



# Electro-optic properties of a side chain poly(norbornene-dicarboximide) system with an appended phenyl vinylene thiophene chromophore



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## ABSTRACT

A side chain EO copolymer series has been synthesized by ROMP using the Grubbs 3rd generation initiator and quenched with ethyl vinyl ether. The copolymers were prepared by combining two norbornene-dicarboximide monomers, one with a cyclohexyl substituent and another substituted with an FTC chromophore. The mol% of the chromophore-substituted monomer was varied from 0.00 mol% to 22.92 mol%, all polymers were obtained in a yield of between 83 and 92% and a purity of between 97 and 98%. The *cis:trans* vinylene ratio remained constant at 1:1, confirming the polymers were amorphous. Peak molecular weights increased from 29,541 g/mol to 142,113 g/mol and the PDI increased from 1.36 to 4.01 respectively. Glass transition and thermal decomposition temperatures decreased from 206 °C to 168 °C and 433 °C to 382 °C as the mol% of the chromophore-substituted monomer was increased. UV–vis absorbance spectroscopy was used to quantify the chromophore content. A close correlation (68–95%) between the measured and calculated absorbance was found. The polymer containing 22.92 mol% of the chromophore-substituted monomer had a maximum  $r_{33}$  of 70 pm/V when polled at an optimum field of 60 V/μm at a polling temperature of 200 °C. This equates to a high polling efficiency of 1.16. High current flow in this polymer film at elevated field strength caused a breakdown of the electrode, preventing access to an elevated electro-optic coefficient. This polymer was found to have an excellent stability of 76% when aged at 85 °C for 1000 h in air.

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## 1. Introduction

Poly(norbornenes) are a family of materials that have been furnished with a diverse range of active substituents to tune the polymer to a desired practical application [1–4]. Due to the high ring strain of norbornene monomers, producing a well-controlled polymer can be difficult. In contrast poly(norbornene-dicarboximide)s (poly(NDI)s) have proved both easier to produce in a well-controlled manner and to functionalize [5–10]. In previous studies it was confirmed that poly(NDI)s can be easily dissolved in common solvents and spin-coated onto the desired substrate giving thin films which are flat, homogeneous and have a high optical quality. These characteristics are essential for utilization in polymer

waveguide, modulator and ring resonator applications [11,12]. Poly(NDI)s with high glass transition ( $T_g$ ) and thermal decomposition ( $T_d$ ) temperatures have been prepared by the attachment of bulky cycloalkanes such as cyclohexyl and adamantyl units [13,14]. Recently we have demonstrated that these polymers can be excellent hosts for phenyl vinylene thiophene (FTC) guest chromophores [15,16]. The well-controlled living ring opening metathesis polymerization (ROMP) of norbornene dicarboximides (NDI)s allow a range of interesting macromolecular architectures to be produced such as homopolymers [17,18], random copolymers [19], polymer brushes [20,21], ladder polymers [22] and many more.

The first electro-optic (EO) devices were derived from inorganic crystalline materials such as lithium niobate (LiNbO<sub>3</sub>) and have since been successfully commercialized [23–25]. Organic EO materials known as chromophores were later found to exhibit many of the same useful properties as lithium niobate. This is a consequence

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of their non-centrosymmetric structure and the abundance of delocalized  $\pi$  electrons. Chromophores are constructed by the linking of an electron donating unit and an electron withdrawing unit. The linker must facilitate electron displacement between the two sections and therefore must be a  $\pi$ -electron bridge [26,27]. Apart from the advantage of solution processability, organic EO materials also exhibit a faster electron displacement than inorganics. Unfortunately chromophores exhibit poor film forming properties, making device fabrication problematic. A non-conjugated organic polymer is a necessary component to offer the required mechanical, and thermal qualities as well as solution processability. The simplest method of inclusion is to blend a suitable polymer and the chromophore in a good solvent, creating a guest-host system [28,29]. Phase separation of the two components can occur at high chromophore concentrations, especially if they have a poor miscibility. Despite the formulation advantages associated with the guest-host approach, such systems are prone to relaxation after polling as the chromophores revert to a random orientation over extended time periods or even when subjected to elevated temperatures below the polymer glass transition temperature ( $T_g$ ) [15,16]. To minimize the degradation, host polymers with a high  $T_g$  ( $>200$  °C) have been utilized. An additional reason is that the blending of a chromophore into a polymer acts as a plasticizer, reducing the  $T_g$  of the polymer/chromophore mixture. Chromophores can also be chemically incorporated into the polymer main chain or as pendant groups producing a side chain EO polymer [30,31], although this requires a greater number of synthetic steps which can be time consuming and costly. Despite this, the use of side chain EO polymers allow the incorporation of higher chromophore concentrations as well as offering an enhanced thermal and temporal stability compared with the guest-host. There are two general methods of producing a side chain EO polymer, the first is to synthesize a polymer which contains a reactive pendant group to which the chromophore can then be attached [30]. This is known as post-polymerization functionalization. The second method is to chemically attach the chromophore to a monomer and then polymerize. This type of pre-polymerization functionalization is much less common in the literature as few polymerization methods allow monomer conversion at lower temperatures necessary to avoid chromophore decomposition. Required initiators often degrade the active chromophore due to its sensitivity. In contrast the high ring strain of NDIs allow polymerization at room temperature under mild conditions [18] using the Grubbs 3rd generation initiator which exhibits little or no affinity for the sensitive chromophore at such temperatures.

