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Dielectric spectroscopy and molecular modeling of branched methacrylic (co)polymers containing nonlinear optical chromophores

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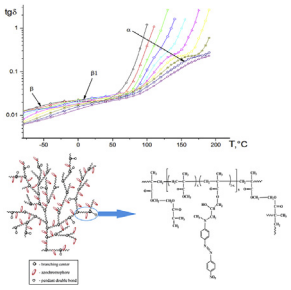
HIGHLIGHTS

- Branched methacrylic copolymers containing NLO chromophores are studied by DS.
- Three relaxation processes, β, β_1 and α, were observed by DS technique.
- Combined DS and MM data relates the processes with mobility of certain polar groups.
- Chromophores mobility occurs at T higher than that for segmental mobility start.

GRAPHICAL ABSTRACT



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ABSTRACT

Molecular mobility in branched methacrylic copolymers with various concentrations of chromophore groups is studied by dielectric spectroscopy. At temperatures from −100 °C to 220 °C and in the frequency range 10^{-1}–$5 \cdot 10^{6}$ Hz three relaxation processes are detected. Molecular mechanisms of local β and β_1 processes and cooperative α process occurring in the glassy and in the rubbery state, respectively, are determined on the basis of the dielectric spectroscopy; molecular modeling results are consistent with experimental data. The mobility of azochromophore groups, which define nonlinear optical properties, begins at temperature 30 °C higher than that for α process.

1. Introduction

Organic polymer materials, exhibiting nonlinear optical (NLO) response to the applied electric field, are at the forefront of research activities in the field of new functional materials for use in photonics and optoelectronics since the mid-1980s [1–4]. In particular, polymer materials with quadratic NLO activity are meant for high-speed waveguide devices, controlling light signals in fiber-optic communication lines. Polymer NLO materials possess a number of essential advantages in comparison with their inorganic analogues traditionally used in the devices for modulation, transmission and storage of light signals: high values of electric susceptibilities, low

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dielectric constant, the ease of fabrication and processing, good compatibility with other structural elements of the devices [2–5]. Molecular sources of the NLO activity are organic chromophores incorporated into polymer material, which should have non-centrosymmetric structure to exhibit quadratic nonlinearity. This is achieved by chromophores orientation in the electric field applied to the polymer heated up to the glass transition temperature, T_g, the so-called poling procedure [1,5]. One of the key tasks in design of polymer materials with quadratic NLO response is to provide optimal relaxational stability of the NLO characteristics achieved during poling.

In order to make the process of orientation of chromophores in the applied electric field possible the chromophores should have sufficient mobility in a polymer matrix at elevated temperature. Dielectric spectroscopy (DS) is widely used to get this information [6]. At studying chromophore-containing polymers it is essential that they contain constant dipoles – polar groups, the orientation of which occurs mainly in the direction of measuring electric field. The orientation has relaxation character, i.e. it depends on the relationship between the electric field frequency and relaxation time τ (or temperature). Relaxation processes reveal themselves in the dielectric spectrum ($\varepsilon'' = \phi(f)$ dependences) as the regions of maxima with the frequency f_{max}, corresponding to the relaxation of dipole polarization of the respective kinetic unit.

An additional tool to study the orientational dynamics of chromophores in a polymer matrix is provided by molecular modeling (MM), which may be helpful for predicting structures with the optimal orientation order of chromophore groups and thus promising NLO response properties [7].

When the chromophore groups concentration in material is rather high, dipole-dipole interactions (DDI) between them may result in the energetically favorable anti-parallel arrangement of chromophores and attenuation of the material NLO response. To prevent or reduce the effect of this detrimental DDI of the chromophores it is suggested to use branched polymer matrices, where the peculiarities of three-dimensional structure provide chromophore isolation [8,9]. The structure of branched polymers determines the effectiveness of poling, which is the necessary step in creation of polymer materials with quadratic NLO activity.

Here we study by DS technique the molecular mobility of branched methacrylic copolymers with methacrylic units containing either aniline groups (**PI**, Fig. 1) or corresponding copolymers obtained by azocoupling reaction producing copolymers with *p*-nitrophenylazobenzene chromophore groups (**FI**, **FIII**, Fig. 1); MM is carried out for **M1** which is a model for **PI,** and for **M2** which is a model for **FI** and **FIII** (Fig. 2).

