Second harmonic generation in polymers containing dithiosquarylium dye

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Polymer layers containing the dye 2,4-bis(1,3,3-trimethyl-2-indolinylidenemethyl)-1,4-dithiosquaraine display second-order nonlinear optical properties. Depending on conditions of preparation of the layers, the monomer form of the dye or the intermolecular charge transfer complex between two dye molecules are responsible for the second harmonic generation.

Key words: 2,4-bis(1,3,3-trimethyl-2-indolinylidenemethyl)-1,4-dithiosquaraine, poly(vinyl acetate), poly(vinyl ethylal), second harmonic generation, surface potential.

Polymer compositions are materials on the basis of which transmission media, active optical elements, and devices for duplication of laser radiation frequencies compatible with modern microelectronic instruments can be developed.

As known,[1–3] polarization ($P(E)$) of the medium occurs in the electric field of laser radiation $E(\omega)$, and donor-acceptor systems exhibit nonlinear effects:

$$P(E) = \chi^{(1)}E(\omega) + \chi^{(2)}E^2(\omega) + \chi^{(3)}E^3(\omega) + \ldots, \quad (1)$$

where $\chi^{(1)}E(\omega)$, $\chi^{(2)}E^2(\omega)$, and $\chi^{(3)}E^3(\omega)$ are volume polarizations; and $\chi^{(1)}$, $\chi^{(2)}$, and $\chi^{(3)}$ are polarizabilities of the first, second, and third orders, respectively. The $\chi^{(2)}$ and $\chi^{(3)}$ values are also named hyperpolarizabilities of the first and second orders. When the $E(\omega)$ vector changes direction to $-E(\omega)$, it can be obtain from Eq. (1) that in centrosymmetrical media, *i.e.*, where $P(+E) = -P(-E)$, the second-order susceptibility $\chi^{(2)} = 0$. Molecules with intramolecular charge transfer and the structure of D—(π-conjugation system)—A (D is a donor and A is an acceptor group) are noncentrosymmetrical. As a result, the $E(\omega)$ field induces anharmonic polarization, and the radiation of oscillating dipoles can be presented by the sum of Fourier components with frequencies ω, 2ω, 3ω, *etc.* The intensity (I) of the second harmonic (SH) measured experimentally is related to the susceptibility by the equation

$$I^{0.5}(2\omega) - \chi^{(2)} = P(2\omega)/E^2(\omega) = N\beta f^2(\omega)f(2\omega)\langle\cos^3\theta\rangle, \quad (2)$$

where N is the number of donor-acceptor groups in the polymer unit volume; $f(\omega) = [n^2(\omega) + 2]/3$ and $f(2\omega) = [n^2(2\omega) + 2]/3$ are dimensionless coefficients relating the external electric field and the internal electric field acting upon the molecule ($n(\omega)$ and $n(2\omega)$ are refractive indices of laser radiation with the main and doubled frequencies, respectively); and θ is the angle between the main axis of an individual molecule and perpendicular to the plane of the polymer layer. The molecular hyperpolarizability of the first order[1–4] is described by the equation

$$\beta(\equiv\beta_{CT}) = \frac{9e^2\hbar^2}{4m}\cdot\frac{W}{[W^2-(2\hbar\omega)^2][W^2-(\hbar\omega)^2]}f\Delta\mu, \quad (3)$$

where e and m are the electron charge and mass, respectively; $\hbar = h/(2\pi)$ (h is Planck's constant); W is the difference of energies between the ground state of the donor-acceptor system $\psi_0 = a\psi(D,A) + b\psi(D^+A^-)$ ($a > b$) and the charge transfer state $\psi(CT) = c\psi(D,A) + d\psi(D^+A^-)$ ($d > c$); $\Delta\mu$ is the difference between the dipole moments of the chromophore molecule in the ground and excited states; f is the strength of the oscillator of the optical charge transfer transition (see, *e.g.*, Ref. 5): $f = 4.32\cdot10^{-9}\varepsilon_{max}\Delta\nu_{1/2}$ (ε_{max} is the maximum extinction coefficient, and $\Delta\nu_{1/2}/\text{cm}^{-1}$ is the half-width of the charge transfer band); and $\hbar\omega$ and $2\hbar\omega$ are the energies of quantum of the main frequency (1064 nm) and SH, respectively.

