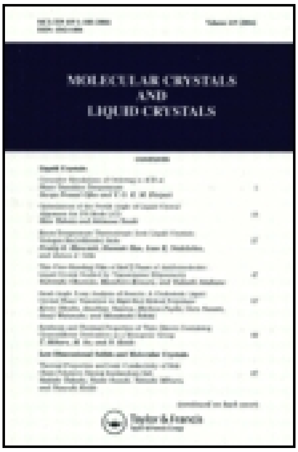

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Impact of Merocyanine Dye Concentration in Ultrathin Polymer Films on Nonlinear Optical Response Due to the Aggregation Effect

V. Ya. Gayvoronsky [a], A. Uklein [a], E. Vishnyakov [a], M. S. Brodyn [a], D. Grynko [b] & O. Kachkovsky [c]
[a] Institute of Physics of NASU, Kyiv, Ukraine
[b] Institute of Semiconductor Physics of NASU, Kyiv, Ukraine
[c] Institute of Organic Chemistry of NASU, Kyiv, Ukraine

Version of record first published: 03 Mar 2011

To cite this article: V. Ya. Gayvoronsky, A. Uklein, E. Vishnyakov, M. S. Brodyn, D. Grynko & O. Kachkovsky (2011): Impact of Merocyanine Dye Concentration in Ultrathin Polymer Films on Nonlinear Optical Response Due to the Aggregation Effect, Molecular Crystals and Liquid Crystals, 535:1, 132-139

To link to this article: http://dx.doi.org/10.1080/15421406.2011.537962

Mol. Cryst. Liq. Cryst., Vol. 535: pp. 132–139, 2011
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.537962

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V. YA. GAYVORONSKY,[1] A. UKLEIN,[1]
E. VISHNYAKOV,[1] M. S. BRODYN,[1]
D. GRYNKO,[2] AND O. KACHKOVSKY[3]

[1]Institute of Physics of NASU, Kyiv, Ukraine
[2]Institute of Semiconductor Physics of NASU, Kyiv, Ukraine
[3]Institute of Organic Chemistry of NASU, Kyiv, Ukraine

Nonlinear optical properties of thin films of the organic merocyanine dye derived from the class of malonodinitrile dyes, as well as its solid guest-host systems based on polymethyl methacrylate are studied. The optical absorption spectra of films with different dye concentrations and of the dye solutions in non-polar solvents are measured. The scattering indicatrices of films are presented. The films demonstrated the efficient photoinduced variation of the refractive index under the pulsed and continuous wave laser excitations. A nonlinear optical response of films under the picosecond range pulsed laser excitation points to the aggregation effects at the 10-wt.% dye concentration and higher.

Keywords Aggregation effects; guest-host nanocomposites; merocyanine dye; nonlinear optical response; polymethyl methacrylate; scattering indicatrices

1. Introduction

Organic materials for nonlinear optical (NLO) applications rely on a noncentrosymmetric ordering of dye molecules [1–3]. A great attention has been paid to donor-acceptor conjugated compounds because of their highly polarizable π-electron systems and a strong correlation between their structure and optical properties [1,2]. It was shown that a combination of these materials with different polymer matrices can improve and purposefully modify their NLO behavior [4]. Such "guest-host" systems can be useful for the frequency conversion, data storage, image processing, optical switching, and optical limiting. For instance, third-order NLO photoinduced changes in the refractive index are fundamental to all-optical switching and computing.

The dye under investigation is of the merocyanine group with donor and acceptor residuals that define its large NLO properties [1]. It is well known that such structures can aggregate and self-organize into microstructures of different types

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Address correspondence to V. Ya. Gayvoronsky, Institute of Physics of NASU, 46, Nauky Prosp., Kyiv 03680, Ukraine. E-mail: vlad@iop.kiev.ua depending on growth conditions, substrate properties, solvents, etc. [2,5,6]. Their THz absorbance spectra are sensitive to the length of their π-conjugated chain [7]. These and other photochemical features make these dyes interesting for various investigations.

