

Thermal degradation of poly(vinyl cinnamate)

Hee-Tak Kim, Jung-Ki Park*

Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, Yusung-gu, Kusung-dong, Daejeon 373-1, Korea

Received: 27 April 1998/Revised version: 25 June 1998/Accepted: 3 July 1998

Summary

The thermal degradation of poly(vinyl cinnamate), which is a representative photo-reactive polymer and a promising candidate as a rubbing-free liquid crystal alignment layer, was investigated by thermal and spectroscopic analysis to envisage the structural changes occurring during cell assembly process. Thermal analysis shows that the poly(vinyl cinnamate) is thermally stable at least upto 200°C. The spectroscopic investigations indicate that above 200°C the cinnamate groups are mainly broken at the carbonyl group and the detached cinnamate groups are evaporated resulting in the weight loss. The crosslinking during thermal degradation seems to be mainly caused not by the cyclobutane ring formation, which readily occurs by UV irradiation, but by the chain transfer of the thermally generated radical.

Introduction

The leading technology for flat, high-resolution computer and television screens is based on twisted nematic liquid-crystal displays (1). The successful operation of these displays requires control of molecular alignment of liquid crystal, which is currently achieved by confining the liquid crystal(LC) between mechanically rubbed surfaces (2). However, in addition to the practical difficulties associated with rubbing (in particular, development of static electricity and appearance of dust particles), the resulting displays suffer from the restricted viewing angles arising from the uniaxial nature of the LC alignment process (3,4).

In the last few years, alignment control of LC molecules on photopolymer substrates has been realized (5~9) and the methods are considered to become a most promising candidate as a post-rubbing technique because it can solve the problems associated with mechanical rubbing (8). Poly(vinyl cinnamate) (PVCi) is a typical polymer which can be photo-crosslinked anisotropically by dimerization of two cinnamate groups with linearly polarized UV light (10~12). Even though the

* Corresponding author

mechanism of LC alignment by photo-crosslinked poly(vinylcinnamate) is still unclear, the anisotropic distributions of the dimerized cinnamate groups and/or the remaining cinnamate groups are considered to be important in LC alignment (10~12).

Besides good LC alignment property, LC alignment layer is required to have good thermal stability, because LCD production includes high temperature process such as cell assembly in which LCD is pressed at rather high temperature. The structural changes in the remaining cinnamate groups of PVCi during the cell assembly process may disrupt the structural anisotropy of the film, which diminishes the uniformity of liquid crystal alignment. In the present article, the structural changes of PVCi at enhanced temperatures were investigated by thermal and spectroscopic analysis. An attempt was also made to elucidate the degradation mechanism of the cinnamate groups of PVCi at higher temperatures.

Experimental

Sample preparation

PVCi, of which weight averaged molecular weight is 200,000, was purchased from Aldrich and used as received. For spectroscopic analysis, the benzene solution of PVCi was spread on the substrate (silicon wafer for FTIR measurement and quartz slide for UV measurement), and dried under atmosphere for 1 day. The remaining benzene was further removed by drying *in vacuo* for 1 day. The powdered PVCi was used for thermal analysis.

Thermal analysis

For thermal analysis, differential scanning calorimetry (DSC) (Thermal Analyst 2000, Dupont) and thermogravimetric analysis (TGA 2950, TA Instruments) were used. All the measurements were carried out at a heating rate of 10°C/min under N₂ atmosphere.

Spectroscopic analysis

FTIR spectra were acquired on a Bomem 102 model fourier transform spectrometer at a resolution of 4cm⁻¹. A minimum of 40 scans was signal-averaged and the spectra were stored on a magnetic disc system. An *in-situ* measurement of FTIR spectra at various temperatures was conducted by using the temperature controllable FTIR kit (Graseby Specac Co.). After the temperature of the kit was completely equilibrated, the films on silicon wafers were inserted into the kit and the spectra were acquired. The time required for obtaining each spectrum was 1 min.

The ¹H NMR spectra were recorded on Bruker AMX 500. Lamor frequency for ¹H NMR was 500MHz. The solvent used for the sample preparation was benzene-d₆. TMS was used as a reference.

Mass spectra were acquired by using a VG Autospec Ultima mass spectrometer. The samples were heated from 50 to 400°C with a heating rate of 10°C/min.

UV spectra were recorded with a Hewlett Packard 8452A spectrometer. All measurements were done with quartz slides as a substrate. The uncoated part of the slide was used as a reference.