The phenyltetraene (CLD) [32] and phenyl vinylene thiophene (FTC) [33] class of EO chromophore's have proved effective benchmarks. Substitution of these molecules with bulky and solubilizing side groups is necessary to prevent strong aggregation caused by antiparallel stacking [34]. Side groups also enhance the polarizability through increasing the strength of the donating unit. Organic EO materials do not possess an inherent activity and therefore they must be polled [35]. This process results in the required non-centrosymmetric alignment. Polling can be achieved by using a strong electric field and must be performed at an elevated temperature which is near to the  $T_g$  of the polymer matrix. The magnitude of the EO coefficient ( $r_{33}$ ) is proportional to the degree to which the chromophores can be aligned under the applied electric field.

By the combination of a cyclohexyl-substituted monomer (**5**) and chromophore-substituted monomer (**9**), a series of well-controlled copolymers (**10b-10g**) have been prepared by utilizing the Grubbs 3rd generation initiator (**G3**) in anhydrous chloroform. After monomer conversion the living polymerization was quenched

by the addition of excess ethyl vinyl ether as shown in [Scheme 2](#). The cyclohexyl substituent of monomer (**5**) imparted an increased solubility to the copolymer as well as elevating both the  $T_g$  and  $T_d$ . The chromophore-substituted monomer (**9**) allowed the chromophore content of the copolymer to be precisely varied. The mol% of monomer (**9**) was increased from 0.00 mol% (**10a**) to 22.92 mol% (**10g**). This was achieved by maintaining a constant mass of monomer (**5**) while gradually increasing the mass of monomer (**9**) in the reaction mixture. A progression in the physical, thermal and electro-optic properties of the series were systematically investigated and are presented herein.

## 2. Experimental procedures

### 2.1. Materials

All common laboratory solvents and reagents were purchased from Tokyo Chemical Industry (TCI) or Kanto Chemical Co and were used as received. Further details can be found in [supporting information section 5](#). The Grubbs 3rd generation initiator (**G3**) was purchased from Sigma-Aldrich and was used as received. The chromophore (**Cr**) was prepared according to previous literature procedures [30,36].

### 2.2. Techniques

Details of instruments used and standard analytical measurement techniques can be found in [supporting information section 6](#). Polymer thin films were prepared by firstly dissolving the polymer (100 mg) in 1,2-dichloroethane (1–2 mL) and stirring at room temperature for 24 h. The solutions were then filtered through a 0.2  $\mu\text{m}$  syringe filter and spin coated onto an Indium Tin Oxide (ITO) coated square glass substrate (2 cm  $\times$  2 cm) at a spin rate of 1000 rpm for a period of 30 s. The films were 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  $\mu\text{m}$  and a scan rate of 50  $\mu\text{m}/\text{min}$ . 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 copolymers were measured at a wavelength of 1.31  $\mu\text{m}$  utilizing a modified Teng-Man reflection technique [37]. The temporal and thermal stability of copolymer (**10g**) was evaluated by placing the polled sample onto a hotplate at 85 °C for a period of 1000 h in air. The  $r_{33}$  was recorded at regular time intervals to produce the decay curve.

### 2.3. Synthesis of precursors (**1**), (**2**), (**3**) and (**4**)

The precursors (**1**), (**2**), (**3**) and (**4**) are necessary components for the synthesis of the cyclohexyl-substituted monomer (**5**) and chromophore-substituted monomer (**9**). Precursor (**1**) which is the starting material was prepared according to a modification of the Castner procedure [38]. This has been further optimized and described in our previous works [16] and the most up to date procedure can be found in [supporting information section 3.1](#). The preparation of precursor (**2**) has been described in our previous work [17]. A more recent experimental procedure can be observed in [supporting information section 3.2](#). The preparation and characterization of precursor (**3**) was previously reported by ourselves [17], the procedure is given in [supporting information section 3.3](#). The synthesis of precursor (**4**) has been reported by other groups [13] as well as being optimized by ourselves [18,19]. For details see [supporting information section 3.4](#).

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