



A norbornene polymer brush for electro-optic applications

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ABSTRACT

Norbornene-dicarboximide derived polymer brushes containing Disperse Red 1 appended chromophores have been prepared by sequential ring opening metathesis polymerization and atom transfer radical polymerization. This brush was then employed as an electro-optic polymer host for high molecular hyperpolarizability phenyl vinylene thiophene vinylene (FTC) bridge chromophores in a binary chromophore system. The r_{33} of the polymer brush/bi-chromophore network was evaluated *via* in situ poling and was measured as 94 pm/V compared to the benchmark polymethylmethacrylate (PMMA) system of 76 pm/V with an identical chromophore. Furthermore, our polymer brush/bi-chromophore network exhibited an enhanced poling efficiency of 1.37 (nm/V)^2 as compared to a simple PMMA - FTC host - guest 0.70 (nm/V)^2 .

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1. Introduction

Electro-optic (EO) organic polymers [1,2] are being intensively investigated because of their potential applications in data processing. Such advanced applications include telecommunications, sensing and next generation computing [3]. In all of these cutting-edge technologies a low driving voltage ($V \pi$) is essential [4]. Over the last decade polymeric materials have been developed with an increasingly high EO coefficient (r_{33}) at telecommunication wavelengths. This enhanced r_{33} is a crucial requirement for the reduction of $V \pi$. The driving voltage may be defined as: $V \pi = \lambda d / (2n^3 r_{33} \Gamma)$, where λ , d , n , L and Γ are the working wavelength, electrode gap, refractive index, interaction length and overlap integral factor, respectively [5].

The most simple and easy to prepare EO polymer system for exploitation in devices is the guest-host. In such materials, the dipolar EO chromophores have been physically incorporated into the host polymer matrix to obtain their maximum EO response. Unfortunately, there is a practical limit for the chromophore loading density beyond which the poling-induced polar order considerably decreases due to the strong intermolecular electrostatic interactions. Thus, research efforts have been focused on increasing the chromophore loading density, and at the same time maintaining high poling efficiencies. Side chain polymer hosts which incorporate chromophore's appended as a side chains were the next logical step forward in the pursuit of more efficient EO materials [6]. Such systems were a dramatic improvement over simple homopolymer hosts, as the chromophore loading concentration could be increased markedly because of a reduced aggregation [7,8]. As

an extension of this technology, the bi-chromophore strategy involves the appending of a small chromophore molecule (usually Disperse Red 1) onto a polymer backbone, thus forming a side chain system. This material was then employed as a host for a more enhanced hyperpolarizability chromophore such as the phenyl vinylene thiophene vinylene (FTC) or phenyl vinylene cyclohex-2-enylidene propenyl (CLD). Bi-chromophore systems have been shown to exhibit an enhanced dielectric constant in the host. This host can in turn enhance the hyperpolarizability of the guest chromophore. Furthermore the appended chromophores of the host polymer enable a large supra-molecular interaction with the guest. These interactions are primarily repulsive and dipole-dipole electrostatic. Guest-host "coupling" becomes feasible in bi-chromophore systems, which has a large impact on the acentric order under the application of an external electric field. These bi-chromophore systems therefore allow higher loading densities without phase separation because of the strong interaction between guest and host chromophores. Additionally, optical poling may lead to an isomerization of the Disperse Red 1 (DR-1) derivative (trans-cis-trans) which also has been shown to enhance the electro-optic activity [9]. Also as chromophore degradation is known to occur by singlet oxygen chemistry, a high T_g and highly networked material such as polymer brushes may prevent this degradation pathway.

Polymer brushes are known to display a highly compact and regular structure [10,11]. The physical characteristics of the polymer brush are governed by a large degree of steric repulsion between the densely grafted side chains. If used as an EO host, polymer brushes should be able to disperse chromophore molecules to a higher degree than a homopolymer, possibly to the same degree or greater than the side chain. Furthermore a well-controlled synthetic process involving chain growth polymerizations sequential ring opening metathesis polymerization (ROMP)/atom transfer radical polymerization (ATRP) may facilitate

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optimization of the brush properties, such as backbone/brush length variation. If utilized in an EO device we would expect polymer brushes to exhibit excellent physical stability, which is a paramount requirement in fabrication processes and long-term operation. Furthermore side chain polymer brushes may offer many of the advantages of the bi-chromophore strategy whilst also providing the beneficial physical characteristics of the brush network. The concept is illustrated in Fig. 1.

Of the various polymer brush morphologies, the so-called cylindrical polymer brush involves a polymer backbone being densely grafted with many polymeric side chains. Owing to the strong steric repulsion between crowded branches, the main chain is extended greatly and the whole polymer displayed a wormlike morphology. Molecular brushes are branched polymers of which polymeric chains are densely tethered by one end to a linear polymer backbone [12]. Three general strategies have been used to synthesize polymer brushes: “grafting through”—the polymerization of a macro monomer, “grafting onto”—the addition of preformed side chains to a backbone and “grafting from”—the polymerization of side chains from a macromolecular initiator backbone [13,14].

