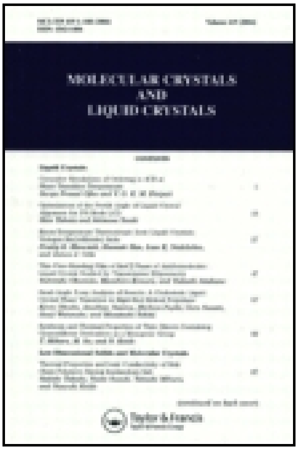

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A Novel Formation Method of Thin Polymer Film with Densely Dispersed Organic Dye by using Vacuum Technique

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A Novel Formation Method of Thin Polymer Film with Densely Dispersed Organic Dye by using Vacuum Technique

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A novel method of thin film formation of organic materials using a vacuum technique is proposed. An organic dye with a high sublimation pressure is loaded in a crucible along with a thin polymer film. After pumping down, the crucible is sealed, then placed in a constant temperature oven. The vapor of dye dissolves into the polymer film, thus forming a thin dye-containing layer.

Keywords: Thin film; Diarylethene; Vacuum technique; Vapor transport; DVD

Introduction

Organic molecules have been widely applied to electronic devices such as liquid crystal displays, electro-luminescence devices, and rewritable compact disks among others. In these applications, the formation of a thin film is the key technique for fabricating complex device structures. Spincoatinging technique which is applicable for dissolving of compounds in a solvent and vacuum deposition applicable to compounds with high vapor pressure are widely employed. In the vacuum deposition process, however, some percentage of organic compounds exhibit decomposition during the evaporation process, and the technique is not suitable for compounds with high sublimation pressures. It is widely believed that the vacuum deposition method be can applied to organic compounds which exhibit a melting point, to fabricate a thin film and attempts have been made since a long time. In the vacuum deposition technique, even for organic compounds, the source material is strongly evaporated by an electric heater to obtain kinetic energy for fabricating a thin film at room temperature. Most of organic compounds, however it has melting points, exhibit decomposition by the heating process. Here, we have developed a novel method, termed the "vapor transportation method", where the maximum temperature of the organic compounds is lower than just below the melting points.[1]

Experimental

Diarylethene,[2] *cis*-1,2-Dicyano-1,2-bis(2,4,5-trimethyl-3- thienyl) ethene($C_{18}H_{18}N_2S_2$; Tokyo Chemical Industry Co., LTD) was selected as a model compound for evaluation of the present method, and was used without further purification. The sublimation temperature of the dye is between 80 and 115 degrees under a base pressure of about 10^{-6} Pa, and the dye exhibited decomposition over the temperature of 120 degrees. Polymer films of poly(methyl methacrylate)(PMMA;Aldrich), poly(benzyl methacrylate)(PBzMA;Aldrich), poly(2-hydroxy propyl methacrylate) (PHPMA; POLYMERSCIENCE INC.) and poly(Bisphenol A carbonate) (PC; Aldrich) were prepared for the present experiment. To study the solubility to polymer films, vacuum hot-press method[2] was employed, which thickness was several tens of . m. To evaluate the detail of dispersion of dye into the poly(Bisphenol A carbonate) layer, a commercial digital video disk (DVD) was employed by means of atomic force microscope (AFM).

A test peace of polymer was loaded in a Pyrex glass tube with a small but sufficient amount of the dye (smaller amount of 1 mg), and the pressure in the tube was pumped down using a vacuum pump (V70; Varian)(Fig.1). After an ultimate pressure was reached, the glass tube was sealed by melting to form an ampoule (diameter of 15 mm and length of about 300 mm)(Fig. 2). For the test piece, the ampoule was set in a constant temperature oven for more than 5 hours, then cooled down slowly over several hours. The dye dispersed into polymer matrix after thermal treatment at 115 degrees for about 24 hours. For the DVD, both temperature of the oven and treatment time was verified.

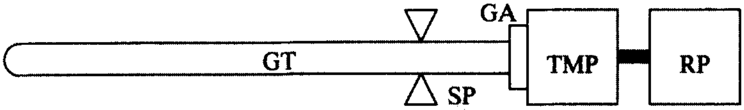

Fig. 1. Schematic drawing of vacuum apparatus; TMP: turbo molecular pump, RP: rotary pump, GT: Pyrex glass tube, SP: sealing point, GA: glass tube adaptor.

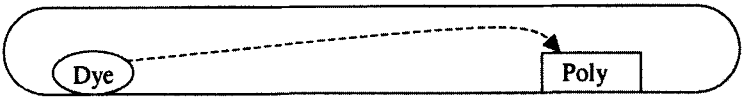

Fig. 2. Details of the glass ampoule; Dye: Powder of dye, Poly: Pellet of polymer, spin-coated polymer film on a glass substrate, or DVD.

Results and discussion

1. Pellet of polymer

Depth of dye-dispersed layer is automatically determined by the total amount of loaded dye and by temperature of oven during treatment.

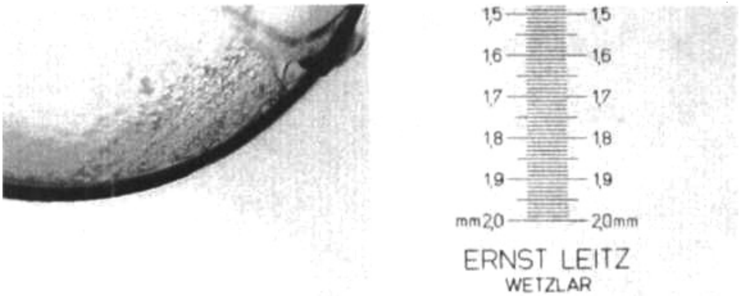

Fig. 3. Cross-sectional view of dye dispersed PC pellet.
(After UV light irradiation)

If small amount of dye is loaded in the ampoule, and treating for a long time (about 1 week), it is observed a clear boundary of dye dispersed layer in the polymer, which suggests that diffusion of the dye adsorbed on the polymer surface is not a dominant process for dispersion of dye molecule (Fig. 3). By comparing several kinds of polymer, it is found that the tendency of dye dispersion into the polymer is as follows; PC > PBzMA > PMMA > PHPMA, where no dispersion is observed for PHPMA under the condition of 115 degrees for 24 hours.