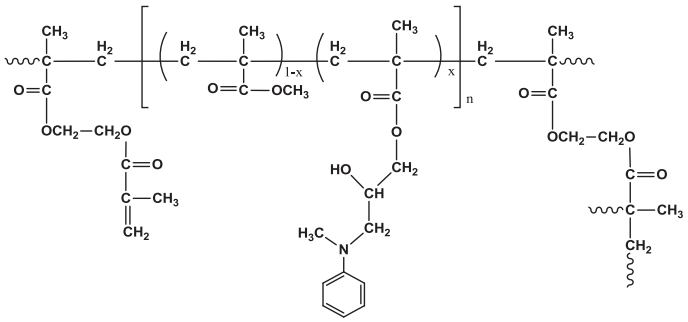
The purpose of this paper is to study local and cooperative forms of molecular mobility in **PI**, **FI, FIII** and clarify the effect of azo-chromophores introduction and their concentration on the kinetic characteristics of molecular mobility by means of Dielectric spectroscopy. We have also performed the Molecular Dynamics (MD) simulation for the **M1** and **M2** model systems and considered its correspondence to the information about molecular mobility based on DS experimental data.

2. Materials and methods

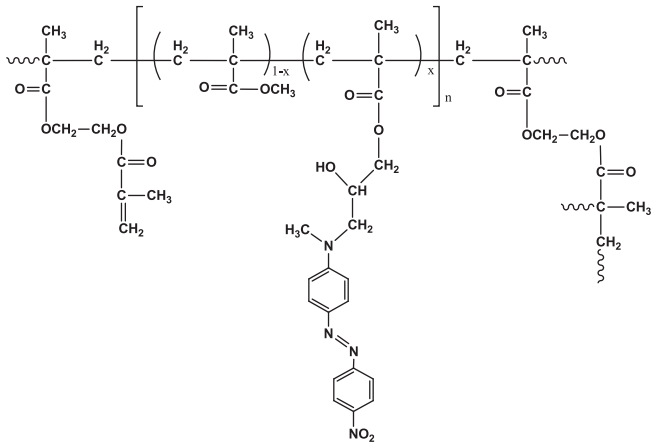
Chromophore-containing branched copolymers were obtained by two-step procedure [10]. At the first stage by radical copolymerization of methylmethacrylate (MMA), *N*-methyl,-*N*-(3-methacryloyloxy-2-hydroxypropyl) aniline (AMA) and ethylene glycol dimethacrylate (EGDMA) as a branching agent in toluene in the presence of 1-decanethiol, DT, as a chain-transfer agent branched aniline-containing copolymers were obtained. As a result, aniline-containing copolymers **PI** and **PIII** are obtained with molar ratios of reagents [MMA]:[AMA]:[EGDMA]:[DT] being equal to 90:10:12:12 and 70:30:12:12, respectively. According to the data of gravimetric analysis, the copolymers yield is 90–95%. As a result of participation of dimethacrylate double bonds in the chain growth reaction the branched polymer architecture is formed; its topology – the length of initial and internodal polymer chains – is determined by the reagents ratio and chain transfer to DT [11].

To obtain copolymers with NLO groups, at the second stage azo-coupling reaction is carried out, branched aniline-containing oligomers **PI** and **PIII** being azo-component and 4-nitrobenzenediazonium tetrafluoroborate being diazocomponent. As a result, polymers **FI** and **FIII** with high yields were obtained; they are red powders well soluble in organic solvents. Structure and content of obtained oligomers are confirmed by physico-chemical techniques [10].

Dielectric spectra were recorded on “Concept-41 Novocontrol Technologies” broadband dielectric spectrometer with ALPHA-ANB high-resolution automatic frequency-analyzer. The measurements were performed under nitrogen in the frequency range 10^2–10^7 Hz



PI



FI x=0.1
FIII x=0.3

Fig. 1. Branched methacrylic (co)polymers studied here.