

# Second-harmonic properties of dendritic polymers skeleton-constructed with azobenzene moiety used for nonlinear optical materials

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## Abstract

A series of dendrons and dendrimers skeleton-constructed with azobenzene moiety were synthesized and doped in a high  $T_g$  polycarbonate (PC) as a host for nonlinear optical (NLO) materials. The optimal loading density and poling conditions were investigated using UV–vis spectral and second-harmonic generation (SHG) measurements. The results showed that the dendrons and dendrimers have good solubility in PC host, which increased with the generation increased. Moreover, the SHG measurements indicated that the dendrons possess higher nonlinearity than the dendrimers. The chromophores of lower generation dendrons were easier to orient along the poling electric field and gave a cone shape with the azobenzene branching units, which coherently contributed to the molecular hyperpolarizability and resulted in the higher SHG intensity. The temporal stability of the dendrons with 15% loading density was also investigated, and showed that the decaying in nonlinearity was slower for higher generation dendrons.

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## 1. Introduction

Polymeric nonlinear optical (NLO) materials have been demonstrated to possess larger nonlinearity, ease of processing, ultra-fast response time and low dielectric constant compared to the traditional

inorganic materials. These advantages make them feasible to be used in a variety of device configurations to achieve a number of functions including electrical-to-optical signal transduction, switching at nodes in optical networks, control of the phase of radio frequency and optical signals, electromagnetic field sensing, etc. [1]. At a molecular level, the large second-order NLO response can be achieved by maximizing the molecular first hyperpolarizability  $\beta$ . To develop high performance NLO materials, large number of chromophores with high  $\mu\beta$  value have

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been designed for achieving the polymeric materials with large nonlinearity, high stability and low optical loss. The chromophores were simply doped into a polymer matrix such as poly(methyl methacrylate) (PMMA) or polycarbonate (PC) [2–4], incorporated into polymer main chains, or attached to main chains as pendants [5–8]. Moreover, the cross-linkable polymers, hyperbranched polymers and dendrimers with NLO chromophores have been developed in this aspect, and show several advantages [9–12].

The monodisperse dendrimers with three-dimensional molecular architecture and starburst topology provide unique properties which can promote the performance of formed NLO materials. Multi chromophores can be incorporated into one dendrimer molecule. The spherical structure of dendrimers results in higher solubility in polymeric hosts. Both lead to higher chromophore loading density, and thus larger nonlinearity. Moreover, the NLO chromophores with high  $\mu\beta$  value can be chemically bonded to dendrimers, which are further doped in polymer matrices. The highly branched structure of dendrimers provides the internal free volume for NLO chromophores, which can be site-isolate arranged through steric interaction [13]. Thus the detrimental intermolecular electrostatic interaction can be reduced and large macroscopic nonlinearity will be realized [3,14–16]. Most of dendrimers involved in this aspect are based on the above concepts but rather few examples could be found for the dendrimers with NLO chromophores as the branching units. Yokoyama et al. synthesized the dendrons bearing up to 15 azobenzene moieties as the branching units. The dendrons in solution existed in a cone shape, and each chromophore unit coherently contributed to form a large electronically dipolar macromolecule system, thus the molecular hyperpolarizability  $\beta$  increased with increasing the generation [17]. Because the second-harmonic generation (SHG) intensity ( $d_{33}$ ) directly depends on the first-order molecular hyperpolarizability, it will be of interest to further investigate the NLO materials formed by dendrons and dendrimers skeleton-constructed with NLO chromophores.

In this paper, the previously synthesized azobenzene skeleton-constructed first to fourth generation dendrons and first to second generation dendrimers were doped in a high glass transition temperature ( $T_g$ ) polycarbonate (PC). The UV–vis spectra were utilized to evaluate the differences in the aggregation behavior of azobenzene moieties for dendrons and dendrimers in PC. The  $d_{33}$  values were obtained

after a corona poling process. The effects of the molecular structure, loading density, and aggregation behavior of chromophores on the  $d_{33}$  value were explored. The thermal stability and relaxation behavior of the dendron films with the same loading density were also investigated.

## 2. Experimental section

### 2.1. Materials

The syntheses of azobenzene-constructed dendrons G1-COOH to G4-COOH and dendrimers G1, G2 have been described previously [18]. Polycarbonate (PC, K-1300  $T_g = \sim 170^\circ\text{C}$ ) was purchased from TEIJIN Ltd., Japan. All the solvents were purchased from Sinopharm Chemical Reagent Co., Ltd., and used as received. The differential scanning calorimetry (DSC) analysis was carried out with a SHIMADZU DSC-60 equipment. All the samples were heated at  $10^\circ\text{C}/\text{min}$  from 20 to  $170^\circ\text{C}$  under nitrogen for the first scan, then cooled to  $20^\circ\text{C}$  at  $10^\circ\text{C}/\text{min}$ , and immediately heated at  $10^\circ\text{C}/\text{min}$  from 20 to  $200^\circ\text{C}$  for the second scan. The UV–vis spectra were measured on a SHIMADZU UV-2401PC ultraviolet–visible spectrometer. The thermogravimetric analysis (TGA) was carried out on a SHIMADZU TG-50 instrument using the heating rate of  $10^\circ\text{C}/\text{min}$  under nitrogen. The film thickness was measured by an Alpha-step 500 Surface Profiler in the SHG intensity measurements.

### 2.2. Film preparation

For the UV–vis analysis and SHG measurements, the films were prepared by a spin-coating method. Firstly PC was dissolved in cyclopentanone (8 wt%), and a given amount of dendron or dendrimer was then added into the solution, and filtered through a syringe filter ( $0.44\ \mu\text{m}$ ) to remove the undissolved particulates. The indium–tin oxide (ITO)-coated glass was pre-cleaned using DMF, acetone, distilled water, and THF sequentially in ultrasonic bath. The obtained homogenous solution was spin coated onto the ITO-coated glass substrate at room temperature with the spinning rate of 800 rpm to give a film, which was dried in a vacuum oven at  $80^\circ\text{C}$  for 12 h to remove the residual solvent. For UV–vis analysis, the film was carefully split from the substrate and then tested to avoid the influence of absorption of the glass.

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