In polymer compositions, due to disordered orientation of dissolved D—A molecules, the average value of $\langle\cos^3\theta\rangle$ in Eq. (2) is equal to 0. Noncentrosymmetry is created by the application to the polymer layer of the dc electric field E, which provides orientational polarization, *i.e.*, rotation of molecules resulting in the predominant arrangement of donor-acceptor groups along the field direction. In this case, the average value $\langle\cos^3\theta\rangle = \mu E/(5kT)$,[1] from where

$$I^{0.5}(2\omega) - \chi^{(2)} = Nf^2(\omega)f(2\omega)f_z(0)E[\beta\mu/(5kT) + \gamma], \quad (4)$$

where $f_z(0) = (\varepsilon + 2)/3$ (ε is the dielectric constant of the polymer matrix), and γ is the second-order molecular hyperpolarizability. This contribution of the third-

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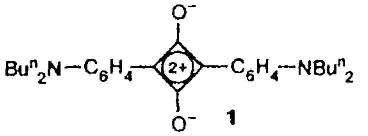
order nonlinearity is due to the action of fields $E \times E^2(\omega)$. Unlike the second-order polarizability, the dc electric field E does not exert an orientation effect, but polarizes the molecule without changing the direction of molecular axes.

The works[6–8] on studying the second-order susceptibility in Langmuir—Blodgett films of squarylium dyes have been published recently. The high $\chi^{(2)}$ value was established in films consisting of 2,4-bis[4-(*N,N*-dibutylamino)phenyl]squaraine molecules (**1**, for the monomeric form, λ_{max} = 656 nm).



$\mathrm{Bu^n_2N{-}C_6H_4{-}\overset{O^-}{\underset{O^-}{C_4^{(2+)}}}{-}C_6H_4{-}NBu^n_2}$

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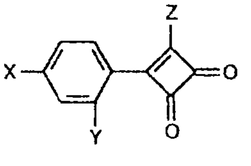
Comparison with the structural analysis data shows that the appearance of SH is due to the formation of noncentrosymmetrical intermolecular donor-acceptor complexes of the "T-form" in which the donor amino group of one molecule is oriented to the central four-membered acceptor fragment (—C_4O_2—) of another molecule. The optical absorption of these complexes corresponds to λ_{max} = 694 nm.



The nonlinear properties of organic crystals of substituted cyclobutynediones[9,10] with the nonsymmetrical structure were studied.

For these compounds, at X = Me_2N, Y = H, and Z = $NHCH_2CH(OH)Me$, the $\chi^{(2)}$ value obtained is 64 times higher than that of the urea crystal ($\chi^{(2)} \sim$ 3 pm V^{-1} at 1064 nm[10] and a thickness of 100 μm).

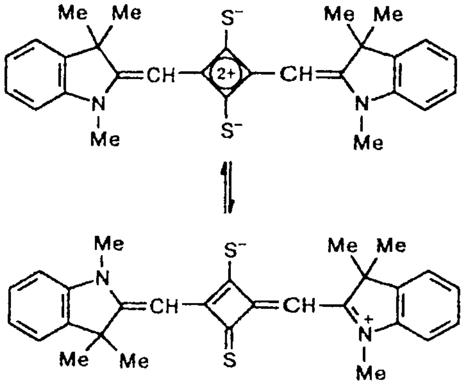
This work is devoted to the study of SH generation (SHG) of laser radiation by polymers containing the squarylium dye. We used the thiosquarylium dye (TSD) 2,4-bis(1,3,3-trimethyl-2-indolinylidenemethyl)-1,4-dithiosquaraine (**2**, Scheme 1), whose synthesis and spectral parameters have been discussed previously.[12,13]

It is known[14] that the Langmuir film of a similar indoline-containing squarylium dye (3) with O atoms instead of S in the central group is decomposed upon compression. This effect is explained by the nonplanar structure of molecule 3 due to the twist-turn of the indoline group about the HC—C bond (of the central square), which is characteristic of crystals of this dye[15] and induced by the mutual repulsion of O atoms and methyl groups. The enhancement of this repulsion on going to TSD **2** should be expected due to the great volume of the C=S group (19.7 Å^3)[16] as compared to that of C=O (5.85 Å^3).[16]

Experimental

Layers consisting of polymer matrices, poly(vinyl acetate) (PVA), poly(vinyl ethylal) (PVE), poly(vinyl chloride) (PVC), and cresol-formaldehyde novolac resin (NR), and additives of

Scheme 1



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TSD **2** were deposited on transparent electrodes of ITO by stretching out from a viscous solution in chloroform. For comparison, a layer of NR and TSD **2** was also deposited from a solution in acetone. Solvents (reagent grade) were additionally purified by distillation. Prior to measurements, layers were stored *in vacuo* for ~20 h at room temperature (freshly prepared layers).

