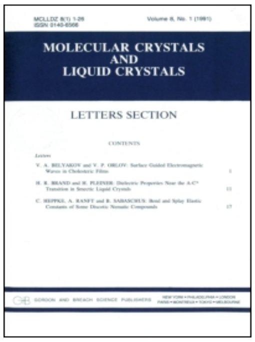

Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

Optical properties of disperse dyes doped poly(methyl methacrylate)

Beata Derkowska-Zielinska, Oksana Krupka, Vitaliy Smokal, Andrzej Grabowski, Mieczyslaw Naparty & Lukasz Skowronski

To cite this article: Beata Derkowska-Zielinska, Oksana Krupka, Vitaliy Smokal, Andrzej Grabowski, Mieczyslaw Naparty & Lukasz Skowronski (2016) Optical properties of disperse dyes doped poly(methyl methacrylate), Molecular Crystals and Liquid Crystals, 639:1, 87-93, DOI: 10.1080/15421406.2016.1254585

To link to this article: http://dx.doi.org/10.1080/15421406.2016.1254585

MOLECULAR CRYSTALS AND LIQUID CRYSTALS
2016, VOL. 639, 87–93
http://dx.doi.org/10.1080/15421406.2016.1254585

Optical properties of disperse dyes doped poly (methyl methacrylate)

Beata Derkowska-Zielinska[a], Oksana Krupka[b], Vitaliy Smokal[b], Andrzej Grabowski[c], Mieczyslaw Naparty[c], and Lukasz Skowronski[c]

[a]Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Torun, Poland; [b]Taras Shevchenko National University of Kyiv, Kyiv, Ukraine; [c]Institute of Mathematics and Physics, UTP University of Science and Technology, Bydgoszcz, Poland

ABSTRACT
In this paper, we investigated Disperse Red (DR1, DR13) and Disperse Orange (DO3, DO13) dyes embedded into poly(methyl methacrylate) (PMMA) polymeric matrix. The linear optical properties such as absorption coefficient, refractive index and energy band-gap of guest-host polymeric thin films were studied using spectroscopy and spectroscopic ellipsometry combined with transmittance measurements.

We found that the refractive index of DR1 is higher than the refractive indices for other studied azo dyes compounds. We also observed that the energy band-gap of studied materials varies from about 2 eV to 2.3 eV.

KEYWORDS
Disperse red; Disperse Orange; PMMA; optical properties

1. Introduction

Disperse Red (DR) and Disperse Orange (DO) are the azobenzene dyes. They can occur in two different geometries: a linear, stretched *trans* configuration and an angular *cis* configuration. The existence of these two isomeric configurations and reversible isomerization of the azo ($-N=N-$) group under UV or visible light are the origin of the photosensitivity. This transformation is connected with its volume change, just change of its rotational mobility. For example there is a ca. 10% decrease of the volume occupied by molecule passing from *trans* to *cis* form. As such conformational changes are connected with the change of π electron conjugation length, as result the material index of refraction is also changing.

Disperse Red (DR) and Disperse Orange (DO) dyes are the most popular materials as nonlinear optical compounds [1–3]. These compounds make an important class of materials due to a wide range of optical applications including optical data storage, surface-relief holographic, optical switching, optical limiting, signal processing, optical modulators and nonlinear optical devices [4–8].

However, the linear optical properties of these materials should be known in order to providing the accurate nonlinear parameters [2–3] for development of future nonlinear devices. Therefore, in this paper, we present the optical properties such as absorption coefficient and refractive index of Disperse Red (DR1, DR13) and Disperse Orange (DO3, DO13) thin films using spectroscopy and spectroscopic ellipsometry (SE) combined with transmittance measurements (T). These azobenzene dyes (as guest materials) were dispersed in poly(methyl

---

CONTACT Beata Derkowska-Zielinska ✉ beata@fizyka.umk.pl

methacrylate) (PMMA) polymer matrix (as host material). PMMA is one of the most commonly used polymeric hosts, which has high optical transparency in the visible spectral range, high optical homogeneity and relatively high laser-damage resistance [9–10].

Therefore, this work allows insight into the linear optical mechanisms of Disperse Red (DR) and Disperse Orange (DO) dyes and helps to understand some of them.

