



Thermo-optical study of UV cured polyether urethane diacrylate films with dispersed octadecanol

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ABSTRACT

Thermally reversible light scattering (TRLS) films are prepared from ultraviolet (UV) curing of polyether urethane diacrylate (PEUDA) with dispersed low molecular weight 1-octadecanol (OD). Depending on the temperature, the OD domains are crystalline or amorphous and this produce opaque or transparent films in a reversible way. Stable optically transparent and light scattering states are obtained after 100 successive heating–cooling cycles. Moreover, morphologies of the OD domains could be varied significantly with the cure temperature and this led to notable discrepancy in optical properties. By using an UV-mask and curing in two steps at different temperatures, complex patterns could be recorded in the film that were encoded at high temperatures (60 °C) and revealed at low temperatures (i.e., at room temperature), which makes the film a candidate for thermo-optical recording medium.

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1. Introduction

Thermally reversible light scattering (TRLS) films repeatedly change their optical properties from light-scattering to translucent and highly transparent states in response to external thermal stimuli. Environmental protection and energy conservation have brought TRLS films into potential applications such as flat-panel displays, shutters, thermal sensors, recording medium, etc. [1–5]. A common composition for TRLS films consists of a support polymer matrix with dispersed domains of relatively low molar mass species, such as hydrogels [6,7], polymer blends [8], liquid crystals [9–12] and phase change materials (PCMs, i.e., inorganic eutectics, paraffins, fatty acids) [13–15]. The switching between transparent and scattering states is achieved either by a change in the refraction index of one or both components, by a change in the aggregate state, or by reversible solid–liquid phase formation of PCMs at different temperatures. Some promising TRLS materials have been reported [16–18], but most of them

require careful control of the cooling/heating rate and complicated devices. The use of PCMs could either avoid using or lower the demand for extra equipments.

Hotta et al. [19–22] reported on a thermo-reversible recording material composed of polymeric films with dispersed fatty acids prepared via thermo-curing method. Transparent and light scattering states can be thermally switched only by changing temperature. Unfortunately, very few materials are candidates for thermo-reversible recording till today to the author's knowledge. In this paper, a novel TRLS film with potential for optical data storage application based on the melting/crystallization of aliphatic alcohols dispersed in a polyether urethane diacrylate (PEUDA) matrix is prepared by UV curing method. Compared with the mentioned above processes, UV curing offers several advantages, such as pollution-free, simple preparation procedures, high-speed processing and high-energy efficiency. Besides, UV-induced polymerization is a preferred method since the curing temperature (T_c) and the rate of polymerization can be chosen independently. This allows a better control of morphology.

To generate a TRLS film based on PEUDA via UV curing method, it is necessary to search for a particular PCM with three main characteristics: (a) highly solubility with

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PEUDA precursors, (b) adequate matching of refractive indices with polymeric PEUDA matrix in the transparent state, (c) the phase change (solid–liquid) temperature should be higher than the glass transition temperature (T_g) of the cured PEUDA. 1-Octadecanol (OD) fulfilled the required conditions and is selected for this study. Two distinct optical states, one is transparent and the other, light-diffusing, can be easily and repeatedly selected just by adjusting the temperature. A thermo-reversible response model based on the polymerization-induced phase separation and phase changing of OD is proposed for the mechanism of the TRLS phenomenon. Moreover, OD crystallite morphologies vary with different preparation T_c s, resulting in a notable discrepancy in optical transparency. This makes the film a candidate for information recording medium. A thermal method for recording information on these films has been developed based on selective exposure of the films to UV irradiation passing through a mask plate at different T_c s.

2. Experimental

2.1. Materials

Polyether urethane diacrylate precursors ($\overline{M}_w = 2000$ –3500, $T_g = -53.6^\circ\text{C}$) was obtained from Chengdu Bysun Hitech Materials Co., Ltd. (PR China). Refractive indices measured for PEUDA precursors and matrix were 1.474 and 1.492, respectively. 1-Octadecanol (OD), 1-hexadecanol (HD), 1-tetradecanol (TD), and 1-dodecanol (DD) were purchased from Bodi Chemicals (PR China). Chemical structures of PEUDA and aliphatic alcohols were depicted in Scheme 1. 2-Hydroxy-2-methyl-1-phenyl-1-propanone (HMPP, Darocur 1173) was obtained from Ciba–Geigy Shanghai, China.

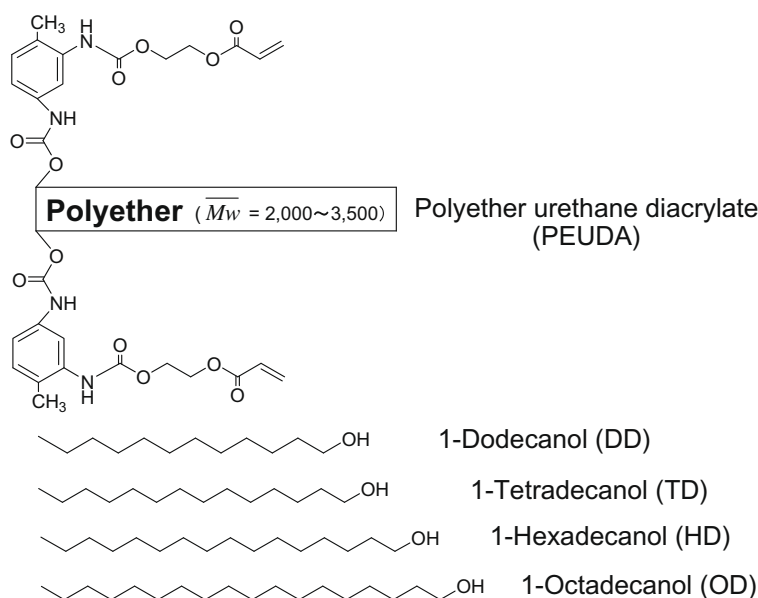
All compounds were of analytical grade and used without further purification.

2.2. Preparation of TRLS film

Films for all measurements were prepared by dissolving aliphatic alcohols in PEUDA precursors. Photoinitiator darocur1173 (~ 3 wt.%) was added, and then the mixture was heated to 70°C with stirring until the aliphatic alcohols were melted and dissolved homogeneously. The solution was then poured into a glass mold (70°C , in dark oven) of the required dimension scale, and covered with a glass plate or polyethylene terephthalate (PET) sheet. After curing with a 1000 W high-pressure mercury lamp (Yaming Lighting Co., Ltd., China) at a distance of 15 cm (UV light intensity: $8.6\text{ mW}/\text{cm}^2$ at 360–410 nm) for 20 s, the formed film was peeled off from the glass mold.

2.3. Measurements

Optical transmittances were measured at a wavelength of 660 nm using a TU-1800 UV–vis spectrophotometer (Purkinje General Instrument Co., Ltd., China) equipped with a heater and a OPTRIS[®] CT infrared thermometer (Opttris GmbH, Germany). Polarized optical microscopy (POM) was performed on a Leica DMLB microscope (Germany) with crossed polarizers, provided with a video camera (Leica DC 100) and a hot stage (Linkam THMS 600), along with a continuously heating/cooling rate of 5°C min^{-1} . X-ray diffraction (XRD) experiments were performed on X' Pert Pro MPD X-ray diffractometer (Philips, Netherlands) using a Cu-K ray. Scanning electron microscopy (SEM) measurement was performed on a JSM-5900LV scanning electron microscope (Kabuskiki Kaisha Co., Ltd., Japanese). Tensile strengths measurements were performed on a Shimadzu



Scheme 1. Chemical structures of polyether urethane diacrylate and aliphatic alcohols.

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