



Development of new nonlinear optical polymers based on epoxy-amine oligomers with Bi-chromophore fragments in the side chain

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ABSTRACT

For the first time bichromophore nonlinear optically active compounds, 3,5-bis [2- (N-ethyl-4- (4'-nitrophenylazo) anilino) ethoxy] benzyl alcohol, **DF1**, and 3,5-bis [6- (N-methyl-4- (4'-nitrophenylazo) anilino) hexaoxy] benzyl alcohol, **DF2**, have been synthesized. The synthesis of the epoxy-amine oligomers containing **DF1** and **DF2** dendritic fragments in the side chain was preceded by molecular design which demonstrated that the hexyl groups, binding the chromophores to the branching center in **DF2**, are able to provide greater mobility of the chromophores compared to the ethyl groups in **DF1**, thus determining the preference of the former from the viewpoint of NLO activity.

Bi-chromophore compounds were introduced into the side chain of epoxy amine oligomers using the esterification reaction under mild conditions by the Steglich method. As a result, oligomers **OAB-DF1** ($T_g = 122^\circ\text{C}$) and **OAB-DF2** ($T_g = 107^\circ\text{C}$) were obtained with good yields, the degree of functionalization was 60 mol% and 45 mol%, respectively. The values of the NLO coefficients, d_{33} , were measured by second harmonic generation technique; they are equal to 29 pm/V for **OAB-DF1** and 40 pm/V for **OAB-DF2**.

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1. Introduction

In recent decades, there is intense interest of researchers in organic polymeric materials exhibiting nonlinear optical (NLO) response to the applied electric field. Primarily, this is due to the possibility of using these materials in telecommunications, digital signal processing, THz generators and photonic devices [1–6]. The quadratic NLO response of polymer materials originates at the molecular level due to organic chromophores introduced into the polymer matrix either as guest molecules or as fragments covalently attached to the bearing chain [2–6]. For the manifestation of a quadratic NLO activity, the chromophores should be non-centrosymmetrically organized in the polymer material what is achieved by their orientation in the applied static electric field [3,6]. The optimal value of NLO response and its relaxation stability are the key characteristics that must be ensured when developing such materials [3,7]. Polymer quadratic susceptibility determining the NLO characteristics depends on the chromophores concentration in a matrix; when some threshold value of chromophores content is

exceeded, detrimental dipole-dipole interactions (DDI) may cause the chromophores partial aggregation, resulting in the decrease of the quadratic NLO response [2,8].

Over the past decade, new approaches have been developed to avoid this undesirable effect and to ensure the optimal macroscopic chromophores order in the polymer matrix. In particular, researchers focus on the following approaches: the use of linear polymers with bichromophore fragments in the side chain [9], the use of branched polymers containing NLO chromophores as peripheral groups [10–13] and of dendronized polymers [6,14–20], or the combination of the latter two strategies consisting in the introduction via covalent coupling of dendritic NLO fragments into the hyperbranched polymers [21]. The structure of such materials provides spatial separation of chromophores, limiting their undesirable DDI. The second approach involves the use of dendrimers with a spherical form or dendronized linear polymers having in the side chain chromophore-containing dendrons of different generations and structure; most of the works are devoted to the synthesis of either multichromophore dendrimers [22–25] or dendritic chromophores with isolating groups [26–28]. The synthesis and electrooptic (EO) properties of dendronized polymers based on polyimide with multichromophore dendrons of the second generation are presented in Refs. [29,30]; at the chromophores content

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58 wt% the EO coefficient $r_{33} = 32$ pm/V is measured. Along with multichromophore dendronized polymers, polymers containing modified dendrons carrying one chromophore and several isolating groups located in the branches of the dendron have been developed [10–13,31–33]; pentafluorophenyl, adamantyl, carbazole bulk groups, as well as various branched alkyl fragments have been used as isolating groups [15,31]. However, despite the positive effect resulting in the decrease of detrimental DDI, the introduction of isolating groups may lead to an undesirable reduction in the NLO activity of the material, if it results in the decrease in the concentration of chromophores; besides, it may cause the complication of the poling process because of the large volume of the dendritic chromophore-containing groups [31].

