

Synthesis and investigation of optical properties of fluorine containing chromophore Disperse Orange DO1

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Abstract:

New electrooptical polymeric material was synthesized on the base of polymethylmethacrylate with fluorine containing chromophore disperse orange DO1 (Disperse Orange 1) in a side chain. It was shown that under the influence of laser radiation with the wavelength 440 nm the polymer translucence takes place, what happens due to not-reversible chromophore DO1 photodegradation. It was found out that during the photodegradation process the polymer refractive index n decreases, at the same time its change on the wavelength 632.8 nm may reach $\Delta n = 0.028$. Using the selective laser action, this allows to produce from the given electro optical material channel waveguides and other integrated optical devices elements.

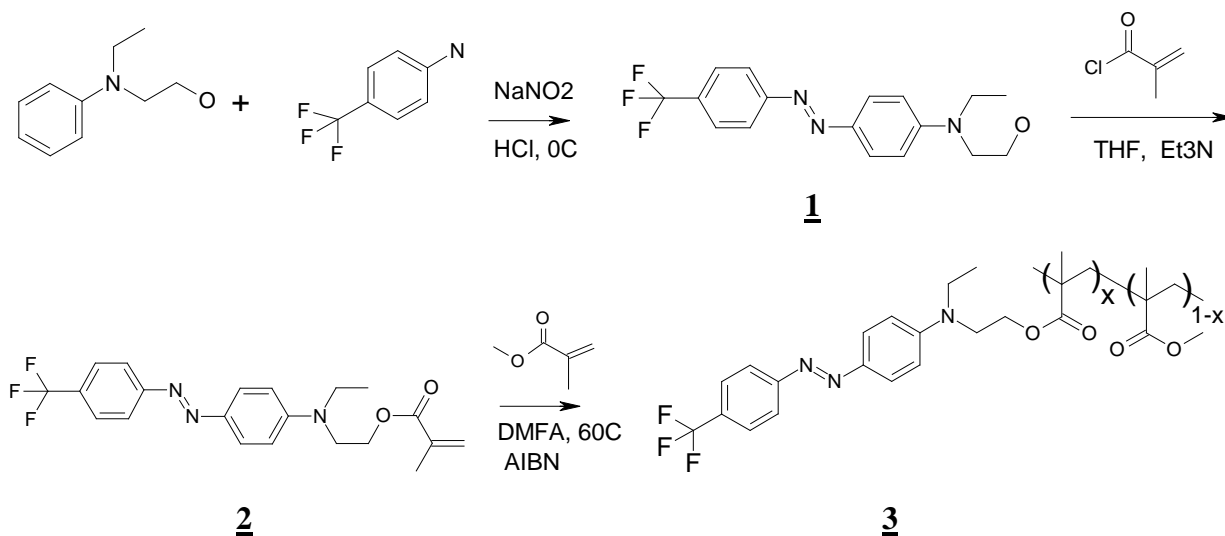
Introduction:

Electro optical polymeric materials find a wide application when producing high-speed integrated-optical modulators for telecommunication C – diapason of wavelength 1530 – 1565 nm [1 - 8]. Such materials are produced either by inputting chromophores molecules, which are able to change its refractive index under the influence of applied electric field into the passive polymeric matrix (guest – host system) [4 - 6], or by its chemical integration into the polymeric macromolecule side chains (side – chain system) [7, 8]. The second approach is more attractive because chromophore inputting in a side chain decreases it's mobility, what prevents chromophores agglomeration. Chromophores agglomeration decreases electric coefficient r_{33} . It is known that hydrocarbonic electrooptical chromophores, such as DR1, DR13 [6, 8], have noticeable absorption in C – band wavelenth range. In view of this, the synthesis of new chromophores, which along with the high electro optical coefficient r_{33} , have high optical transparency in the given spectral range is important. We suggest to use fluorine containing chromophores in order to increase optical transparency of electrooptical polymeric materials in telecommunication C – band wavelength. The idea of such approach is that the substitution of more lightweight hydrogen atoms on more heavy fluorine atoms leads to oscillative overtones dislocation to the side of longer wavelenth [9]. As a result the refractive index of a polymeric material in C – spectrum field decreases.

