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Generation of the second harmonic of laser radiation in noncentrosymmetrical polymeric systems

A V Vannikov, A D Grishina, R W Rychwalski, A T Ponomarenko

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Abstract. Second-order nonlinear optical properties in polymeric media and the mechanisms of generation and relaxation of the second harmonic of a polarised laser beam are discussed. The relationships between the chemical structures of the polymeric systems and the transport characteristics of the charge carriers are considered and the influence of the captured charges on the parameters of the second harmonic relaxation are analysed. It is shown that the kinetics of second harmonic relaxation in the polymeric systems of the host – guest type is determined entirely by the decay kinetics of the surface potential. The bibliography includes 98 references.

I. Introduction

Optical second harmonic generation (SHG) consists in the medium assisted transformation of two photons with the frequency ω into one photon with the frequency 2ω. The generation of the second harmonic (SH) results from the dispersion of light in the medium and occurs under the action of polarised laser radiation, as a rule, in the spectral range of polymer transparency where both single- and multi-photon absorption by the medium are absent. This range corresponds to the radiation of the near-IR lasers. Physicochemical basis of SHG is considered in detail in several monographs [1–4] and reviews [5–8] and numerous papers. Preparation of polymeric systems with nonlinear optical properties that are used for SHG requires first of all that an oriented molecular structure was formed. These structures are produced under the action of an external electric field. The charges left after the electric field is switched off determine in some cases kinetic characteristics of SHG.

A V Vannikov, A D Grishina A N Frumkin Institute of Electrochemistry, Russian Academy of Sciences, Leninskii prosp., 31, 117071 Moscow, Russian Federation. Fax (7-095) 952 08 46. Tel. (7-095) 952 24 28. E-mail: vanlab@glas.apc.org (A V Vannikov)
R W Rychwalski Chalmers University of Technology, S-41296 Gothenburg, Sweden. Fax (31) 772 38 72
A T Ponomarenko Institute of Synthetic Polymeric Materials, Russian Academy of Sciences, ul. Profsoyuznaya 70, 117393 Moscow, Russian Federation. Fax (095) 420 22 29

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This review is devoted to the analysis of the influence of captured charges in polymers on the characteristics of the SH relaxation. Some general information on the mechanism of the SH generation and relaxation in polymeric media is considered at the beginning of the paper.

The SHG phenomenon is caused by the nonlinear polarisability of conjugated molecules containing donor and acceptor *para*-substituents when the electric field is applied. It is known that a dipole moment is induced in a molecule placed in the electric field E

$$\vec{p} = \mathrm{e}x = \alpha E \cos\theta \,, \tag{1}$$

where e is the electronic charge, x is the displacement of a bound electron in the electric field, α is the polarisability, θ is the angle between the direction of the electric field and the induced dipole moment. In the rectilinear coordinates, the projections of the vector $\vec{p}$ are equal to

$$p_i = \alpha_{ix}E_x + \alpha_{iy}E_y + \alpha_{iz}E_z \,, \quad i = x, y, z \,, \tag{1a}$$

where α_{ij} is the coefficient of linear polarisation along the axis i with electric field acting along the axis j; this is a second rank tensor or the tensor of linear polarisability

$$\alpha_{ij} = \begin{vmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{vmatrix}$$

Macroscopic polarisation (P) per unit volume of a substance containing N chromophore molecules along the direction of the applied field is the sum of the projections of dipole moments for each individual molecule onto this direction under conditions of dipole – dipole interaction. Under the action of the laser radiation, nonlinear effects along with linear dependence $P = \chi^{(1)}E$ take place in donor – acceptor systems

$$P = \chi^{(1)}E + \chi^{(2)}EE + \chi^{(3)}EEE + \ldots \,. \tag{2}$$

Here $\chi^{(1)}E$, $\chi^{(2)}EE$, and $\chi^{(3)}EEE$ are the polarisations, and $\chi^{(1)}$, $\chi^{(2)}$, $\chi^{(3)}$ are the susceptibilities of the first, second, and third order, respectively. The nonlinear terms, $\chi^{(2)}EE$ and $\chi^{(3)}EEE$, are also called hyperpolarisabilities of the second and third orders.

Under the action of a monochromatic electromagnetic wave $E(\omega) = E_1\cos(\omega t) = 0.5E_1(\mathrm{e}^{i\omega t} + \mathrm{e}^{-i\omega t})$, dipoles oscillating with a frequency ω in small fields appear provided $P(\omega) \approx \omega^{(1)}E_1\cos(\omega t)$. The donor – acceptor systems discussed below exhibit nonlinear

response to laser radiation, which is caused by the nonlinear electronic polarisation

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

or

$$P(\omega) = \chi^{(1)}E_1\cos(\omega t) + 0.5\chi^{(2)}E_1^2\cos(2\omega t) + \quad (3a)$$

$$+ 0.5\chi^{(2)}E_1^2 + \frac{\chi^{(3)}}{4}E_1^3[\cos(3\omega t) + 3\cos(\omega t)] + \ldots$$

The expressions for the nonlinear polarisation in media with symmetrical polarisability with respect to the inversion centre, where $P(+E) = -P(-E)$, cannot contain even terms, *i.e.*, $\chi^{(2)} = 0$ in Eqns (3) and (3a). In such media, nonlinear effects are caused by the third order polarisation. The second-order polarisation is induced in noncentrosymmetrical systems, where $P(+E) \neq -P(-E)$. According to the formula (3), the nonlinear response of a centrosymmetrical system causes the generation of the third harmonic (3ω) of the fundamental frequency of the laser radiation. In a noncentrosymmetrical medium, the radiation spectrum of the assembly of the oscillating dipoles contains a second harmonic caused by the second order nonlinear polarisation

$$P(2\omega) = 0.5\chi^{(2)}E_1^2\cos(2\omega t)\,. \quad (3b)$$

The anharmonic character of the polarisation induced by the polarised light $E(\omega)$ is illustrated in Fig. 1.[1,8] The polarisation along a donor–acceptor molecule D–B–A (D is the donor fragment, B is the bridging spacer group with the system of conjugated π-bonds, A is the acceptor fragment) is caused by the fact that the charge displacement from A to D is smaller than in the opposite direction. In this case, an expression for the polarisation is represented by a Fourier series. The terms of the series possess the frequencies ω, 2ω ... 0 (see Fig. 1).

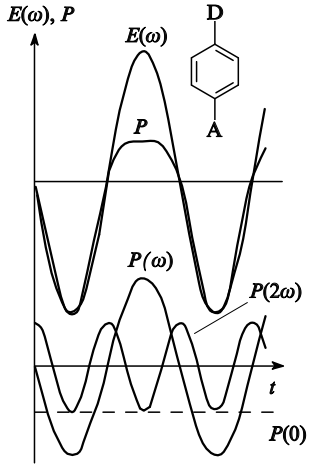


Figure 1. Polarisation (P) in a molecule D–B–A induced along the direction from A to D by the electric field $E(\omega)$ of a light wave (upper x axis) and the expansion of $P(\omega)$ as a Fourier series with the frequencies 2ω,ω, and 0 (bottom x axis).

$$P = P(\omega) + aP(2\omega) + \ldots + вP(0)\,.$$

The dipole oscillations with the frequency 2ω (second term of the series) induce the generation of the second harmonic 2ω under the action of the fundamental frequency ω.