The new approach aimed at the development of NLO materials exploits linear block copolymers with dendritic chromophore-containing fragments; in such copolymers linear polymer blocks are responsible for solubility and good film-forming properties, and the dendritic block - for the manifestation of the NLO effect [34]. In Refs. [35,36] the study of linear-diblock copolymer [poly(styrene-*b*-4-vinylpyridine)] and linear-dendritic (poly(methyl methacrylate)-dendron) block copolymer with chromophores coupled via hydrogen bonding was described.

For the development of NLO materials epoxy-amine oligomers and polymers are widely used due to the easy synthesis, relatively high glass transition temperature (about 130 °C), good film-forming properties, and processability of the resulting materials. The synthesis of epoxy amine oligomers is based on the poly-addition reaction between the epoxy and amino groups, diglycidyl esters of various structures and aniline being most often used as monomers. After further modification of the polymer, for example, azo-coupling reaction with various diazotizing agents, one obtains NLO polymers with aniline as a donor moiety of the chromophore, that is chromophores donor group becomes the part of the polymer backbone [37–42]. Such polymers exhibited rather high values of the NLO coefficient: up to 60 pm/V when a chromophore with nitro group is used [42] and up to 66 pm/V in the case of a chromophore with a tricyanovinylene acceptor group [37]. As already noted, the value of the NLO coefficient depends on many factors, in particular, on the effectiveness of poling, which, in its turn, is determined by the local mobility of the chromophore groups in the polymer matrix. The introduction of chromophores into the main chain of the polymer matrix somewhat limits the mobility of NLO-active units. This has led to the assumption that the introduction of chromophores into the side chain of the polymer through the spacer groups will increase the mobility of chromophores, which, in turn, will allow to perform more effective poling. The introduction of NLO-active fragments into the side chain of the oligomer requires the presence of reactive groups. Earlier on the basis of diglycidyl ether of bisphenol A (DGEBA) and *p*-aminobenzoic acid (*p*-ABA), we synthesized a new reactive polyether polyol **OAB** [43,44], into which using polymer-analogous reactions various NLO-units were incorporated. The bi-chromophore fragments of various structures were shown to be effective in the search for new NLO-active moieties with improved physical-chemical properties [45,46]. Here we use epoxy-amine oligomers with bichromophore moiety in the side chain for the development of polymer NLO material.

2. Materials and methods

2.1. Materials

Solvents used in the work, THF, DMF, hexane, cyclohexanone, acetone, chloroform, methylene chloride, ethyl acetate, butanol, were purified by standard procedures. *p*-Aminobenzoic acid was recrystallized twice from water, $T_m = 191$ °C.

N-methylaniline was purified by distillation on a water jet pump from a flask equipped with a needle reflux condenser, selecting the fraction with $T_b = 76$ °C/10 mm. Hg; $n_D^{25} = 1.5710$.

4,4'-Methylenediisocyanate (MDI) was purified by recrystallization from hexane according to the technique [47].

1,3-Dicyclohexylcarbodiimide (DCC) was purified by fractional distillation under reduced pressure on the oil pump, selecting the fraction with $T_b = 95$ –100 °C/0.1 mm. Hg.

Bisphenol A diglycidyl ether (DGEBA) from ACROS Organics with 99% substance content, 4-Dimethylaminopyridine from ACROS Organics with 99% substance content, *N*-ethyl-, *N*-hydroxyethyl-aniline from ACROS Organics with a substance content of 96%, 6-chlorohexane-1-ol from ACROS Organics with a substance content 95%, 1,3-dichloropropane-2-ol from ACROS Organics with a substance content of 99%, were used without preliminary purification. 4-Nitrobenzenediazonium tetrafluoroborate was synthesized according to the procedure described in Ref. [48].

