

## New epoxy-amine oligomers with chromophore-containing dendritic fragments in the side chain and determination of their nonlinear-optical characteristics

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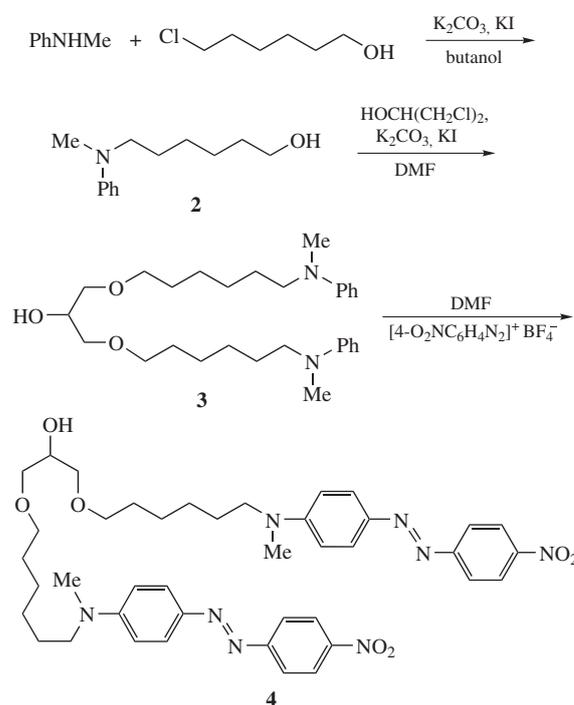
New epoxy-amine oligomers with azochromophore-containing dendritic fragments in the side-chain are synthesized and characterized; nonlinear-optical coefficients of the obtained oligomers are equal to 20 pm V<sup>-1</sup>.

Design of polymer materials exhibiting quadratic nonlinear-optical (NLO) response to the applied intense electric field is based on the incorporation of special organic chromophores into the polymer matrix.<sup>1,2</sup> Recently the research has been focused on molecular systems with higher content of chromophores in polymer matrix, and at the same time with minimized detrimental intermolecular interactions between them.<sup>2–4</sup> One type of such systems is based on the use of chromophore-containing dendritic fragments covalently attached to the bearing chain. The structure of such fragments provides spatial isolation of chromophores with reduced dipole–dipole interaction.<sup>2,3</sup> Since materials with quadratic NLO activity should be non-centrosymmetric, the chromophores are oriented along the direction of the electrostatic field applied to the material heated to the temperature close to the glass transition one.<sup>1</sup> Epoxy-amine matrices are widely used for the development of polymer materials with quadratic NLO activity due to the easiness of their processing and poling as well as to low optical loss of this class of polymers. Conventionally chromophore groups are incorporated into the polymer in such a way that their electron-donor groups constitute parts of the bearing chain.<sup>1</sup>

Here we present the synthesis of new epoxy-amine oligomers (OAB-AzoDF) **1** on the basis of Bisphenol A diglycidyl ether (DGEBA) and *p*-aminobenzoic acid with azochromophore-containing dendritic fragments in the side chains, and study of their quadratic NLO characteristics. In their structure, 4-amino-4'-nitro-

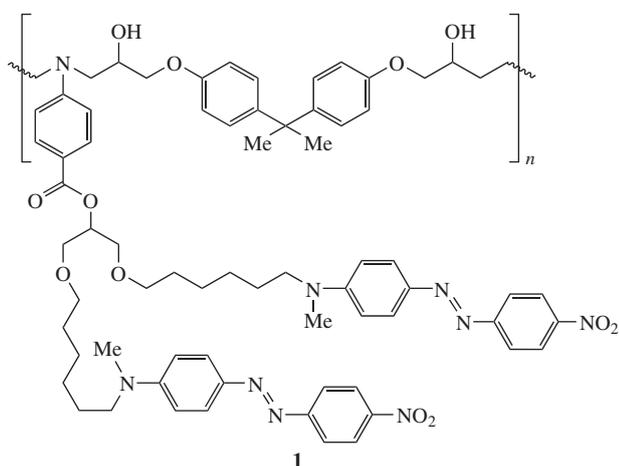
azobenzene chromophores are the NLO-active units, 1,3-dioxypropyl group is a branching center with which azochromophores are coupled through hexamethylene tether groups.

Synthesis of the required intermediates is outlined in Scheme 1. 6-(*N*-Methyl-*N*-phenylamino)hexan-1-ol **2** was obtained as described.<sup>5</sup> Further preparation of compound **3** is given in ref. 6. The dendritic fragment **4** was prepared using diazotization method.<sup>†</sup>

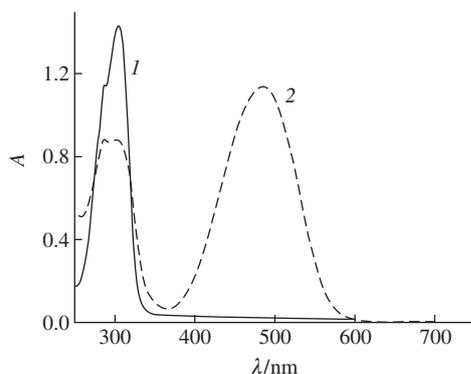


Scheme 1

<sup>†</sup> Compound **4**. 4-Nitrobenzenediazonium tetrafluoroborate (0.61 g, 2.556 mmol) was introduced with stirring into the solution of **3** (1.00 g, 2.13 mmol) in 60 ml of DMF. Sodium acetate (0.35 g, 4.26 mmol) was added to the reaction mixture in two portions: in 10 and 30 min after addition of diazonium salt. The reaction was performed at room temperature for 3 h. The obtained product was isolated by precipitation from water. The precipitate was filtered off, washed with water and purified by hexane precipitation from THF solution. The product yield was 69%. <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>) δ: 1.44 (m, 8H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.68



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**Figure 1** UV-VIS spectra of (1) OAB and (2) functionalized OAB-AzoDF oligomers in THF.