II. The relationship between microscopic and macroscopic polarisation

The dipole polarisation of an isolated chromophore molecule in a linear range can be written as follows [see formula (1a)]

$$p_i(\omega) = \alpha_{ij}(\omega)E_j(\omega)\,.$$

Here i and j are the molecular coordinates that fix the orientation of the induced dipole moment $p_i(\omega)$ and the direction of the electric field $E_j(\omega)$, respectively. In the range of the appearance of the nonlinear effects, the expression for the dipole polarisation takes the form

$$p_i(\omega) = \alpha_{ij}(\omega)E_j(\omega) + \beta_{ijj}(-2\omega,\omega,\omega)E_j(\omega)E_j(\omega) + \quad (4)$$

$$+ \gamma_{ijjj}(-3\omega,\omega,\omega,\omega)E_j(\omega)E_j(\omega)E_j(\omega) + \ldots$$

Here $\beta_{ijj}(-2\omega,\omega,\omega)$ and $\gamma_{ijjj}(-2\omega,\omega,\omega)$ are the polarisabilities of the second and third orders or hyperpolarisabilities of the second and third orders (the coefficients β_{ijj} and γ_{ijjj} are the tensors of the third and fourth rank), respectively.

In the macroscopic coordinates XYZ, the macroscopic polarisation of a dielectric, *e.g.*, in the direction Z, is determined by the local internal field $F_Z(\omega)$, which is linked with the external field by the expression

$$F_Z(\omega) = E_Z(\omega) + \frac{4\pi}{A}P_Z(\omega) = E_Z(\omega)\left[1 + \frac{4\pi}{A}\chi_{ZZ}^{(1)}(\omega)\right],$$

where A is a coefficient depending on the system geometry: for sphere $A = 3$, for ellipsoids of polarisation this factor is tabulated and can be found in the reference books. Using the relationship between the dielectric constant $\varepsilon_Z(\omega)$ and the susceptibility

$$\varepsilon_Z(\omega) = 1 + 4\pi\chi_{ZZ}^{(1)}(\omega)\,,$$

the expression in square brackets can be written in the form[5]

$$\mathrm{f}_Z(\omega) = 1 + \left[\frac{\varepsilon_Z(\omega) - 1}{A}\right] \quad (5)$$

and

$$F_Z(\omega) = \mathrm{f}_Z(\omega)E_Z(\omega)\,. \quad (5a)$$

If $A = 3$, then

$$\mathrm{f}_Z(\omega) = \left(\frac{\varepsilon_Z(\omega) + 2}{3}\right), \quad (5b)$$

where $\varepsilon_Z(\omega) = n^2(\omega)$, and $n(\omega)$ is the refractive index for the fundamental frequency. It thus follows that the linear polarisation can be represented by the relation [see also formula (1)]

$$P_Z(\omega) = N\alpha_{ij}\mathrm{f}_Z(\omega)E_Z(\omega)\langle\cos\theta_{Zi}\rangle\,.$$

Thus, the first-order susceptibility is linked with the linear polarisability of an individual molecule α_{ij} by the relation

$$\chi_{ZZ}^{(1)}(\omega) = N\alpha_{ij}\mathrm{f}_Z(\omega)\,\langle\cos\theta_{Zi}\rangle\,. \quad (6)$$

Consequently, the second-order macro-scopic polarisation is linked with β_{ijj} by the relation

$$P_Z(2\omega) =$$

$$= N\beta_{ijj}E_Z(\omega)\mathrm{f}_Z(\omega)\langle\cos\theta_{Zi}\rangle E_Z(\omega)\mathrm{f}_Z(\omega)\langle\cos\theta_{Zi}\rangle\mathrm{f}_Z(2\omega)\langle\cos\theta_{Zi}\rangle,$$

where $\mathrm{f}_Z(2\omega)$ is determined according to the formula (5b) at the frequency 2ω.

The second-order polarisability along the direction of the macroscopic axis Z, which is averaged along all orientations of the individual molecules D–B–A, is determined by the expression

$$\beta_i = \beta_{iii} + \tfrac{1}{3}\left[\sum(\beta_{ijj} + \beta_{jij} + \beta_{jji})\right].$$

The molecules D–B–A are chromophores, since they contain donor and acceptor groups, and a conjugated chain; they absorb visible light. Below we call these molecules nonlinear optical NLO-chromophores or just chromophores.

A component of the second-order susceptibility along the direction Z is determined by the polarisability β_i according to the relation

$$\chi^{(2)}_{ZZZ} = \\ = N\beta_i(-2\omega,\omega,\omega)f_Z(\omega)\langle\cos\theta_{Zi}\rangle f_Z(\omega)\langle\cos\theta_{Zi}\rangle f_Z(2\omega)\langle\cos\theta_{Zi}\rangle,$$

i.e., in a quasi one-dimensional molecule (in which dipole moment is directed along the axis of symmetry and the β_{iii} dominates)

$$\chi^{(2)}_{ZZZ} = N\beta_{iii}(-2\omega,\omega,\omega)f^2_Z(\omega)f_Z(2\omega)\langle\cos^3\theta_{Zi}\rangle\,, \quad (7)$$

$$\chi^{(2)}_{ZXX} = \chi^{(2)}_{ZYY} = \quad (7a)$$

$$= \frac{1}{2}N\beta_{iii}(-2\omega,\omega,\omega)f^2_Z(\omega)f_Z(2\omega)(\langle\cos\theta_{Zi}\rangle - \langle\cos^3\theta_{Zi}\rangle).$$

III. The polarisability of polymeric donor-acceptor systems

Doubling of the laser radiation frequency was observed for the first time for quartz crystals [9] ($d_{33} = 0.5$ pm V^{-1})†. Nowadays, a large number of inorganic crystals that generate the SH of the fundamental frequency of the laser radiation are known. However, of special interest are polymeric systems as that it is in these media the maximum intensities of the SH corresponding to $d_{33} = 200$ pm V^{-1} are obtained. Organic polymers are processable and blend well with integrated film optical systems.

