



Design and preparation of novel polyarylene ether materials based on Diels–Alder reaction as the crosslinker for electrooptical modulators



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ARTICLE INFO

Article history:

Received 28 March 2016

Received in revised form

6 April 2016

Accepted 7 April 2016

Available online 16 April 2016

Keywords:

Optical materials

Electro-optical modulators

Optical properties

Thermal properties

Glass transitions

ABSTRACT

Novel crosslinkable organic linear electro-optical (EO) material based on polyarylene ether as the main chain host polymer was designed and prepared. The host polymer with rigid aromatic has demonstrated a good compatibility with the guest chromophore. Long side chain with anthracene ensured the cross-linkable reaction and appropriate glass transition temperature of the host polymer (55 °C). The EO r_{33} tensor coefficient for this novel EO material has been magnitude of 66 pm/V at 1310 nm and the excellent long term stability at 85 °C. These parameters permit to consider their application in fabrication of organic electro optical devices. The semi-empirical and DFT quantum chemical simulations were performed for 4 principal chromophores to clarify a role of cross-linker in the enhancement of the ground state dipole moments and effective hyperpolarizabilities.

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1. Introduction

Integrated optical devices based on organic second-order nonlinear optical (NLO) chromophores have emerged as one of the enabling elements for a new generation of optical communications, which needs fast modulation and switching of optical signals at the speed of at least 100 Gbit/s to accommodate anticipated growth in data traffic [1,2].

Particular role with respect to second order susceptibility efficiency plays an interface between the chromophore and polymers [3,4].

The main requirement for such kind of effects is an existence of charge density acentricity [5] and high frequency of switching [6] together with decrease of operating voltages [7]. So the organic EO chromophore cause an enhanced interest over the past two decades [8] and favor explorations boom of materials with large electro-optics (EO) tensor coefficients for the near infrared

wavelengths (1 ... 1.5 μm) [9]. The search and design of novel materials for laser modulators, triggers and deflectors is developed both at molecular level by enhancement of second order hyperpolarizability (β) and as processed materials (r_{33}) [10–12].

Organic NLO chromophores possess many benefits with respect to other ones having a large EO activity, high working bandwidth, low prices, and easy integration with traditional semiconductor devices [13].

Though large number of organic NLO chromophores with large first order hyperpolarizability has been reported [14]. Many new approaches were developed to apply a strong inter-molecular electrostatic interaction among the chromophore molecules. Among them it is necessary to emphasize such as modification of the guest chromophores, side chain attachment of the host polymers, hyper-branched polymers, molecular self-assembly etc. [15–17]. However, the long-term thermal stability of this kind of materials remains still a principal restraining factor which significantly restrains a wide application of organic EO polymer-chromophore in different optoelectronics waveguides [18,19]. Some works about solving the long term stability of organic EO materials have been reported and polymer crosslinking system

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used in this paper is considered as the best method [20].

Polymer crosslinking process is a chemical process in which the basic NLO chromophore might be destroyed. So a crosslinking reaction with mild reaction condition and without by-product should be chosen. Diels–Alder reaction is an optimal choice for this reason. Some crosslinkable EO polymers have been just reported using Diels–Alder reaction as the crosslinker. However, most of host polymers have flexible main chains such as polymethylmethacrylate [21].

In the present work to get a host polymer with good compatibility with the guest NLO chromophores, polyarylene ether with rigid aromatic structure was prepared and anthracene was introduced to this polymer as a side chain Diels–Alder crosslinker. This novel EO polymer system is shown in Scheme 1. Rigid aromatic structure could ensure the phase matchable conditions between the host polymer and guest chromophore and also improve the loading density of the NLO chromophores and crosslinkers.

2. Results and discussion

2.1. Synthesis of polymer P2

Two methods are usually used to prepare polyaryl ether. 1) Friedel–Crafts reaction: sulfonyl chloride reacted with aromatic compounds by electrophilic substitution reactions; 2) the activation of di-halogen monomers reacted with aromatic bisphenol by nucleophilic substitution reaction. The second method was used in this paper, due to its simple operation. The basic principle of this reaction is that: 1) bisphenol monomer reacted with potassium carbonate forming negative oxygen ions; 2) the negative oxygen ions used as nucleophilic reagents reacted with aromatic ring by addition reaction forming Meisenheimer complex; 3) finally one of the substituent was eliminated and the nucleophilic substitution reaction was finished. In the whole reaction process, the formation of Meisenheimer complex intermediate requires higher energies, and this step was considered as the determining step.

