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Crosslinked poly(norbornene-dicarboximide)s as electro-optic chromophore hosts

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ABSTRACT

A series of crosslinked poly(norbornene-dicarboximide)s have been prepared by ring opening metathesis polymerization. Increasing quantities of a bifunctional norbornene-dicarboximide crosslinker was doped into a high T_g cyclohexyl-substituted norbornene-dicarboximide monomer before polymerization. The wt% of the crosslinker was increased from 0.00 to 4.40 wt%, after which the polymers became gelated. Polymer molecular weights increased drastically from 23,500 to 2,135,000 g/mol, the polydispersities increased from 1.18 to 73.47 and the viscosities increased from 5.27 to 538.7 mPa·s as the wt% of the crosslinker was increased. The *trans:cis* vinylene ratio remained constant at 1:0.18 as well as the T_g and T_d with average values of 210 °C and 392 °C being measured. Five of the crosslinked polymers and the reference homopolymer were utilized as hosts for the high activity *tert*-butyldiphenylsilyl substituted FTC chromophore guest. The polymer host containing 1.96 wt% crosslinker was found to have a maximum r_{33} of 78 pm/V when polled at 150 °C with an electric field strength of 100 V/μm. The r_{33} increased linearly from 63 to 78 pm/V as the wt% of the crosslinker was increased from 0.00 to 1.96 wt%. The thermal and temporal stability was found to increase slightly with the 0.00 wt% polymer exhibiting a stability of 77%, while the 1.96 wt% polymer exhibited a stability of 79% when both were heated to 85 °C and aged for 500 h in air.

1. Introduction

Ring opening metathesis polymerization (ROMP) has become a reliable and well-controlled polymerization technique since the availability of active and tolerant ruthenium based Grubbs initiators [1,2]. When a strained cyclic alkene is initiated, the release in energy acts as the driving force for the polymerization. Norbornene-dicarboximides (NDIs) are a well suited class of cyclic alkene because of their high ring strain and easy to functionalize dicarboximide unit, consequently they have been prepared with a large number of active substituents enabling them to be utilized in applications spanning the boundaries of chemistry, physics and biology [3–5]. For electro-optic (EO) applications such as ring resonators [6], Mach-Zehnder interference modulators [7] and waveguide modulators, the organic components must be soluble in common solvents for spin coating. Resulting thin films must exhibit minimal surface roughness, be homogeneous and have a high optical quality. As well as possessing all of these essential qualities, poly(NDI)s incorporating cycloalkanes have been shown to exhibit very high glass transition (T_g) and thermal decomposition (T_d) temperatures [8,9]. By trial and error methods we have found that cycloalkane-substituted poly(NDI)s are able to be doped with a high (> 35 wt%) concentration of the phenyl vinylene thiophene (FTC) chromophore while still maintaining a high T_g, T_d and excellent film quality [10,11]. This is due to the microstructure of poly(NDI)s which leads them to be highly amorphous. The choice of Grubbs initiator can influence this microstructure, with varying degrees of *trans* and *cis* vinylene units being possible, depending on the specific ligand. The high miscibility between EO chromophores and poly(NDI)s has served as the basis for a number of investigations [12–16].

Inorganic crystalline and organic EO materials have been developed, with Lithium Niobate ($LiNbO_3$) having successfully yielded numerous commercial products [17–19] Despite this success, organic chromophores are currently a major focus of research efforts as they offer excellent solution processability, and a faster electron displacement. Chromophores include an electron donating unit separated from an electron withdrawing unit by a π electron bridge, delocalized π

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electrons and a non-centrosymmetric structure are responsible for their high EO activity [20,21]. For utilization in devices it is essential to include a non-conjugated organic polymer, preferably with a high T_g and T_d as a passive matrix. This can be achieved by blending the polymer and chromophore together in a good solvent yielding a guest-host system [22,23,10,11] or by chemically attaching the chromophore to the polymer backbone generating a side-chain system [24,25]. Phase separation at high chromophore concentrations can occur in guest-host systems if the two species have a poor miscibility and such systems are more prone to relaxation after poling, especially over extended time periods at elevated temperatures [11,10]. One strategy to minimize this degradation is to use a very high T_g polymer (> 200 °C). Various research groups have also explored the use of crosslinking as a method to realize a high stability EO material [26–29]. Thermally initiated cycloaddition reactions have been widely employed, however if the crosslinking begins at temperatures lower than the poling temperature of the EO material, then polling can be problematic. In such cases, poling and crosslinking must be undertaken simultaneously. Thus far soluble crosslinked polymers have not been widely investigated as an EO host material. Here we have attempted to demonstrate the feasibility of a highly amorphous and soluble, crosslinked polymer which can be utilized as a host for high EO activity FTC [30] chromophore guests. The FTC chromophore employed in this investigation was modified to incorporate a bulky *tert*-butyldiphenylsilyl side group to minimize the chromophore aggregation caused by antiparallel stacking [31]. An additional consequence of the side group is an enhanced polarizability of the molecule due to increasing the strength of the donating unit.

The polling process of EO materials induces the non-centrosymmetric alignment of the chromophore molecules in the polymer matrix. This is achieved by sandwiching the material between gold electrodes and applying a high electric field [32]. An elevated temperature is also necessary to give chromophores the necessary freedom of movement. This temperature is commonly close to the T_g of the mixture in a guest-host system and is best found by trial and error methods. If chromophores in the EO material are able to be aligned to a high degree, then the EO material will exhibit a high EO coefficient (r_{33}). Minimizing the required strength of the applied field is desirable to avoid dielectric breakdown at the EO polymer/electrode interface and so materials with a high polling efficiency are desirable.