2. Experimental

The chromophores, DR and DO were purified by a recrystallization from an absolute methanol solution. And then these dyes have been doped in polymer matrice PMMA (polymethylmethacrylate). The concentration of DR and DO to PMMA was 5 wt%. The DR and DO and PMMA are commercially available in Aldrich. The DR and DO (5 g/L), PMMA (100 g/L) were dissolved in trichloroethane and the resulting solution was filtered through a 0.4 µm pore size nylon syringe filter. Spin deposition was used to fabricate thin films with controlled thickness on the glass slides. The principle of spin deposition is based on a homogeneous spreading out of the solution on the rotating substrate with an angular speed of 1000 rpm. Immediately after deposition, the thin films were cured in an 80°C oven for 1 hour to eliminate any remaining solvent.

Ellipsometric and transmission measurements were performed in the spectral range 300–2000 nm using the V-VASE device (J.A.Woollam Co., Inc.) and spectrophotometer Cary 5000 (Agilent), respectively. Ellipsometric azimuths, Ψ and Δ, were measured for three angles of incidence (65°, 70° and 75°). The optical constants were determined using the four medium optical model of the sample (glass/polymer layer (d_p)/rough layer (d_r)/ambient). The optical response in the transparent spectral range was parameterized using Sellmeier dispersion relation of the refractive index. To describe the absorption of these materials, a sum of Gaussian-type oscillators was used [11].

3. Results and discussion

Figure 1 shows the chemical structures of pseudo-stilbene type azobenzene dyes DR1, DR13, DO3 and DO13. We can see that DR 1 contains disparate electron affinities on the opposite sites of benzene rings (two polar end groups: an electron accepting group ($-NO_2$) and an electron donating group ($-NR'R$ where $R' = CH_2CH_3$, $R = CH_2CH_2OH$)) connected by a delocalized, conducting π-electron system ($-N=N-$). Therefore, it consists of an azo group ($-N=N-$) between two benzene rings, and push-pull donor and acceptor groups on the opposite sides of the benzene rings. The high charge-transfer interaction occurring between the electron-donor group (amino) and electron-acceptor group (nitro) which is characteristic for the pseudo-stilbene type azobenzene dyes.

The difference between DR13 and DR1 is that we have chlorine substituent (Cl) in ortho position of benzene ring. The Cl group in DR13 is an electron-withdrawing substituent, and its presence raises the oxidation potential. In the case of DR13 and DR1 molecules hydrogen atoms of amine group have been replaced by a substituent such as two alkyl groups. Whereas, in the case of DO3 we have primary amine group ($-NH_2$). Therefore, DO3 exhibits a push-pull π-conjugated system, having an electron-acceptor nitro group and an electron-donor amino group. The electron charge-transfer occurs from amino to nitro group through the π-conjugated system. While DO13 belongs to azo disperse dyes, which are based on disazo structures i.e. dye with two azo groups.

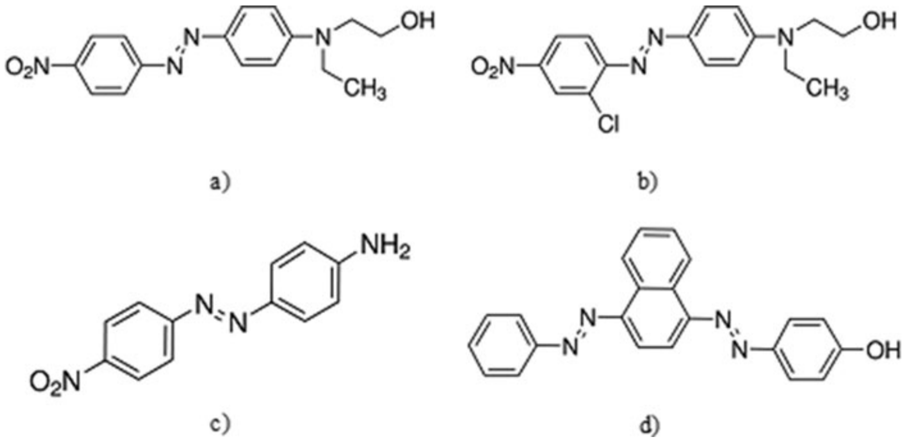

Figure 1. Chemical structures of DR1 (a), DR13 (b), DO3 (c) and DO13 (d).