Polymethyl methacrylate (PMMA) is one of the most versatile polymeric materials convenient for applications in various technological areas including optics and nonlinear optics [4]. In this work, we study the linear and nonlinear optical properties of thin films ($\sim$20–100 nm) of the investigated dye "guest-host" compounds with PMMA as a matrix, as well as of a solid dye film condensed on a glass substrate. The dependences of the NLO response on the dye concentration in films give possibility to judge about the aggregation effects in samples [8].

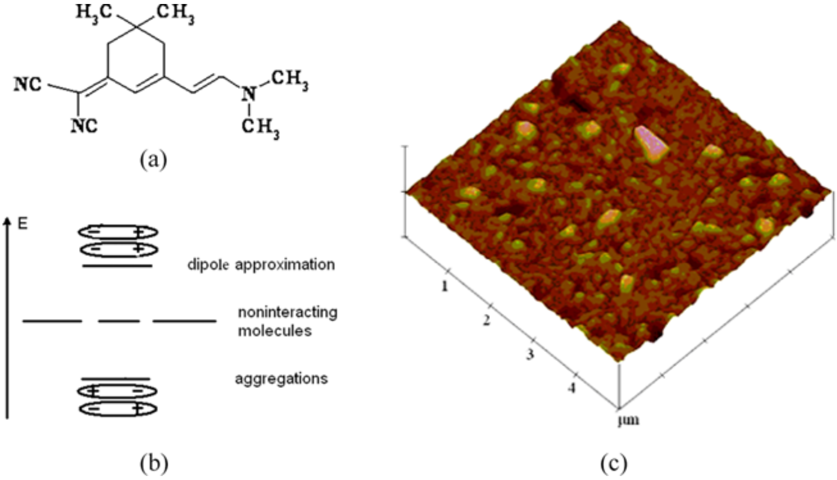
To analyze the third-order NLO coefficients of nanosized films with different concentrations of the dye, as well as those of condensed dye films, we performed measurements of the on-axis transmittance under a single pulse excitation with the second harmonic (532 nm) of a mode-locked Nd:YAG laser. The NLO properties of samples under a continuous wave (CW) laser excitation are presented. An impact of dye nanoclusters on the NLO response, linear absorption spectra, and optical scattering indicatrices is observed.

2. Experimental Section

2.1. *Samples Preparation*

The investigated dye is derived from the class of malonodinitrile dyes. It was synthesized via the condensation of dimethylacetal dimethylformamide and 2-(3,5,5-trimethylcyclohex-2-enyliden)-malonodinitrile in acetonitrile. Its composition and THz properties were studied in [7] (dye No. 3). Its chemical formula is shown in Figure. 1(a).

The nanosized "guest-host" compound films with different wt. concentrations (0%, 0.1%, 1%, 10%, and 50%) of the studied dye in PMMA were prepared, by using



(a)

(b)

(c)

Figure 1. (a) Chemical formula of the investigated merocyanine dye, (b) energy level splitting in the weak dipole-dipole interaction approximation, (c) AFM image of the condensed dye film.

the spin-coating method. Solutions of the polymer matrix mixed with the dye at certain concentrations were dried on a spin dryer at 200°C to produce the nanosized films.

The solid dye film was obtained via the sublimation in vacuum, transfer of molecular compounds in the form of a molecular beam, and following condensation on a glass substrate in vacuum $(1–3) \cdot 10^{-4}$ mmHg with a residual pressure not worse than $1 \cdot 10^{-5}$ mmHg [6]. The film mass and the molecular beam density were measured *in situ* using the quartz crystal microbalance technique.

A morphology of the obtained ultrathin films was examined by means of optical microscopy, scanning microinterferometry, and atomic force microscopy (AFM). In Figure. 1(c), an AFM image of the condensed dye film is presented, and aggregated molecular nanoclusters are clearly seen on the surface. The thicknesses of films were evaluated using a contact-free interferometric automatic profilometer "Micron-Alpha" (Ukraine) with an accuracy of 4 nm. They turn out to be 92 nm, 47 nm, 46 nm, and 16 nm for PMMA films with dye concentrations of 0.1%, 1%, 10%, and 50%, respectively; 47 nm for pure PMMA and 40 nm for the condensed dye film.

