

Imaging on a Vapor Deposited Film by Photopolymerization of a Rod-Like Molecule Consisting of Two Diacetylenic Groups

Ji Young Chang*, Kyung Seo, Hyun Ju Cho, and Cheol Ju Lee

*School of Materials Science and Engineering, and Hyperstructured Organic Materials Research Center,
College of Engineering ENG445, Seoul National University, Seoul 151-744, Korea*

Changjin Lee, Yongku Kang, and Jaehyung Kim

Advanced Materials Division, Korea Research Institute of Chemical Technology, P.O. Box 107, Yusong, Taejon 305-600, Korea

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Abstract : A linear rod-like molecule, bis[4-(1,3-octadynyl)phenyl] terephthalate (**2**), consisting of two diacetylenic groups, was prepared. The unsymmetric diacetylene was prepared by the Cadiot-Chodkiewicz coupling reaction of 1-bromohexyne with 4-ethynylphenol and linked to a benzene core by an esterification reaction with terephthaloyl chloride in tetrahydrofuran. The thin film (200 nm thickness) of compound **2** was fabricated by the physical vapor deposition on a glass plate with a thermal evaporator. In the X-ray diffraction (XRD) study, the vapor deposited film on the glass plate showed peaks with *d* spacings of 19.4, 5.7, and 4.5 Å. This XRD pattern was quite different from that observed for compound **2** isolated by recrystallization from methylene chloride/hexane. The vapor deposited film was polymerized by UV irradiation. Photopolymerization was carried out through a photomask, resulting in a patterned image, where the irradiated part became isotropic.

Keywords : photoimaging, vapor deposited film, rod-like diacetylene molecule.

Introduction

Photopolymerizable molecules have attracted great attention because of their potential applications. One of the most interesting applications is photoimaging, which is mainly based on the optical property changes upon polymerization.¹⁻⁴ Photopolymerization of diacetylenes has been extensively studied due to their unique reactivity, and the interesting properties of the resulting polymers.^{5,6} The polymerization of a diacetylene is known to proceed topochemically via a 1,4-addition pathway by irradiation, and thus has been widely used for preparing ordered macromolecules. The topochemical polymerization of diacetylenes can be carried out in the solid state. A diacetylene single crystal is polymerized to give a single crystal of a polymer, when a crystal structure satisfies the requirements for the topochemical polymerization. Such requirements can be also met in Langmuir-Blodgett films,⁷⁻⁹ self-assembled monolayers,^{10,11} and vesicles.¹² It was reported that in a liquid crystalline state, the 1,4- polymerization also occurred to give highly ordered polymers.¹³⁻¹⁷

In this work, we prepared a linear rod-like molecule, consisting of two diacetylenic groups, and examined its UV polymerization in the solid state. Thin films of the monomer were prepared by a physical vapor deposition or solution casting method. Interestingly the solid state polymerization occurred only in the vapor deposited film. Unlike the polymerization of diacetylenic compounds with one polymerizable group, yielding the polymers with ordered structures, the polymerization of this bisdiacetylenic compound was expected to occur at two sites, and thereby disrupting the aligned molecules in a microdomain, and being isotropic. We applied this reaction to obtain a patterned image.

Experimental

Instrumentation. ¹H and ¹³C NMR spectra were recorded on a Jeol JNM-LA 300 (300 MHz) spectrometer or BRUKER Avance DPX-300 (300 MHz) at room temperature. IR spectra were obtained with the use of a PERKIN ELMER Spectrum GX I spectrometer. UV-Vis spectra were obtained with the use of a HEWLETT-PACKARD HP8452A. Powder X-ray diffractograms were obtained by using a Bruker Xps GADDS (Cu K_α radiation, λ = 1.54 Å). An optical microscopy study was performed with a Leica

*e-mail : jychang@gong.snu.ac.kr

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MPS 30. Elemental analyses were performed at the National Center for Inter-University Research Facilities of Seoul National University, Seoul, Korea.

