European Polymer Journal 63 (2015) 207–216

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Testing of the ways for synthesis of new nonlinear optical epoxy-based polymers with azochromophores in the side chain

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ARTICLE INFO

Article history:
Received 21 July 2014
Received in revised form 14 October 2014
Accepted 2 December 2014
Available online 23 December 2014

Keywords:
Side-chain polymers
Second-order nonlinear optical properties
Azochromophore
Epoxy–amine oligomers

ABSTRACT

New polymer materials with quadratic nonlinear optical (NLO) response were synthesized on the basis of bisphenol A diglycidyl ether and *p*-aminobenzoic acid oligomers with azochromophores in side chains. The reactive polyether polyols were obtained either in solution, or in the bulk, the latter approach being found to be preferable as it provides obtaining oligomers with rather high molecular weight and high yield. The incorporation of chromophores into the oligomers side chain was carried out by etherification reaction using two synthetic approaches: in two steps, when an aniline-containing oligomer precursor is first obtained and then used in an azo-coupling reaction, giving the desired azochromophore-containing oligomer, or in one step via a direct attachment of a hydroxyl-containing azochromophore to the reactive oligomer. The advantage of the one-stage procedure is established, since the oligomer functionalization degree with chromophore groups reached 70 mol% in this case. The synthesized oligomers are characterized by high thermal stability and heat resistance; they demonstrate good film-forming ability. NLO coefficients, d_{33}, of corona-poled films of the materials based on linear oligomers and cross-linked polymers amount to ~22 and 35.2 pm/V, respectively. The cross-linked materials are shown to have moderate temporal stability of the second-order nonlinear optical characteristics.

1. Introduction

A predominant number of researches on polymer materials exhibiting the second-order nonlinear optical (NLO) activity dealt with guest–host systems or side-chain polymers where chromophore groups in side chains are covalently attached to the backbone ([1–6], and references therein). The benefits of the latter class of polymers are generally recognized due to a number of factors. The interest in these materials is caused by a possibility of obtaining the polymer systems with higher nonlinearity and better temporal and thermal stability of the NLO response as compared to guest–host composites with chromophore guest molecules dispersed in host polymer matrices. The determining advantage of side-chain polymers is that a high concentration of chromophore groups can be achieved without crystallization, phase separation or the formation of concentration gradients inside the polymer matrix. In addition, dye-polymer covalent attachment is

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http://dx.doi.org/10.1016/j.eurpolymj.2014.12.003
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shown to be highly efficient for minimizing near-IR losses [7].

Side-chain NLO polymers based on various classes of polymer matrices including those with low T_g (polystyrene, PMMA), relatively high T_g (polyurethanes), and high T_g (polyimides, etc.) have been synthesized and studied [1–3]. Polymers with high T_g are considered promising as they provide high orientational stability of chromophore groups achieved during thermo-poling of polymer films under an external electric field producing their non-centrosymmetric organization necessary to exhibit the second-order NLO activity. However, to provide chromophores orientation in such high T_g matrices, the poling procedure should be performed at high temperatures above or close to the matrix T_g value, that may cause chromophores destruction during poling. Furthermore, polymers with high T_g values sometimes possess a rather high polymer chain rigidity, leading to poor film-forming properties, brittleness, etc. Thus, the choice of a suitable polymer backbone is a complicated task. In a number of works, more specific matrices were used. For instance, in [5] the synthetic strategy was considered which is based on the post-functionalization of poly-(N-vinylcarbazole) to yield an NLO polymer with a high chromophore density (52 mol%), having rather high d_{33} = 20 pm/V and good relaxational stability. Taking into account the necessity of getting high quality films, polymers with very flexible polysiloxane and polyphosphazene backbones were studied in [5], the latter one being characterized by a d_{33} value equal to 32 pm/V.