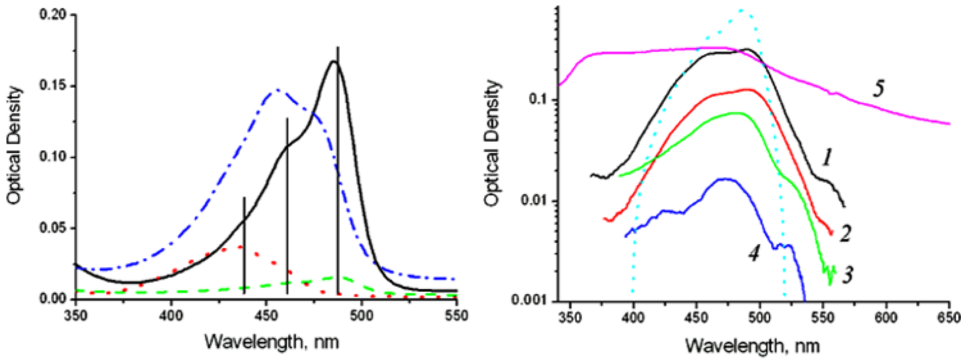
The scattering indicatrices of all investigated samples were measured using the experimental technique described in [9]. To study NLO refractive index variations, the far-field spatial profile analysis [1,10] is used. Photoinduced changes in the total transmittance correspond to certain NLO absorption coefficients [1,11]. The NLO properties of samples are studied under two types of excitation: CW (532 and 633 nm) and the second harmonic of a mode-locked Nd:YAG pulse laser (532 nm, 30 ps FWHM).

3. Results and Discussion

3.1. *Absorption Spectra*

In organic molecular solids, the dye molecules can form aggregates due to specific and nonspecific interactions. Their structure essentially depends on both the kinetics of the formation of ultrathin films and the nature of molecular interactions at interfaces. In the approximation of a weak dipole-dipole interaction between dye molecules, the first excited level is split into three components shown in Figure. 1(b) [12]. These components manifest themselves in the absorption spectrum of any compound containing the dye. The contribution of each component, i.e., its relative intensity, is a function of the mutual orientation of dipoles in aggregates, and the spectral splitting value is a characteristic of their interaction energy. In condensed molecular media, the inhomogeneous broadening and a small shift of spectral lines are present due to a configurational disorder in the system and due to the dielectric environment of aggregates. In Figure. 2, the optical density is plotted for the different dye solutions (a) and for thin PMMA films with different dye concentrations (b). In Figure. 2(a), the positions of spectral components are clearly shown.

The type of a solvent significantly affects the nature of the dye aggregation [12]. In acetonitrile, aggregates with the prevailing motive "head-to-tail" are quite significant at dye concentrations of 10^{-5} mol/liter and higher. The same type of aggregates is prevalent for solutions in acetone and isopropyl alcohol. However, the prevalent type of aggregates in aromatic solvents is a "stack" that is manifested by the dominance of high-energy absorption components in the spectrum. The investigated dye is soluble in toluene and limitedly soluble in benzene, precipitating as a separate phase at concentrations of order of 10^{-4} mol/liter.



(a) (b)

Figure 2. Absorption spectra of the dye-containing (a) solutions: solid line – in acetonitrile, dots – in benzene, dashes – in isopropyl alcohol, dash-dots – in toluene; (b) films: 1 – PMMA with 0.1-% dye concentration, 2 – with 1-%, 3 – 10-%, 4 – 50-%, and 5 – condensed dye film (100%), dots – the dye solution in acetonitrile.

For solid films based on PMMA, the predominant type of aggregates and the phase composition are also significantly dependent on the dye concentration. While spectra of a 1-% solid film are similar to those of solutions in acetone, an increase of the dye concentration leads to the growth of high-energy components and to significant inhomogeneous broadening. 50-% concentration film is most likely a two-phase system. The presence of the second phase was observed using an interference microscope with 400 zoom. The significant scattering and the spectral broadening argue for the same result.

3.2. *Scattering Properties*

The aggregation effects can stimulate phase precipitation and therefore a rapid growth in the intensity of light scattered by a sample with increase in the dye concentration in samples. We measured the optical scattering indicatrices of the films under study, and some of them are presented in Figure 3. It is clearly seen that the condensed film scatters much more light than other samples.