Results and Discussion

Thermal stability of PVCi

The conventional PVCi is actually the copolymer of vinyl cinnamate and vinyl alcohol. The chemical structure of PVCi used in this study was characterized by ^1H NMR spectrum given in Fig. 1. The peaks for the methine and hydroxy protons of the vinyl alcohol unit are revealed at around 4.3 ppm. The peak at 6.0 ppm corresponds to the methine proton of the vinyl cinnamate unit. The relative mole fraction of the vinyl cinnamate unit in the copolymer, which was determined from the relative area of these peaks, was 76%. Detailed peak assignments of PVCi, which are based on the ^1H NMR spectra of pure poly(vinyl alcohol) and monomeric cinnamic acid, are also given in Fig. 1.

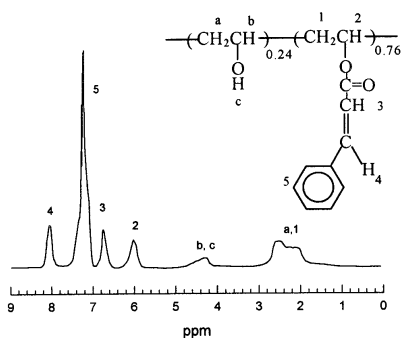


Fig. 1 ^1H NMR spectrum of poly(vinyl cinnamate)

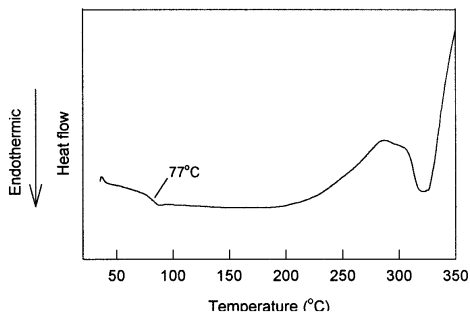


Fig. 2 DSC thermogram of poly(vinyl cinnamate)

Figure 2 shows the DSC thermogram of PVCi. The glass transition temperature of PVCi was found to be 77°C . Broad exothermic peak was revealed above 200°C , which would be attributed to the thermal degradation of PVCi. The degradation process above 200°C was evidenced by TGA thermogram shown in Fig. 3, from which the slow weight loss in the temperature range of $200\text{--}270^\circ\text{C}$ and the abrupt weight loss in the temperature range of $280\text{--}340^\circ\text{C}$ are apparent.

From these thermal analyses, it can be concluded that PVCi used in this study is thermally stable at least upto 200°C . The cell assembly temperature above 200°C would cause the structural changes of PVCi which can influence liquid crystal alignment.

Structural changes of PVCi during thermal degradation

To know the structural changes during the degradation processes, the FTIR spectra of PVCi obtained during isothermal heating at various temperatures were

examined. Figure 4 shows the FTIR spectra of PVCi heated at 200, 250, and 300°C in the range of 1400~1900 cm^{-1} . The intense peaks at 1710 cm^{-1} and the peaks at 1640 cm^{-1} correspond to the C=O and C=C stretching vibrations of the cinnamate units in PVCi respectively. Apparently, the spectra did not change with heating time at 200°C, while significant changes of the spectra were found with time at 250 and 300°C. The peak intensities of the C=C and C=O stretching vibrations of the cinnamate units were decreased with time under isothermal heating at 250 and 300°C. The new peaks, which would be attributed to the ketone or carboxylic acid groups produced from thermal degradation of PVCi, were revealed at 1780 and 1680 cm^{-1} , and their intensities increased with heating time.

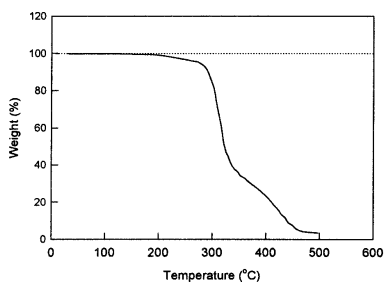


Fig. 3 TGA thermogram of poly(vinyl cinnamate)

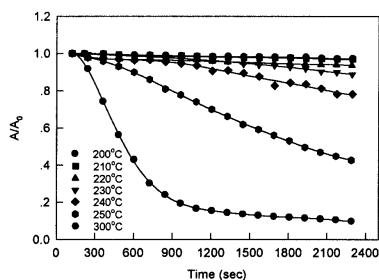


Fig. 5 Time dependent changes of the intensity of the C=C stretching vibration

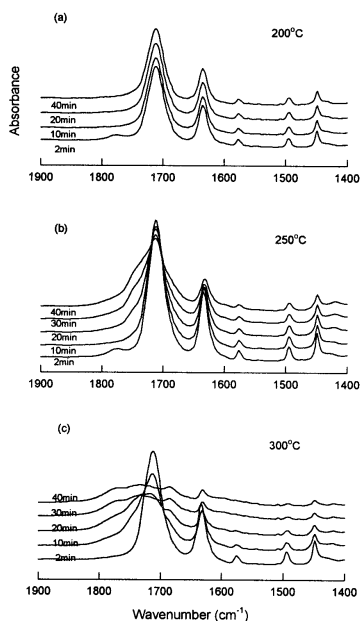


Fig. 4 Change of FTIR spectrum in the range of 1400~1900 cm^{-1} of poly(vinyl cinnamate) during isothermal heating at (a) 200°C (b) 250°C (c) 300°C