In this investigation we have prepared and characterized a norbornene-dicarboximide (NDI) polymer brush containing the associative chromophore Disperse Red 1 methacrylate (DR1-MA) in the side chains. We initially supposed that the addition of this DR1-MA molecule may have numerous beneficial effects, such as increasing the T_g , T_d and interacting strongly with other chromophores used as guests by increasing the dielectric constant of the host polymer and the enhancement of supra-molecular interactions between host and guest [15]. Initially the poly(norbornene-dicarboximide) backbone was prepared by the ROMP of NDI monomer (**1**) using Grubbs 1 (**G1**) in chloroform at room temperature. The resulting macro-initiator (**2**)

underwent ATRP with DR1-MA and methyl methacrylate (MMA) in the presence of catalyst to prepare the EO polymer brush as our host. The three FTC chromophores (**C1**, **C2** and **C3**) were prepared according to the literature procedures [6,16]. These guest chromophores were mixed with the EO polymer brush at a chromophore wt% of 25 in a solvent of cyclopentanone to form EO materials respectively.

2. Experimental details

2.1. Synthesis

The monomer (**1**) was prepared according to literature procedures [17,18].

Macro-initiator (**2**) synthesis; The NDI monomer (**1**) was dissolved in chloroform and stirred for 10 minutes. The **G1** initiator was transferred to a separate vessel and dissolved in chloroform. The initiator **G1** solution was transferred quickly to the reaction vessel *via* syringe and the polymerization was allowed to proceed at room temperature for 60 minutes. After this time, quenching was achieved by the addition of an excess of ethyl vinyl ether. After stirring for 30 minutes the desired polymer was isolated by precipitation into methanol.

Polymer brush (**P3**) synthesis; The macro-initiator (**2**) N, N, N', N'-pentamethyldiethylenetriamine (PMDETA), MMA, DR1-MA, and anisole were transferred to a Schlenk tube. The materials were degassed, after which CuBr was added [19]. The polymerization to yield polymer brush (**P3**) was then carried out at 50 °C for 8 hours. The crude material was purified by passing through a neutral alumina plug and the obtained solution was precipitated into methanol.

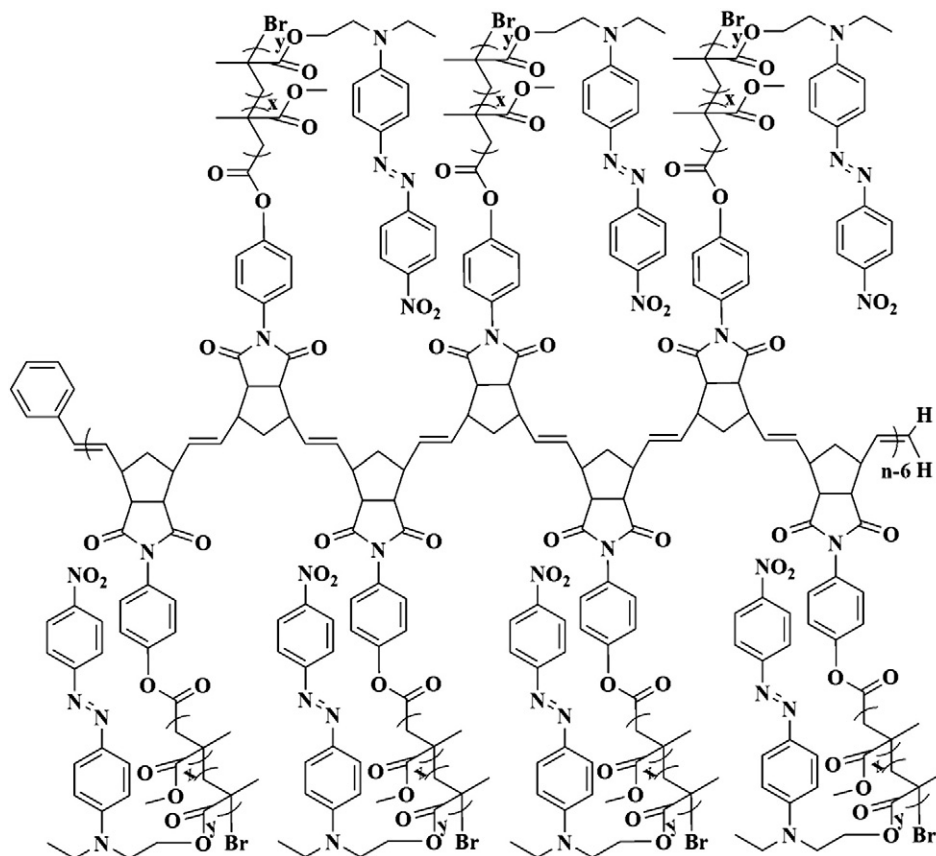


Fig. 1. Graphical representation of the polymer brush/bi-chromophore network.

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