In the present article it is reported about the synthesis of a new fluorine-containing chromophore disperse orange DO1 (Disperse Orange 1). Polymeric material, that is represented as polymethyl acrylate with covalently joined chromophore DO1 in the side chain was obtained. Light-guiding films with the thickness 0.5 – 4 μm were prepared from this material. It was shown that under the laser radiation with the wavelength 440 nm influence, polymer clarification happens. Such clarification is explained by not-reversible chromophore DO1 photodegradation. It was found out that during the photo degradation process, the refractive index n of polymeric material decreases and the n variation may achieve $\Delta n = 0.028$. That allows, using the selective laser photo clarification of the polymer PMMA/DO1, to prepare channel optical waveguides, waveguide splitters, directional couplers and also Mach-Zender interferometers, required for the high-speed integrated optical modulators production for the telecommunication C-band wavelenths.

1. Synthesis of polymethyl acrylate with covalently integrated fluorine containing chromophore DO1

The synthesis of PMMA with fluorine containing electrooptical chromophore in a side chain was held in three stages. Chromophore DO1 was synthesized at the first stage (compound **1** in the Pic. 1). At the second stage, the given chromophore was covalently integrated to methacryloyl chloride molecule. At the third stage, the radical thermal polymerization with electrooptical polymer PMMA/DO1 formation was held. The described stages are shown in the Pic. 1.



Pic. 1. Scheme of the PMMA polymer with fluorine containing electrooptical chromophore DO1 in the side chain synthesis. Compound **1** – chromophore DO1, **2** – methacrylic ether with covalently integrated chromophore DO1, **3** – polymer PMMA/DO1.

1, **2**, **3** compounds' ¹H NMR spectra were recorded on Bruker AM300 (300 MHz) in CDCl₃.

4-(4-trifluoromethylphenylazo)-N-ethyl-N-(2-hydroxyethyl)aniline (**1**)

4-trifluoromethylaniline (5 g.) were dissolved in 3,7 ml of concentrated HCl and 11,2 ml of water. The solution was cooled to 0°C and there was being added 2,21 g. of NaNO₂ in small portions during 1 hour. The solution was being mixed during 30 min at 0°C. N-ethyl-N-hydroxyethylaniline was dissolved in 15 ml of 10% HCl, this solution was being added during 10 min to the reaction mixture and mixed at 0°C during 1 hour. 10% solution of sodium hydroxide was being added until pH 8 and precipitate formation, which was filtered and dried on

air to the constant weight. It was obtained 5,85 g. of compound **1** in the form of dark-orange crystals, melting temp. 95-98°C. Yield 55,8%.

¹H NMR spectra: 1.22(t, 3H), 3.6(m, 4H), 3,85(t, 2H), 6.8(d, 2H), 7,75(d, 2H), 7.9(m, 4H).

4-(4-trifluoromethylphenylazo)-N-ethyl-N-(2-metacryloyloxyethyl)aniline (2)

Compound **1** (2,84 g.) was dissolved in 5 ml of tetrahydrofuran, than there were added 1,3 ml of triethylamine. Solution was cooled to 0°C. Freshly distilled methacryloylchloride solution (1 ml) was added in drops into 3 ml of tetrahydrofuran and mixed during 24 hours at room temperature. After that, the precipitate was filtered, washed with tetrahydrofuran and filtrate was steamed under vacuum to the constant weight. The rest was dissolved in CHCl₃, the solution was washed with water (3 x 20 ml) and steamed to the constant weight at 40°C. 1,54 g of the product **2** were obtained in the form of orange crystals, melting temp. 73-75°C. Yield 57%.

