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Synthesis and second-order nonlinear optical properties of a crosslinkable functionalized hyperbranched polymer

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ABSTRACT

A new implementation of copper-free thermal Huisgen 1,3-dipolar crosslinking reaction into a high T_g hyperbranched polyimide polymer in order to stabilize the electro-optic (EO) activity of second-order non linear materials is reported. Towards this goal, two different synthetic approaches were explored. The first strategy is based on the post-functionalization of the polymer with mixtures of DR1 azido derivative and propargylic alcohol, whereas, the second consists in the preparation of two complementary functionalized hyperbranched polymers that are mixed just before the preparation of films. Materials exhibit good second-order nonlinear optical coefficients (d_{33}) close to 30 pm/V at the fundamental wavelength of 1064 nm. Moreover, the thermal stability of the NLO properties of these materials reaches temperatures as high as 150 °C, and probably higher. This represents the highest thermal stability of crosslinkable EO polymers based on the crosslinking Huisgen reaction.

1. Introduction

The development of organic second-order nonlinear optical (NLO) polymers has received significant attention for the past two decades. They represent promising candidates as active materials in photonic devices, such as electro-optic (EO) modulators since they display faster response times, larger bandwidths, higher EO coefficients and better processability in comparison with NLO inorganic crystals [1,2]. These materials are generally composed of push–pull organic chromophores, in which a π-conjugated bridge is end-capped by donor and acceptor moieties, hosted in the polymeric matrix [2–4]. Considerable efforts have been made in order to translate the molecular optical nonlinearities, corresponding to the scalar product of chromophores off-resonance hyperpolarizability (β) and ground state dipole moment (μ), into macroscopic EO coefficients (r_{33}) [2,5]. Recently, very elegant strategies based on supramolecular construction of the EO materials were published, but these new approaches may not easily be scalable for low-cost industrial applications [3,6]. While the latter relies on the use of well efficient NLO-phores, the thermal stability of the dipole alignment and the poling efficiency depend on both the polymer backbone and the shape of the chromophore [2,3,7,8]. Accordingly, the development of new host matrices is certainly of crucial importance to reach applications with these promising materials. In most cases, NLO-phores are incorporated in a linear polymer as side-chain pendant groups [2–4,7,9,10]. However, they strongly interact with

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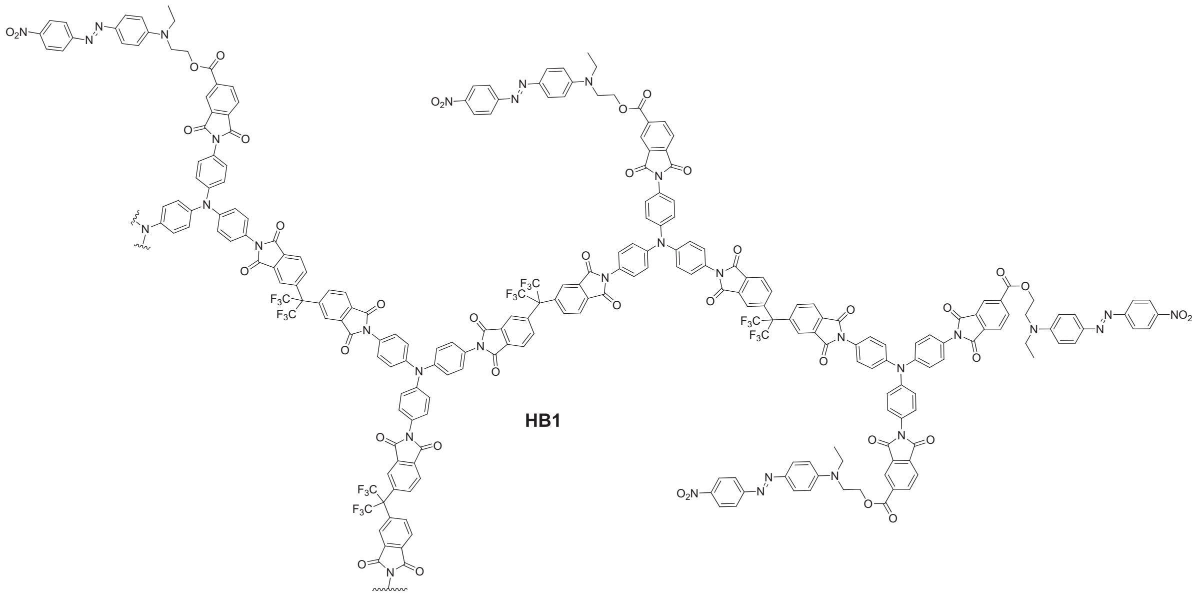