Figure 2 presents transmission spectra (*T*) of DR1, DR13, DO3 and DO13 thin films in PMMA matrix in the spectral range 300–2000 nm. As we know from our previous papers [12, 13] PMMA is transparent from about 380 to 2000 nm. While, in the case of DR- and DO-PMMA, we can notice two absorption bands at about 490 nm and about 300 nm. The absorption band in the range 400 – 600 nm is assigned to π-π^* electronic transitions due to the strong internal charge transfer (ICT) character of pseudo-stilbene azobenzene dyes, and n-π^* transition, which is hidden [14]. They are assigned to π-π^* electronic transitions occurring in aggregated and free azobenzene chromophores. Whereas, the absorption band at about 300 nm is π-π^* transition. The feeble n-π^* transition, forbidden in strictly planar

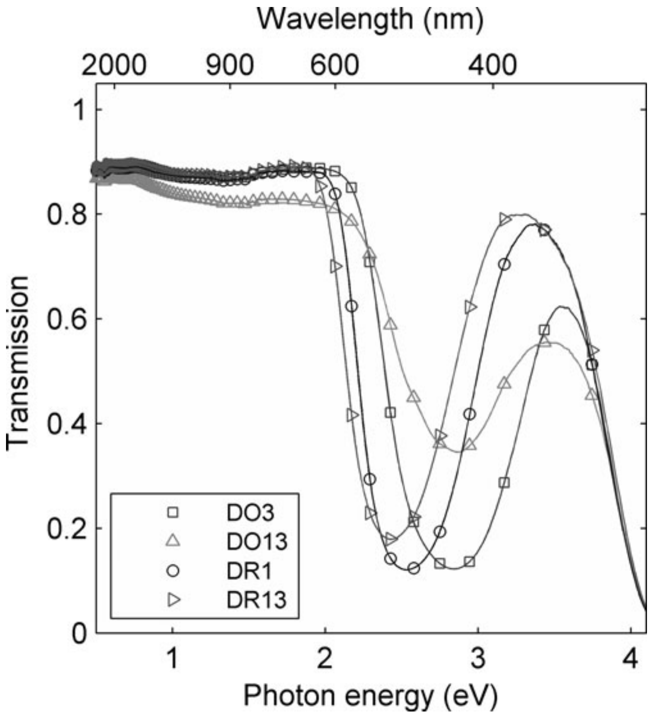

Figure 2. Transmission of DR1, DR13, DO3 and DO13 thin films in PMMA matrix.

molecules by symmetry selection rules, and insensitive to push-pull substitution is not explicitly identified from the spectra because it remains hidden under the strong π-π^* band. DR and DO moieties are of pseudo-stilbene type, which means that the high-energy π-π^* transition is overlapping the low-energy n-π^* transition. This leads to a large structureless band in the spectra of the trans isomer with an absorption maximum strongly depending on the polarity of the host material which may be either a polymer or a solvent [15]. The electron-donor and electron-acceptor substituents are increasing the charge transfer character of the π-π^* transition and consequently shifting the π-π^* band to the red compared to PMMA.

From Figures 2 and 3 we can see that the maximum of absorption band is at 492 nm for DR1. In the case of DR13, we have band at about 512 nm. The Cl group in DR13 is an electron-withdrawing substituent, and its presence raises the oxidation potential. This causes the bathochromic shift of absorption spectrum. In the case of DO3 the maximum of absorption band is at 452 nm, and for DO13 at 437 nm. Therefore, when we have primary amine group (DO3) or two azo groups (DO13) we observe the hypsochromic shift of absorption spectrum compare to DR1.