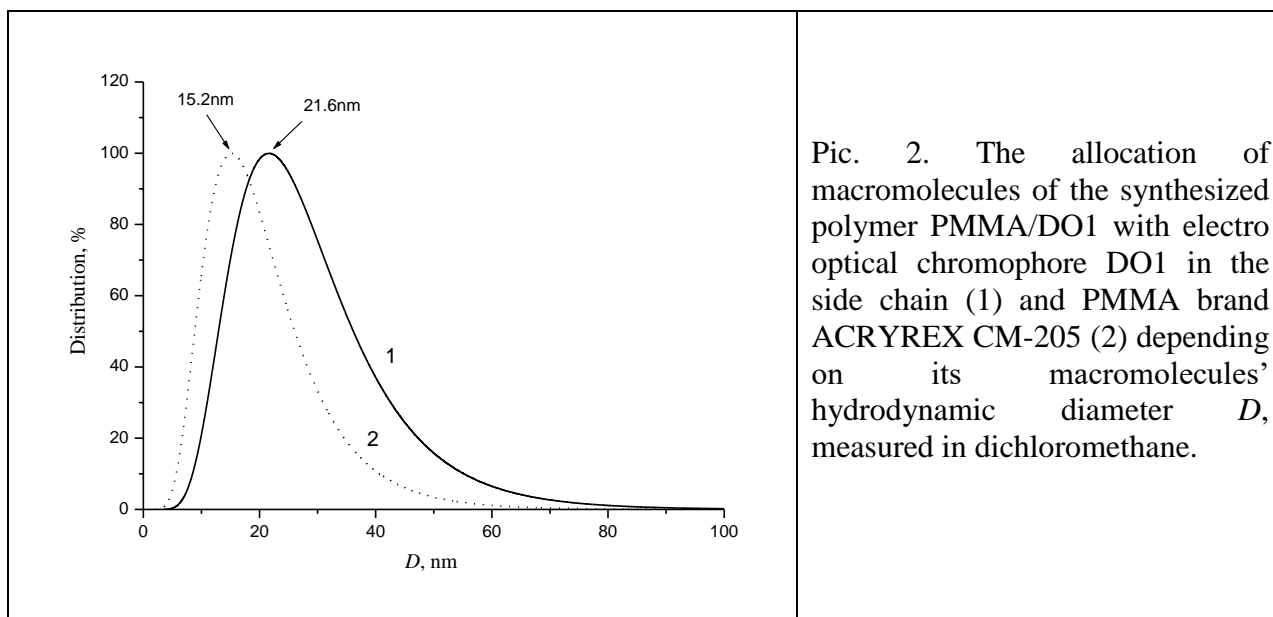
¹H NMR Spectra: 1.28(t, 3H), 3.55(q, 2H), 3.75(t, 2H), 4.4(t, 2H), 5.6(s, 1H), 6.13(s, 1H), 6.8(d, 2H), 7,73(d, 2H), 7.95(m, 4H).

Ether's copolymer 2 with methyl methacrylate (3)

Compound **2** (0,75 g, 1.85 mM) was dissolved in 4 ml of DMF, there was added 1,77 ml (16,7 mM) of methyl methacrylate and 75 mg. of AIBN. After mixing at 60°C during 24 hours the reaction mixture was put in cooled up to 0°C methanol, the precipitate was filtered, washed with methanol and dried on air to the constant mass. 2,05 g. of the product **3** ($x = 0.08$) were obtained. Yield 85%. Consequently, chromophore molar concentration in PMMA/DO1 polymer was equal $\approx 8\%$.

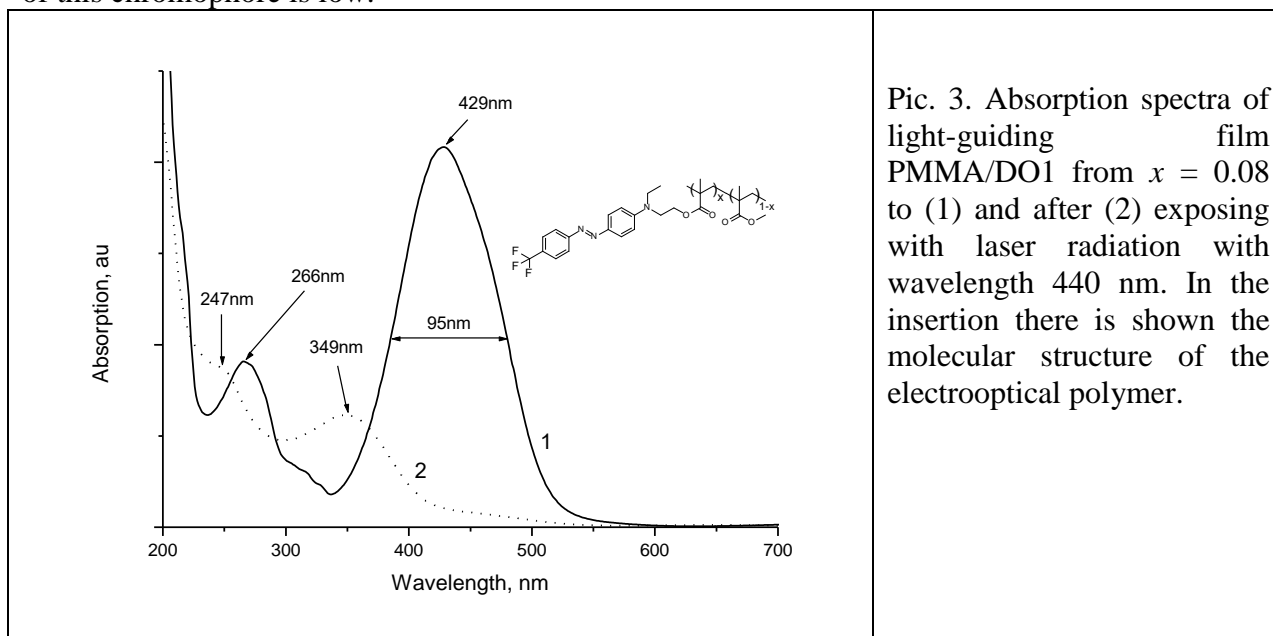
¹H NMR spectra: 1.28(t, 3H), 1,75(m, CH₃ chain), 7H(2CH₂N+3CH₃O chain), 4,2(m, 2H), 6.8(d, 2H), 7,73(d, 2H), 7.95(m, 4H).

