

EFFECTS OF COVALENT BONDING BETWEEN DYES AND POLYURETHANES ON SPECTRAL, PHOTOPHYSICAL AND GENERATION PROPERTIES

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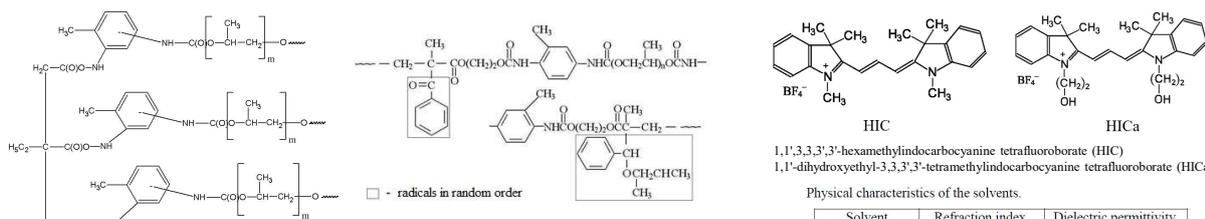
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Introduction

The main reason of fluorophore decay is local (near an organic dye molecule) heating of solid-state media due to dissipation of absorbed (and not converted to the generation) energy, and as a result of intramolecular vibrational relaxation at the transition to the lowest vibrational level of the S_1 state. The problem is partially solved by a use of sol-gel matrices with high thermal conductivity, but this technology does not get a wide application, since it requires complex technological processes and strong inorganic acids as catalysts. Doping the polymer matrix by silica nanoparticles also decreases mentioned local heating and degradation, and improves efficiency of dye lasers. Chemical bonding of a dye with a polymer chain allows distributing dye molecules in the polymer bulk more homogeneously and provides additional channels for dissipation of absorbed energy, not converted into generation.

The aim is to study possibility for a use of the polyurethane as a matrix in the cyanine-based active media, where the direct covalent bonding between dye molecules and polymer chains is realized. The work presents investigations of the spectral (absorption and luminescence), photophysical (stability under powerful irradiation) and lasing (conversion efficiency and operation lifetime) properties for such dye-doped polymers. The effects of the polyurethane synthesis method used and the presence of hydroxyl-containing substituents in the cyanine dye molecules are also analyzed. Results of the study can reveal the ways to produce efficient dye-doped solid-state materials with improved optical and photophysical characteristics for the promising applications in laser active elements.

Materials



The polyurethane (PU) is produced by the polycondensation reaction from a macrodiisocyanate, based on oligourethane glycol of $M=1000$, 2,4-toluene diisocyanate and trimethylolpropane.

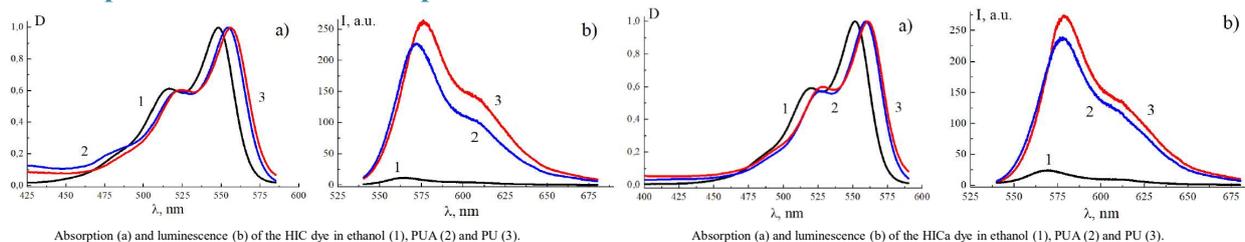
The polyurethane (PUA) material is produced by means of a radical photopolymerization (benzoin isobutyl ether initiator) of oligourethane acrylate, synthesized by a reaction between 2,4-toluene diisocyanate with a oligomer polyol (polypropylene glycol) and 2-hydroxyethyl methacrylate.