Polymeric matrices containing low-molecular-weight chromophores and polymers containing chromophores in the side groups or in the main chain belong to the polymeric media that include D–B–A chromophores.[1,5] It is essential that these molecules possess dipole moments in the ground state. As a rule, the initial polymeric films are disordered and, consequently, are centrosymmetrical systems. Intensive studies of the second harmonic generation in the polymeric donor–acceptor systems began after 1979,[10–12] when an earlier developed rather simple method for transformation of the centrosymmetrical systems into noncentrosymmetrical ones due to predominant orientation of the dipole chromophore molecules under the action of a constant electric field at the glass transition temperature T_g was applied to the polymers (see references cited in the Ref. 6). A decrease in the temperature of such orientational poling in a constant field down to 20 °C and below can be achieved if the polymer layer is plasticised by the introduction of the CO_2 under high pressure. After polarisation the CO_2 is removed by the evacuation, and the polymer is restored its to initial glassy state that is now polarised.[13]

When the constant field E is applied, the potential energy of a molecule with the dipole moment μ is changed by the quantity

$$U(\theta) = -\mu F\cos\theta\,,$$

where $F = Ef(0)$, $f(0) = (1/3)(\varepsilon + 2)$ [*cf.* formulas (5) and (5a)] and ε is the dielectric constant of the polymeric matrix. According to the Boltzmann distribution law the number of particles oriented at an angle θ to the direction of the field E is proportional to $\exp(-U(\theta)/kT)$ and the mean values of $\langle\cos^n\theta\rangle$ are determined according to the formula

$$\langle\cos^n\theta\rangle \equiv L_n\left(\frac{\mu F}{kT}\right) = \frac{\int_0^\pi \{\exp[(-\mu F\cos\theta)/kT]\cos^n\theta\cdot\sin\theta\}\,d\theta}{\int_0^\pi \{\exp[(-\mu F\cos\theta)/kT]\sin\theta\}\,d\theta},$$

† The second harmonic nonlinear coefficient $d_{ZZ} = 0.5\chi^{(2)}_{ZZZ}$ is often used as the SHG characteristics in equations (3a) and (3b). In the studies that are aimed at practical application, the symbols 123 are used, as a rule, instead of XYZ for the designation of the nonlinear coefficient coordinates; *i.e.*, $d_{ZZ} \equiv d_{33}$.

representing the Langevin functions $L_n(\mu F/kT) \equiv L_n(u)$. This function is represented [1] in the form of the Legendre polynomial $L_n(u)$, where $u = \mu F/kT$ when the mean values of $\langle\cos^n\theta\rangle$ are calculated. For $n = 1$,

$$L_1(u) = \frac{u}{3} - \frac{u^3}{45} + \ldots \simeq \frac{u}{3}\,,$$

Hence, in the first approximation $\langle\cos\theta\rangle \approx \mu F/3kT$ in the relation (6). For $n = 3$,

$$L_3(u) = \left(1 + \frac{6}{u^2}\right)L_1(u) - \frac{2}{u} + \ldots = \\ = \left(1 + \frac{6}{u^2}\right)\left(\frac{u}{3} - \frac{u^3}{45} + \ldots\right) - \frac{2}{u} + \ldots \simeq \frac{u}{5}\,,$$

i.e., $\langle\cos^3\theta\rangle \approx \mu F/5kT$ in the relation (7).

Thus,

$$\chi^{(2)}_{ZZZ} = N\beta_{iii}(-2\omega,\omega,\omega)f^2_Z(\omega)f_Z(2\omega)f_Z(0)\frac{\mu E}{5kT} \quad (7b)$$

and

$$\chi^{(2)}_{ZXX} = \chi^{(2)}_{ZYY} = \frac{1}{3}\chi^{(2)}_{ZZZ}\,.$$

If a constant electric field E is applied the second harmonic may contain a contribution of the third-order nonlinearity

$$\Delta P(2\omega) = N\gamma(-2\omega,\omega,\omega,0)f_Z(2\omega)E^2_Z(\omega)f^2_Z(\omega)Ef(0),$$

where $N\gamma(-2\omega,\omega,\omega,0)f_Z(2\omega)f^2_Z(\omega)f(0)$ is the contribution of the third-order susceptibility.

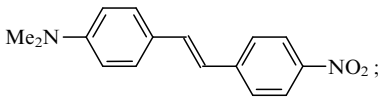
In this case, the constant electric field E excites rather than orients the molecule. Thus,[14]

$$\chi^{(2)}_{ZZZ} = NE_Zf(0)f_Z(2\omega)f^2_Z(\omega)[\beta_{iii}(-2\omega,\omega,\omega)\frac{\mu E}{5kT} + \quad (7c)$$

$$+ \gamma(-2\omega,\omega,\omega,0)]\,.$$

The contribution of the third-order nonlinearity expressed by the term $\gamma(-2\omega,\omega,\omega,0)$ appears and disappears simultaneously as the constant electric field E is switched on and off irrespective of the degree of orientation of the chromophores.

Considerable attention is paid to the D–B–A chromophores such as *para*-substituted stilbenes, where B is $-C_6H_4-CH=CH-C_6H_4-$, for example, 4-dimethylamino-4′-nitrostilbene (DANS),



arylamines, where B = $-C_6H_4-$, polyconjugated systems with B = $-C_6H_4(CH=CH)_n-C_6H_4$ ($n \geqslant 2$), $C_6H_4-N=CH-C_6H_4$ or $C_6H_4-N=N-C_6H_4$, *etc.* *J*-Aggregates of dyes are also effective chromophores.[15]

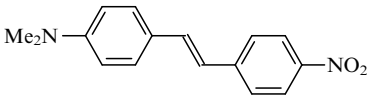
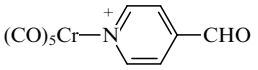
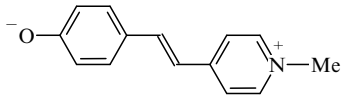
For the molecules D–B–A it is established [16,17] that the second-order polarisability β can be represented in the form of two terms

$$\beta = \beta_{ad} + \beta_{ct}\,,$$

where β_{ad} is the additive part resulting from the interaction between the substituents and the systems of conjugated bonds, and β_{ct} is the contribution for which the donor–acceptor interaction is responsible. As the molecular structure in the case of full charge transfer from D to A corresponds to the structure of the excited molecule then according to the concepts developed in the publications [5–8,16–24]

$$\beta_{ct} = \frac{3e^2h^2}{2m}\,\frac{W}{[W^2 - (2h\omega)^2][W^2 - (h\omega)^2]}\,f\Delta\mu_{ex}\,, \quad (8)$$

Table 1. β Values for the chromophores with different relationships between μ_e and μ_g.

Chromophore	Relationship between μ_e and μ_g	μ_g /D	μ_e /D	$10^{-30}\beta$ /cm^5 C^{-1}
	$\mu_e > \mu_g$	+9.85	+23.5	+73
	$\mu_e \simeq \mu_g$	+7.84	−10.5	−12
	$\mu_e < \mu_g$	+22.6	+13.7	−100

Note. Signs + and − denote the direction of the vectors $\vec{\mu}$ and $\vec{\beta}$ in chromophore.[8]

where h is the Planck constant, m is the mass of an electron, W is the distance between the ground-state level and the first excited level of an intramolecular DA-complex, ω is the fundamental frequency of the laser radiation, f is the oscillator strength for the transition from the ground state to the excited state, $\Delta\mu_{ex} = -\mu_e - \mu_g$ is the difference in dipole moments of the DA-complex in the ground state and excited state, respectively.

It follows from formula (8) that weak ($\mu_e \gg \mu_g$) and weak 'reverse' complexes ($\mu_e \ll \mu_g$), where the electron transfer is only possible in one direction from D to A or from $A^{-\bullet}$ to $D^{+\bullet}$, respectively should exhibit the highest nonlinearity. On going to the molecules $D^{\delta+}A^{\delta-}$ with the degree of transfer $\delta \simeq 0.5$, $\mu_e \approx \mu_g$, the charge displacement in both directions is possible where upon application of the electric field, one should expect the weakening of nonlinear characteristics. Indeed, when the weak complexes ($\mu_e < \mu_g$) are replaced by molecules with close values of μ_e and μ_g, the contribution of β_{ct} decreases drastically, but on going to the reverse complexes ($\mu_e > \mu_g$) this contribution increases considerably (Table 1).