The specific synthesis process of the preparation of polymer P2 is as the following: 1) 2, 6-Difluorobenzoic acid reacted with

thionyl chloride affording us 2,6-Difluorobenzoyl Chloride; 2) 2,6-Difluorobenzoyl Chloride reacted with 6-Chloro-1-hexanol affording us 6-chlorohexyl 2,6-Difluorobenzoate under the catalyst of potassium carbonate; 3) polymer P1 was prepared by the nucleophilic substitution reaction between bisphenol A and 6-chlorohexyl 2,6-Difluorobenzoate; 4) anthracene was introduced to polymer 1 by Williamson reaction affording us Polymer P2 (see Scheme 2).

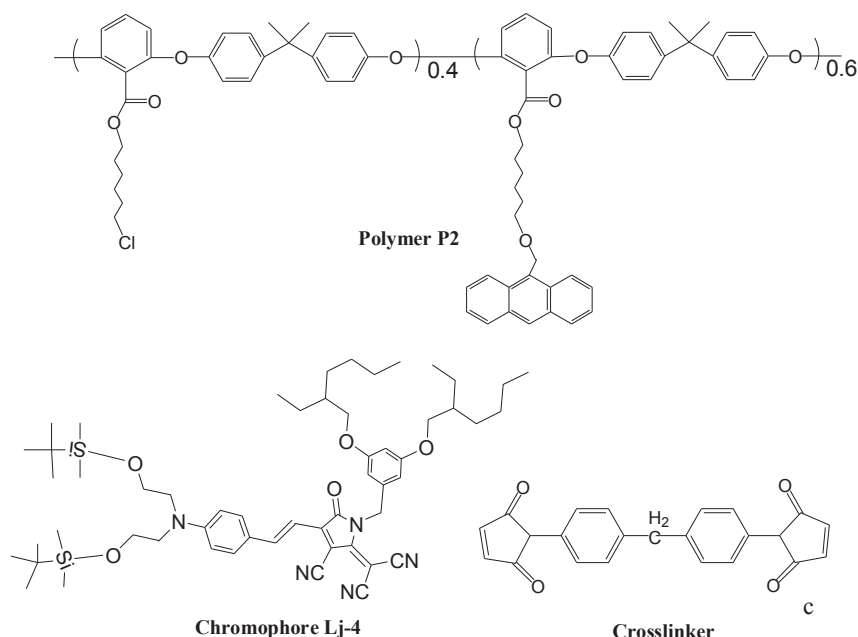
2.2. Structure characterization of polymer P2

The Fourier Transform Infrared (FT-IR) spectroscopy of polymer P1 and P2 is depicted in Fig. 1. The IR absorption peak of the C–Cl vibration at 796 cm^{-1} was very strong for polymer with spectral resolution 1 cm^{-1} . After the addition of anthracene, this absorption peak becomes very weak for polymer P2. However, a strong IR peak at 1105 cm^{-1} appears which confirms formation of C–O–C and existence of reaction between polymer P2 and the reaction between 9-anthracenemethanol and polymer P1. The content of anthracene in polymer P2 was additionally monitored both by $^1\text{H NMR}$ and UV–Vis spectra. In polymer 2, the chemical shifts were equal to 3.75 and 3.68 respectively for the H in Cl–CH₂ and O–CH₂ groups. From the ratio of HNMR integral at 3.75 and 3.86, we can establish a mole ratio of 6-hexyl chloride and anthracene which was equal to about 4: 6.

The molecular weight and molecular distribution were estimated by gel permeation chromatography (GPC) on the basis of PS standards. The result was shown in Table 2. The obtained polymer P2 possessed molecular weight in the range of 8950–26360, and molecular weight distributions near 1.58. The molecular weight was a little bit smaller than we expect. Some advanced methods would be used for improving the molecular weight in our following reported.

2.3. Crosslinking process for polymer P2

To determine the condition of preparation of EO films, the crosslinking process for the polymer P2 was studied in details. 0.4 g polymer P2 and 0.1 g 4,4'-dimaleimidophenylmethane were



Scheme 1. The molecular structure of polyaryl ether cross linked system.

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