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Vertical alignment of liquid crystals on polymer films containing renewable cardanol moieties

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ABSTRACT

Liquid crystal (LC) alignment behaviors of poly(methyl methacrylate) derivative films containing different amounts of plant-based and renewable cardanol moieties were studied for the first time. The poly(methyl methacrylate) derivatives containing the cardanol moieties (HCP#) were prepared using 2-hydroxy-3-cardanylpropyl methacrylate (HCPM) and methacrylate (MMA) as monomers. These polymer films exhibited good optical transparency in the visible light region. The LC cells made from the polymer having 100 mol% of 2-hydroxy-3-cardanylpropyl methacrylate (HCP100) as the alignment layer showed vertical LC alignment having a pretilt angle of about 90°, while those made from HCP# films having smaller than 69 mol% of 2-hydroxy-3-cardanylpropyl methacrylate exhibited random planar LC alignment behavior. The vertical LC alignment behavior on the HCP100 film was ascribed to the hydrophobic HCP100 surface generated by the nonpolar cardanol groups in the polymers. The thermal stability of the LC cell made from UV irradiated HCP100 film (HCP100C) was enhanced compared with HCP100 due to the formation of the cross-linked structure of the unsaturated hydrocarbon in the cardanol group. Good electro-optical characteristics, such as voltage holding ratio (VHR) and residual DC voltage (R-DC), were observed for the LC cells fabricated using the HCP100 as a LC alignment layer. This can give the basic idea for the design of LC alignment layers based on renewable cardanol resource containing polymer films.

1. Introduction

The alignment technologies of liquid crystal (LC) molecules has been intensively studied due to the scientific and technical interest in the liquid crystal display (LCD) industry [1]. Vertical LC alignment methods on alignment layer surfaces have been known to produce LC cells with better electro-optical (E-O) performance, such as higher contrast ratio due to the clear dark state without electric field, than those prepared using planar LC alignment methods [2,3]. Polyimide derivatives containing hydrophobic long alkyl side chains such as *n*-octadecyl groups and (*n*-decyloxy)biphenyloxy side groups have been synthesized in order to use them as vertical LC alignment layers [4–7]. Hard baking processes using high temperature usually over 200 °C are commonly used to produce polyimide alignment layers, while the baking temperature is too high for manufacturing flexible plastic devices. Therefore, vertical LC alignment was also achieved by using comb-like polymers, irradiating with UV light, doping an organic compound or nanoparticles, or fabricating micro and nanostructures, as previously reported by us and others [8–16].

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For example, comb-like polystyrenes having *n*-alkylsulfonylmethyl-, *n*-alkylthiomethyl- and 4-alkylphenoxymethyl-substituted side groups showed the vertical LC alignment behavior [9,10].

Cardanol is one of the important renewable resources having an unsaturated hydrocarbon chain with one to three double bonds at the *meta*-position of the phenol group and it can be readily obtained by the distillation of cashew nut shell liquid (CNSL) produced as a byproduct in the cashew nut production process [17–19]. Cardanol based materials including polymers have been studied as coatings and surfactants in the various industrial applications due to the attractive characteristics such as self-cross-linkable, antibacterial, and chemically modifiable properties [20–24]. Furthermore the physico-chemical properties of the cardanol based polymers have been improved by cross-linking reaction of the unsaturated hydrocarbon chain in the cardanol upon UV irradiation [20,24].

In this paper, the LC alignment behavior of the LC cell produced using the poly(methyl methacrylate) derivatives containing cardanol side groups as an alignment layers was studied. The synthesis and characterization of these polymers and E-O characteristics of the LC cells fabricated with the polymer films are also included. Vertical LC alignment layers were produced from the LC cell through a non-rubbing process and the thermal stability of the LC cell was found to be improved by the UV irradiation on the polymer film. To the best of our knowledge, it is the first time to report the LC alignment behavior on the plant-based and renewable resources-based films for eco-friendly display applications.

2. Experimental part

2.1. Materials

Cardanol was provided by Mercury Co., Ltd. Glycidyl methacrylate and triethylamine were purchased from TCI Co., Ltd. Methyl methacrylate (MMA), 2,2′-azobisisobutyronitrile (AIBN), acryloyl chloride, and acetyl chloride were purchased from Sigma–Aldrich Co., Ltd. Potassium hydroxide (KOH) and sodium hydroxide (NaOH), *N*,*N*′-dimethylacetamide (DMAc) were obtained from Daejung Chemicals & Metals Co., Ltd. Tetrahydrofuran (THF) was dried by refluxing over sodium and benzophenone followed by distillation. Toluene was distilled over calcium hydride. *Escherichia coli* (*E. coli*; ATCC 8739) were obtained from American Type Culture Collection (ATCC). Bacto™ Agar and Difco™ Nutrient Broth were obtained from Becton, Dickinson and Company (BD). All other reagents were obtained from standard vendors and used as received.

2.2. Synthesis of 2-hydroxy-3-cardanylpropyl methacrylate (HCPM)

To a DMAc solution (30 mL) containing cardanol (10 g, 33 mmol) and potassium hydroxide (1.85 g, 33 mmol), glycidyl methacrylate (9.44 g, 66 mmol) was added and reacted under nitrogen (N_2) atmosphere for 24 h at room temperature. The reaction was finished by dropping a few drops of a concentrated HCl solution and then DMAc was evaporated in a low-pressure environment. The crude product was dissolved in methylene chloride (MC) and transferred to a separatory funnel. After extraction with 0.5 *N* HCl solution, the MC layer was dried over anhydrous magnesium sulfate and filtered. The obtained product was purified by silica gel column chromatography (ethyl acetate : *n*-hexane = 1 : 6 vol.%). The yield was 49% (7.18 g).