The oscillator strength f is proportional to $(eRV_{01})^2W$, where R is the distance between the groups D and A, V_{01} is the energy of the exchange interaction between D and $A^{-\bullet}$: $V_{01} = V(R_0)\exp[-(R-R_0)/\zeta]$, R_0 is the sum of Van der Waals radii of D and $A^{-\bullet}$, ζ is the parameter of damping of the wave functions.[20,21] Taking this into account, one can represent formula (8) as follows

$$\beta \propto (eRV_{01})^2 \frac{\Delta\mu_{ex}}{W^2}$$

[in a static approximation, $h\omega = 0$ (see Ref. 8)]. The parameter ζ decreases if delocalised π-electrons of the bridging group B in the molecule D−B−A take part in the exchange interaction

$$V_{01} = V_{01}(D,M^{-\bullet})V_{01}(M^{-\bullet},A^{-\bullet}) .$$

The parameter ζ is determined by the structure of the bridging group. Weakening of the exchange interaction at a large distance between D and A leads to the decrease in β_{ct}.

It is seen from the formula (8) that the contribution of β_{ct} increases with a decrease in the distance between the ground and excited levels, which determines the longwave optical absorption of the intramolecular DA complex. The experimental data showing the increase in $\log\beta_{ct}$ with the increase in the wavelength of the optical absorption for *para*-substituted benzenes and stilbenes are presented by Kanis *et al*.[8]

The charge displacement from D to A in the D−B−A molecules in the ground state is determined by the difference in the Hammett constants (σ_x). For example, for *para*-substituted π-conjugated molecules [8]

$$\sigma_n = \sigma_{n,a} - \sigma_{n,d} ,$$

where σ_n is the empirical Hammett constant, $\sigma_n = \log K_X - \log K_H$, where K_X and K_H are the ionisation constants for *para*-substituted and nonsubstituted benzoic acids, respectively. The Hammett constants are positive for the acceptors [$\sigma_{n,a}$ (NO_2) = 0.778] and negative for the donors [$\sigma_{n,d}$ (NH_2) = −0.66].[25] It is shown [8,26] that β_j increases linearly from $\sim 4\times10^{-30}$ to 40×10^{-30} cm^5 C^{-1} at $h\omega = 0.65$ eV as σ_n increases from 0.4 to 1.5 for mono- and di-substituted stilbenes (the axis Z is directed along the dipole moment of a molecule).

IV. Typical experimental procedure

A typical SHG process includes two stages: the first one is orientational polarisation of a polymer in the external electric field, and the second one is the measurement of the intensity of the SH in the course of the polarisation or after the electric field is switched off. Two methods for the potential application to the polymeric film are used. The first one is a contact method where the potential difference is applied to the transparent electrodes with the polymeric film placed between them. In_2O_3/SnO_2 (ITO) or a semitransparent metal film, for example, gold are used as the transparent electrodes. The second method is the corona discharge, the charges are deposited onto the free surface of a polymer instead of the upper contact electrode. These charges result from the corona discharge (ionisation of a gas in the measurement chamber by high voltage applied to the corona electrode). This method is well developed in electrophotography.[27] The principal scheme of the experimental set-up for second harmonic generation with the potential application of the corona discharge method is shown in Fig. 2.[28] The specimen consists of a transparent ITO electrode as a substrate and a polymeric layer that generates the second harmonic. A positive or negative charge is applied to the surface of the polymeric layer by the corona discharge method. The surface potential U is registered using the ring electrode and an electrometer.

Linearly polarised laser radiation with the fundamental wavelength λ (as a rule, λ lies, in the near-IR range and is equal to 1064 nm) is applied to the sample. The intensity of the second harmonic $I(-2\omega)$ that is selected by the $\lambda/2$ interference filter (532 nm) is measured with a photomultiplier and a digital voltmeter. The effects due to the fluctuation of the incident radiation can be excluded if the intensity of the second harmonic is measured relative to the intensity of the fundamental wavelength signal taken out by the reference channel (see Fig. 2).

The intensity $I(-2\omega)$ is related to the second-order susceptibility by the expression [1,29]

$$[I(-2\omega)] \propto [\chi^{(2)}_{ZZZ}E(\omega)E(\omega)]^2 . \quad (9)$$

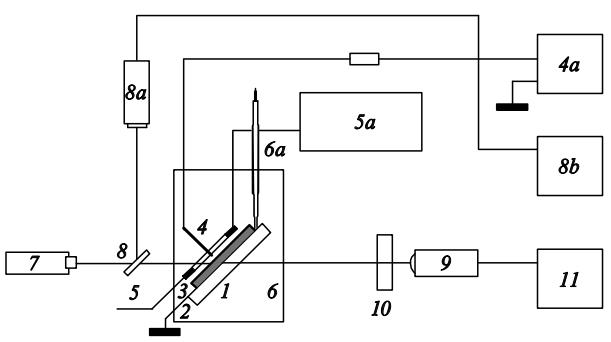


Figure 2. Schematic diagram of the experimental set-up for the second harmonic generation with the potential application by the corona discharge.
(*1*) — substrate, (*2*) — transparent electrode, (*3*) — polymeric layer, (*4*)— corona electrode, (*4a*) —source of stabilised voltage, (*5*) — ring electrode, (*5a*) — electrometer, (*6*) — temperature controlled chamber, (*6a*) — thermometer, (*7*) — laser, (*8*) — laser beam splitter, (*8a*) *and (9*) — photomultipliers, (*8b*) and (*11*) — pulse voltmeters, (*10*) — interference light filter for 532±10 nm.

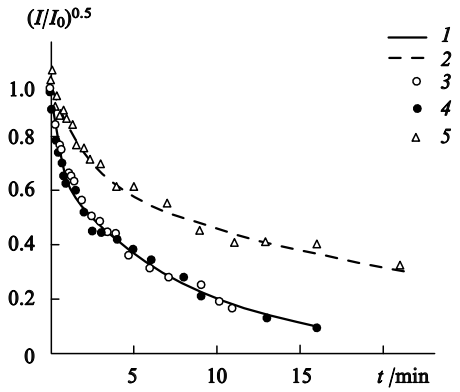


Figure 3. The kinetics of the decay of the second harmonic signal after the switch-off of the corona discharge for the sample of PVAC + 5 - mass % of DO3.
(*1*) equation (19) with parameters $\varphi = 0.33$, $\tau_1 = 0.52$ min, $\tau_2 = 8.3$ min; (*2*) equation (19) with parameters $\varphi = 0.35$, $\tau_1 = 2.1$ min, $\tau_2 = 28$ min; (*3*) keeping at 43 °C for 5 min, then charging by the corona discharge for 2 min at 35 °C, measurement at 35 °C; (*4*) keeping at 43 °C for 5 min, then charging by the corona discharge for 2 min at and then 2 min at 35 °C, measurement at 35 °C; (*5*) keeping at 43 °C for 5 min, then keeping at 35 °C for 4 h, charging by the corona discharge for 2 min at 35 °C, measurement at 35 °C.