The simplified scheme of measurement of SHG is presented in Fig. 1 (the detailed scheme is presented in Ref. 17). A sample consisting of a glass support, a grounded transparent electrode of ITO, and a supported polymer layer (*1*) was irradiated by single pulses of an Nd:YAG laser (*2*) (λ = 1064 nm, 50 mJ pulse^{-1}, a pulse duration was 15 ns, and a beam diameter was ~0.3 cm). The sample was placed at an angle of 45° to the laser beam direction. A portion of the laser radiation with the main frequency was directed through a light-dividing plate (*3*) to a photoamplifier and a digital voltmeter (*4*) to estimate the stability of the laser. The intensity of polymer layer-generated radiation with the wavelength of 532 nm (I_{532}/mV), which was picked out by an interferential light filter (*5*) at the wavelength $\lambda/2$ nm, was measured using a photoamplifier and a digital voltmeter. A negative potential was applied on the polymer layer surface by the corona discharge method: ionization of the gas upon application of a high voltage (from a source (*8*)) to a steel needle (*7*). This method is well developed in electrophotography.[18] The temperature of the sample was controlled by a heated nitrogen jet directed to the sample in a reservoir (*9*).

The surface potential and its decrease after switching off the high-voltage source was estimated in parallel experiments by measuring dark xerographic discharge curves. The negative charge was applied to the polymer layer surface within 10 s in a coronator. A potential close to the saturation potential was achieved within this time period. The sample was removed from the coronator into a measuring cell within less than 10 ms. The decrease in the surface potential in time was measured on a vibration-snap electrometer.

Optical spectra were recorded on a Beckman DU-7 spectrometer. The thickness of layers was measured on a MII-4 Linnek microinterferometer.

Results and Discussion

The changes in the second harmonic intensity, I_{532}, in the freshly prepared layer of PVA containing TSD **2** (sample A) under conditions of switching on and switching off the corona discharge (see Fig. 1) and upon increasing the measurement temperature are shown in Fig. 2, *a*. In the absence of TSD, the polymer matrices irradiate no SH. It is seen that the I_{532} value decreases to 0 when the orienting field E is switched off (in region *A*) and due to the increase in the temperature of the sample (in region *B*), and decreases gradually during measurement of SH. The curve of $(I/I_0)^{0.5}$ decrease in region *A* (Fig. 2, *a*) is compared in Fig. 2, *b* to the curve of surface potential (U/U_0) obtained under similar conditions. Here I_0 and U_0 are the initial values measured in the moment of switching off the corona discharge. At 18 °C, the surface potential is U_0 = 136 V (the layer thickness is 11 μm, hence, the orienting permanent field is E = 0.124 MV cm^{-1}). The similar run of these curves indicates that the decrease in SH is controlled by the decrease in the E field. The decrease in the $(I/I_0)^{0.5}$ value is compared in Fig. 2, *c* to the decrease in the surface potential U due to the increase in the temperature of the sample (see region *B* in Fig. 2, *a*). The activation energy of the temperature decrease in SH, $\Delta E = 0.2[\Delta(\log I^{0.5})]/[\Delta(10^3/T)] \approx 1$ eV, exceeds the activation energy of the decrease in the surface potential U (ΔE = 0.66 eV). The sharp decrease in SH and potential U begins near the glass transition temperature of the polymer ($T_g \approx$ 30—32 °C), from which we can conclude that the temperature decrease in SH intensity is determined, as shown below, by both the decrease in the content of the active form of the dye and the decrease in the surface potential.

It has been shown previously for poly(isobutyl methacrylate) containing the chromophore dimethylaminonitrostilbene[19] that traces of chloroform (the dipole moment of the molecule (μ) is 1.01 D) are retained in the freshly prepared layers. Under the action of the orienting field E, CHCl$_3$ molecules are selectively accumulated around dipolar chromophore molecules due to diffusion from the nonpolar polymer. As a result, a "heterogeneous" structure is formed, in which the internal electric field weakening the effect of the orienting

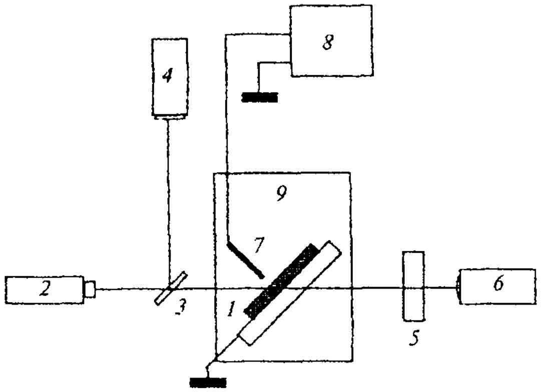

Fig. 1. Simplified scheme of measurement of SH of laser radiation with λ = 1064 nm: *1*, sample; *2*, Nd:YAG laser; *3*, light-dividing plate; *4*, *6*, photoamplifiers and digital voltmeters; *5*, interferential light filter at the wavelength λ/2 nm; *7*, steel needle; *8*, high-voltage source; and *9*, reservoir.