Scattering losses for all the investigated samples were calculated by the integration of the light power dP scattered into a solid angle $d\Omega$ (normalized to the incident power P_0) over a part of the forward hemisphere that corresponds to the non-ballistic propagation of photons:

$$\Delta P_{scatt} = \frac{2\pi}{P_0} \int_{\theta_{\min}}^{\pi/2} \frac{dP}{d\Omega} \sin\theta \cdot d\theta.$$

The calculated scattering losses are 3% and 5.5% for the 1- and 50-% wt. concentration films and 13% for the solid dye film. We note that the thickness of the 50-% film is 16 nm against ~40 nm for the 1- and 100-% concentration (condensed) films. So, it can be stated that the rapid growth of scattering losses starts at ~10 wt.%, and the aggregation effects are present in films with higher dye concentrations.

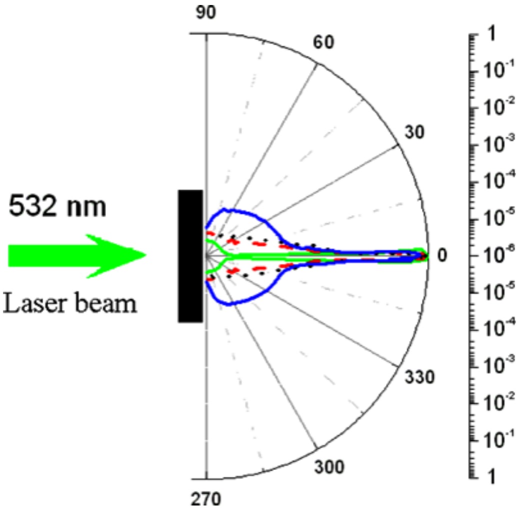
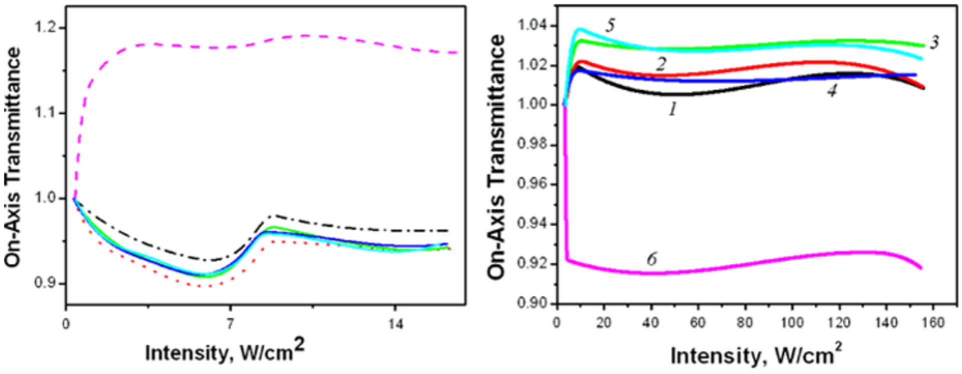


Figure 3. Scattering indicatrices of the investigated films: light solid line – freely propagated 532-nm laser beam, dashes – PMMA with 1-% dye concentration, dots –50-% concentration, dark solid line – condensed dye film (100-% concentration).

3.3. *NLO Properties under CW Laser Excitation*

The refractive NLO responses of the films were studied under the CW laser excitation by He-Ne (633 nm, 15 mW) and DPSS diode (532 nm, 70 mW) laser sources. The on-axis transmittances versus the input laser intensity for all the investigated samples are presented in Figure. 4. It can be seen that the effect is similar for all PMMA-based compounds, whereas, for the condensed film, the effect is extremely high and has the opposite sign.



(a) (b)

Figure 4. Photoinduced on-axis transmittance versus the laser intensity in the far field under CW laser excitation (a) at a wavelength of 633 nm: dashes – condensed dye film (100-% concentration), dash-dots – pure PMMA film, dots – 0.1-% concentration, solid lines – rest of the studied concentrations (1%, 10%, and 50%); (b) at a wavelength of 532 nm: 1 – pure PMMA, 2 – 0.1-% concentration, 3 – 1-%, 4 – 10-%, 5 – 50-%, 6 – condensed dye film.

