

## FTIR investigation of molecular mobility in glassy epoxy-amine oligomers with azo-chromophores

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**Abstract.** Molecular mobility in glassy epoxy-amine oligomer with covalently attached 4-amino-4'-nitroazobenzene NLO chromophore fragments has been studied by conformational probes method. The conformational transitions in the probes (1,2-dichloroethane and chlorocyclohexane) embedded in the oligomer have been studied in the temperature range from -160°C to +20°C. The freezing of conformational transitions has been observed by FTIR at temperature near  $T_f = -90^\circ\text{C}$ . This value is correlated with the secondary relaxation transition temperature in the oligomer. The comparison of the activation volumes of the mobile groups in the probes with volumes of mobile groups in the oligomer allows us to conclude that there is the freezing of benzene rings mobility near  $\beta$ -process temperature.

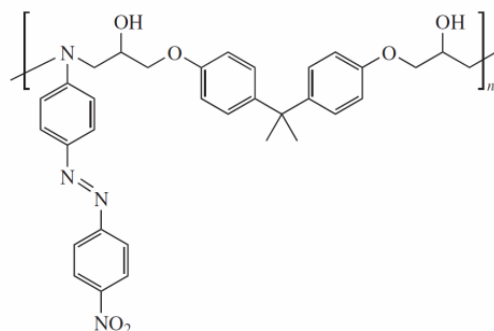
### 1. Introduction

In the recent decades the interest to organic polymer materials with high quadratic nonlinear-optical (NLO) coefficients raised significantly. This is due to the possibility of their application in photonics and optoelectronics [1]. Molecular sources of NLO response are organic chromophores. Such molecules possess large dipole moments in the ground state. Non-centrosymmetric arrangement of dipole chromophores is formed in an electric field. The second harmonic generation (SHG) is observed in the medium. There are a lot of references concentrated on the investigation of the SHG in polymer matrix with NLO chromophores [1-4]. The great attention is given to the increasing of the relaxation stability of NLO response.

Epoxy polymer matrices based on bisphenol-A diglycidyl ether with aniline fragments in the main chain are promising materials. Organic chromophores are embedded as guest-molecules or covalently attached to the main or side chain of the polymer. The relaxation stability of the NLO response is an important issue related to the mobility of the polymer chain fragments.

In the present work  $\beta$ -process in epoxy-amine oligomer with covalently attached 4-amino-4'-nitroazobenzene NLO chromophore fragments with donor groups introduced into the main chain (CFAO) is studied (figure 1).





**Figure 1.** The structure of the monomer unit of CFAO.

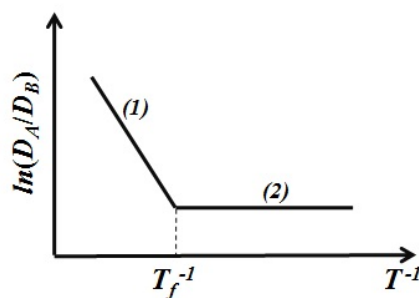
## 2. The method of conformational probes

The molecular mobility of low- and high-molecular-weight glass forming liquids has been extensively studied by different physical methods, including those based on molecular probes. In particular, it was proposed to use compounds with conformational flexibility as probes in glassy solids [5]. The approach is based on embedding a small amount of the probe into the studied glass forming liquid (hereafter “matrix”) and following the temperature dependences of its conformationally sensitive bands in FTIR spectra. If at a certain condition the probe molecules can transform from one conformation (*A*) to another (*B*) within the observation time, *i.e.*, the conformers are in equilibrium, then the integrated intensities of the IR bands of the conformers,  $D_A$  and  $D_B$ , follow the relation [6]:

$$\ln \frac{D_A}{D_B} = \frac{\alpha_A}{\alpha_B} + \frac{\Delta S_0}{R} - \frac{\Delta H_0}{RT} \quad (1)$$

where  $\Delta S_0$  and  $\Delta H_0$  are the entropy and enthalpy differences of the conformers, respectively,  $\alpha_A$  and  $\alpha_B$  are the absorption coefficients of the conformer's bands under study,  $T$  is the temperature and  $R$  is the gas constant. The dependence  $\ln(D_A/D_B)$  upon  $1/T$  is shown in figure 2, branch 1.