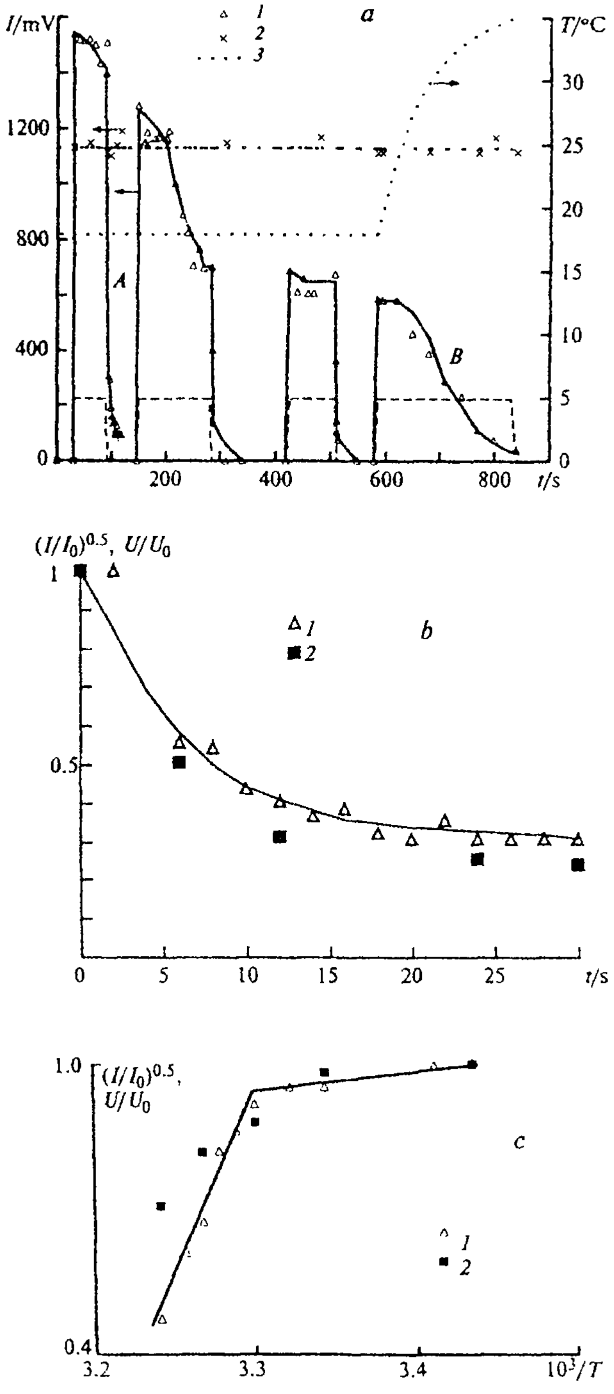

Fig. 2. *a*. Change in the second harmonic intensity I_{532} in sample A during orientational polarization (*1*); change in the signal of the main frequency I_{1064} in channel *3*—*4* Fig. 1 (*2*); and change in the temperature of the sample (*3*). Switching on and switching off the corona discharge are shown by the dashed line. *b*. Comparison of the decrease in $(I/I_0)^{0.5}$ (*1*) in region *A* in Fig. 2, *a* with a decrease in the surface potential (U/U_0) (*2*) after switching off the corona discharge. *c*. Temperature dependence of the decrease in $(I/I_0)^{0.5}$ in region *B* in Fig. 2, *a* (*1*) and surface potential U/U_0 (*2*).