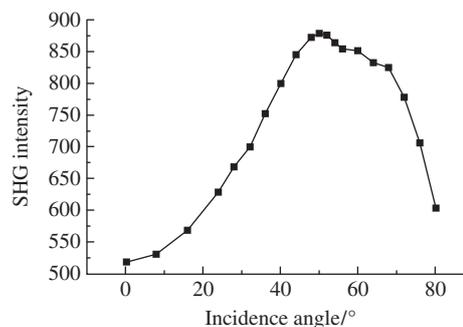
OAB oligomers were synthesized by the reported procedure.<sup>7</sup> The oligomers are cream-coloured powder products highly soluble in polar organic solvents. The incorporation of chromophores into the oligomers side chains was performed by esterification of oligomer carboxyl group by hydroxyl-containing AzoDF.<sup>‡</sup>

The structure of OAB-AzoDF was confirmed by physicochemical analysis. UV-VIS spectra of initial OAB and functionalized OAB-AzoDF oligomers (Figure 1) demonstrate the appearance of the band with  $\lambda_{\max} = 481$  nm in the visible range, which is characteristic of azochromophore fragment. According to elemental analysis (nitrogen content) and <sup>1</sup>H NMR data the degree of oligomers functionalization is 58 mol%. The introduction of AzoDF fragment results in the essential enhancement of oligomer thermal stability and thermal endurance: glass transition temperature,  $T_g$ , increases for 30 °C and becomes equal to 129 °C, while  $T_{10\%}$  grows twice from 120 °C for OAB up to 260 °C for OAB-AzoDF. Chromophores content in OAB-AzoDF is 34.3 wt%.

Polymer films were spin-cast from 7% solution of polymer in cyclohexanone according to the elaborated technique;<sup>8,9</sup> films were characterized by AFM technique: thickness was 300 nm, roughness was 3.5 nm. Films were poled at the corona-triode setup in the corona discharge field, voltage 6.5 kV, poling time ~20 min, and the distance from the tungsten needle electrode to the surface of the film being 1 cm; the field was applied to the films heated to temperatures close to  $T_g$ . The quality of orientation was controlled by the absorption change in UV-VIS spectra detected before and after poling,<sup>10</sup> and characterized by the order parameter,  $\eta$ ; for the studied films  $\eta = 0.33$ .

(m, 8H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$ ), 2.91 (s, 6H, Me), 3.17 (t, 4H,  $\text{NCH}_2$ ), 3.37 (t, 4H,  $\text{CH}_2\text{O}$ ), 3.55 [d, 4H,  $\text{CH}_2\text{CH}(\text{OH})\text{CH}_2$ ], 3.84 [s, 1H,  $\text{CH}(\text{OH})$ ], 6.91 (d, 4H,  $\text{H}_{\text{Ar}}$  ortho to NMe), 7.93 (d, 4H,  $\text{H}_{\text{Ar}}$  ortho to N=N), 8.30 (d, 4H,  $\text{H}_{\text{Ar}}$  meta to N=N), 8.39 (d, 4H,  $\text{H}_{\text{Ar}}$  meta to NMe).

<sup>‡</sup> DMAP (0.055 g, 0.45 mmol), DCC (0.16 g, 0.77 mmol) and compound **4** (AzoDF, 0.5 g, 0.65 mmol) were added with stirring to the solution of OAB (0.28 g, 0.59 mmol) in 30 ml of THF. The esterification was carried out at room temperature for 170 h. The formed dicyclohexylurea was filtered off, and the oligomer product was precipitated into hexane. The obtained oligomer was purified by twice-repeated THF dissolution–hexane precipitation, and was dried *in vacuo* till constant weight. The oligomer yield was 59%.



**Figure 2** The dependence of SHG signal intensity on the angle of the laser radiation falling on the poled OAB-AzoDF film.

Polymer NLO coefficients,  $d_{33}$ , were measured by the second harmonic generation (SHG) technique; pulse  $\text{Nd}^{3+}$ :YAG laser radiation [ $\lambda = 1064$  nm, pulse duration 15 ns, power density at the sample  $10 \text{ kW cm}^{-2}$ ;  $\alpha$ -quartz ( $x$ -cut) plate used as a standard] was employed. The observed dependence of SHG signal intensity on the angle of the laser radiation falling on the film (Figure 2) is typical of poled polymer films with chromophores oriented perpendicular to the film plane; the angle at which the SHG intensity is maximal is  $\sim 57^\circ$ . The determined value of  $d_{33}$  was  $20 \text{ pm V}^{-1}$ , this result being quite satisfactory. However, more thorough selection of parameters defining the poling regime, as well as the determination of optimal content of azochromophore-containing dendritic fragments would allow one to enhance the  $d_{33}$  values for this type of oligomers.

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