1-Bromo-1-hexyne. 4-Trimethylsilylethynylphenol and 4-ethynylphenol were prepared according to our previous report.¹⁷ Bromine (39.9 g, 0.25 mol) was added to a vigorously stirred solution of potassium hydroxide (37.5 g) in water (100 mL) with cooling at 0 °C.¹⁸ 1-Hexyne (0.15 mol) in dioxane (80 mL) was added dropwise to the above mixture over 2 h. The reaction mixture was stirred for 40 h without further cooling. Then the mixture was extracted with chloroform. The organic layer was dried with MgSO₄, filtered, concentrated and vacuum-dried (yield 90%).

¹H NMR (CDCl₃, 300 MHz): δ 2.20 (t, 2H, CCH₂), 1.54-0.91 (m, 7H, alkyl chain protons).

1-(4-Hydroxyphenyl)-1,3-octadiyne (1). Methanol (35 mL), a solution of hydroxylamine·HCl (0.75 g) in water (10 mL), 70% aqueous solution of ethylamine (4.75 g), and copper (I) chloride (0.11 g) were placed in the flask and 4-ethynylphenol (14.9 mmol) was added in one portion.²⁴ Then 1-bromohexyne (14 mmol) was added over about 1 h, while keeping the temperature at 35 °C. After 6 h, a solution of KCN (0.37 g) and NH₄Cl (1.50 g) in water (50 mL) was added with vigorous stirring. The mixture was extracted with chloroform, dried with anhydrous MgSO₄ and filtered. After evaporation of the solvent, the product was isolated by column chromatography on silica gel (25% ethyl acetate in hexane) in 43% yield.

¹H NMR (CDCl₃, 300 MHz): δ 7.37, 6.77 (dd, 4H, C₆H₄), 5.59 (s, 1H, OH), 2.35 (t, 2H, CCH₂), 1.60-0.90 (m, 7H, alkyl chain protons).

Bis[4-(1,3-octadynyl)phenyl] terephthalate (2). To a solution of compound **1** (0.73 g, 3.68 mmol) in THF (100 mL) was added NaH (0.106 g, 4.4 mmol). After the mixture was stirred for 1 h at room temperature, a solution of terephthaloyl chloride (0.403 g, 1.84 mmol) in THF (50 mL) was added. The solution was stirred for 6 h. After evaporation of the solvent, the product was isolated by column chromatography on silica gel (methylene chloride/hexane = 5/1 v/v) and further purified by recrystallization from methylene chloride/hexane to give 0.63 g (yield 65%).

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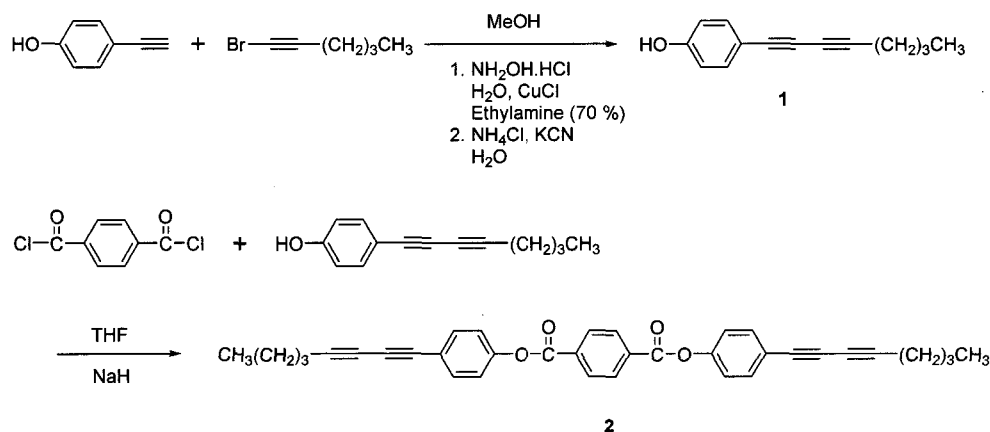
Anal. calcd for C₃₆H₃₀O₄: C, 82.11; H, 5.74. Found: C, 81.06; H, 5.71. ¹H NMR (CDCl₃, 300 MHz): δ 8.32 (s, 4H, C₆H₄), 7.57, 7.22 (dd, 8H, C₆H₄), 2.38 (t, 4H, CCH₂), 1.62-0.91 (m, 14H, alkyl chain protons). ¹³C NMR (CDCl₃, 300 MHz): δ 163.8, 150.8, 133.8, 133.7, 130.3, 121.7, 120.2, 85.2, 74.8, 73.7, 64.9, 30.2, 21.9, 19.2, 13.5. IR (KBr pellet, cm⁻¹) 2934, 2862, 2241, 2141, 1741, 1595, 1500, 1247, 1193.