field E is created around the chromophore, which results in a decrease in the SH intensity according to Eq. (4). In our system, this effect is disguised by the decrease in the optical density of chromophores. This is shown in Fig. 3, *a*, which presents the optical spectra of the starting freshly prepared sample **A** before measuring SH, after completion of the measurements (see Fig. 2), before the repeated measurement of SH after storage of sample **A** for 15 days (sample **A**^{1}), and after 30-day storage (sample **A**^{2}) before and after measurements of SH. The maximum of optical absorption of TSD **2** in freshly prepared samples corresponds to 662 nm. The spectra were recorded in the region of the corona discharge effect. As can be seen in Fig. 3, *a*, keeping the dc electric field and heating of the sample led to a decrease in the optical absorption density at 662 nm and appearance of a new band with a maximum at 637 nm and an additional long-wave shoulder in the region of 680—750 nm. During all transformations of the spectrum, the optical density at 590 nm remains unchanged. In the spectrum of dye **3** close in structure to TSD **2**, this band is assigned to dimers due to dipole-dipole interactions of central C—O groups, and the absorption with a maximum at 662 nm corresponds to the monomeric form of the dye.[14,20]

Figure 3, *b* shows the optical spectrum of the layer of PVA and TSD **2** (sample **B**) heated at 42 °C for 4 h, which before heating had the optical density in the maximum D_{662} = 0.75. As can be seen, heating results in the disappearance of the maximum at 662 nm, appearance of a band with a maximum at 637 nm, and a decrease in the optical density in the maximum to D_{637} = 0.2. The spectrum also exhibits a shoulder at 680—750 nm. In addition, Fig. 3, *b* presents the optical spectrum of the freshly prepared composition (sample **C**) consisting of the novolac resin and TSD **2** obtained from an acetone solution. (The low optical density is determined by a poor solubility of the dye in acetone.) It is seen that the spectrum contains bands assigned to the absorption of dimers in the 560—620 nm region and monomers with a maximum ~640 nm and a band in the region of 680—750 nm. This band can be compared to the long-wave absorption with a maximum at 694 nm in the Langmuir—Blodgett films of dye **1**.[6—8] This absorption, as mentioned above, is due to the formation of noncentrosymmetrical intermolecular complexes with the "T-form" responsible for efficient SHG.

The change in the second harmonic intensity in sample **B** during polarization in the dc electric field E and after its switching off differs considerably from that observed for the freshly prepared samples. As shown in Fig. 4, unlike the freshly prepared sample (see Fig. 2, *a*, *b*), after heating of the layer of PVA and TSD, the I_{532} value does not decrease, but increases somewhat during polarization, and the decrease in I_{532} becomes more prolonged after switching off the dc electric field.

The dependence of the maximum intensity $I^{0.5}$ on the optical density in the absorption maximum of the

