SOLVENT PARAMETERS AS AN IMPORTANT FACTOR FOR THE PHOTOPHYSICAL PROPERTIES OF THE ORGANIC DYES IN POLYMER MATRICES

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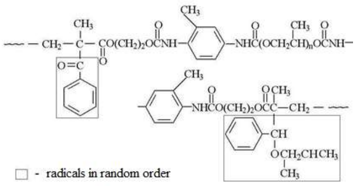
Introduction

The study of molecule associates for complex organic compounds in liquid media was carried out in numerous works, and quite negligible interest was attracted to the aggregate states in polymer matrices. Laser dye associations in a form of dimers quench fluorescence, and consequently, worsen generation characteristics of dye lasers. To incorporate dyes to the polymer materials, the most widespread methods are the following: direct dissolving of the dye in one of liquid monomers, monomer mixture or inserting in the polymer composition of the preliminary prepared intermediate liquid solution of a dye with a subsequent removal of a solvent by vacuum topping. The authors used the following solvents: chloroform, methanol, moderately polar 1-methyl-2-pyrrolidone, cyclohexanone, or added trace amounts of dimethyl sulfoxide, in order to improve dye solubility in the methyl methacrylate and polymethyl methacrylate. The latter solvent increases significantly dye solubility, but the problem of its removal form the mixture appears due to its high boiling temperature t = 189 °C.

The method with a use of solvents is preferable due to the more uniform distribution of dyes in the polymer matrices. The carried out analysis of literature data has shown, that the choice of specific solvents is arbitrary, since the main attention is paid only to their removal from the mixtures before the polymerization reaction. **Aimed** to optimize the choice of the solvent type, this work contains investigations of how the solvents, strongly different by physical parameters, affect spectral, photophysical and lasing properties of Rhodamine dyes, doped to the polymer polyurethane matrix.

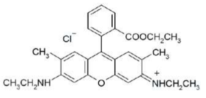
Materials

Polymer matrix



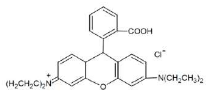
The polyurethane (PUA) material is produced by means of a radical photopolymerization (benzoin isobutyl ether initiator) of oligourethane acrylate, synthesized by a reaction between 2,4-toluene diisocyanate with a oligomer polyol (polypropylene glycol) and 2-hydroxyethyl methacrylate.

Organic dyes



Rh6G

Rhodamine 6G (Rh6G, chloride)



RhB

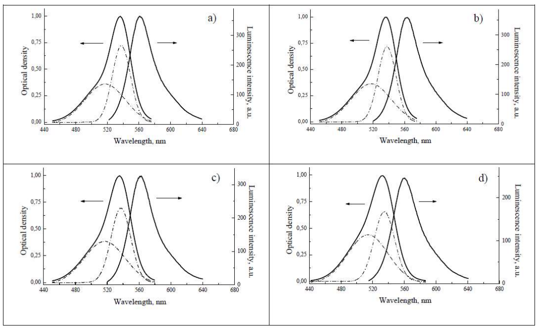
Rhodamine B (RhB, chloride)

To study the effects of a solvent type on the properties of Rhodamines in the PUA, the dyes have been incorporated to this polymer matrix with a use of different liquids

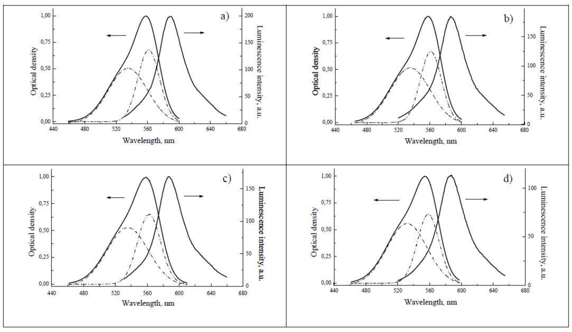
Solvents

Solvent	Dielectric permittivity, ε	Refractive index, **n**	**F_1(ε,n)**	**F_2(ε,n)**	Boiling point, **t_{boil}**, °C
Acetonitrile	37.5	1.344	0.87	0.67	81.6
Dichloromethane	8.9	1.424	0.59	0.58	40.1
Ethanol	24.3	1.361	0.81	0.65	78.4
Ethyl acetate	6.0	1.372	0.49	0.50	77.2