HIC
1,1',3,3,3',3'-hexamethylindocarbocyanine tetrafluoroborate (HIC)
HICa
1,1'-dihydroxyethyl-3,3',3'-tetramethylindocarbocyanine tetrafluoroborate (HICa)

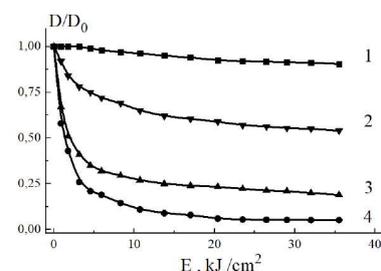
Physical characteristics of the solvents.

Solvent	Refraction index, n	Dielectric permittivity, ϵ
Ethanol	1.3610	24.3
PUA	1.4870	4.1
PU	1.5002	6.6

Absorption and luminescence spectra



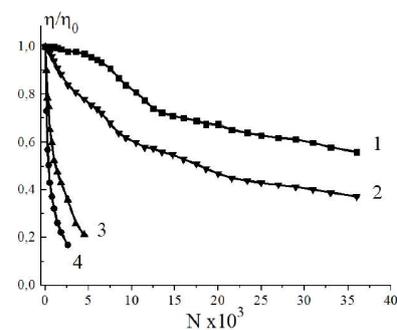
Photostability of laser dyes in polyurethane matrices



Photobleaching kinetic curves for the HICa (1, 3) and HIC (2, 4) dyes in the PU (1, 2) and PUA (3, 4) polymer matrices in the dependence on the irradiation energy dose.

Photostability measurements for the dyes in the PUA and PU matrices have been made by integral irradiation from a DRK-120 ultrahigh pressure mercury lamp. Ultraviolet and visible light of the mentioned lamp is mainly used for irradiation into the $S_0 \rightarrow S_1, S_2$ transitions. Photostability of the dyes in the PU (curves 1, 2) is considerably higher, than that in the PUA matrix (curves 3, 4), where dye photodecay occurs quite rapidly. Stability growth is caused by an absence of radicals in the PU, contrary to the PUA material, hardened by means of radical polymerization. In addition, the PU has an advantage over the PUA not only in the polymerization method, but also in its higher polarity. Moreover, under ultraviolet light irradiation, higher excited electronic states of the dye molecules can be deactivated nonradiatively in the processes of vibrational relaxation and internal conversion through the high-excited vibrational states of polymers with a formation of macromolecule free radicals. Since the dye absorption bands in the ultraviolet region overlap with the corresponding bands of polymers more strongly in the PUA, compared to the PU, probability of radical formation should be higher in the polyurethane acrylate; this conclusion is proved by the photodestruction curves.

Generation properties of laser dyes in polyurethane matrices



Operation lifetime dependencies of the conversion efficiency, normalized on the initial value in the dye laser for the HICa (1, 3) and HIC (2, 4) dyes in the PU (1, 2) and PUA (3, 4) polymers.

Operation lifetime of laser active media is known to depend on the pumping energy fluence and average power. Severe pumping conditions have been specially applied to test operational capability under powerful excitation and to obtain express information about operation lifetime of our laser elements, based on the two dye-doped polymer matrices. High beam strength of the used polyurethanes allows imposing such powerful pumping in the same local sample area at a small polymer thickness (~ 2 mm) in the triplex. Lifetime dependencies, η/η_0 , as functions of pumping radiation conversion to the generation versus a number of pulses, N , is shown in Fig. Decrease of the η value with the N growth for all the samples occurs due to the dye bleaching without any polymer matrix damage. Systematic significant increase of the operation lifetime is observed for the PU active laser media, compared to the PUA ones. Initial conversion efficiency, η_0 , is also higher in the PU-based materials. The higher initial efficiency in the PU samples can be explained by the absence of the dye decay in this polymer even on a production stage. Dye degradation occurs also during a synthesis process of the dye-doped materials by means of radical thermopolymerization, when the PMMA polymer is used. Dye decay products absorb in a generation region in the both cases of the PMMA and PUA matrices. Contrary to the PMMA and PUA samples, the PU-based active media are synthesized by the polycondensation reaction, and so the HIC and HICa dyes do not decay during the production process.

Conclusions

Formation of the covalent bonding between the HICa hydroxyethyl auxochrome and PU isocyanate component changes considerably photophysics of the dye molecules; photostability, generation conversion efficiency and operation lifetime have been significantly improved. This chemical bonding is possible due to a presence of the hydroxyl group in the hydroxyethyl auxochrome $-(CH_2)_2OH$.