In order to count the overage molecular weight M_w of synthesized PMMA/DO1 polymer the hydrodynamic diameter D was measured in dichloromethane. Dichloromethane was chosen as a solvent because PMMA/DO1 is easily dissolved in it, at the same time the dichloromethane refractive index $n_D = 1.4244$ at 20 °C varies from the PMMA/DO1 refractive index $n = 1.538$. In the Pic. 2 macromolecules distribution of the given polymer in dependence to D is shown. By way of comparison, in this picture the macromolecules distribution for polymer PMMA brand ACRYREX CM-205 is given. As it is shown in the picture 2, the Z-average diameter of the molecules PMMA/DO1 is equal to $D_{avr} = 21.6$ Nm, when for ACRYREX CM-205 $D_{avr} = 15.2$ Nm. On the assumption that the density of polymeric globules PMMA/DO1 and ACRYREX CM-205 in dichloromethane are similar, we can conclude that the average macromolecule PMMA/DO1 length three times outweighs the average length of macromolecule ACRYREX CM-205. Taking into account that for the last polymer $M_w \approx 5 \times 10^5$ g/mole [10], molecular mass of the polymer PMMA/DO1 can be calculated as $M_w \approx 1.5 \times 10^6$ g/mole.



Pic. 2. The allocation of macromolecules of the synthesized polymer PMMA/DO1 with electro optical chromophore DO1 in the side chain (1) and PMMA brand ACRYREX CM-205 (2) depending on its macromolecules' hydrodynamic diameter D , measured in dichloromethane.

Using the centrifuge method the light-guiding films were formed from the synthesized electrooptical polymer with thickness H_f from 0.5 to 4 μm from solutions PMMA/DO1 in chlorobenzene on quartz substrates, and also on silicon substrates with thermal grown oxide layer. Absorption spectrum of freshly applied on the quartz substrate film PMMA/DO1 is illustrated by the curve 1 in the Pic. 3. We can see that electrooptical polymer has intensive absorption in the visible area and in UV area with the centers near 429 nm and 266 nm, which are due to the light absorption by chromophore molecules. It should be noted that electrooptical chromophore DO1 has visible absorption only in the visible and UV areas of the spectrum, whether in the telecommunicational C – diapason of wavelength 1530 – 1565 nm the absorption of this chromophore is low.