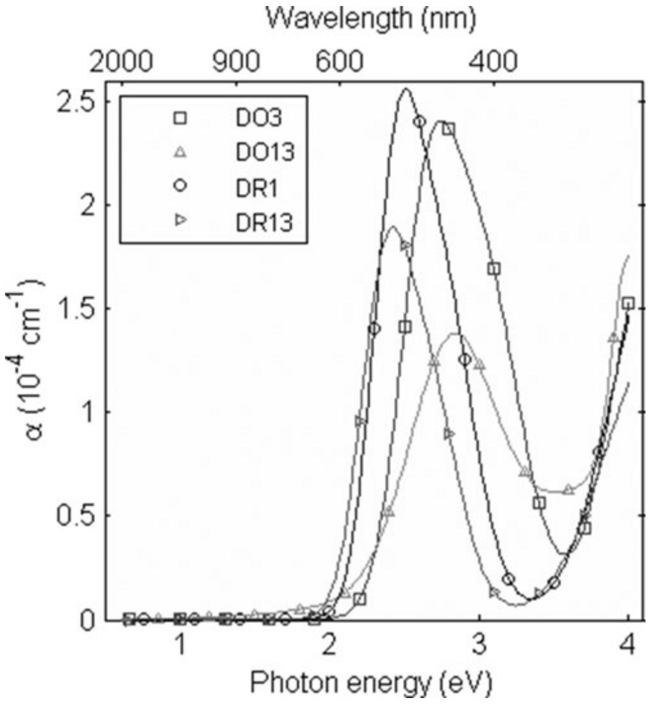

Figure 3. Absorption coefficient (α) of DR1, DR13, DO3 and DO13 thin films in PMMA matrix.

Figure 4 shows the refractive index (n) of DR1, DR13, DO3 and DO13 thin films in PMMA matrix obtained from spectroscopic ellipsometry (SE) measurements. SE yields information on the dispersion behavior of the real (n) and the imaginary (k) parts of the complex refractive index $\tilde{n}$. Parameters n and k are often referred to as refractive index and extinction coefficient [16, 17]:

$$\begin{cases} \tilde{n} = n + i\kappa \\ \kappa = \frac{\alpha\lambda}{4\pi} \end{cases} \tag{1}$$

where κ is the extinction coefficient, α is the absorption coefficient, λ is wavelength of light in vacuum. The real and imaginary parts of $\tilde{n}$ are related via the Kramers-Kronig relations and are associated with the absorption and the dispersion of the electromagnetic radiation respectively.

The refractive index (n) is a fundamental material property that is used in the design of optical devices. From Figure 4 we can see that the value of the refractive index for DR1 is the highest for all studied compounds in non-absorbing range (i.e. for $h\nu < 2$ eV, see Fig. 3). We can notice the following relationship in the case of value of the refractive index: $n_{\mathrm{DR1}} > n_{\mathrm{DR13}} > n_{\mathrm{DO3}} > n_{\mathrm{DO13}}$ in the spectral range 600–700 nm.

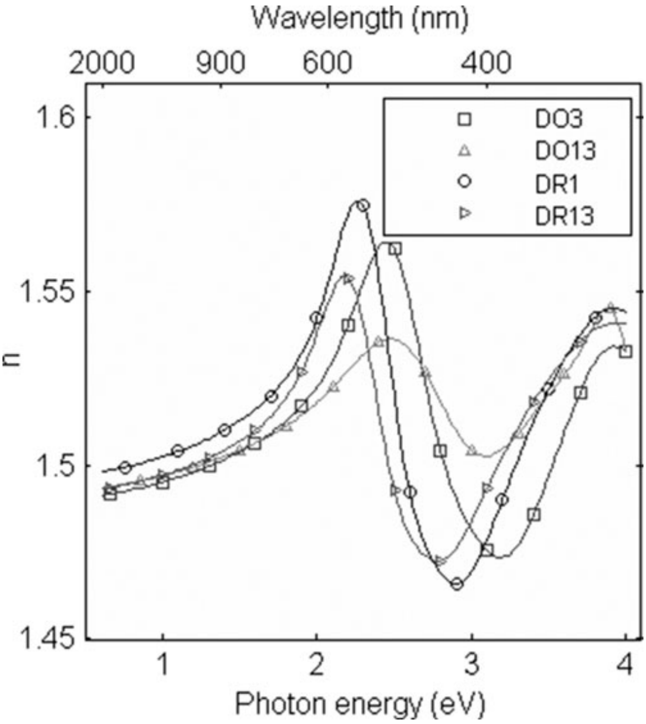

Figure 4. Refractive index (n) of DR1, DR13, DO3 and DO13 thin films in PMMA matrix.