The conformational transitions in the probe molecules are possible only if the molecules of the surrounding matrix (or their fragments) exhibit sufficient mobility and if such mobility leads to creation of free volume entities large enough for the probe molecules to transform. Lowering the temperature may cause freezing-in of the molecular mobility of the matrix and this in turn may freeze-in the conformational transitions in the probe. Then below a certain temperature  $T_f$  the plot of the  $\ln(D_A/D_B)$  upon  $1/T$  should be a straight line parallel to the horizontal axis (figure 2, branch 2). Then, knowing the “activation volume” (*i.e.*, the minimum volume required for conformational transitions to occur), one can estimate the size of the mobile units of the matrix which also froze-in at  $T_f$ .



**Figure 2.** The dependence of  $\ln(D_A/D_B)$  upon  $T^{-1}$ .

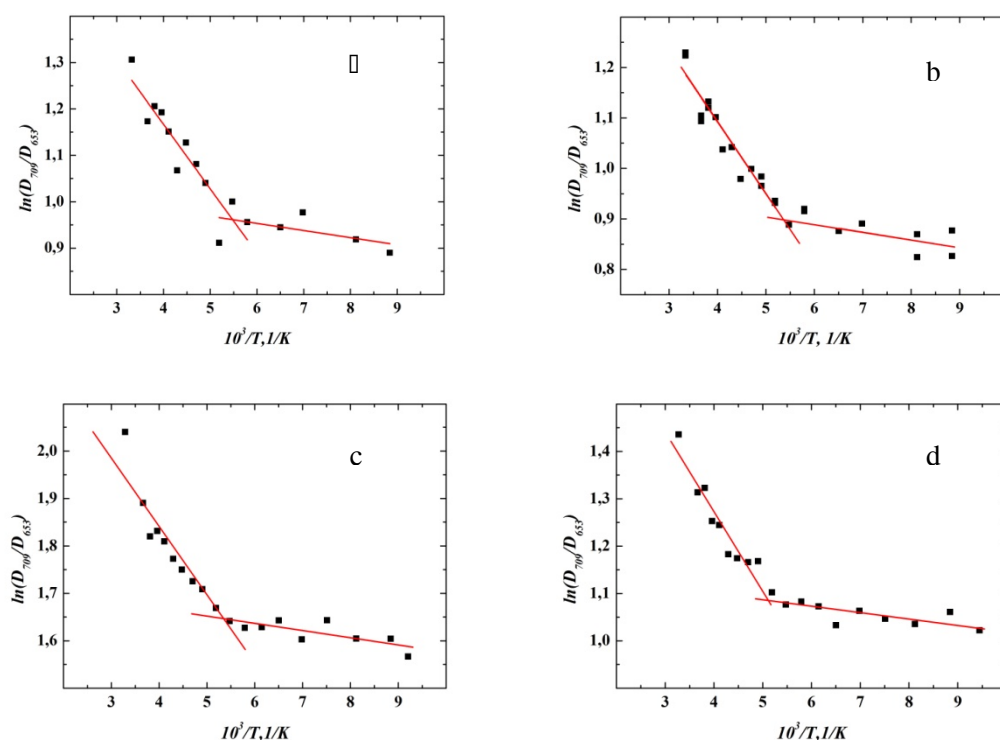
### 3. Experimental part

The synthesis of **CFAO** is described in [7].

1,2-dichloroethane (**DCE**) and chlorocyclohexane (**CCH**) (products of Sigma–Aldrich) were used as the probes to study the conformational mobility of the oligomer. The polymer films were created from the **CFAO** solution in cyclohexanone. The films were kept in the atmosphere of the **DCE** vapour during few hours. Then the samples were kept in the air during 24 hours. The thickness of the films with **DCE** was about 30 – 90  $\mu\text{m}$ . The concentration of **DCE**,  $[C]$ , was estimated to be in the range 1 – 3 vol%. To introduce **CCH** into **CFAO**, mixture of **CFAO** with probe was dissolved in tetrahydrofuran. The liquid solution was spread on KBr plates and kept at room temperature during 24 hours in order to remove the solvent. The concentration of **CCH** in **CFAO** was about 6 vol%, film thickness ca. 150  $\mu\text{m}$ .