Absorption and luminescence spectra

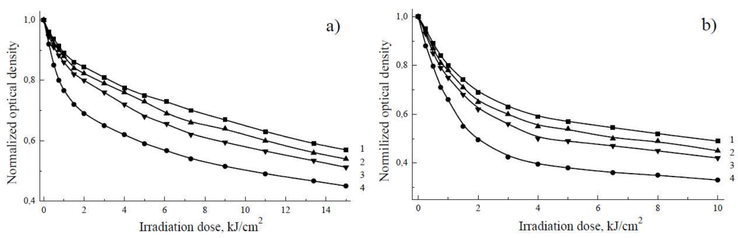


Absorption and luminescence spectra of the Rh6G dye in the PUA, incorporated from acetonitrile (a), ethanol (b), dichloromethane (c), ethyl acetate (d).



Absorption and luminescence spectra of the RhB dye in the PUA, incorporated from acetonitrile (a), ethanol (b), dichloromethane (c), ethyl acetate (d).

Photostability and generation properties of laser dyes in polyurethane matrices



Dependencies of normalized optical density, **D/Do**, on irradiation dose for the Rh6G (a) and RhB (b) dyes in the PUA, made with a use of acetonitrile (1), ethanol (2), dichloromethane (3) and ethyl acetate (4).

Basic generation characteristics of the active elements.

PUA-based active element, dye/solvent	Initial efficiency of generation, **η_o**, %	Number of pulses, caused **η_o** twice drop, **N**
Rh6G / Ethyl acetate	26	830
Rh6G / Dichloromethane	30	1200
Rh6G / Ethanol	31	1340
Rh6G / Acetonitrile	33	1400
RhB / Ethyl acetate	23	600
RhB / Dichloromethane	25	850
RhB / Ethanol	27	900
RhB / Acetonitrile	28	960

Conclusions

Effects of the solvents, different by physical parameters, on the spectral, photophysical, lasing properties and molecule associations of the Rhodamine dyes, incorporated to the polyurethane acrylate matrix were investigated. The role of the solvent polarity in the dye luminescence, photostability and generation of the dye-doped polymer active media was studied.

Aggregation of dyes in the polymer matrix is found out in the present investigations to be one of the main reasons of photostability decrease on a production stage, changes in spectral luminescence, photophysical and generation properties of laser active elements, based on Rhodamine dyes in the polyurethane acrylate matrix. Quite high concentrations of the dyes ($1x10^{-4}$ mol/L), which are typical of laser active media are investigated in this work. Increase of the Rh6G and RhB concentrations enlarges possibility for the appearance of ion pairs, including contact ones, where an electron is phototransfered from an anion to a cation and a formation of active neutral radicals is realized.

Effects of the solvents, possessed different polar properties and used in the production of laser dye-doped polymer active elements, on the spectral, photophysical and generation characteristics of these materials have been investigated for the first time. This study shows that in order to obtain high gain of active media in polymer matrices and prevailing quantity of monomers over the dimers for the dyes of a xanthene type, auxiliary solvents of high polarity should be applied. Such method allows to improve photostability, efficiency and operation lifetime of solid-state active elements in the dye lasers. The use of these solvents provides minimal photodestruction of the dyes during production of the laser active elements, based on radically hardened polymer compositions.

Development of optimal production methods for optically transparent materials, containing dye molecules, and investigations of their spectral optical properties are of great interest from both scientific and technological aspects. This is caused by prospectivity of such approach in practice, in particular, for the devices of quantum electronics.