Vapor Deposition. The thin film (200 nm thickness) of compound **2** was fabricated by the physical vapor deposition on a glass, quartz, or NaCl plate with a thermal evaporator (Thermal Evaporator System KVT-420, Korea Vacuum Co.). After placing compound **2** approximately 15 cm above the tungsten boat and evacuating the chamber to 7 × 10⁻⁶ torr, the compound was deposited at a rate of 0.2 nm/sec.

UV Polymerization. A vapor deposited film of compound **2** on a glass plate was placed under an UV lamp (100 W short arc mercury lamp). The polymerization was carried out for 30 min at room temperature under nitrogen atmosphere.

Results and Discussion

The diacetylenic monomer, **2**, was synthesized according to Scheme I. 4-Trimethylsilylethynylphenol was prepared by the coupling reaction of 4-iodophenol with trimethylsilylacetylene in the presence of a palladium catalyst.¹⁹⁻²¹ The trimethylsilyl group was easily removed under basic conditions, to give 4-ethynylphenol. The unsymmetric diacetylene, **1**, was prepared by the Cadiot-Chodkiewicz coupling reaction²²⁻²⁴ of 1-bromohexyne with 4-ethynylphenol. The coupling reaction yielded three different diacetylene products, and the desired unsymmetrical diacetylene was isolated by column chromatography on silica gel. Compound **1** was linked to a benzene core by an esterification reaction with terephthaloyl chloride in tetrahydrofuran. The structure of



Scheme I

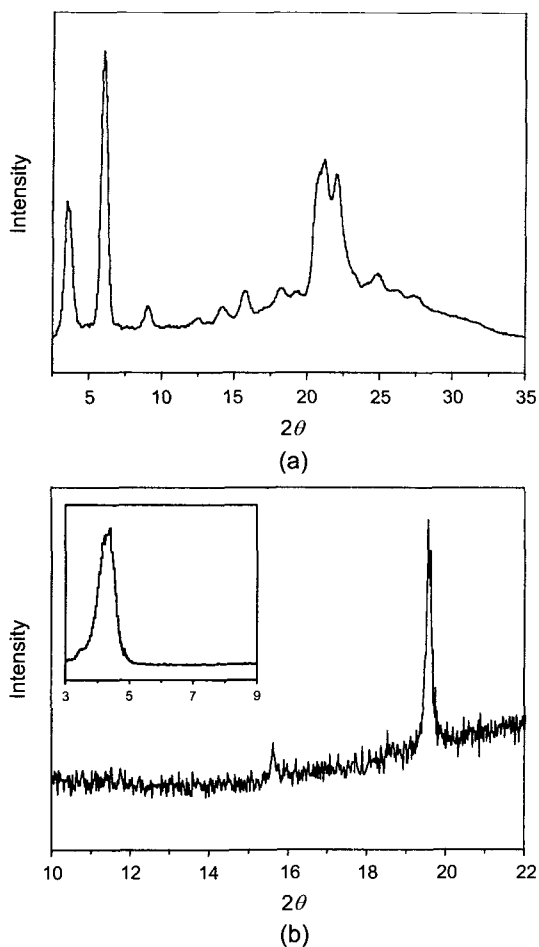


Figure 1. X-ray diagrams of (a) compound **2** isolated by recrystallization from methylene chloride/hexane and (b) the vapor deposited film on the glass plate; the inset shows a small angle region.

compound **2** was confirmed by ^1H and ^{13}C NMR spectroscopy, and elemental analysis.