Considering the role of the cinnamate group in PVCi on the liquid crystal alignment, it would be important to investigate the time-dependent changes in the intensity of the C=C stretching peak. Figure 5 shows time dependent changes of the intensity of the C=C stretching peak at various heating temperatures. The double bond of the cinnamate groups is nearly stable upto 210°C. Above 220°C, considerable decreases in intensities of the C=C stretching peak with heating time were observed: heating at 250°C for 30 min resulted in the decrease of the cinnamate groups by half of the initial content and only 13% of the initial cinnamate groups remained after the heating at 300°C for 30 min.

Figure 6 shows the mass spectra of the poly(vinyl cinnamate) obtained at 250 and 300°C. At both temperatures, the strongest peak was observed at $m/e=147$ which

exactly corresponds to the one cleaved at the ester linkage of the cinnamate group. The peak at $m/e=103$ also comes from the cleaved one of the cinnamate group. It suggests that the main thermal degradation process of PVCi is the breakage of the cinnamate group.

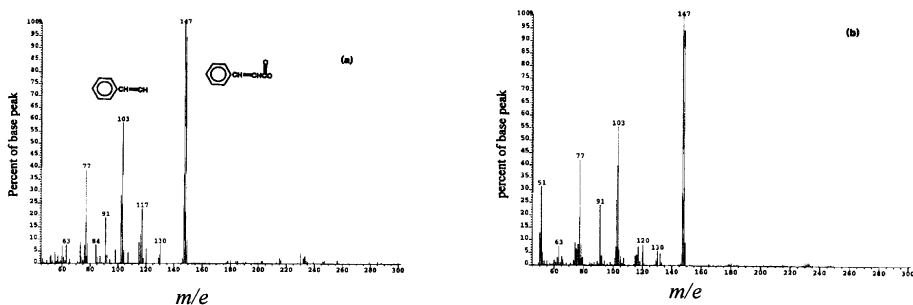


Fig. 6 Mass spectra of poly(vinyl cinnamate) at (a) 200°C (b) 250°C

Figure 7 shows the time-dependent changes of the FTIR spectra of PVCi in the range of $2500\sim 4000\text{ cm}^{-1}$ acquired during isothermal heating at 200, 250, and 300°C. The spectra were nearly unchanged with time at 200°C, which is reconfirmation on stability of the polymer at this temperature. One thing to be noted here is the relative changes of the peak intensities with time for the OH stretching ($3400\sim 3630\text{ cm}^{-1}$), CH stretching of benzene ($3000\sim 3150\text{ cm}^{-1}$), and CH stretching of the main chain ($2850\sim 3000\text{ cm}^{-1}$) at 250°C. The CH stretching vibration intensities of the benzene group decreased more significantly with heating time than the intensities of the OH stretching vibration and the CH stretching vibration of the main chain. With the results on the reduction in peak intensities of the C=C and C=O stretching in PVCi at 250°C, it represents that the thermal degradation at 250°C is dominated by the degradation of the vinyl cinnamate unit while the vinyl alcohol unit is relatively stable at this temperature. However, the intensity of the OH stretching peak from the vinyl alcohol unit was greatly reduced at 300°C. The 30min heating led to almost complete degradation of the vinyl alcohol unit in PVCi.

Crosslink formation during thermal degradation

The heating at 250 and 300°C caused the crosslinking of PVCi, which was confirmed by insolubility of the heated PVCi. Among the PVCis heated at 200, 250, and 300°C for 5min, only the PVCi heated at 200°C was soluble in benzene, whereas the other two samples showed swelling behavior evidencing the occurrence of crosslinking reaction. The degree of swelling of the PVCi heated at 300°C was lower than that heated at 250°C, which seems to be due to higher crosslinking density of the PVCi heated at 300°C. The solubility test shows that the degradation results in crosslinking which increases with increasing the degradation temperature. It can be simply explained by the thermal generation of radical and subsequent chain transfer of the radical to the other chains as is the case for polyacrylate (13-16). However, it is also possible that the dimerization of cinnamate group can cause crosslinking by

cyclobutane ring formation which is known to readily occur by UV irradiation (7,10~12).