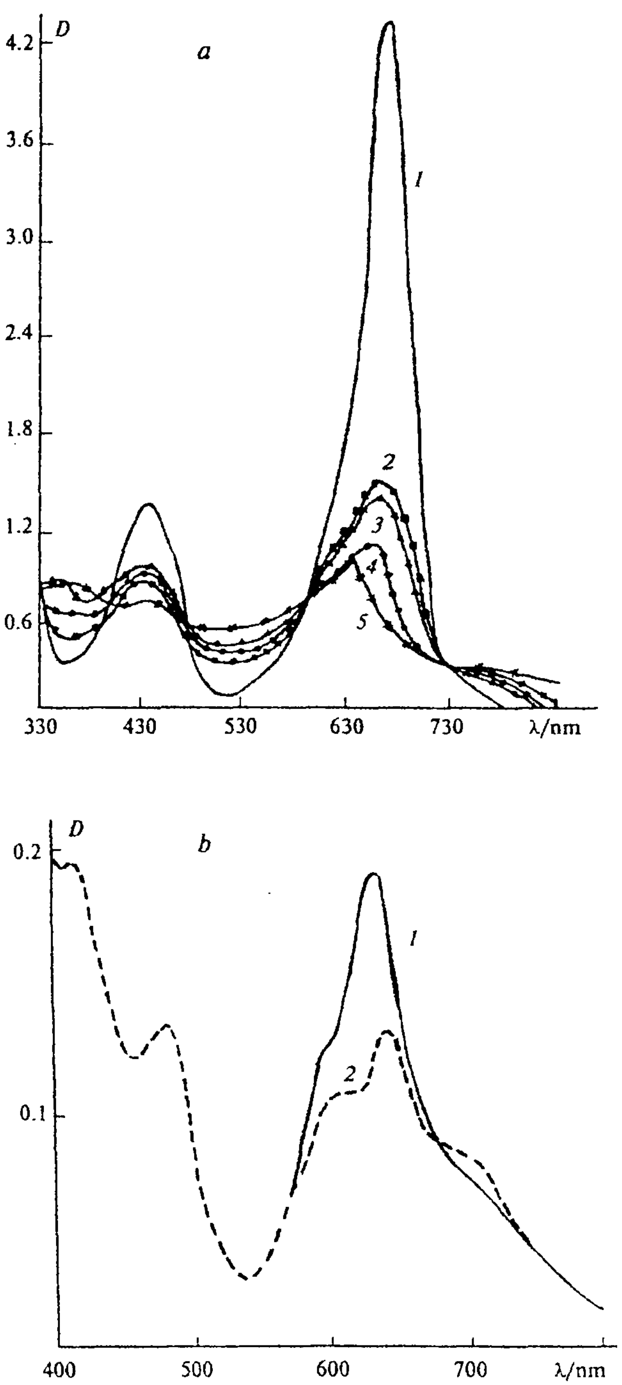

Fig. 3. *a*. Optical spectra of the starting freshly prepared sample **A** before measurement of SH (*1*); after completion of measurements illustrated in Fig. 2 (*2*), after 15-day storage of the sample (*3*), after 30-day storage (*4*) and after measurement of SH (*5*). *b*. Spectra of the layer of PVA and TSD **2** prepared from a solution in chloroform and heated at 42 °C for 4 h (sample **B**) (*1*) and a freshly prepared composition consisting of novolac resin and TSD **2** obtained from an acetone solution (sample **C**) (*2*).

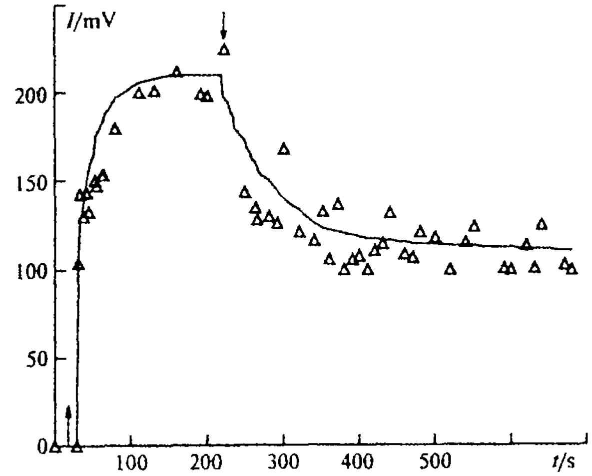

Fig. 4. Dependence of the second harmonic intensity I_{532} on the duration of orientational polarization in sample **B**. Switching on (↑) and switching off (↓) the corona discharge are shown by arrows.

freshly prepared samples is presented in Fig. 5 along with the $I^{0.5}$ values for samples **A**, **A**^{1}, and **A**^{2}. It is seen that for the samples with the predominant monomeric form of TSD **2**, a similar linear dependence of $I^{0.5}$ on the optical density in the absorption maximum of the dye in the region of $D_{662} < 2.4$ is observed for both freshly prepared layers and after a considerable decrease in D_{662} due to polarization, heating (see Fig. 2, *a*), and prolonged storage (within 15 and 30 days).

The linear dependence of $I^{0.5}$ on the optical density of the monomeric form of TSD **2** indicates that the optical transition at 662 nm is determined by the intramolecular electron transfer and, hence, the TSD form presented in the lower part of equilibrium in Scheme 1 predominates. It is established[21] by NMR spectroscopy that dye **1** forms, with chloroform, associates responsible for the bathochromic shift of the optical spectrum of the monomeric form. It can be assumed that the optical absorption of TSD **2** with λ_{max} = 662 nm is due to the formation of associates between the dye and $CHCl_3$, and the hypsochromic shift to 637 nm can be related to complete evaporation of solvent traces.

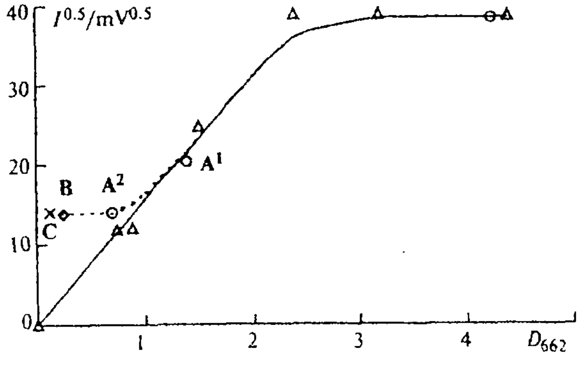

Fig. 5. Dependence of the maximum intensity $I^{0.5}$ on the optical density D_{662} in the absorption maximum of freshly prepared samples. The $I^{0.5}$ values of samples **A**, **A**^{1}, **A**^{2}, **B**, and **C** are shown (see text).