The thin film (200 nm thickness) of compound **2** was fabricated by the physical vapor deposition on a glass, quartz, or NaCl plate with a thermal evaporator. In the X-ray diffraction (XRD) study (Figure 1), the vapor deposited film on the glass plate showed peaks with d spacings of 19.4, 5.7, and 4.5 Å. The films deposited on the quartz and NaCl plate showed the same results. This XRD pattern was quite different from that observed for compound **2** isolated by recrystallization from methylene chloride/hexane. The recrystallized compound showed several peaks including the peaks with d spacings of 25.1, 14.8, 9.8 Å in the small angle region.

The vapor deposited film was exposed to UV light for 30 min at room temperature under nitrogen atmosphere. In the IR spectra (Figure 2), two weak bands at 2141 and 2241 cm^{-1} , corresponding to the diacetylenic groups, almost disappeared, and a weak band at 2202 cm^{-1} emerged. The band at

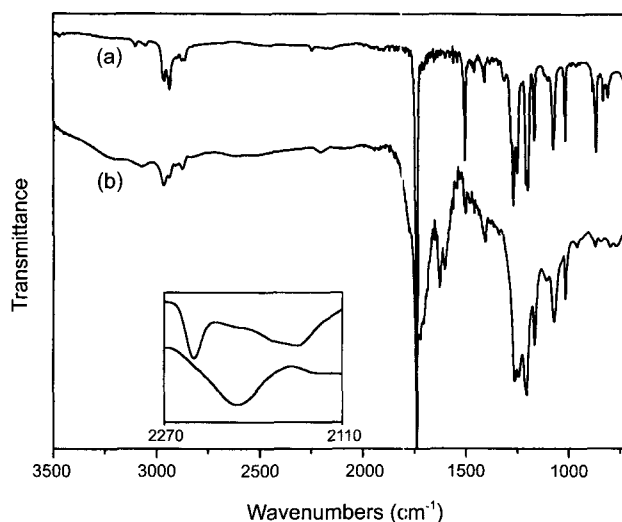


Figure 2. IR spectra of (a) compound **2** (KBr) and (b) the vapor deposited polymer film on a NaCl plate; the inset shows the IR spectra of the diacetylene vibration range.

1620 cm^{-1} became broader and stronger due to the formation of the C-C double bonds. These IR results show that photopolymerization occurred via the 1,4-addition reaction. The polymer conversion was estimated to be higher than 90% based on the decrease in the intensity of the diacetylene peaks. The deposited film initially looked opaque, but became transparent after polymerization. In the X-ray diffractogram of the polymer film, the peaks observed for the vapor deposited monomer film, completely disappeared, indicating that the morphology of the polymer became amorphous. UV-Vis spectroscopy showed an absorption limit of about 400 nm for the vapor deposited monomer film, whereas absorption of the UV polymerized film occurred up to about 600 nm. Since there were no significant absorptions between 500 to 700 nm, we assumed that cross-linking of the bisdiacetylene produced only short conjugated polydiacetylene backbones.

It is noteworthy that the polymerization did not occur in the film prepared by methylene chloride solution casting. We believe that the vapor deposition process provided the molecular arrangement suitable for the solid state polymerization, while the solution casting method did not. Since the deposited film appeared opaque, it is likely that crystalline domains were grown during the deposition process, which had a structure different from that out of a solution.