V. Relationship between the second harmonic and the relaxation characteristics of a polymeric matrix

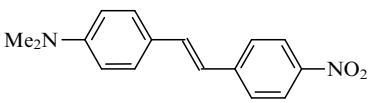
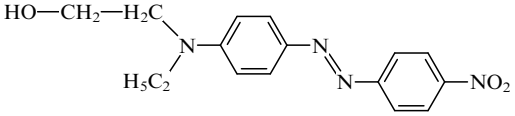
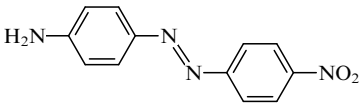
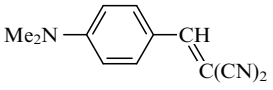
A detailed analysis of studies on the second harmonic generation in polymeric systems performed before 1994 is presented in a review by Burland *et al.*[5] It is noted that one of the main problems in the consideration of the nature of SHG in polymeric materials is the elucidation of the role of charges in the stabilisation and kinetic characteristics of the second-order susceptibility.

The coincidence of the decay of the second-harmonic intensity when the corona discharge is switched off and decay of the surface potential U in a poly(vinyl acetate) film containing 2 mass % of DO3 (Table 2) is established.[28] The plots $[I(-2\omega,t)]^{0.5}$ and $U(t)$ (Fig. 3) coincide over all time of measurement (22 min) after the corona electrode is switched off and correspond to a biexponential dependence. Thus, the susceptibility $\chi^{(2)}$ is completely controlled by the surface potential U. A biexponential decay of the surface potential in the polymeric films is observed for a large number of polymers[30] and can be associated with two processes, *viz.*, autolocalisation of the charge carriers in the polymeric dielectric responsible for the initial fast region (τ_1), and a charge carrier drift responsible for the decay of the potential with the time constant τ_2.

Only in a few studies[31–35] the kinetics of the decay of the susceptibility $\chi^{(2)}$ and a decrease in the residual electric field were measured simultaneously[35] to take account of the effect of trapped charges in the relaxation processes. It was assumed earlier that the contact method entirely excludes the influence of the residual electric field after the cut-off of the potential difference. However, the electric current passing through a cell with poly(isobutyl methacrylate) (PIBMA) and a chromophore DANS (1 mass %) placed between the ITO electrodes has been registered.[32–34] It was concluded that ITO is an injecting electrode and the current is caused by the ionic impurities in the polymeric matrix. In this case, a residual charge, which can significantly influence the characteristics of the SH relaxation remains in the sample. An attempt was made to exclude the influence of captured electrons on the SH relaxation introducing an insulating SiO_2 interface between the ITO anode and the polymer.[32–34]

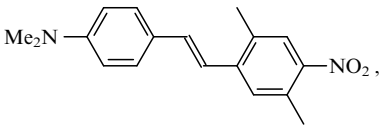
The effect of traces of solvent (chloroform) on the kinetics of SH decay was observed.[33] In the authors opinion, the solvent

Table 2. Relative contribution of the third-order nonlinearity into $\chi^{(2)}_{ZZZ}$ (see Ref. 37).

Chromophore	Name	Abbreviation	$\frac{\gamma}{\gamma + \beta\mu/5kT}$
	4-dimethylamino-4′-nitrostilbene	DANS	0.2 ± 0.03
	(*N*-ethyl)-*N*-(2-hydroxyethyl)-4-(p-nitrophenylazo)aniline, dispersion red dye 1	DR1	0.12 ± 0.02
	4-(*p*-nitrophenylazo)aniline, dispersion orange dye 3	DO3	0.16 ± 0.03
	4-(dimethylamino)benzylidene-malononitrile	DMN	0.06 ± 0.02

diffuses from a nonpolar polymer into a microvolume that surrounds the chromophore with a high dipole moment. This leads to the change in the dielectric constant and also to the significant decrease in viscosity in the microenvironment of the chromophore. As a consequence, this results in a decrease in the activation energy of the chromophore orientational relaxation. The content of traces of solvent is difficult to monitor. Therefore, the experimental results are often irreproducible. In this connection, one should pay attention to the dry process for the fabrication of films with oriented chromophores by spray-coating the polymer onto the electrode.[36]

According to the formula (7c), the second harmonic contains the contribution of the third-order nonlinearity, which has to be taken into account in the analysis of the relaxation processes. The kinetics of the decay of $\chi^{(2)}_{ZZZ}$ in polymeric matrices (PMMA, poly(methyl methacrylate) (PEMA), and PIBMA) containing 2 mass % of a chromophore at 30 °C was measured after the constant electric field was switched off.[37] Depending on the nature of the chromophore (see Table 2), the susceptibility $\chi^{(2)}_{ZZZ}$ decreases by 6%–20% over the period 10^{-4}–0.5 s and then slowly diminishes over 10^3–10^4 s. Fast decrease in the susceptibility after the cut-off of the constant field E is related to the disappearance of the contribution of the third-order nonlinearity. This contribution $\gamma/(\gamma + \beta\mu/5kT)$ for different donor-acceptor molecules are also listed in Table 2. The value of this contribution depends only slightly on the nature of the polymeric matrix: in the PEMA and PIBMA containing 2 mass % of 4-tricyanovinyl-*N*-ethyl-*N*-(2-hydroxyethyl)aniline (TC1) this contribution was 4% at 30 °C.[38] For polyamide $[-CONH-X-HNCO-(CH_2)-]_n$, where the chromophore X was of the following structure,



the initial fast decay of the second-harmonic intensity $[I(-2\omega,t)/I(0)]^{0.5}$ down to 25% of the initial value was also explained[39] by the disappearance of the contribution of the molecular third-order susceptibility γ. Here $I(0) \equiv I(-2\omega,0)$ is the second-harmonic intensity at the moment of the polarising field cut-off. This decay continues for $\sim$ 20 s after the cut-off of the constant electric field. Possibly, such a delay is caused by the gradual drain of the surface charge deposited by the corona discharge.[40]

The rate of the decay of the second-harmonic intensity after the real removal of the electric field is caused by the orientational relaxation of the chromophore and is determined by its structure, the character of the linkage with the polymer, and free volume of the polymer. The investigation of the kinetics of this process is an informative method of analysis of the polymer dynamics. The measurement of the SH after the switch-off of the electric field may last from $\sim$ 0.5 s to an indefinitely long time. Different mechanisms of the relaxation of the system chromophore–polymer are found in the measurement.

