cinnamic group is known to be a perpendicular director⁴⁻⁵ while coumarin moiety to be a parallel director⁹ after polarized UV exposure. Since PCCMMA has two different chromophores such as cinnamic and coumarin, it can be either a perpendicular director or a parallel director for liquid crystal. When we prepared LCD cells to check thermal stability of PCCMMA, 700s exposure time was selected giving high dichroic ratio. As shown in Figure 6, PCCMMA seems to be a parallel director controlled by coumarin group. However, when the PCCMMA film was exposed longer time, *i.e.* 2000s, it turned out to be a perpendicular director as given in Figure 7, which indicates the cinnamic group controls the LC alignment direction. The coumarin group

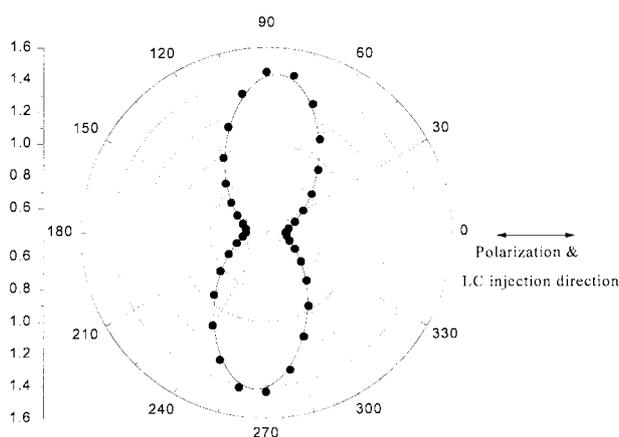


Figure 7. Polar plot of methyl violet absorbance in LCD cell with PCCMMA photoalignment layer. PCCMMA film was exposed on polarized UV for 2000s before LCD cell assembly. With longer UV exposure time, LC alignment direction was changed to perpendicular.

may be assumed to be more easily photocyclizable than cinnamic group. If this assumption is true, the dichroic ratio of coumarin group must become bigger than that of cinnamic group at relatively short exposure time. According to Figure 3, the dichroic ratios of both groups give no significant difference. Hence, both groups have similar photo-reactivity and the assumption is excluded. At this point, we can not deduce any reason why the LC direction can be changed from parallel to perpendicular by the exposure time. Further detailed experiments may need to clarify this issue. We tried to prepare the LC cell with UV bandpass filter in order to control the wavelength of UV, but it was not successful because the absorption maxima of cinnamic and coumarin group were not far from each other. The precise control may be performed using UV laser and it will be reported later.

Conclusions

Three different photopolymers, PMCMMA, PACMMA,

PCCMMA have been successfully synthesized. All three polymers can be used as a photoalignment layer for liquid crystal. Among them, PACMMA and PCCMMA have better thermal stability up to 120 °C. This observation may be attributed to the glass transition temperature elevation due to the bulky size and another photocrosslinking site of anthracene or coumarin group. PMCMMA and PACMMA were a perpendicular director whereas PCCMMA was either parallel or perpendicular director depending on the exposure time.

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