The surface morphology of the thin film on the quartz substrate was investigated with a scanning probe microscope (Park Scientific, auto probe CP). Figure 3 shows the surface morphologies after the deposition and the photopolymerization at room temperature. The vapor deposited film had a very smooth surface, indicating that initial binding of the molecules onto the substrate occurred evenly and closely. After UV polymerization, surface roughness was increased,

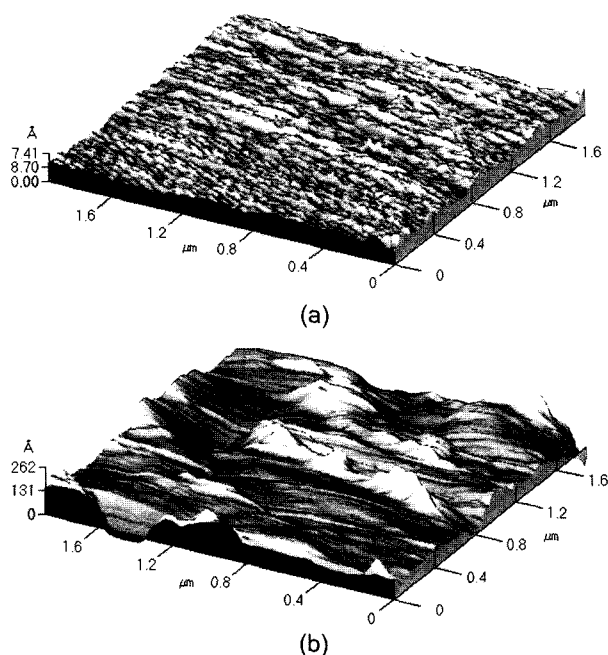


Figure 3. SPM images of (a) after deposition of compound **2** on a quartz plate and (b) after photopolymerization.

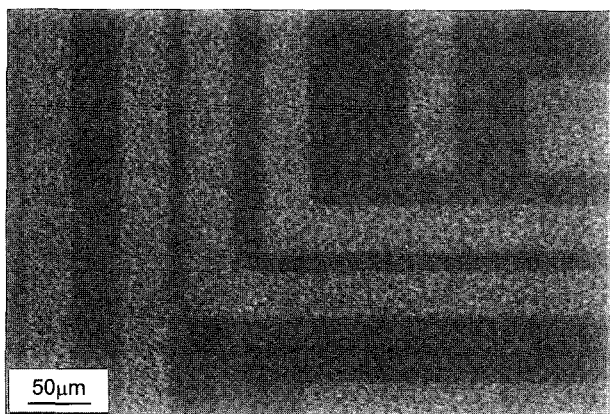


Figure 4. Image patterns observed under polarized optical microscopy. The patterns were obtained with the vapor deposited film of compound **2** by UV irradiation through a photomask at room temperature for 30 min.

probably due to migration and rearrangement of the molecules.

Since the thin film of compound **2** was easily fabricated by physical vapor deposition and photopolymerization in the film yielded an amorphous polymer, the compound was considered as a good optical material for photoimaging. After the thin film was prepared by the physical vapor deposition on a glass plate, photopolymerization was carried out for 30 min through a photomask, with a UV lamp (100 W short arc mercury lamp) at the room temperature under

nitrogen atmosphere. Figure 4 shows the image pattern observed under polarized optical microscopy. A patterned image was obtained where the irradiated part became dark, and the masked part remained birefringent, under polarizing microscopy. This result is ascribed to the photoreaction at two sites on the molecule, resulting in a crosslinked polymer. Since two diacetylenic units comprise a rigid part of the molecule, the crosslinking reaction eventually disrupted aligned molecules in a microdomain to be isotropic.