The photoinduced variations of the refractive index Δn were derived from the data in Figure. 4 according to the technique described in [1,10] and presented in Table 1. The estimations were performed for the initial intensity ranges of the presented experimental dependences (at the intensities $I \sim 1\,\mathrm{W/cm^2}$ and $I \sim 5\,\mathrm{W/cm^2}$ for the 633-nm and 532-nm excitations, respectively). The obtained extremely high magnitudes of the Δn without irreversible changes of the NLO response testify to a non-local response mechanism in ultrathin films. When the layer thickness becomes smaller than the wavelength, the internal electric field in the film can be considered as a sum of direct and backward waves. Under certain conditions, the waves can constructively interfere, by producing a huge non-local enhancement of the internal field [13].

The films demonstrate photoinduced changes of a spatial beam profile in the far field. In our opinion, the obtained extremely high magnitudes of variations Δn in the photoinduced refractive index can be attributed both to the CW resonant excitation of the high-polarizable π-electron systems of dyes and to the non-local mechanism of response in ultrathin films.

The 532-nm excitation wavelength lies inside the absorption band (see Fig. 2b) of the guest-host films. A non-monotonic dependence of the Δn (positive values attribute to the self-focusing effect) on the dye concentration C can be explained by a high sensitivity of the resonance excitation to the detuning from the transitions of the dye subsystem in the matrix. The off-resonance excitation by a He-Ne laser exhibits the almost monotonic enhancement of the NLO response with increase in C. It is worth to point out the different signs of the refractive NLO response at the 532- and 633-nm CW excitations, which corresponds to self-focusing and self-defocusing effects. Such a kind of the NLO response sign switching is typical of the case of the near-resonance excitation – typical behavior of the NLO response due to the tuning from the above to the below to the intrinsic resonance frequency for various systems [10].

High magnitudes of the NLO response in the condensed film are most likely the manifestation of aggregates. In Figure. 4, it can be seen that all the PMMA-based samples demonstrate the self-defocusing effect under the 633-nm CW excitation,

Table 1. Variations Δn of the photoinduced refractive index for the films with various organic dye wt. concentration C due to the self-action of the continuous wave laser excitation at 633 and 532 nm; the real and imaginary parts of the cubic NLO susceptibility $\chi^{(3)}$ for the pulsed laser excitation at 532 nm, d stands for the film thickness

Excitation		633 nm, CW	532 nm, CW	532 nm, pulsed (30 ps)	
C, wt.%	d, nm	Δn	Δn	Re($\chi^{(3)}$), 10^{-4} esu	Im($\chi^{(3)}$), 10^{-6} esu
PMMA (0%)	47	−0.01	0.04	−0.02	−0.4
0.1%	92	−0.02	0.02	−1.7	−0.7
1%	47	−0.02	0.04	−3.8	−0.8
10%	46	−0.02	0.02	−5.2	−1.3
50%	16	−0.08	0.15	−9.9	−1.4
100% (condensed)	40	0.30	−0.40	−13.0	−16.0

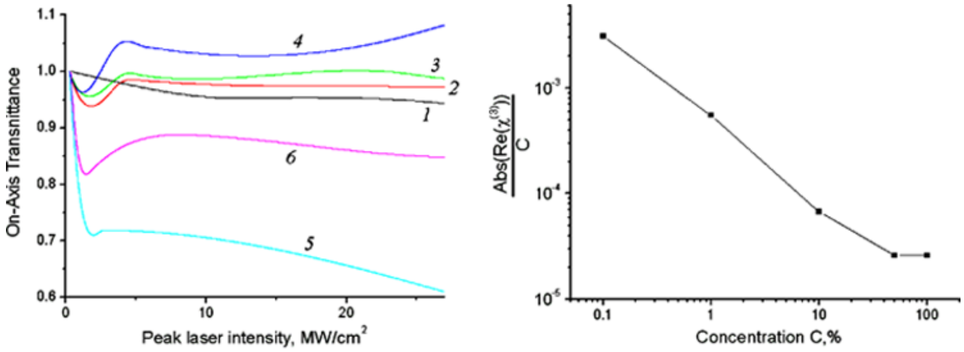
while the solid film is self-focusing. It is of interest that, at the 532-nm excitation, the situation is quite opposite.

