Polymer Bulletin 42, 149–152 (1999)

Polymer Bulletin

Hydrogenation of poly(vinyl cinnamate) thin layer

Eung Jin Kim[1], O Ok Park[2,*], Yukio Kawanami[3], Hirokazu Furue[4], Shunsuke Kobayashi[4]

[1] Flat Display Laboratory, Technology Division, Samsung Display Devices Co. LTD,
575 Shin-Dong, Paldal-Gu, Suwon 442-390, Korea
[2] Center for Advanced Functional Polymers, Department of Chemical Engineering,
Korea Advanced Institute of Science and Technology, 373-1 Kusong-dong, Yusong-gu,
Taejon 305-701, Korea
[3] Department of Materials Science and Engineering, Science University of Tokyo
in Yamaguchi
[4] Department of Electronics and Computer Science, Science University of Tokyo
in Yamaguchi, 1-1-1 Daigaku-dori, Onoda, Yamaguchi 756-0884, Japan

Received: 24 November 1998/Revised version: 6 January 1999/Accepted: 12 January 1999

Summary

Hydrogenation of poly(vinyl cinnamate) was performed with $RhH(CO)(PPh_3)_3$ catalyst with intent to clarify the photoalignment mechanism of liquid crystals on poly(vinyl cinnamate) alignment layer. The hydrogenated cinnamate side group shows the characteristic peaks at 2.9 ppm and 2.5 ppm in ^{1}H-NMR spectrum, and a decreasing peak at 280 nm in UV spectrum. This reaction can reveal the role of dimerized or residual cinnamate groups in the applications of the polymeric layer for electronic devices.

Introduction

After its successful preparation(1), poly(vinyl cinnamate) (PVCi) has played an important role in various applications, such as a photoresist(2), a nonlinear optical (NLO) polymer(3) and, recently, a liquid crystal (LC) alignment layer(4). In the LC photoalignment applications, a spin-coated layer is exposed to linearly polarized UV light in order to induce anisotropic characteristics in the polymeric layer. LC molecules are aligned in a specific direction when they are placed between two such layers, separated by micron spacers. In the case of PVCi, LC molecules are aligned in the direction normal to the UV polarization.

It is generally believed that the controlling force of photoalignment is the dispersion interaction between the photopolymer and LC molecules. However, two distinct explanations are possible for the origin of the PVCi photoalignment effect: it is either caused by the interaction with the photoproducts or with the unreacted side groups. The first explanation suggested by Schadt(5) was that the photoproducts would show directional preference perpendicular to the direction of UV polarization. On the other hand, others(6) implied that the residual side groups remaining after anisotropic depletion could be responsible for the alignment of LC molecules. The side groups whose axis is normal to the polarization would be hardly affected by the polarized irradiation so that they would induce alignment of LC molecules. Another mechanism considers the trans-cis transformation of the residual cinnamate groups(7), but it may be included in the role of

---

[*] Corresponding author

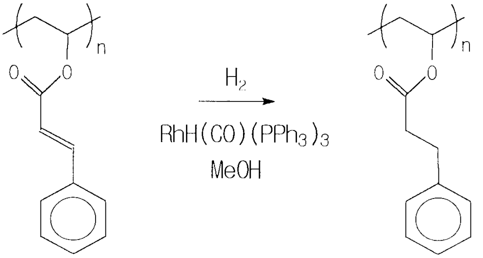
the side groups in this step.

It is important to clarify which component is responsible for the alignability of the photopolymer for further improvement of the photoalignment technique(8,9). In order to remove completely one anisotropic contribution, surface hydrogenation of the cinnamate side groups is appropriate because it can remove the rigidity of the side groups by saturating the double bonds while the reaction keeps the photoproducts still intact(10,11). Such a modification can give a preferential change to the residual cinnamate groups after [2+2] cycloaddition. In this communication, we are going to demonstrate that such solid state hydrogenation can be performed and confirmed by spectroscopic observations. The detailed mechanism of photoalignment is discussed elsewhere(12).