Conclusions

We have demonstrated a method for photoimaging on a vapor deposited film. A rod-like molecule, having two photoreactive diacetylenic units, was prepared, and fabricated into a thin film by physical vapor deposition. The vapor deposition is a relatively simple and clean process for generating a thin film. Photopolymerization was carried out by UV irradiation through a photomask, resulting in a patterned image, where the irradiated part became isotropic.

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References

- (1) T. J. Trout, J. J. Schmieg, and W. J. Gambogi, *Adv. Mater.*, **10**, 1219 (1998).
- (2) J. Y. Chang, S. W. Nam, C. G. Hong, J.-H. Im, J.-H. Kim, and M. J. Han, *Adv. Mater.*, **13**, 1298 (2001).
- (3) M. Nakagawa, S.-K. Oh, and K. Ichimura, *Adv. Mater.*, **12**, 403 (2000).
- (4) U. Theissen, S. J. Zilker, T. Pfeuffer, and P. Stroehriegel, *Adv. Mater.*, **12**, 1698 (2000).
- (5) G. Wegner, *Naturforsch.*, **24b**, 824 (1969).
- (6) *Advances in Polymer Science*, H.-J. Cantow, Ed., Springer-Verlag, Berlin, 1984, Vol. 63.
- (7) B. Tieke, H. J. Graf, G. Wegner, B. Naegele, H. Ringsdorf, A. Banerjee, D. Day, and J. B. Lando, *Colloid and Polym. Sci.*, **255**, 521 (1977).
- (8) B. Tieke, G. Wegner, B. Naegele, and H. Ringsdorf, *Angew. Chem.*, **88**, 805 (1976).
- (9) V. N. Kruchinin, S. M. Repinsky, and L. L. Sveshnikova, *Thin Solid Films*, **240**, 131 (1994).
- (10) D. N. Batchelder, S. D. Evans, T. L. Freeman, L. Haussling, H. Ringsdorf, and H. Wolf, *J. Am. Chem. Soc.*, **116**, 1050 (1994).
- (11) T. Kim and R. M. Crooks, *Tetrahedron Lett.*, **35**, 9501 (1994).
- (12) B. M. Peek, J. H. Callahan, K. Namboodiri, A. Singh, and B. P. Gaber, *Macromolecules*, **27**, 292 (1994).
- (13) J. Tsibouklis, *Adv. Mater.*, **7**, 407 (1995).
- (14) A. F. Garito, C. C. Teng, K. Y. Wong, and O. Z. Khamiri,

- Mol. Cryst. Liq. Cryst.*, **106**, 219 (1984).
- (15) P. T. Hammond and M. F. Rubner, *Macromolecules*, **28**, 795 (1995).
- (16) J. Y. Chang, J. H. Baik, C. B. Lee, M. J. Han, and S.-K. Hong, *J. Am. Chem. Soc.*, **119**, 3197 (1997).
- (17) J. Y. Chang, J. R. Yeon, Y. S. Shin, M. J. Han, and S.-K. Hong, *Chem. Mater.*, **12**, 1076 (2000).
- (18) L. Brandsma, *Preparative Acetylenic Chemistry*, 2nd Ed., Elsevier Science, New York, 1988.
- (19) J. Y. Chang, H. J. Ji, and M. J. Han, *Bull. Korean Chem. Soc.*, **16**, 674 (1995).
- (20) S. Takahashi, Y. Kuroyama, K. Sonogashira, and N. Hagihara, *Synthesis*, 627 (1980).
- (21) W. B. Austin, N. Bilow, W. J. Kellaghan, and K. S. Y. Lau, *J. Org. Chem.*, **46**, 2280 (1981).
- (22) E. Barbu and J. Tsibouklis, *Tetrahedron Lett.*, **37**, 5023 (1996).
- (23) M. D. Mowery and C. E. Evans, *Tetrahedron Lett.*, **38**, 11 (1997).
- (24) J. M. Montierth, D. R. DeMario, M. J. Kurth, and N. E. Schore, *Tetrahedron*, **54**, 11741 (1998).