



Relaxation behavior and nonlinear properties of thermally stable polymers based on glycidyl derivatives of quercetin



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ABSTRACT

Cross-linked polymers on the basis of di-, tri and tetraglycidyl ethers of quercetin (3,3',4',5,7-pentahydroxyflavone) were synthesized, and then, poled in electrical field of corona discharge. Investigations of structural, thermal and optical parameters of the polymer films were carried out. It was found that the polymers obtained from di- and triglycidyl quercetin ethers had high values of macroscopic quadratic susceptibilities and substantial stability of nonlinear optical (NLO) properties after the poling. Tetraglycidyl ether of quercetin forms the polymer of lower quadratic susceptibility, which demonstrates noticeable relaxation process resulting in decrease of the NLO effect.

It is supposed that the difference of the NLO properties is due to peculiarities of physical network of the polymers, namely to the ratio between numbers of hydrogen bonds formed by hydroxyl groups of chromophore fragments and by the ones of interfragmental parts of the polymeric chains.

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1. Introduction

In recent years, photonics is one of the most developed fields of science and technology. A very important photonics area is design and use of the new functional optically transparent polymeric materials with nonlinear optical (NLO) properties, also having good thermal and long-term structural stability [1,2]. Such NLO materials can be obtained by electrical poling of cross-linked polymers [3].

There are several ways to obtain polymeric NLO materials such as doping of the polymeric matrices by organic chromophore molecules or design of the polymers containing chromophore fragment in the main or side chains. The last way requires synthesis of the corresponding chromophore-containing monomers [4–7].

Disadvantage of the doped cross-linked polymers is that they can contain limited amount of the chromophore dopant. At high concentrations, highly polar dopant molecules are in intense dipole-dipole interactions [8,9], that can hinders their optimal packing (alignment) and results in decrease of the NLO activity.

Since the chromophore molecules incorporated in the polymer matrix are not covalently bonded with the latter, they maintain a high mobility and quickly reorient after electrical poling. This leads

to decrease of macroscopic NLO activity of the polymer materials [10].

In the polymers with covalently bonded chromophore fragments, the NLO properties substantially depend on location of these fragments [11]. The polymers with chromophore fragments in side chains are more inclined to form unidirectional orientation of the chromophore dipoles during the poling procedure. In other hand, the polymers with chromophore fragments built into main chains keep for a long time ordered orientation of the chromophore fragments that increases temporal stability of the NLO properties [12]. However, relaxation is unavoidable in the both cases.

Recently, we have obtained monomers functionalized by glycidylation of 3,5,7,3',4'-pentahydroxyflavone (quercetin). Recently, we have obtained monomers functionalized by glycidylation of 3,5,7,3',4'-pentahydroxyflavone (quercetin). Quercetin and its derivatives are asymmetric molecules including electron-withdrawing bicyclic chromone fragment, whose electron acceptor properties increase substantially upon the molecule excitation. A side dihydroxyphenyl ring is electron-donating fragment in all the electronic states. Such a structure causes a high dipole moment of quercetin in the ground and excited states. Thus, quercetin molecule and its substituents, containing acentric and polar chromophore, could be described by third rank tensors and, therefore, used for design of the NLO polymers [13]. Structures of

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the quercetin glycidyl ethers used for following synthesis of the cross-linked polymers are depicted in Fig. 1.

The obtained quercetin-containing cross-linked polymers have chromophore fragment built into the main chains. These polymers have high thermal stability and, after the poling, they demonstrate optical anisotropy and the NLO properties.

In this paper we report our investigations of the NLO relaxation behavior of the polymers based on glycidyl derivatives of quercetin.

2. Experimental

2.1. Materials

Di-, tri- and tetraglycidyl ethers of quercetin (2GEQ, 3GEQ, 4GEQ) used as monomers were synthesized by method reported previously in Ref. [13] according to a scheme showed in Fig. 1. Commercial diethylenetriamine (DETA) (Dow Chemical) was used as a hardener. Acetone used as solvent for formation of thin films was previously dried and distilled.