2. Spin-coated polymer film on a glass substrate

It was employed a spincoated PMMA film to determine an optimum temperature of dispersion and concentration of the dye. The optimum temperature for Diarylethene is about 110 degrees (Fig. 4.), which correspond to an estimated decomposition temperature of the dye.

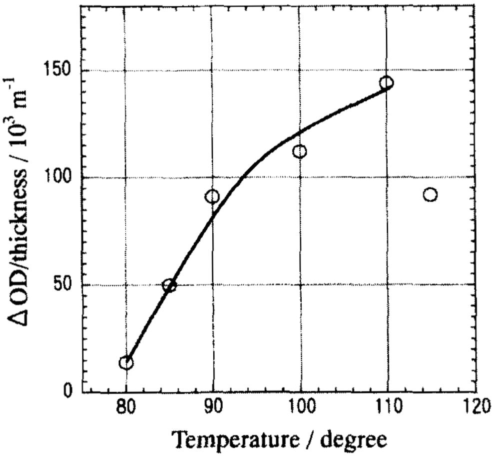

Fig. 4. Normalized OD of obtained film as a function of treatment temperature.

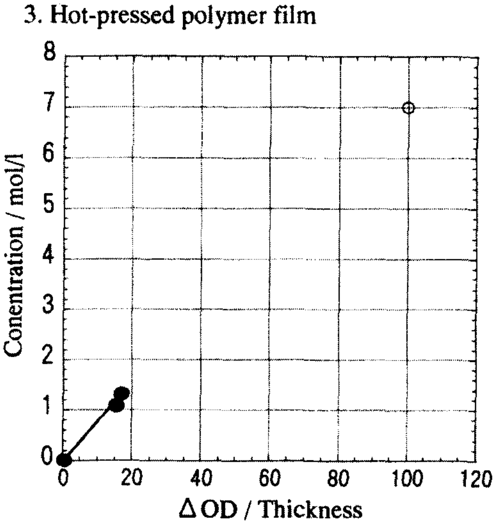

Fig. 5. Estimation of ultimate concentration of Diarylethene in polymer matrix under thermal equilibrium conditions.

To determine concentration of the dye dispersed into the polymer film, the hot-press method was employed.[3] Weighted powder of both the dye and PMMA were formed a thin film of about 50 . m thickness between two cover glasses. By measuring the transmittance, it is obtained that the ultimate value of normalized optical density (OD/thickness) under dispersed state with thermally equilibrium is around 100 [x10^3 m^{-1}]. The concentration of dye dispersed into a PMMA film was determined as about 7 mol/l.

Glass transition temperature (T_g) of the PC with containing the dye was measured by thermal analysis of the polymer, and concluded that T_g was reduced approximately 70 degrees than PC without the dye. As *the property of the thin layer of polymer surface with the dye is* drastically changed, the dye-dispersed layer will exhibits clear boundary as shown in Fig. 3. The mechanism of dispersion of Diarylethene into polymer surface following to adsorption of vapor of the dye on polymer surface will become clear in near future.

4. DVD

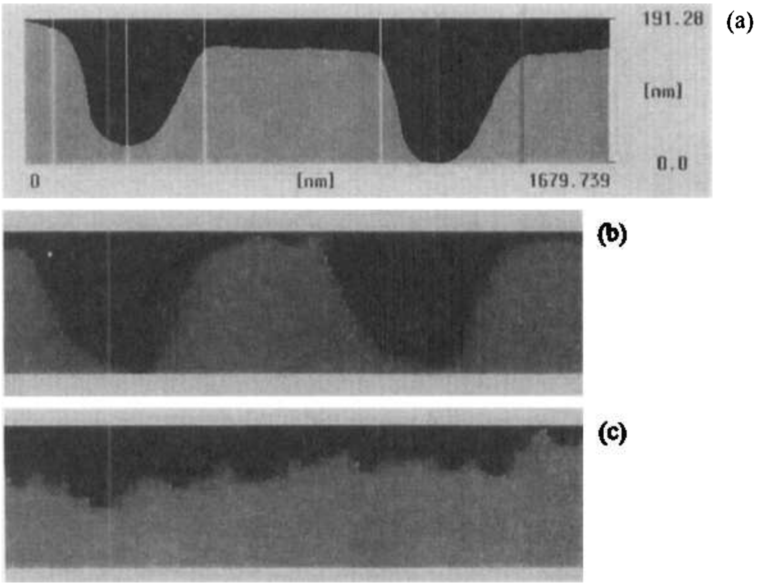

Fig. 6. AFM images of DVD after dispersion of the dye. (a) 30 minutes at 80 degrees, (b) 2hours at 110 degrees without the dye as a reference, and (c) 2 hours at 110 degrees.

Present method is evaluated the by DVD as shown in Fig. 6. Under the condition of 30 minutes at 80 degrees where the dispersion rate was about ten times smaller than at 110 degrees, the shape was kept as same as a reference (b). Under the condition of 2 hours at 110 degrees, however, land-groove was disappeared.

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