We can also notice that the refractive indices of studied films decrease continuously as the wavelength increases thus displaying normal dispersion in the spectral range 600–2000 nm. This behaviour of n is typical for dielectrics for wavelengths longer than the absorption threshold [18–20].

To determine the optical energy band-gap (E_g) we used the Tauc method. Figure 5 presents the Tauc plot of studied compounds dispersed in PMMA. From the extrapolation of the linear part of dependence $(\alpha h\nu)^2$, which is plotted as a function of photon energy, we can determine the value of the optical energy band-gap of DR1, DR13 and DO3 thin films. Therefore, in the case of DR13 we can observe that adding Cl group into DR1 causes the shift of energy band-gap to a shorter energies compared to DR1 ($E_{g(\mathrm{DR1})} = 2.10$ eV $> E_{g(\mathrm{DR13})} = 2.01$ eV). Whereas, the changing amino group in DR1 causes the shift of E_g to a longer energies DO3 ($E_{g(\mathrm{DO3})} = 2.26$ eV). In the case of DO13 the band-gap energy can be estimated at about 2.2 eV ($E_{g(\mathrm{DO13})} \approx 2.2$ eV), however we could not precisely determine this optical energy band-gap due to the difficulty of matching a straight line to the experimental data (the Tauc plot in Fig. 5). The value of $E_{g(\mathrm{DO13})}$ cannot be treated as exact absorption-threshold. For energies below $E_{g(\mathrm{DO13})}$

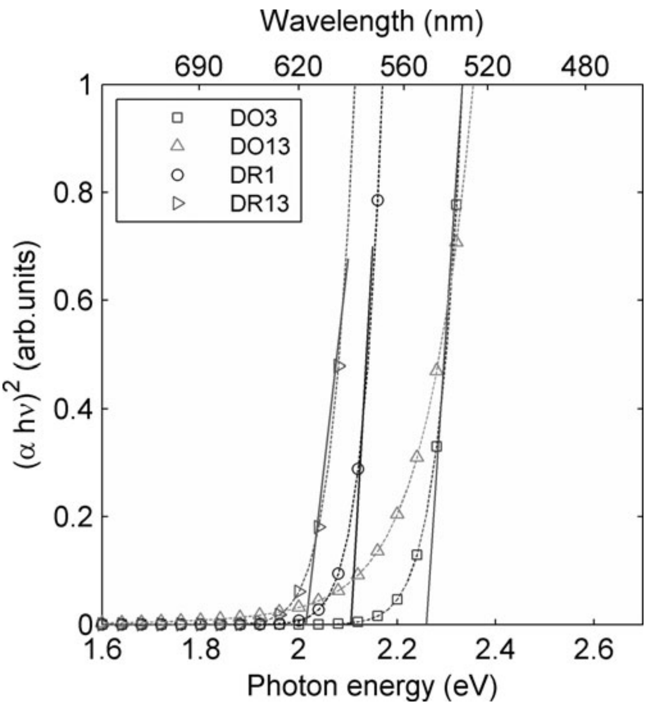

Figure 5. Tauc plot of DR1, DR13, DO3 and DO13 thin films in PMMA matrix.

the absorption coefficient is very low, however it is still higher than 0 (see Fig. 3). In turn, for energies above $E_{g(\mathrm{DO13})}$ the dramatic increase of α can be observed. Therefore, for DO13 the behavior of α can be explained as absorption associated with disazo structure (for $h\nu > E_{g(\mathrm{DO13})}$) and sub-bandgap absorption (for $h\nu < E_{g(\mathrm{DO13})}$). The existence of sub-bandgap absorption is also visible in the transmission spectra – T values decrease for energies below 2.2 eV (see Fig. 2).

4. Conclusions

The present study is an observation of the linear optical properties of guest-host system with different azobenzene dyes thin film. We observe that presence a chlorine substituent (Cl) in ortho position of benzene ring into DR1 causes the bathochromic shift of absorption spectrum. Whereas, we can observe the hypsochromic shift of absorption spectrum compare to DR1 when the molecule has primary amine group (DO3) or has two azo groups (DO13). Similar behavior is observed in the case of energy band-gap (E_g).