Fig. 1. Previously studied post functionalized hyperbranched polyimide (**HB1**).

one another due to their high ground state dipole moment and adopt a head-to-tail organization limiting the poling efficiency [2–4,11]. Theoretical and experimental studies suggest that, into dendritic or hyperbranched architectures, intermolecular electrostatic interactions are minimized due to the steric hindrance generated by the spherical molecular shape [2–4,9,12]. [13] This dentritic effect allows higher poling efficiency and therefore, an enhancement of the macroscopic optical nonlinearity. Nevertheless, the synthesis of dendritic materials could be a time-consuming task, requiring multi-step syntheses and tedious purifications [14], while hyperbranched polymers can be prepared with a minimum of synthetic efforts, in a single step [15]. That is why we selected the polyimide developed by Xu and Economy owing to its one-pot synthesis, high glass transition temperature (T_g), high solubility and filmability (Fig. 1) [16].

We recently reported the peripheral post functionalization of a hyperbranched polymer by a DR1 derivative chromophore [13]. The post functionalization was performed according to two different routes, the esterification of the polymeric carboxylic acid group by alcohol derivatized chromophores or by "click chemistry" based on copper-catalyzed 1,3-dipolar Huisgen cyclo-addition. Both strategies exhibit high d_{33} coefficients, up to 65 pm V^{-1} measured at the fundamental wavelength of 1064 nm by second harmonic generation (SHG). In addition, the latter remains stable until 130 °C (corresponding to the loss of 5% of the initial SHG signal). The two most practical strategies to slow down the chromophores relaxation are the utilization of a high T_g polymer [2–4,17,18] or the introduction of post-poling crosslinking systems into the materials [8,9,19,20]. Herein, we have decided to couple both strategies into a single material by implementing the previously reported copper-free thermal Huisgen 1,3-dipolar cyclo-addition [21] into an EO hyperbranched polyimide polymer in order to enhance the thermal stability of the chromophores alignment. This objective was tackled according to two synthetic strategies. The first one consists in condensing on the hyperbranched polymer an equimolar mixture of an azido derivative of DR1 and propargylic alcohol (Fig. 2, Strategy 1). The second approach (Fig. 2, Strategy 2) consists in the preparation of two complementary hyperbranched polymers, respectively functionalized with azido DR1 (**HB3**) and propargylic alcohol (**HB4**). Thus, the latter will be mixed just before the preparation of the films avoiding any undesired crosslinking during storage.

2. Experimental part

2.1. Materials

Compounds **1** [22], **HB0** [16] and **HB4** **[13]**, dimethoxytriazine-*N*-methylmorpholinium chloride were prepared according to the methods described in the literature.

2.2. Methods

^{1}H NMR spectra were recorded using a Bruker 300 MHz instrument (ARX-300, Bruker) with tetramethylsilane (TMS) as the internal standard and $CDCl_3$ as the solvent. The IR spectra were recorded using a FTIR spectrometer (Clark-MXR CPA). UV–Vis. absorption spectra were recorded on an UV-2401PC Shimadzu spectrophotometer. Thermal analyses were performed using a TA instruments Q100 in a nitrogen atmosphere at a heating rate of 10 °C/min. The number- and weight-average molecular weights and molecular weight distributions were determined using a size exclusion chromatography (SEC) on a system equipped with a SpectraSYSTEM AS 1000 autosampler, with a guard column (Polymer Laboratories, PL gel 5 μm guard column)