2. Experimental

PVCi (Aldrich) was spin-coated onto glass substrates (20 nm) and quartz plates (30 nm) at 3000 rpm for 25 seconds using a 2 wt.% solution of 2-6-Thinner (Nissan Chem. Co.), and then was baked at 150 °C for one hour to ensure removal of the solvent.

After purging an autoclave with hydrogen gas, the layers were immersed into the solution of 0.6 nmol $RhH(CO)(PPh_3)_3$ (Wako Co.) per unit area (cm^2) of PVCi; At first, 3.7 mg of the catalyst was dissolved into 3.3 ml of distilled methylene chloride, then a small portion of the solution (10 µl) was rapidly transferred to 20 ml of methanol with a microsyringe. The pressure was kept to 70-75 kg/cm2 at 50 °C for 24 hours.

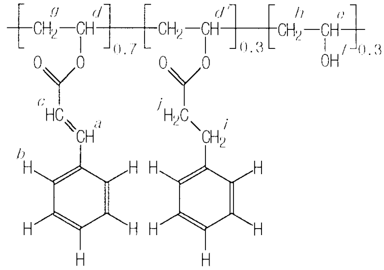


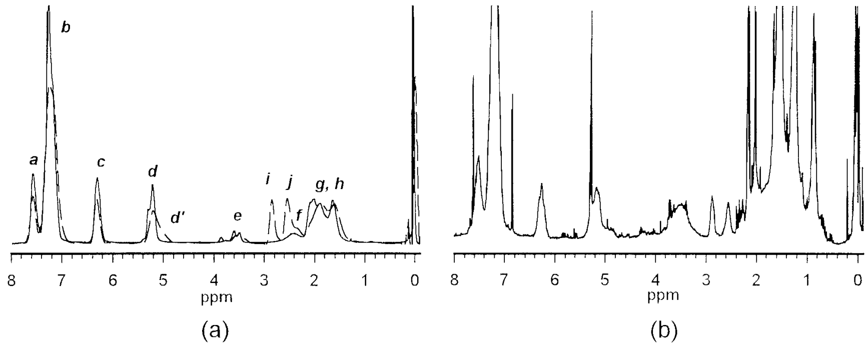
After the reaction the layers were rinsed with fresh methanol and were dried for two hours at 50 °C. The reaction was confirmed by ^{1}H-NMR (270 MHz, JNM-EX270S, JEOL) after collecting the hydrogenated layer in $CDCl_3$.

For comparison, 20 mg of PVCi was hydrogenated in 20 ml of toluene with 9.2 mg of the catalyst at 50 °C for 24 hours. After the reaction, the solution was poured into methanol for precipitation and was dried in vacuum at 50 °C. ^{1}H-NMR spectrum was measured and compared with PVCi.

3. Result and discussion

Figure 1 reports the assignments and numbering scheme used in this paper. About 76 % of the hydroxyl groups were esterified to cinnamate in the PVCi used [Figure 1(a), solid line]. Most significant are the new peaks around 2.9 and 2.5 ppm in the hydrogenated PVCi, which are assigned to newly formed 3-phenylpropionyl groups (H^i and H^j) [Figure 1(a), dashed line]. The decreases of H^a and H^c, and the shift of H^d from 5.2 to 5.0 ppm also mean the saturation of the double bonds. Hydrogenation proceeded to 30 mol. % in toluene, which showed lower yield than in other polar solvents(11).





(a) (b)

Figure 1. ^1H NMR spectra: (a) virgin PVCi (solid) and PVCi hydrogenated in toluene (dashed); (b) PVCi layer hydrogenated in methanol

The new peaks of H^i and H^j were also found in the solid-state hydrogenation in methanol [Figure 1(b)]. A large number of scans (8250 scans) was done, and the vertical scale was enlarged because the amount of the sample was so small. Also seen in the signal were other compounds, such as methylene chloride, acetone, and chloroform which might be included during the sample collecting process. Inspection of the peaks, H^a, H^c, H^d, H^i, and H^j indicates that 20 % of double bonds have been saturated by the mild condition in methanol.