In this investigation a series of soluble crosslinked poly(norbornene-dicarboximide)s (**7a-t**) have been prepared by the doping of ascending amounts of a bifunctional norbornene-dicarboximide monomer (**4**) into a high T_g cyclohexyl-substituted norbornene-dicarboximide monomer (**6**). The mixture was then polymerized by using the Grubbs 1st generation initiator (**G1**) in anhydrous chloroform and the living polymerization was quenched by the addition of an excess ethyl vinyl ether. The reaction pathway can be observed in the Scheme 1. By increasing the wt% of crosslinker (**4**) from 0.00 to 4.40 wt%, the degree of crosslinking was precisely controlled until an insoluble gel resulted. An easily processed selection of the crosslinked polymers were then themselves doped with 35 wt% of a high EO activity *tert*-butyldiphenylsilyl substituted FTC chromophore. The effect of the increased crosslinker wt% on the physical and EO properties of the guest-host polymers was evaluated and the results are presented herein.

2. Experimental procedures

2.1. Materials

Common laboratory solvents and reagents were procured from Tokyo Chemical Industry (TCI) or Kanto Chemical Co and were used as received. Details can be observed in supporting information Section 5.1. The Grubbs 1st generation initiator (**G1**) was purchased from Sigma-Aldrich and was used as received. The *tert*-butyldiphenylsilyl substituted FTC chromophore was prepared according to previous literature procedures [31].

2.2. Techniques

The details of commonly utilized analytical techniques can be found in supporting information Section 5.2. Guest-host mixtures were prepared by dissolving the crosslinked polymer (65 mg) and the chromophore (35 mg) in 1,2-dichloroethane (1 mL) and stirring at room temperature for 24 h. The solutions were then filtered through a 0.2 μm syringe filter and spin coated onto an Indium Tin Oxide (ITO) coated square glass substrate (2 cm × 2 cm) at a spin rate of 1000 rpm for a period of 30 s. The films were then placed on a hotplate and dried firstly at 85 °C for 30 min in air and then transferred to a vacuum oven and dried at 85 °C for a further 24 h. The film thickness of the polymers were measured using a KLA Tencor P-15 surface profiler with a scan size of 100 μm and a scan rate of 50 μ/min. Gold contacts were deposited on top of the polymer film using a magnetron sputter, for a period of 6 min at 40 mA. The circular gold electrode had a radius of 2 mm. The electro-optic coefficient (r_{33}) of the guest-host systems were measured at a wavelength of 1.31 μm utilizing a modified Teng-Man reflection technique [33]. Temporal and thermal stability of the materials were evaluated by placing the polled sample onto a hotplate at 85 °C for a period of 500 h in air. The r_{33} was re-measured at regular time intervals to produce a decay curve.

2.3. Synthesis of precursors (1), (2), (3), (5) and monomer (6)

The precursors (**1**), (**2**), (**3**) and (**5**) are necessary components for the synthesis of the high T_g cyclohexyl-substituted monomer (**6**) and the bifunctional crosslinker (**4**). The starting material precursor (**1**) was prepared according to a modification of the Castner procedure [34]. The updated procedure can be seen in supporting information Section 5.3. Precursor (**2**) and precursor (**3**) have been prepared and characterized previously by ourselves [12] and the current procedures can be observed in supporting information Section 5.4 and Section 5.5 respectively. Precursor (**5**) was prepared in a manner consistent with the Contreras procedure [8]. The slight modification employed by ourselves can be observed in supporting information Section 5.6. Monomer (**6**) has been prepared and extensively characterized by ourselves [10,13] as well as other groups [9,8]. The most recent procedure can be observed in supporting information Section 5.7.

2.4. Synthesis of crosslinker (4)

1,8-Dibromooctane (6.55 g, 24.09 mmol), potassium carbonate (33.00 g, 238.78 mmol) and precursor (**3**) (12.30 g, 48.18 mmol) were dissolved in acetonitrile (200 mL) and heated under reflux for 48 h. After allowing to cool to room temperature the acetonitrile was evaporated using a rotary evaporator and the remaining mixture was poured into a beaker of stirred de-ionized water. This was stirred for 1 h to ensure the potassium carbonate had dissolved. The organics were then extracted into dichloromethane and washed several times with brine. The dichloromethane fraction was collected and dried using anhydrous magnesium sulfate. Filtration and evaporation of the dichloromethane allowed isolation of the crude product. This was purified using column chromatography in a solvent system of ethyl acetate and hexane. The off-white solid was finally recrystallized from a mixture of boiling ethanol and tetrahydrofuran to give the pure product in a yield of 67% [35]. ^{1}H-NMR (400 MHz, CD_3OD) δ: 7.13 (d, J = 9.2 Hz, 4H), 7.00 (d, J = 8.7 Hz, 4H), 6.36 (m, 4H), 3.99 (t, J = 6.8 Hz, 4H), 3.19 (s, 4H), 2.81 (s, 4H), 2.50 (m, 4H), 1.72 (m, 4H), 1.42 (m, 8H) p.p.m. ^{13}C-NMR (125 MHz, CD_3OD) δ: 189.59, 170.96, 150.32, 140.71, 137.25, 127.16, 80.25, 59.97, 57.45, 55.21, 41.23, 41.10, 37.95 p.p.m.