^{1}H NMR (300 MHz, $CDCl_3$, trimethylsilane (TMS) ref): $\delta = 0.88$ (t, $J = 6.78$ Hz, 3 H, $\text{—C}\mathit{H}_3$), 1.20–1.40 (m, $CH_3(C\mathit{H}_2)_{12}$-CH_2—), 1.60 (m, 2 H, $CH_3(CH_2)_{12}C\mathit{H}_2CH_2$—), 1.97 (s, 3 H, $\text{—OC(O)C(C}\mathit{H}_3\text{)=CH}_2$), 2.02 (m, $\text{—CH}_2\text{CH}_2\text{C}\mathit{H}_2\text{CH=CHCH}_2\text{—}$), 2.57 (t, $J = 8.04$ Hz, 2 H, $\text{—OC}_6\text{H}_4\text{C}\mathit{H}_2\text{—}$), 2.75–2.90 (m, $\text{—CH}_2\text{CH=CHC}\mathit{H}_2\text{CH=CH—}$), 3.94–4.40 (m, 5 H, $\text{—OC}\mathit{H}_2\text{C}\mathit{H}\text{(OH)C}\mathit{H}_2\text{OC(O)—}$), 4.97–5.80 (m, $\text{—CH}_2\text{C}\mathit{H}\text{=C}\mathit{H}\text{CH}_2\text{—}$), 5.62 and 6.26 (s, 2 H, $\text{—OC(O)C(CH}_3\text{)=C}\mathit{H}_2$), 6.67–6.83 (m, 3 H, aromatic), 7.19 (t, $J = 7.5$ Hz, 1 H, aromatic). FT-IR: 3471 cm^{-1} (O—H stretching vibration), 3010 cm^{-1} (C—H vibration of the unsaturated hydrocarbon), 1720 cm^{-1} (C=O stretching vibration (α,β-unsaturated ester), 1261 cm^{-1} (C(Ar)—O—C asymmetric stretching vibration (m-alkyl phenol)), 1049 cm^{-1} (C(Ar)—O—C symmetric stretching vibration (m-alkyl phenol)), 775 cm^{-1} ($\text{—CH}_2\text{—}$ rocking vibration), 721 cm^{-1} ($\text{— (CH}_2)_n\text{—}$, $n > 3$; rocking vibration), 694 cm^{-1} (aromatic out of plane C—H deformation vibration of *meta*-substituted benzene).

Mass *m*/*z* calculated $C_{28}H_{44}O_4^+$: 444.3, found 444.0.

2.3. Synthesis of poly(2-hydroxy-3-cardanylpropyl methacrylate-co-methyl methacrylate) (HCP#)

The copolymers containing HCPM and MMA monomeric units were abbreviated as HCP#, where the # is the molar compositional ratio of HCPM in the polymers. The following procedure was used for the preparation of HCP47 containing 47 mol% of HCPM and 53 mol% of MMA monomeric units, respectively. HCPM (3.0 g, 6.75 mmol), MMA (0.675 g, 6.75 mmol), AIBN (120 mg, 0.70 mmol), and THF (18 mL) were added to a round-bottomed flask equipped with a condenser and a magnetic stirring bar. The flask was purged with N_2 and sonicated for 10 min to degas the mixture and remove dissolved oxygen. Then, the mixture was refluxed with stirring. After 24 h of polymerization, the solution was exposed to air. The crude product was poured into excess of distilled water/methanol (2/1). The dissolution–precipitation procedure was repeated three times, yielding a yellowish wax (2.37 g). The M_n and PDI of HCP47 (gel permeation chromatography (GPC), polystyrene standards, THF as an eluent) were 4,900 g mol^{-1} and 1.51, respectively. Other HCP#s with different compositions were prepared using the same procedure except the monomer feed ratio (Table 1).

^{1}H NMR (300 MHz, $CDCl_3$, TMS ref): $\delta = 0.8$–1.1 (3 H, $\text{—C}\mathit{H}_3$), 1.20–1.90 (m, $CH_3(C\mathit{H}_2)_{12}CH_2$— and backbone), 1.55 (m, 2 H, $CH_3(CH_2)_{12}C\mathit{H}_2CH_2$—), 2.01 (m, $\text{—CH}_2\text{CH}_2\text{C}\mathit{H}_2$-$\text{CH=CHCH}_2\text{—}$), 2.54 (2 H, $\text{—OC}_6\text{H}_4\text{C}\mathit{H}_2\text{—}$), 2.75–2.90 (m, $\text{—CH}_2\text{CH=CHC}\mathit{H}_2\text{CH=CH—}$), 3.59 (3 H, $\text{—OC(=O)C}\mathit{H}_3$), 3.90–4.40 (m, 5 H, $\text{—OC}\mathit{H}_2\text{C}\mathit{H}\text{(OH)C}\mathit{H}_2\text{OC(O) —}$), 4.96–5.80 (m, $\text{—CH}_2\text{C}\mathit{H}\text{=C}\mathit{H}\text{CH}_2\text{—}$), 6.50–6.83 (m, 3 H, aromatic), 7.16 (1 H, aromatic).