The $I^{0.5}$ values in samples **B** and **C** are presented in Fig. 5. As can be seen, they are close and exceed substantially the $I^{0.5}$ values corresponding to the run of the linear dependence $I^{0.5} \sim D_{662}$. Since the optical densities in the 680—750 nm region for samples **B** and **C** also have close values (see Fig. 3, *b*), it can be assumed that the above-mentioned intermolecular charge transfer complexes of the "T-form" responsible for this optical absorption make the main contribution to the second harmonic.

When the layers are obtained from a solution in chloroform with replacement of PVA by PVE, PVC, and NR, both the position of the maximum in the optical spectrum in the freshly prepared samples (λ_{max} = 662 nm) and its hypsochromic shift upon heating accompanied by a decrease in the optical density are retained. In all polymer matrices, when the temperature increases, SH decreases sharply to zero in the region of T_g. The next decrease in the temperature to values $< T_g$ results in the appearance of SH, whose intensity is lower than the initial one and proportional to the optical density at 662 nm. The specific features of SH generation by TSD **2** molecules in the PVE matrix are shown in Fig. 6. The measurements were carried out 18 h after 2-s polarization of the sample in the dc electric field E at room temperature. The presence of SH at the beginning of measurements without the electric field indicates that orientational ordering of dye molecules due to preorientation in the electric field E is retained in this matrix. Figure 6 shows the subsequent increase in I_{532} both upon switching on the E field and during orientation of TSD molecules at increased temperatures. A sharp decrease in I_{532} is observed when the temperature approaches T_g (68 °C). After orientation at increased temperatures, the SH signal was also observed in the absence of the electric field during ~30 days.

These changes in the SH parameters on going from PVA to PVE can be related to the dependence of the rate of rotational diffusion of TSD **2** molecules on the nature of the polymer matrix. According to the concept of free volume, the movement of a molecule in amorphous media becomes possible in the case where a microcavity whose volume (V_{mc}) exceeds that of a diffusing molecule appears near a diffusing molecule due to the thermal redistribution of the free volume. The molecular volume (V_{in}) calculated by the increment method[16] for TSD is equal to 340 Å^3, which corresponds to the van der Waals volume of ~0.14 cm^3 in 1 cm^3 of polymer at the concentration of 0.06 mol dm^{-3} (D_{662} = 4, the thickness of the sample is 7 μm, ε_{max} = $0.95 \cdot 10^5$ dm^3 mol^{-1} cm^{-1}). In PVA, the free volume at room temperature is ~0.35 cm^3 in 1 cm^3 of polymer.[16] The free volume of PVE calculated without taking into

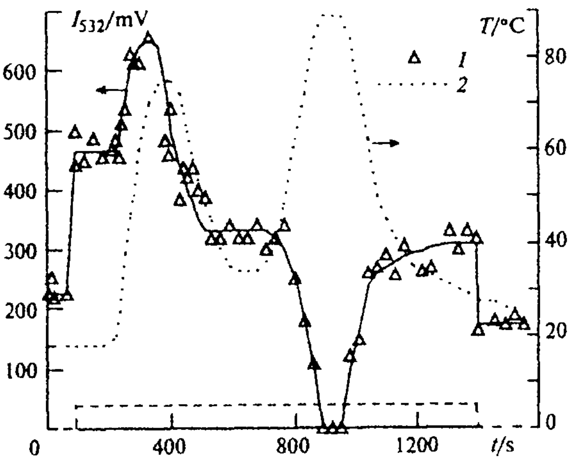

Fig. 6. Change in the I_{532} value (*1*) in TSD **2** in the PVE matrix under the action of the electric field and changing the temperature of the sample (*2*). Switching on and switching off of the corona discharge are shown by the dashed line.

account the formation of hydrogen bonds is close to this value. However, PVE contains vinylethylal (79—83 mol.%) and vinyl-alcohol units (~18—14 mol.%), which can form intermolecular hydrogen bonds and thus restrict the volume of an individual microcavity V_{mc}. Most likely, this is the reason why orientation of TSD molecules in PVE is "frozen" after heating in the orienting field E, and SH is observed for a long time and in the absence of polarization in the dc electric field.