In the case of the refractive index we can notice that its value decreases (for select wavelength in the certain range) as follows: DR1 > DR13 > DO13 > DO3.

References

[1] Czaplicki, R., Krupka, O., Essaidi, Z., El-Ghayoury, A., Grote, J. G., Kajzar, F., & Sahraoui, B. (2007). *Optics Express*, *15*, 15268.

[2] Smokal, V., Derkowska, B., Czaplicki, R., Krupka, O., Kolendo, A., & Sahraoui, B. (2009). *Optical Materials*, *31*, 554.

[3] Smokal, V., Czaplicki, R., Derkowska, B., Krupka, O., Kolendo, A., & Sahraoui, B. (2007). *Synthetic Metals*, *157*, 708.

[4] Kajzar, F., Krupka, O., Pawlik, G., Mitus, A., & Rau, I. (2010). *Molecular Crystals and Liquid Crystals*, *522*, 180.

[5] Krupka, O., Derkowska, B., Czaplicki, R., Rau, I., El-ghayoury, A., Grote, J. G., Kajzar, F., & Sahraoui, B. (2007). *SPIE* 6470–13.

[6] Ubukata, T., Seki, T., & Ichimura, K. (2000). *Advanced Materials*, *12*, 1675.

[7] Ichimura, K. (2000). *Chemical Reviews*, *100*, 1847.

[8] Lagugne-Labarthet, F., Bruneel, J. L., Rodriguez, V., & Sourisseau, C. (2004). *The Journal of Physical Chemistry B.*, *108*, 1267.

[9] Getsova, M., Kircheva, V., Zaharieva, J., Manolov, I., Naruke, H., & Milanova, M. (2012). *Journal of Optoelectronics and Advanced Materials*, *14*, 685.

[10] Costela, A., Garcia-Moreno, I., Figuera, M., Amat-Guerri, F., & Sastre, R. (1998). *Laser Chemistry*, *18*, 63.

[11] J. A. Woollam Co., Inc., (2010). Guide to Using WVASE32, Wextech Systems Inc.; 310 Madison Avenue, Suite 905, New York, NY.

[12] Derkowska-Zielinska, B., Krupka, O., Wachowiak, A., Smokal, V., & Grabowski, A. (2015). *IEEE* 2015, 978-1-4673-7879-6/15.

[13] Derkowska-Zielinska, B., Skowronski, L., Kozlowski, T., Smokal, V., Kysil, A., Biitseva, A., & Krupka, O. (2015). *Optical Materials*, *49*, 325.

[14] Poprawa-Smoluch, M., Baggerman, J., Zhang, H., Maas, H. P. A., De Cola, L., & Brouwer, A. M. (2006). *The Journal of Physical Chemistry A*, *110*, 11926.

[15] Rau, H. (1990). In *Photochemistry and Photophysics*, Rabeck, F.J. (Ed.), Vol. II, Chapter 4, CRC, Boca Raton, FL, 119.

[16] Wojdyła, M., Derkowska, B., Bała, W., Bratkowski, A., & Korcala, A. (2006). *Optical Materials*, *28*, 1000.

[17] Skowronski, L., Krupka, O., Smokal, V., Grabowski, A., Naparty, M., & Derkowska-Zielinska, B. (2015). *Optical Materials*, *47*, 18.

[18] Skowronski, L., Trzcinski, M., Antończak, A., Domanowski, P., Kustra, M., Wachowiak, W., Naparty, M. K., Hiller, T., Bukaluk, A., & Wronkowska, A. A. (2014). *Applied Surface Science*, *322*, 209.

[19] Wronkowska, A. A., Skowroński, Ł., Wronkowski, A., Firszt, F., Męczyńska, H., Strzałkowski, K., & Arwin, H. (2008). *Physica Status Solidi A*, *205*, 854.

[20] Wronkowska, A. A., Arwin, H., Firszt, F., Wronkowski, A., & Skowroński, Ł. (2011). *Thin Solid Films*, *519*, 2795.