3.4. *NLO Response under Picosecond Pulse Laser Excitation*

The concentration dependence of the NLO response of studied films was also explored under the mode-locked Nd:YAG laser excitation at 532 nm (30 ps FWHM, repetition rate 5 Hz). The experimental setup and technique are described in [1]. The measured on-axis transmittances versus the peak laser intensity are presented in Figure. 5(a). All the curves were normalized to the NLO total transmittances that were simultaneously measured, and the values of on-axis transmittance at low intensities were normalized to unity.

In all the samples containing the dye, the self-defocusing effect is present at low intensities, and then it turns to the self-focusing one at intensities of ~2 $\mathrm{MW/cm^2}$. The magnitude of the switching threshold depends on the dye content in the matrix. It decreases, as the concentration increases. The pure PMMA matrix exhibits the monotonous self-defocusing effect.

Values of the real and imaginary ($\mathrm{Re}(\chi^{(3)})$ and $\mathrm{Im}(\chi^{(3)})$) parts of the cubic NLO susceptibility of the films under the 30-ps pulsed laser excitation are presented in Table 1. The estimations were performed below the switching threshold of the NLO refractive response (low intensity range). The concentration dependence of the specific NLO response $|\mathrm{Re}(\chi^{(3)})/C|$ calculated for low intensities is plotted in Figure. 5(b) on a double logarithmic scale. Despite the specific NLO response reduction for each dye molecule, an increase in the dye concentration *C* leads to an enhancement of the macroscopic NLO response. This can be attributed to the formation of aggregates, which changes the dipole moments of the subsystem of dye molecules. At concentrations above 10%, the slope of the dependence $\mathrm{Re}(\chi^{(3)})/C$ on C changes. This corresponds to the transition from $\mathrm{Re}(\chi^{(3)}) \sim C^{1/4}$ to $\mathrm{Re}(\chi^{(3)}) \sim C^{1/3}$. The effect can be explained with the dye precipitation as a separate phase. The same peculiarity at 10% is observed for $|\mathrm{Re}(\chi^{(3)})|$ under the CW laser excitation (Table 1).



(a) (b)

Figure 5. The nonlinear optical response of the samples under 532-nm picosecond pulse excitation. (a) On-axis transmittance versus the peak laser intensity of the films: 1 – pure PMMA, 2 – 0.1-% dye concentration, 3 – 1-%, 4 – 10-%, 5 – 50-%, 6 – condensed dye film. (b) The specific NLO response versus the dye concentration *C*.

The imaginary part of the NLO cubic susceptibility Im($\chi^{(3)}$) exhibits not so abrupt change at the transition from pure PMMA to PMMA with dye. However, its concentration dependence also changes at a dye content higher than 10% wt. (Table 1). Typical Im($\chi^{(3)}$) values are of order $\sim 10^{-6}$ esu, and their magnitudes enhance with increase in the dye concentration in the films.

4. Summary

Optical and nonlinear optical properties of PMMA-based nanocomposite ultrathin films with a merocyanine dye at various concentrations are studied along with a condensed dye film. The efficient photoinduced variation of the refractive index due to the CW laser radiation self-action was observed. The magnitude and the sign of the NLO response can be controlled by the dye concentration and the laser frequency position against the absorption band of the nanocomposite system. High magnitudes of the refractive cubic NLO response Re($\chi^{(3)}$)$\sim$ - $(1 \div 10) \cdot 10^{-4}$esu were achieved with the excitation by picosecond laser pulses at 532 nm.

Signatures of the aggregation effect of the dye in a matrix were observed with the use of the spectroscopic and scattering indicatrix analyses. The impact of the effect is clearly shown in the concentration dependences of variations of the photoinduced refractive index under the CW and pulsed laser excitations.

Acknowledgment

We are grateful to O. Yaroshchuk for the preparation of samples and to A. Shkurinov for the fruitful discussions.

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