As a rule, the study of the second-harmonic relaxation is based on the concept that these processes are caused by the rotational diffusion of chromophore. When the electric field is applied, they are described in the framework of the Smoluchowski model by equation[5, 31, 41]

$$\frac{\partial G(\theta,t)}{\partial t} = D_{\rm rot}\,\frac{1}{\sin\theta}\,\frac{\partial}{\partial\theta}\left\{\sin\theta\left[\frac{\partial}{\partial\theta}G(\theta,t) + \frac{G(\theta,t)}{kT}\,\frac{\partial}{\partial\theta}V(\theta,t)\right]\right\}, \qquad (10)$$

where $G(\theta,t)$ is the distribution function of the orientations of the dipole moment of the chromophore as the projection of the solid angle θ at the moment t; θ is the angle between the macroscopic axis Z normal to the film surface and coinciding with the direction along the constant electric field E, and the long axis of the chromophore, $D_{\rm rot} = \langle[\theta(t)-\theta(0)]^2\rangle/4\tau$ is a coefficient of the rotational diffusion of the chromophore, τ is the relaxation time, and $V(\theta,t) = -\mu E\cos\theta$ is the potential energy of the chromophore. The change in the chromophore orientation after the switch-off of the constant field at the moment $t = 0$

$$\frac{\partial G(\theta,t)}{\partial t} = D_{\rm rot}\,\frac{\partial G(\theta,t)}{\partial(\sin\theta\,{\rm d}\theta)^2} \qquad (11)$$

(the second Fick law) determines kinetics of the decay of the second-order susceptibility according to the expression[5, 40–42]

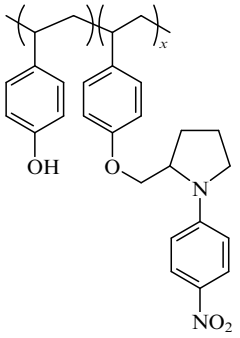
$$\frac{\chi^{(2)}(-2\omega,\omega,\omega,t)}{\chi^{(2)}(-2\omega,\omega,\omega,0)} = A\exp(-2D_{\rm rot}t) + B\exp(-12D_{\rm rot}t)\,. \qquad (12)$$

Here [see Eqn (7)],

$$\frac{\chi^{(2)}(-2\omega,\omega,\omega,t)}{\chi^{(2)}(-2\omega,\omega,\omega,0)} \equiv \left(\frac{I(-2\omega,t)}{I(0)}\right)^{0.5} \equiv \frac{\langle\cos^3\theta,t\rangle}{\langle\cos^3\theta,0\rangle}\,.$$

The representation of the function $G(\theta,t)$ in the form of the Legendre polynomial is used in the calculation and the same $D_{\rm rot}$ value is assumed for all chromophores. The latter condition is more characteristic of the temperatures higher than $T_{\rm g}$.

The kinetics of the decay of the second harmonic intensity ($\lambda/2$ = 532 nm) in the polymer with the pendent chromophoric groups has been studied by Firestone *et al.*[40–42] Polyhydroxystyrene (PHS) with the portion of hydroxy group (x) esterified with *N*-(4-nitrophenyl)-(*S*)-proline [(*S*) = NPP] was the object of the investigations



The kinetics was measured over a wide range of temperatures near the $T_{\rm g}$ of the polymer, which depends on the degree of substitution x, and decreases from 146 °C at x = 12% to 134 °C and 96 °C at x = 36% and 90%, respectively.[41]

The calculations have shown[5, 40] that the relationship between pre-exponential factors in Eqn (12) depends on the poling field strength and at $E = 2.5\times10^5$ V cm^{-1} (at $D_{\rm rot} = 1.5\times10^{-5}$ rad^2 s^{-1}) the kinetics of the decay of the $\chi^{(2)}_{ZZZ}$ is mainly characterised by the stretched exponent: $A \simeq 1$, $B \simeq 1.5\times10^{-5}$ at 130 °C. If the poling field increases by an order of magnitude the contribution of the fast exponent increases to $B = 0.0712$. Thus, one should expect the first-order exponential orientational relaxation of the chromophores after the switch-off of the constant field. The experimentally measured decay of the SH intensity $[I(-2\omega,t)]^{0.5}$ in (*S*)-NPP-PHS with x = 36% at temperatures higher than the $T_{\rm g}$ for this polymer (134 °C) after the cut-off of the field $E = 1.1\times10^6$ V cm^{-1} is mainly characterised by the fast exponent only at 153 °C: $B = 0.998$, $A \simeq 0.0016$, and $D_{\rm rot} = 9.7\times10^{-3}$ rad^2 s^{-1} [or in Eqn (12) the relaxation time $\tau_2 = (1/12)D_{\rm rot} = 8.6$ s]. The contribution of the slow relaxation increases with the decrease in the temperature of the measurement: at 149 °C $B = 0.88$, $A \simeq 0.12$, and $D_{\rm rot} = 8.7\times10^{-3}$ rad^2 s^{-1} ($\tau_2 = 9.6$ s), and at 134 °C $B = 0.52$, $A \simeq 0.43$, and $D_{\rm rot} = 2.3\times10^{-3}$ rad^2 s^{-1} ($\tau_2 = 36.2$ s). Revealing the biexponential relaxation instead of the calculated monoexponential process suggests in the authors' opinion[40–42] the presence of two fractions

in the structure of the polymer, *viz*., the liquid one responsible for the fast relaxation and the glassy one responsible for the slow orientational relaxation of chromophores.

The contribution of the liquid fraction increases with the increase in temperature and prevails at $T_g + 19$ °C. It was also noted that this two-fraction consideration is possibly unnecessary as the model of rotational diffusion itself predicts the biexponential relaxation according to the relation (12).

The temperature dependence of the orientational relaxation of chromophores in the range higher than T_g does not obey the Arrhenius law and is well described by the Williams–Landel–Ferry formula

$$\lg\left(\frac{\tau(T)}{\tau(T_g)}\right) = -\frac{C_1(T-T_g)}{C_2+(T-T_g)}, \qquad (13)$$

where C_1 and C_2 are empirical coefficients, and τ is the relaxation time. The values $C_1 = 17.44$ and $C_2 = 51.6$ °C are typical of polymers. In the measurement of the kinetics of $\chi^{(2)}_{ZZZ}$ decay at different temperatures these coefficients are as follows: $C_1 = 1.94$ and $C_2 = 39.1$ °C, *i.e*., measurement of the second harmonic gives information on the relaxation in the local chromophore microenvironment rather than the universal macroscopic relaxation.[40,42]

In viscous media, the individual chromophores differ in their orientational relaxation time and a distribution of the relaxation processes can be represented by the empirical Kohlrausch–Williams–Watts (KWW) function[42]

$$\frac{\chi^{(2)}(t)}{\chi^{(2)}(0)} \equiv \left(\frac{I(-2\omega,t)}{I(0)}\right)^{0.5} \equiv G(t) = \exp\left(-\frac{t}{\tau_{KWW}}\right)^b, \qquad (14)$$

where τ_{KWW} is the mean relaxation time [the time counted from the moment of the field cut-off to the moment of a 2.7-fold decrease in the distribution function $G(t)$], parameter b characterises the width of the distribution of chromophores according to the orientational relaxation time. The values of the coefficient b vary from 0 to 1. At temperatures higher than the glass transition temperature $b \approx 1$, *i.e*., all chromophores are characterised by the same τ_{KWW}. The decrease in b as the temperature decreases indicates a growing deviation of the relaxation time of the individual chromophore from the mean value. In a number of publications (see, for example, Ref. 13), difficulties in the transformation of the experimental results to the form of function (14) using a single value of τ_{KWW} are noted. It is suggested to use of a bimodal representation in order to avoid difficulties

$$G(t) = \varphi_1 \exp\left(-\frac{t}{\tau_{1,KWW}}\right)^{b_1} + \varphi_2 \exp\left(-\frac{t}{\tau_{2,KWW}}\right)^{b_2}. \qquad (14a)$$

Here, parameters $\tau_{1,KWW}$, b_1, and $\tau_{2,KWW}$, b_2 show the presence in the polymer of domains with the fast and slow relaxations distributed according to the energies.