Some typical examples of side-chain polymers having various backbones and different chromophores are summarized in [6]. One of the most popular classes of chromophores contains azobenzene moieties though they are characterized by rather moderate molecular nonlinearities. The reported synthetic strategies used for the chromophore binding to the polymer backbone involve either the polymerization of azobenzene-functionalized monomers, or a polymer reaction, also called post-functionalization, which allows pendent azo-groups to be attached. The first method is sometimes preferable since it is rather simple and makes it possible to introduce chromophore groups into each monomer unit. However, chromophore-containing monomers are often difficult to polymerize, they produce, as a rule, low-molecular weight polymers with poor film-forming properties. The second method has no these drawbacks but it involves polymer functionalization reactions proceeding often with limited yields [8].

Epoxy–amine matrices are intensively used for the synthesis of polymer materials with the second-order NLO response due to their easy processing and poling, as well as low optical losses observed for this class of polymers [1]. Usually, chromophore groups in such polymers are covalently attached to the main chain, so that donor end-group is embedded into the main polymer chain [9–14]. Such materials are characterized by rather high values of NLO coefficients, in particular, when chromophores with acceptor nitro- and tricyanovinylene groups were used, d_{33} values amounted to ~60 pm/V (λ = 1064 nm) [13,14] and ~66 pm/V (λ = 1542 nm) [10,11], respectively. The value of the NLO coefficient is known to depend essentially on the poling efficiency, which is defined by the local mobility of chromophore groups in polymer matrix. One may suggest that introducing chromophores into the side-chain through long tether groups will provide their increased mobility and higher nonlinearity as a result of more efficient poling. To test the validity of this suggestion here we present the synthesis and studies of NLO characteristics of epoxy oligomers on the basis of bisphenol A diglycidyl ether (DGEBA) and *p*-aminobenzoic acid, which were functionalized by chromophores with long tether groups. As far as we know, similar oligomers were not studied before.

2. Materials and methods

2.1. Materials

Solvents used in the work, THF, DMFA, hexane, cyclohexanone, were purified by standard techniques, *p*-aminobenzoic acid was recrystallized twice from water.

DGEBA was isolated by vacuum distillation on oil pump from epoxy resin ED-24 as colorless transparent solidifying mass, the first fraction being collected with boiling temperature, T_b, 218–220 °C/0.1 mm Hg. IR-spectrum, cm^{-1} (drop on NaCl): 2967, 2928, 2872 (CH_3, CH_2); 1608, 1582, 1510 (Ph); 1247 (epoxy and ether groups, broad band); 915, 831 (epoxy group).

^1H NMR (acetone-d_6); (δ, ppm/I, Hz): H1, d, 4H (7.17/8.80); H2, d, 4H (6.87/9.17); H3, dd, 2H (4.27/2.93; 11.37); H3, dd, 2H (3.87/6.23; 11.37); H4, m, 2H (3.29); H5, t, 2H (2.82/4.77); H6, dd, 2H (2.69/2.56; 5.14); H7, s, 6H (1.64).

The synthesis of 4-nitrobenzenediazonium tetrafluoroborate was carried out according to the technique described in [12]. DR1 and N-ethyl-N-hydroxyethylaniline (Acros), 4-dimethylaminopyridine (DMAP) (Panreac Sintesis) and 1,3-dicyclohexylcarbodiimide (DCC) (Aldrich) were used without additional purification.

2.2. Synthesis

2.2.1. Synthesis of polyether polyol on the basis of DGEBA and p-aminobenzoic acid (OAB)

1 g (2.9 mmol) DGEBA and 0.403 g (2.9 mmol) *p*-aminobenzoic acid were poured into an ampoule, thoroughly shaken at room temperature, and purged with argon for 15 min. The ampoule was sealed and placed into an oven. The reaction was carried out at 100 °C for a variable time period. Then, the obtained oligomer was purified by triple reprecipitation from THF to hexane. The isolated oligomer was dried in vacuum oven till constant weight. The oligomer yield was 67–96%, depending on the reaction conditions.

2.2.2. One-stage functionalization of OAB with DR1 chromophore

The oligomer functionalization was carried out in a flat-bottom flask at room temperature for 22 h. 1 g (2.1 mmole) OAB was dissolved in 60 ml THF. Then, 0.12 g (0.99 mmole) DMAP, 0.56 g (2.72 mmole) DCC, and 0.72 g (2.31 mmole) DR1 were added in this sequence to the oligomer solution