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Thus, it is shown in this work that polymer layers containing TSD exhibit second-order nonlinear optical properties. The TSD molecules oriented in the dc electric field E are responsible for generation of second harmonic (532 nm) of laser radiation with the fundamental frequency of 1064 nm. The TSD molecules exist, depending on conditions of layer preparation, either in the monomeric form with optical absorption at λ_{max} = 662 nm, or as intermolecular complexes having absorption in the region of 680—750 nm. In the PVA layers, the kinetics of SH relaxation is determined completely by the kinetics of the decrease in the dc electric field. Unlike PVA, in the PVE matrix containing vinylethylal and vinyl-alcohol units, SH and, hence, ordered orientation of TSD molecules are retained for a long time after the action of the electric field E ceased. This occurs most likely due to the formation of hydrogen bonds, which restrict the volume of microcavities of polymer and thus decrease the rate of disordering of dye molecules.

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References

1. D. M. Burland, R. D. Miller, and C. A. Walsh, *Chem. Rev.*, 1994, **94**, 31.
2. G. A. Lindsay, *Trends Polym. Sci.*, 1997, **5**, 91.
3. A. V. Vannikov, A. D. Grishina, R. W. Rychwalski, and A. T. Ponomarenko, *Usp. Khim.*, 1998, **67**, 507 [*Russ. Chem. Rev.*, 1998, **67**, 451 (Engl. Transl.)].
4. J. F. Nicoud and R. J. Twieg, in *Nonlinear Optical Properties of Organic Molecules and Crystals*, Eds. D. S. Chemla and J. Zyss, Academic Press, New York, 1987, Ch. 4.
5. J. G. Calvert and J. N. Pitts, *Photochemistry*, Wiley, New York, 1965, Ch. 3.
6. G. J. Ashwell, G. Jefferies, D. G. Hamilton, D. E. Lynch, M. P. S. Roberts, G. S. Bahra, and C. R. Brown, *Nature*, 1995, **375**, 385.
7. G. J. Ashwell, *Adv. Mater.*, 1996, **8**, 248.
8. G. J. Ashwell, G. S. Bahra, C. R. Brown, D. G. Hamilton, C. H. L. Kennard, and D. E. Lynch, *J. Mater. Chem.*, 1996, **6**, 23.
9. G. Seitz and P. Imming, *Chem. Rev.*, 1992, **92**, 1227.
10. L. S. Pu, *J. Chem. Soc., Chem. Commun.*, 1991, **6**, 429.
11. J.-M. Halbout and C. L. Tang, in *Nonlinear Optical Properties of Organic Molecules and Crystals*, Eds. D. S. Chemla and J. Zyss, Academic Press, New York, 1987, Ch. 7.
12. V. V. Kurdyukov, M. A. Kudinova, and A. I. Tolmachev, *Fizika i khimiya polimetinovykh krasitelei, Tez. dokl.* [*Physics and Chemistry of Polymethine Dyes, Abstrs.*], Moscow, 1996, 18 (in Russian).
13. S. H. Kim, S. K. Han, J. J. Kim, and S. H. Hwang. *Syntheses, Optical Properties, and Applications of Near-Infrared Dyes in High Technology Fields. NATO Advanced Research Workshop*, Czech Republic, 1997, P-16.
14. K.-Y. Law and C. C. Chen, *J. Phys. Chem.*, 1989, **93**, 2533.
15. Y. Kobayashi, M. Goto, and M. Kurahashi, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 311.
16. A. A. Askadskii and Yu. I. Matveev, *Khimicheskoe stroenie i fizicheskie svoistva polimerov* [*Chemical Structure and Physical Properties of Polymers*], Khimiya, Moscow, 1983, Ch. 4 (in Russian).
17. A. V. Vannikov, K. Klason, E. I. Mal'tsev, R. W. Rychwalski, and V. V. Savel'ev, *Vysokomol. Soedin. A*, 1997, **39**, 1038 [*Polymer Sci. Russ., Ser. A*, 1997, **39**, 705 (Engl. Transl.)].
18. P. M. Borsenberger and D. S. Weiss, *Organic Photoreceptors for Imaging Systems*, Marcel Dekker, New York, 1993, Ch. 1.
19. S. Schüssler, R. Richert, and H. Bässler, *Macromolecules*, 1995, **28**, 2429.
20. M. Matsumoto, T. Nakamura, M. Tanaka, T. Sekiguchi, H. Komizu, S. Y. Matsuzaki, E. Manda, Y. Kawabata, M. Saito, S. Iizima, and M. Sugi, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 2737.
21. K.-Y. Law, *J. Phys. Chem.*, 1989, **93**, 5925.
22. V. G. Rostiashvili, V. I. Irzhak, and B. A. Rozenberg, *Steklovanie polimerov* [*Vitrification of Polymers*], Khimiya, Leningrad, 1987, 190 pp. (in Russian).

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