The relationships of the type (14a) bear little information as they contain a large number of parameters and, naturally, allow one to describe any experimental dependence.

The process of the chromophore orientation immediately after the switch-on of the poling constant field can be represented by the modified KWW function

$$[I(-2\omega,t)]^{0.5} = 1 - \exp\left(-\frac{t}{\tau_{KWW}}\right)^b. \qquad (14b)$$

It was mentioned above that the exponential dependence corresponding to $b = 1$ in Eqn (14) is found in (*S*)-NPP-PHS with $x = 36\%$ at $T_g + 19$ °C.[40] As temperature decreases, b gradually decreases, which indicates a deviation of the relaxation time of individual chromophores from the mean value. The empirical functions (14) and (14b) describe well the process of the depolarisation/polarisation at the temperatures smaller than T_g. The decay of the second harmonic intensity measured after the switch-off of the poling field ($E = 1.25 \times 10^6$ V cm^{-1}, poling time 20 min) at $T_g = 134$ °C corresponds [see Eqn (14)] to the values $\tau_{KWW} = 63$ s, $b = 0.61$, and at 120 °C $\tau_{KWW} = 972$ s, $b = 0.5$. The growth of $[I(-2\omega,t)]^{0.5}$ after the switch-on of the field corresponds to the dependence (14b) with the parameters $\tau_{KWW} = 79.8$ s, $b = 1$ at T_g and $\tau_{KWW} = 3126$ s, $b = 0.41$ at 120 °C.[42] The decrease in the coefficient b with the decrease in temperature, *i.e*., the broadening of the distribution function of the chromophores according the orientational relaxation times and the increase in the mean duration of relaxation τ_{KWW} in both processes (polarisation and depolarisation) indicate the heterogeneous character of the distribution of the microdomain sizes at temperatures below T_g.

An Arrhenius-type temperature dependence of the orientational processes was established at temperatures below T_g.[40,42]

$$\lg\left(\frac{\tau}{\tau_0}\right) = \frac{E_a}{kT}, \qquad (15)$$

where τ_0 is a constant, E_a is the activation energy. In the samples of (*S*)-NPP-PHS with $x = 36\%$ $E_a = 24.7 \pm 2.6$ kcal mol^{-1} either at a growth or decay of $[I(-2\omega,t)]^{0.5}$, *i.e*., upon switch-on and off of the poling field.

According to the principles developed by Turnball and Cohen and Chalykh,[43–45] molecular diffusion is determined by the free volume of the polymer. Migration of a molecule in amorphous media becomes possible if a microcavity the volume of which exceeds some critical value $V' \simeq V_m$ (V_m is the volume of the diffusing molecule) appears in the vicinity of the diffusing molecule as a result of the thermal redistribution of the free volume.[44] In this case, the diffusion coefficient (D) is proportional to the probability of redistribution of the free volume and is determined by the relation

$$D \propto \tau^{-1} \propto \exp\left(-\frac{cN_A V'}{V_{fr}(T)}\right), \qquad (16)$$

where $c \simeq 0.5-1$ is a factor of the overlap of the microcavities, $V_{fr}(T) = [V(T) - V_v]$ is the molar free volume of the polymer repeating unit, $V(T)$ is the molar volume of the polymer at given temperature, and V_v is the Van der Waals molar volume of the repeating unit.

An analysis of the decay kinetics carried out by Firestone *et al*.[40–42] demonstrated the link between the characteristics of the second harmonic and relaxation processes in the polymer. However, the authors failed to rationalise the disagreement between theoretical order of the exponential dependence of the orientational relaxation of chromophores using diffusional model and the measured biexponential dependence of the decay of the susceptibility $\chi^{(2)}_{ZZZ}$. In the authors opinion, the theoretical consideration carried out is simplified as it does not take into account different specific effects, for example, the interaction of the chromophore dipoles with the polymeric matrix or with each other.

An analysis of the relaxation processes gives a good correspondence[35] between the experimental results and calculations based on a Gaussian distribution of the activation energy E_a (see Refs 32–34) or according to Eqn (15)

$$\Phi(t) = \left(\frac{I(-2\omega,t)}{I(0)}\right)^{0.5} = \int_{-\infty}^{\infty} \Gamma(\ln\tau)\exp\left(-\frac{t}{\tau}\right)d\ln\tau = \qquad (17)$$

$$= \pi^{-1/2}\int_{-\infty}^{\infty} \exp(-u^2)\exp\left[\left(-\frac{t}{\tau_G}\right)e^{-\sigma_G u}\right]du.$$

Here $\Gamma(\ln\tau) = (\pi\sigma_G^2)^{-1/2}\exp(-u^2)$ is the Gaussian distribution of $\ln\tau$, $u^2 = (\ln\tau - \ln\tau_G)^2/\sigma_G^2$, σ_G is the half-width of the distribution at $\Gamma_{max}/2.7$, and τ_G is the most probable relaxation time. Verbiest

et al.[35] have used the Eyring theory of absolute reaction rates according to which

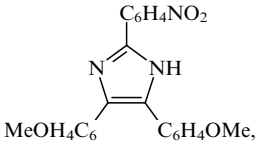
$$\ln \tau = \ln \frac{2\pi h}{kT} - \frac{\Delta S}{R} + \frac{\Delta H}{RT},$$

where R is the gas constant, ΔS and ΔH are the entropy and enthalpy of activation, respectively. Therefore, the thermal characteristics of the processes are estimated according to the dependence

$$\ln(\tau T) = \ln \frac{2\pi h}{k} - \frac{\Delta S}{R} + \frac{\Delta H}{RT}.$$

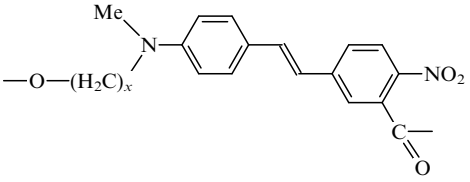
On the basis of the fact that $E_a = \Delta H + RT$ and in majority of cases $\Delta H \gg$ RT the authors suppose that $E_a \simeq \Delta H$.

The distribution function (17) and the empirical KWW function (14) are characterised by two parameters, *viz.*, τ_G, σ_G and τ_{KWW}, b, respectively. The parameters of the Gaussian distribution τ_G and σ_G were compared with the coefficients τ_{KWW} and b for the decay curves $[I(-2\omega,t)]^{0.5}$ measured at different temperatures in a polyetherimide containing chromophore lophine 1 (L1)[35]



and also in PMMA containing dye DR1 (see Table 2). It was shown that as the temperature increases the increase in b from 0.2 to 1 corresponds to a decrease in σ_G from 10 to 0. In the range of $\sigma_G = 0-2$ the value of $\ln(\tau_{KWW}/\tau_G)$ is equal to zero and then decreases linearly down to -1.3 with an increase in σ_G to 10.