UV spectrum (UV-3100PC, Shimazu Co.) also confirms the hydrogenation reaction, as shown in Figure 2, where all double bonds have been saturated through the entire layer with the increased amount of the catalyst (36.8 μmol per cm2 PVCi) within five hours.

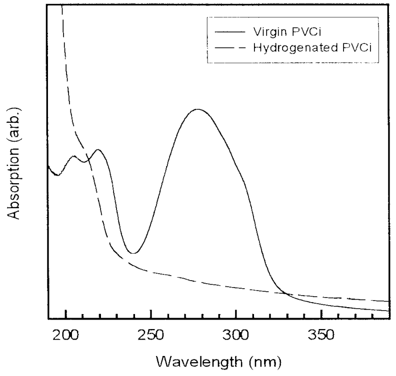


Figure 2. Spectra of UV spectroscopy for virgin and hydrogenated PVCi thin layer.

The decreasing peak at 280 nm shows the disappearance of the double bonds, and the increasing peak below 190 nm represents the generation of new side groups. The spectra of the hydrogenated layers in UV or IR spectroscopies are similar with those of the irradiated layers. The phenylpropionyl group and the cyclobutane ring seem to have identical absorption bands. The layer thickness (< 30nm) was under the penetration depth of the catalytic solution even after photo-curing of the layers and methanol would be the most effective polar solvent for the solid-state hydrogenation of PVCi(11).

Photoaligned LC cells using the hydrogenated PVCi showed complete change of the microscopic texture(12). By the hydrogenation reaction, PVCi cannot retain the dimerizable cinnamate side groups and UV irradiation does not generate photoproduct. It showed that the PVCi layer does align LC molecules less and less as hydrogenation proceeds. The progress of the saturation reaction makes direct effects to the layer/surface properties of PVCi. Most of all it offers an experimental tool to settle the arguments on the photoalignment of LC. It can also be used directly in clarifying the role of the dimerized cinnamate groups questioned in NLO application(3).

Acknowledgment

The authors express special appreciation to Professor Keiji Yamamoto for his valuable advice and offering experimental instruments. Eung Jin Kim expresses heartful thanks to Mr.Choi Su An and many members of Science University of Tokyo in Yamaguchi for their encouragement and kindness. He is also deeply grateful to the Korea Science and Engineering Foundation (KOSEF) for supporting his stay at SUT in Yamaguchi.

References

1. Minsk LM (1955) US Patent 2,725,377.
2. Reiser A, Egerton PL (1979) Photogr Sci Eng 23: 144.
3. Skloss TW, Haw TW (1994) Macromolecules 27: 6998.
4. Dyadynsha A, Khizhnyak A, Marushi T, Renznikov Y, Yaroshchuk O (1995) Mol Cryst Liq Cryst 263: 399.
5. Schadt M, Schmitt K, Kozinkov V, Chigrinov V (1992) Jpn J Appl Phys 31: 2155.
6. Bryan-Brown GP, Sage IC (1996) Liq Cryst 20: 825.
7. Ichimura k, Akita Y, Akiyama H, Kudo K, Hayashi Y (1997) Macromolecules 30: 903.
8. Schadt M, Seiberle H, Schuster A (1996) Nature 381: 212.
9. Yoshida H, Koike Y (1997) Jpn J Appl Phys 36: L428.
10. Collman JP, Hegedus LS, Norton JR, Finke RG (1987) Principles and Applications of Organotransition Metal Chemistry, University Science Books, California, pp 524.
11. Schulz DN (1987) Hydrogenation In: Kroschwitz JI(ed), Encyclopedia of Polymer Science and Engineering, 2nd VII/807, Wiley-Interscience Publication.
12. Kim EJ, Park OO, Li HF, Kawanami Y, Furue H, Kobayashi S, Mol Cryst Liq Cryst in press.