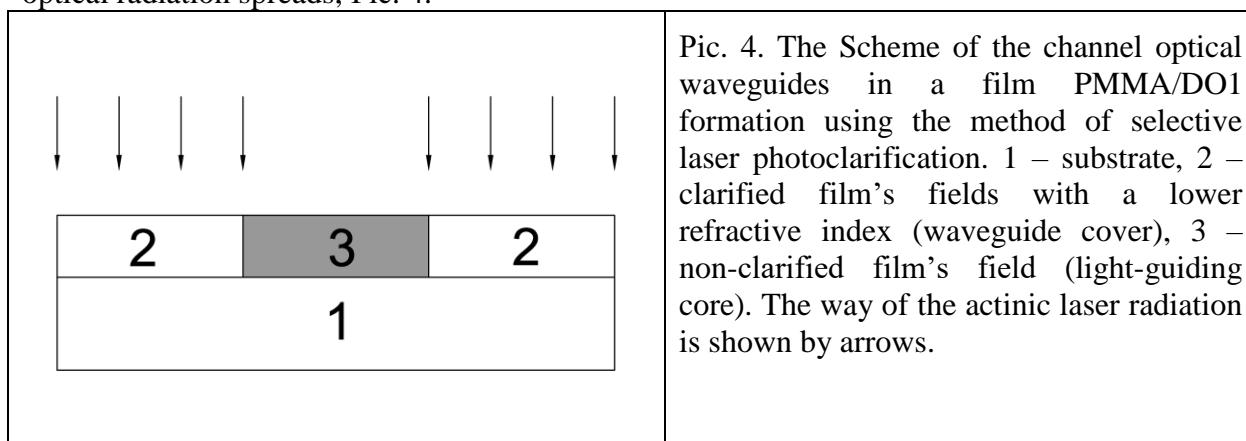


Pic. 3. Absorption spectra of light-guiding film PMMA/DO1 from $x = 0.08$ to (1) and after (2) exposing with laser radiation with wavelength 440 nm. In the insertion there is shown the molecular structure of the electrooptical polymer.

In the Pic. 3 there is shown the absorption spectrum of the given film after exposing by diode laser radiation with the wavelength 440 nm, located near the absorption peak of chromophore DO1. From curves 1 and 2 comparison it follows that during the exposing process, the absorption band intensity with the centers near 429 and 266 nm decreases, however new

absorption bands with centers near 349 and 247 nm appears. Such spectrum absorption variation is due to inconvertible chromophore DO1 photodegradation with the loss of color (photo bleaching effect [6, 11]).

Chromophore DO1 molecules photodegradation is accompanied by their polarization capacity changes, and as a consequence, changes of refractive index n of polymeric material. In order to measure the refractive index Δn , using the centrifuge method on silicon substrate with thermal grown «fat» oxide layer (oxide layer thickness 2.1 μm) there were prepared films from the polymer PMMA/DO1 with the thickness $\approx 2 \mu\text{m}$. The measurement of the refractive index of polymer during the photo clarification was held using the method of waveguide modes resonance activation in the film on the wavelength 632.8 nm using prismatic communication device Metricon2010M. It was found out that the polymer PMMA/DO1 refractive index decreases monotonically during the photoclarification process, at the same time reduction may reach $\Delta n = 0.028$. Such refractive index variation is enough for the formation of channel optical waveguides with numerical aperture $\text{NA} = 0.29$. We have to note that under the influence of actinic laser radiation in the film PMMA/DO1 there are formed fields with the lower refractive index, used as waveguide's cover, weather unexposed electrooptical material is a light-guiding core, in which optical radiation spreads, Pic. 4.



Pic. 4. The Scheme of the channel optical waveguides in a film PMMA/DO1 formation using the method of selective laser photoclarification. 1 – substrate, 2 – clarified film's fields with a lower refractive index (waveguide cover), 3 – non-clarified film's field (light-guiding core). The way of the actinic laser radiation is shown by arrows.

Consequently, by using the space lattice – selective laser photoclarification of electrooptical polymer films PMMA/DO1 there can be produced channel optical waveguides, and also other elements of integral-optical devices: waveguide splitters, directional couplers and so on. Using this method, Mach-Zender interferometers can be formed.

Conclusion.

The new fluorine containing electro optical chromophore DO1 was synthesized. The methodology of producing PMMA polymer with covalently integrated chromophore DO1 in the side chain was developed. Light-guiding films were prepared from this polymer. It was shown that under the influence of the laser radiation with the wavelength 440 nm, photo bleaching of the polymer PMMA/DO1 happens, which is accompanied by n material refractive index decrease. The measured decrease of n on the wavelength 632.8 nm was equal to $\Delta n = 0.028$, what allows to form different waveguides elements of integral optical devices in the given electrooptical material under the influence of the laser radiation.

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