The effect of chromophores concentration on the nonlinear optical activity of methacrylic copolymers with azochromophores in the side chain

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Abstract. Quadratic nonlinear-optical characteristics of thin films based on methacrylic copolymers with of chromophore-containing monomers incorporated at various concentrations are measured by Second Harmonic Generation technique. Optimal chromophores content is obtained to be about 17 mol%, rather high values of nonlinear-optical coefficient, $d_{33}$, up to 60 pm/V, are determined.

1. Introduction

Nonlinear optical (NLO) characteristics of polymer materials originate from organic dipolar chromophores which are incorporated into the polymer by various ways [1,2]. Aggregation of these dipolar chromophores represents one of the governing factors in the development of polymer NLO materials limiting the accessible concentration of the chromophores in the polymer matrix; the aggregation was shown to occur even at moderate chromophores content [3,4]. Thus the determination of optimal chromophore concentration for a material to exhibit maximal quadratic NLO activity is a burning problem. This problem is realized by the researchers, however the systematic studies of the concentration dependence are rare in literature [3,5,6]. In these works different aspects of the development of electro-optic materials connected with the aggregation problem are considered: determination of the concentrations at which maximal quadratic electric susceptibility, $\chi^{(2)}$, is realized [5]; relaxation stability of the poling order [3,6]; the ways for revealing chromophores aggregation [3,6]; the influence of pre-poling history on the effectiveness of chromophores orientation and $\chi^{(2)}$ value [6]; the effect of poling regimes on the $\chi^{(2)}$ value and temporal relaxation of the response [3,5,6]. Optimization of all mentioned factors may essentially enlarge NLO response and improve material properties. Conventionally in these papers the traditional polymer/dye systems are studied, both guest-host and polymers bearing chromophores in the side chain. Somewhat apart the researches stand where the new way of incorporation of chromophores is implemented, namely by means of noncovalent interactions between chromophores and polymer matrix [4,7]. The study of a tendency of
aggregation in such systems depending on the nature of a polymer matrix is performed [4,7]. In all these studies the so-called azo-chromophores were used as NLO-active groups.

Methacrylic copolymers with incorporated organic NLO chromophore groups represent one of the classes of organic materials with quadratic NLO response to the applied electric field (see [1] and references therein). However, some problems still attract attention, in particular, the analysis of interplay between chromophores concentration and aggregation. Here we study the effect of chromophores concentration on the \( \chi^{(2)} \) values by the example of methacrylic (co)polymers with azochromophores in the side chain, the concentration of chromophore-containing comonomer (MAZ) being 5 mol%, 8 mol%, 17 mol, 37 mol% and 43 mol% (see figure 1).

2. Experimental section
The synthesis of the studied methacrylic copolymers with various concentrations of MAZ monomers was carried out by the procedure described in [8].

\[
\left[ \begin{array}{c}
\text{CH}_3 \\
\text{H}_2\text{C} - \text{C} \\
\text{O} = \text{C} - \text{OCH}_3
\end{array} \right] \times \left[ \begin{array}{c}
\text{CH}_3 \\
\text{H}_2\text{C} - \text{C} \\
\text{O} = \text{C} - \text{OCH}_3\text{CH}^- \text{OH}
\end{array} \right]_x \times \left[ \begin{array}{c}
\text{CH}_3 \\
\text{H}_2\text{N} - \text{CH}_3 \\
\text{NO}_2
\end{array} \right]_n
\]

MMA-MAZ : \( x=0.05; 0.08; 0.1; 0.17; 0.37; 0.43, n=60 \)

**Figure 1.** Methacrylic copolymers with azochromophores in the side chain.

Polymer films were spin cast on glass plates from 7% solution of polymer in cyclohexanone (~5000 rpm during 60-90 sec); then the samples were kept in vacuum desiccator (drying oven) at room temperature for 10-16 hours followed by a soft bake at 50 °C during two hours. Film thickness was measured by AFM technique in tapping mode.

Since the material should be noncentrosymmetric in order to exhibit significant quadratic NLO activity, the polymer materials were converted into the so-called electret state with “frozen-in” macroscopic polarization appearing due to the orientation of dipole chromophores in the corona-discharge field [1,9]. This alignment was achieved in the electric field applied to the material heated to the temperature close to the glass transition temperature, \( T_g \), the field was applied during ~20 min (\( t_p \)), after that the temperature was decreased with the field still on, when the room temperature was reached the field was switched off. Poling was carried out at the corona-triode setup, the corona discharge field voltage being 7 kV (positive corona), the distance from the tungsten needle electrode to the surface of the film being 1 cm. The orientation order parameter, characterizing the quality of chromophore poling, was controlled by UV/vis-spectroscopy by the change in absorbance values before (\( A_0 \)) and after (\( /A \)) poling: \( \eta=I-I/A/A_0 \) [10]. Parameters characterizing poling regime are presented in table 1.