2.2. Synthesis of bi-chromophore compounds

2.2.1. Synthesis of 3,5-bis[2-(*N*-ethyl-4-(4'-nitrophenylazo)anilino)ethoxy]benzyl alcohol (DF1)

For the synthesis of dendritic compound **DF1** the procedure was elaborated with the account of those described in Refs. [43,49,50].

2.2.1.1. *N*-ethyl-*N*-(2-chloroethyl)aniline. The procedure described in Ref. [49] was used to prepare *N*-ethyl-*N*-(2-chloroethyl)aniline. A solution of POCl₃ (3.30 g, 0.021 mol) in 10 mL of THF was added dropwise to a solution of *N*-ethyl-*N*-(2-hydroxyethyl)aniline (5.00 g, 0.03 mol) in THF under intensive stirring at room temperature for one hour. The reaction mixture was stirred for 4 h. The solvent was evaporated, the residue was diluted with an aqueous solution of NaHCO₃, the product was extracted with CH₂Cl₂ (20 mL). The extract was dried over MgSO₄, filtered, and the solvent was distilled off in a vacuum of a water jet pump. The product was purified by vacuum distillation, selecting the fraction with $T_b = 65$ –73 °C/0.4 mm Hg. Yield: 3.5 g (60%), a liquid of a yellow color was obtained.

¹H NMR (400 MHz, acetone d₆; δ , ppm; J, Hz): 1.14 (t, 3H, -CH₃, J = 7.1), 3.45 (q, 2H, N-CH₂-CH₃, J = 7.1), 3.66 (s, 4H, -N-CH₂CH₂-Cl), 6.63 (t, 1H, *p*-Ar-H(-N), J = 8.9), 6.72 (d, 2H, *o*-Ar-H(-N), J = 8.9), 7.17 (t, 2H, *m*-Ar-H(-N), J = 8.9).

2.2.1.2. Synthesis of 3,5-bis[2-(*N*-ethyl-anilino)ethoxy]benzyl alcohol. A mixture of *N*-ethyl-*N*-(2-chloroethyl)aniline (4.04 g, 0.022 mol), 3,5-dihydroxybenzyl alcohol (1.40 g, 0.010 mol), anhydrous potassium carbonate (10 g), potassium iodide (0.5 g) and 30 mL of acetone was heated at 56 °C under an argon atmosphere with intense stirring for 48 h. The reaction mixture was poured into 500 mL of water, the product was extracted with CH₂Cl₂ (20 mL). The extract was concentrated to 5 mL and precipitated with petroleum ether. The precipitate was filtered off and dried at 70 °C in a vacuum oven for 48 h and purified by recrystallization. Yield 1.3 g (30%), transparent crystals were obtained, $T_m = 110$ °C (toluene). ¹H NMR (400 MHz, acetone d₆; δ , ppm; J, Hz): 1.21 (t, 6H, -CH₃, J = 7.0), 3.48 (m, 4H, N-CH₂-CH₃), 3.71 (t, 4H, N-CH₂CH₂-O, J = 7.1), 4.11 (t, 4H, N-CH₂CH₂-O, J = 5.9), 4.59 (s, 2H, Ar-CH₂-OH), 6.32 (s, 1H, *l*-Ar-H(CH₂OH)), 6.47 (s, 2H, *o*-Ar-H(CH₂OH)), 6.78 (t, 2H, *l*-Ar-H(N), J = 7.3), 6.94 (d, 4H, *o*-Ar-H(N), J = 7.9), 7.28 (t, 4H, *m*-Ar-H(N), J = 7.3).

2.2.1.3. Synthesis of DF1. Into the solution of 3,5-bis[2-(*N*-ethyl-anilino)ethoxy]benzyl alcohol (0.11 g, 0.253 mmol) in 3 mL of DMF the estimated quantity of 4-nitrobenzenediazonium tetrafluoroborate (0.13 g, 0.558 mmol) was introduced under stirring. After 10 and 30 min in two portions sodium acetate (0.04 g,

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