The cyclobutane ring formation by UV irradiation is frequently confirmed by the changes in UV spectra of PVCi (7). Figure 8 compares the UV spectra of the unheated, the heated at 250°C and the UV irradiated PVCis. The intense peak at 270nm corresponds to the cinnamate group. As indicated by the comparison of the UV spectra of the unheated PVCi (Fig. 8 (a)) with that of the UV-irradiated PVCi (Fig. 8 (f)), the cyclobutane ring formation by the dimerization of two cinnamate groups causes the decrease in absorbance of the band at 270nm and the increase in absorbance of the band at 190nm that is attributed to the cyclobutane ring. Interestingly, the overall features of UV spectrum of PVCi were nearly unchanged by the heating at 250°C, even though slight increase of the absorbance at 190nm was observed. This result indicates that the dimerization reaction does not readily occur by heating and the crosslinking would be mainly caused by the radical generation and the successive chain transfer reaction to the other chains.

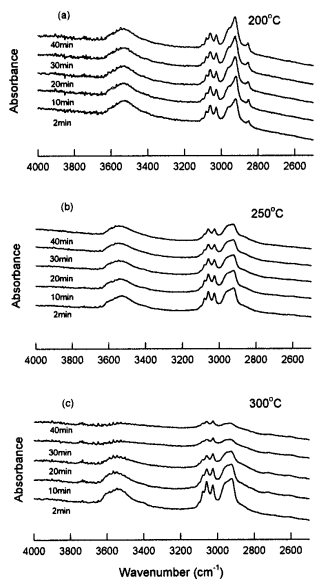


Fig. 7 Change of FTIR spectrum in the range of 2500~4000 cm^{-1} of poly(vinyl cinnamate) during isothermal heating at (a) 200°C (b) 250°C (c) 300°C

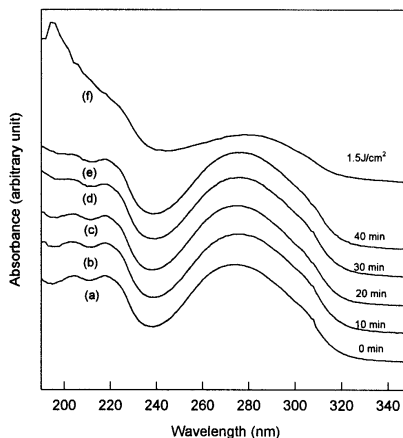
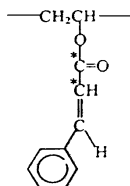


Fig. 8 Comparison of UV spectra of the thermally degraded and photo-crosslinked poly(vinyl cinnamate) (a) unheated (b) heated at 250°C for 10 min (c) heated at 250°C for 20 min (d) heated at 250°C for 30 min (e) heated at 250°C for 40 min (f) UV-irradiated poly(vinyl cinnamate) (irradiation energy : 1.5J/cm²)

Conclusion



The poly(vinyl cinnamate) was found to be thermally stable at least up to 200°C, which indicates that the cell assembling temperature above 200°C may cause the structural changes of PVCi. The thermal degradation of PVCi is caused by the cleavage of the cinnamate unit from the main chain. The bond breaking mainly occurs at the marked sites as shown in the left side.

The dimerization of two cinnamate groups in PVCi by thermal heating was found to be not so significant compared with that by UV irradiation.

Acknowledgment

This work was supported by Center for Advanced Functional Polymers at KAIST.

Reference

1. M Schadt, W J Helfrich (1971) *Appl Phys Lett* 18 : 127
2. J Cognard (1982) *Molec Cryst Liq Cryst Suppl Ser* 1 : 1
3. D Meyerhofer (1977) *J. Appl. Phys.*, 48 (1977) 1179
4. F C Luo (1990) *Liquid Crystals Vol. 1* p397World Scientific Singapore
5. W Gibbons, P J Shannon, S T Sun, B J Swelin (1991) *Nature* 351 : 49
6. Y Iimura, J Kusano, S Kobayashi, Y Aoyagi, T Sugano (1993) *Jpn J Appl Phys* 32 : L93
7. M Schadt, K Schmitt, V Kozinkov, V Chigrinov (1992) *Jan J Appl Phys* 1 : 2155
8. Y Iimura, T Saitoh, S Kobayashi, T Hashimoto (1995) *J Photopolym Sci Technol* 8 : 257
9. M Hasegawa, Y Taira, (1995) *J Photopolym Sci Technol* 8 : 241
10. Y Iimura, S Kobayashi, T Hashimoto, T Sugiyama, K Katoh (1996) *IEICE TRANS ELECTRON E-79-C* : 1040
11. G Bryan-Brown, L C Sage (1996) *Liquid Crystals* 20 : 6
12. J Chen, D L Johnson, P J Bos, X Wang, J L West (1996) *Physical Review E* 54 : 2
13. N Grassie, J G Speakman (1971) *J Polym Sci A1* : 9
14. N Grassie, J G Speakman (1971) *J Polym Sci A1* : 919
15. N Grassie, J G Speakman (1971) *J Polym Sci A1* : 931
16. N Grassie, J G Speakman (1971) *J Polym Sci A1* : 949