2.2. Polymer films preparation

Glycidyl ethers of quercetin (GEQ) were dissolved in acetone with concentration of 0.1 g/mL. DETA was added to achieve a stoichiometric ratio DETA:GEQ close to 10:1 w/w. Glass microscope coverslips (used as a substrate for the polymer films) with thickness of 170 μm were cleaned by sonication in detergent solution for about 10 min. After that they were rinsed in deionized water and then, in boiling ethanol, and finally dried at 90 $^{\circ}\text{C}$ for 10 min. Thereafter, thin films were spin-coated onto the pre-cleaned coverslips at 1000 rpm for 0.5 min and cured at the room temperature for 24 h in vacuum. To remove residual solvent, the polymer films were then annealed for 3 h at 100 $^{\circ}\text{C}$. Presence of the residual solvent traces in the polymer films was monitored using FTIR-ATR spectroscopy. Quantification of the residual solvent was based on the values of optical density at 1720 cm^{-1} – in the absorption band maximum of acetone carbonyl group stretching. The thickness of the obtained polymer films was 1.0 μm .

2.3. Polymer films poling

The polymer films were poled by the corona poling technique at

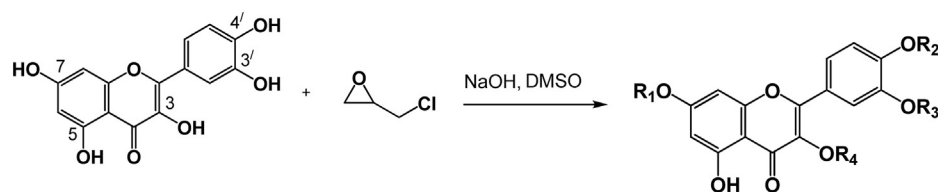
elevated temperature simultaneously with curing reaction. A thin tungsten needle placed 10 mm above the polymer films and oriented perpendicularly to their surface was used as positive corona electrode. The corona current was 2.5 μA with an electrode potential of 6 kV.

Electrical field of the corona discharge was imposed for 1 h to the films preheated to 200 $^{\circ}\text{C}$. Then, in the presence of the corona discharge the films were cooled to the room temperature.

2.4. Characterization

UV–visible spectra of the polymer films were recorded by UV–VIS Spectrophotometer Hitachi-U3210 in the range of 210–500 nm. Mathematical treatment of the spectra was performed using Spectra Data Lab software package [14]. FTIR-ATR (attenuated total reflection) spectra were registered on ALPHA FT-IR Spectrometer with a diamond crystal in the range of 400–4000 cm^{-1} with resolution of 4 cm^{-1} and averaging 32 scans of the spectra. Decomposition temperature (T_d) and glass-transition temperature (T_g) of the polymers were obtained by thermal analysis. The heating thermogravimetric (TG) curves were obtained using Netzsch STA 409 PC Luxx thermal analyzer with samples weights of 20–25 mg over the temperature range from 20 to 900 $^{\circ}\text{C}$ and with heating rate equal to 20 $^{\circ}\text{C}/\text{min}$. The measurements were carried out in synthetic air atmosphere (flow rate – 80 mL/min) using a corundum crucible. Differential scanning calorimetry (DSC) analysis was carried out by Q 2000 thermal analyzer with samples weights of 9–6 mg over the temperature range from 0 to 180 $^{\circ}\text{C}$ and with the heating rate of 10 $^{\circ}\text{C}/\text{min}$. Densities of the polymer films were determined using pycnometer method in accordance with DIN EN 725–7. The thickness of the films was measured with an interferometer of the Linnik type. The refractive indices determined according to [15] were used for the further calculations of macroscopic quadratic susceptibilities.

Cross-linking degree was investigated using conventional gel content determination by means of acetone extraction of the cured films using Soxhlet apparatus at 56.2 $^{\circ}\text{C}$ for 24 h. The process was performed according to ASTM D 2765. Then, the specimens were dried at 80 $^{\circ}\text{C}$ for 3 h approximately until their weight stayed constant. The gel content (a) was calculated as the ratio of the final weight to the initial weight, as described in Eq.:



where

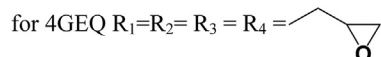
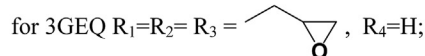
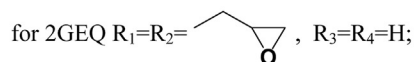


Fig. 1. Scheme of synthesis of quercetin glycidyl ethers.

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