NLO coefficients of the studied polymers were measured by the Second Harmonic generation (SHG) technique (Nd:YAG laser, \( \lambda=1064 \) nm; 10 ns). The essence of the method is that we measure...
the intensity of SH-beam from the investigated polymer film and compare it with that of a standard. As a standard sample the alpha-quartz plate (X-cut) was used, the value of its nonlinear-optical coefficient $d_{11}$ is equal to 0.3 pm/V [12]. Maximal intensity of the generated second harmonic beam was shown to be measured at the incident laser radiation angle of about 57°.

3. Results and Discussion

The optical absorption spectra of the obtained films are presented in figure 2 and demonstrate a small blue shift of absorption maximum for all the chromophores molar contents up to 37 mol%, this observation being consistent with those made in [4,11]. When chromophores concentration exceeds 37 mol% the absorption decreases; $\lambda_{\text{max}}$ shows the red shift in this case, giving evidence to the chromophores aggregation [3]. The decrease of the $d_{33}$ value, presented in table 2, starts already for the film with chromophores content of 37 mol% and in general is in agreement with this observation.

Poling procedure results in the modification of the film surface (see figure 3); film roughness increases nearly twice.

The dependence of the obtained NLO coefficients $d_{33}$ for the studied polymer films on the concentration of chromophores is presented in table 2. Increase of $d_{33}$ value is observed up to level of concentration of 17 mol%, this being consistent with the formula for relation of molecular hyperpolarizability with quadratic electric susceptibility, obtained in the framework of the approach of non-interacting dipoles [2]. Maximum of $d_{33}$ curve is observed near 17 mol%; then $d_{33}$ decreases tending to saturation. Similar evidence was obtained in [5] for PMMA-DR1 side chain polymers, where optimal chromophores content was estimated to be 15%. However, both in our case and in [5] films with limited number of various chromophores concentrations were studied, and the agreement between these conclusions could be considered reasonable.

The change of $d_{33}$ values in table 2 is consistent with that obtained in [6] for guest-host films with pre-poling history. This fact gives hope to get higher nonlinearity when examining freshly-prepared films without pre-poling period during which spatial entanglements of polymer chains and head-to-tail arrangement of dipoles, hindering poling process, may take place [6]. Besides, optimization of poling protocol ($T_p$ increase) may also serve to the achievement of this goal.

Table 1. Characteristics of the studied polymer films.

| MAZ concentration (mol%) | Film thickness (nm) | $\lambda_{\text{max}}$ (nm) | $T_g$ (°C) | $T_p$ (°C) | $t_p$ (min) | Order parameter, $\eta$ |
|-------------------------|---------------------|-----------------|--------|--------|--------|-----------------|
| 5                       | 700                 | 475             | 126    | 125    | 20     | 0.04            |
| 8                       | 570                 | 475             | 128    | 112    | 20     | 0.33            |
| 17                      | 410                 | 472             | 131    | 125    | 20     | 0.32            |
| 37                      | 410                 | 468             | 138    | 127    | 20     | 0.36            |
| 43*                     | 250                 | 470             | 124    | 125    | 20     | 0.23            |

* - the procedure of film development differs in this case [8].
Table 2. The dependence of nonlinear optical coefficient $d_{33}$ on molar concentrations of the chromophores in the side chain (MMA-MAZ). The numbers in brackets are standard deviations.

| MAZ concentration (mol%) | $d_{33}$ (pm/V) |
|--------------------------|-----------------|
| 5                        | 21 (2)          |
| 8                        | 46 (5)          |
| 17                       | 60 (6)          |
| 37                       | 53 (5)          |
| 43*                      | 46 (5)          |

* - the procedure of film development differs in this case [8].

Thus, polymer materials based on methacrylic copolymers with different azochromophore molar contents, exhibiting relatively high values of NLO coefficients (up to 60 pm/V), were created.

Optimal concentration of chromophores in the studied methacrylic copolymers providing the highest value of the NLO coefficient is about 17 mol%.

Possible ways of enhancing quadratic nonlinearity are considered.

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