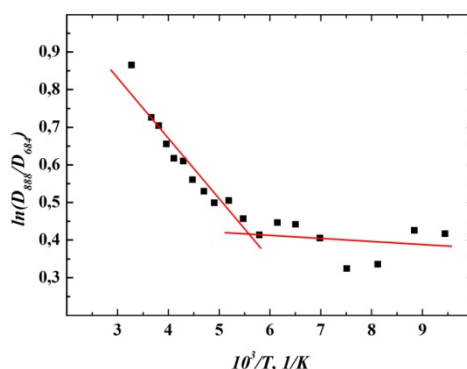
The absorption bands at 709  $\text{cm}^{-1}$  Q(CCl) (*t*-conformation), 653  $\text{cm}^{-1}$  Q(CCl) (*g*-conformation) [8] of **DCE** and 684  $\text{cm}^{-1}$  Q(CCl) (*a*-conformation), 888  $\text{cm}^{-1}$  Q(CC) (*e*-conformation) [9] of **CCH** were chosen as analytical bands. These absorption bands fall within the “transparency windows” of **CFAO**.

The study of conformational dynamics was carried out in the temperature range from -160°C to +20°C. The experimental dependences  $\ln(D_A/D_B)$  upon  $1/T$  for **DCE** dissolved in **CFAO** are represented in figure 3. The enthalpy difference of the conformers was determined for the temperature range -80°C - +20°C. The obtained value appeared to be  $\Delta H_{\text{ig}} = 300 \pm 40 \text{ cal mol}^{-1}$ . The freezing-in of the conformational transitions was observed at  $T_f = -88 \pm 8^\circ\text{C}$ .



**Figure 3.** The dependence of  $\ln(D_t/D_g)$  upon  $T^{-1}$  for **DCE** embedded in **CFAO**: a)  $T_f = -93^\circ\text{C}$ , film thickness  $d = 90 \mu\text{m}$ ,  $[C] = 1 \text{ vol}\%$ ; b)  $T_f = -89^\circ\text{C}$ ,  $d = 30 \mu\text{m}$ ,  $[C] = 2,5 \text{ vol}\%$ ; c)  $T_f = -90^\circ\text{C}$ ,  $d = 90 \mu\text{m}$ ,  $[C] = 2 \text{ vol}\%$ ; d)  $T_f = -81^\circ\text{C}$ ,  $d = 35 \mu\text{m}$ ,  $[C] = 2,5 \text{ vol}\%$ .

The similar dependences were obtained for **CCH** embedded into **CFAO** (see figure 4). Enthalpy difference is  $\Delta H_{ed}=320\pm 40$  cal mol<sup>-1</sup>. The freezing-in of the conformational transitions was observed at  $T_f=-93\pm 10^\circ\text{C}$ .



**Figure 4.** The dependence of  $\ln(D_f/D_g)$  upon  $T^{-1}$  for **CCH** embedded in **CFAO**:  $T_f=-93^\circ\text{C}$ ,  $d=155\mu\text{m}$ ,  $[C]=6$  vol%.

It can be seen that the conformational mobility of **DCE** and **CCH** is freezing-in at the similar temperature, around  $T_f=-90^\circ\text{C}$ . According to [10]  $\beta$ -process in **CFAO** takes place in this temperature range.

Each probe is characterized by the activation volume  $V_p^\ddagger$ , which is defined as a minimal free volume necessary for the internal rotation of definite groups of the probe molecule resulting in the transition from one conformation to another [5]. To estimate activation volumes for  $\text{H}_2\text{Cl}$  group in **DCE** and  $\text{ClCH}$  groups in **CCH**, we have used the method of increments [11, 12], the obtained values being equal to  $24 \text{ \AA}^3$  and  $31 \text{ \AA}^3$ , respectively. The freezing of such probe molecules gives evidence to the termination of local mobility of the groups of similar and greater volume; the groups having lower volumes preserve their local mobility and freeze at lower temperatures. The smallest kinetic unit of the oligomer under study is the end  $\text{NO}_2$  group having the activation volume  $14 \text{ \AA}^3$ . Taking into account the above consideration, one may conclude that the freezing of the probe mobility is not connected with the motion of these groups. Other groups with larger activation volumes, which provide the free volume generation in the oligomer, are the benzene rings in the main and side chains. The “kinetic volume” of benzene ring ( $\text{C}_6\text{H}_4$ ) is estimated to be equal to  $59 \text{ \AA}^3$ . Since at  $T_f \sim -90^\circ\text{C}$  the local mobility of the probe with smaller activation volume terminates, this gives evidence to the lack of the free volume in the oligomer. This statement is in agreement with the conclusion made in [10] on the basis of molecular simulation study, that relaxation  $\beta$ -process in **CFAO** is related to the freezing of the benzene rings motion.

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