The characteristics of the orientational relaxation of chromophores in co-polymers consisting of the repeating units (P1, $x = 2$ and 6) with the following structure



and polymers including DANS, whose donor fragment is incorporated into the main chain (P2), and also containing DR1 (see Table 2) in the side chain (P3)

$$[-CH_2-CRMe-]_{60}-[CH_2-CR'Me-]_{40},$$

where R = $-C(O)-O-(CH_2)_2-R''$ (R'' = carbazolyl) and the chromophore R' = $-C(O)-O-(CH_2)_2-N(Et)-C_6H_4-N=N-C_6H_4-NO_2$ are the side substituents have been studied.[46] The susceptibility was measured when the poling electric field was switched on at room temperature, then the temperature was gradually increased to T_g, the sample was kept at this temperature until the constant value of $\chi^{(2)}$ was achieved, then the temperature was decreased again to 20 °C. The decrease in the temperature was accompanied, according to relation (7a) by an increase in the susceptibility to the limiting value $\chi^{(2)}_{max}$, which could be achieved upon prolonged poling at the temperatures near the T_g. Then the poling electric field was switched off. It is established that in all polymers $\chi^{(2)}$ was increased up to 60% of $\chi^{(2)}_{max}$ in 30 s at 20 °C. As this value exceeds a possible contribution of the third-order susceptibility (20%, see Table 2) the fast rise of $\chi^{(2)}$ was related [46] to the local motion of the chromophore in the free volume of the polymer. It was found that upon cut-off of the electric field in the samples cooled down to room temperature the value of the fast decay is less than 60%; for the P1 polymer this value is ~ 20% of $\chi^{(2)}_{max}$. In the authors opinion such a decrease in the contribution of the fast component of $\chi^{(2)}$ is caused by the decrease in the free volume, which resulted from the poling at T_g. The 'memory effect'‡ in PIBMA containing DANS, *i.e.*, the increase in the duration of the decay of the second harmonic intensity τ in repeated cycles on-off of the polarising field at $T = T_g + 27$ °C [for the relationship between τ and V_{fr}, see Eqn (16)] was explained by the decrease in the free volume.[34] A gradual increase in τ_{KWW} after keeping a poly(arylene ether) composition doped by 10% of chromophore DANS ($T_g = 185$ °C) in a constant electric field at 45 °C (*i.e.*, at $T_g - 140$ °C) was also related to the decrease in the free volume.[47] The composition was preliminarily poled for 25 min at 190 °C (*i.e.*, at $T_g + 5$ °C). It was shown that upon keeping at 45 °C τ_{KWW} increases from 0.27 to 4.06 h after 31 h.

Polymers with $T_g = 82.7$ °C containing donor carbazole groups in the main chain substituted at positions 2 and 3 by acceptor substituents have been synthesised.[48] In contrast to the majority of polymeric systems with quasi-unidimensional chromophores, the direction of the dipole moment vector in these polymers does not coincide with the direction of the charge transfer, which results in an contribution of a nondiagonal coefficient of the second harmonic d_{ZX} is increased. The authors assume that the biexponential decay of $[I(-2\omega,t)]^{0.5}$ after the cut-off of the poling electric field measured at temperatures from 20 °C to 100 °C ($T_g + 17.3$ °C) is caused by two effects, *viz.*, the fast decay is determined by the movement of chromophore in a local free volume, and the slow decay is related to the recombination of the injected charges.[48]

The values of τ_{KWW} and b in Eqn (14) obtained in the measurement of the second harmonic decay and an analysis of the electrochromic relaxation at 85–105 °C of a system consisting of PMMA and 1 mass % of nitroaminostilbene (NAS) ($T_g = 117$ °C), have been compared.[49,50] These compositions possess electrochromic properties, *i.e.*, upon application of the poling field the optical density of the chromophore decreases reversibly. It is established [50] that the relaxation time (τ) of the NAS chromophores after the switch-off of the electric field estimated from the decay of the second harmonic intensity coincides with the time of the electrochromic relaxation. For such polymers as PMMA, poly(vinyl chloride) (PVC), and polycarbonate (PC) the time τ increases by an order of magnitude near the T_g on going from PVC to PMMA in the series PVC < PC < PMMA. This increase is believed to be caused by the decrease in the free volume of polymers [see relation (16)].[50] Such a conclusion provokes objections that the free volume is increased rather than decreased as on going from PVC to PMMA and makes up 18.56 and 23.17 cm^3 mol^{-1} at 20 °C, respectively (see Ref. 51). As the thermal extension coefficients for these polymers are similar [$(2.7-2.9)\times 10^4$ K^{-1}] (see Ref. 52), and the T_g of (PVC + NAS) is equal to 59 °C (see Ref. 49), which is almost half the T_g of (PMMA + NAS) (117 °C), the relation V_{fr}(PVC) < V_{fr}(PMMA) holds and at elevated temperatures, too. It is possible that the captured charges determine the significant increase in the relaxation time on going from PVC to PMMA. It is to the accumulation of charges captured during poling that the memory effect in these compositions is related. [50]

In the high-temperature corona poling, the sharp initial increase in $[I(-2\omega,t)]^{0.5}$ is followed by its gradual decay both in the polymers with the chromophores in the main chain [53] and in the doped polymers.[31] Such behaviour of the polarisation curves can be caused by the decrease in the surface potential under equilibrium conditions due to the penetration of deposited charge into the bulk of the polymer and the increase in the film electric conductivity in the constant field due to the thermal increase in the crystallinity of the materials.

‡ The manifestation of this effect is that the repetition of the cycles polarisation/cut-off of the electric field results in the increase in the time of electrochromic relaxation, while optical density is not restored to the initial value.[50]

The dynamics of the dipole reorientation at different temperatures in pure polymers, *viz*., PMMA, PC, and polyimide (PI, T_g = 207 °C) not-doped with chromophores has been investigated.[54] The characteristics obtained by the method of the generation and decay of the second harmonic (532 nm) and by the method of the dielectric relaxation were compared. The values of $\chi^{(2)}$ appeared to be small, however, it was established that the decay plots of $[I(-2\omega,t)]^{0.5}$ can be described by the dependence (14). Two effects have been found. The first one lies in the fact that the decay time of the second harmonic τ_{KWW} measured in PI is increased by an order of magnitude when the same on-off cycle is repeated. The temperature dependences of the decay time for the second harmonic intensity τ(SH) and the dielectric relaxation time τ(DR) at the temperatures higher than T_g for all polymers are described by Eqn (13). The second effect is illustrated by the example of PVC where τ(SH) is five orders of magnitude higher than τ(DR) at T_g + 23 °C. This difference gradually decreases as the temperature decreases, and τ(SH) $\approx$ τ(DR) at T_g. Both effects were explained by the influence of the captured charges on the decay time of $[I(-2\omega,t)]^{0.5}$ after the cut-off of the poling electric field. Presumably, the significant difference in the relaxation times is caused by the fact that at temperatures higher than T_g the polymeric chains are mobile and only captured charges hold the dipole in the oriented state thereby decreasing the orientational relaxation time τ(SH).[54] At T_g, where the mobility of the polymeric chains is restricted, the role of the captured charges in the stabilisation of the oriented dipoles decreases.

Unfortunately, as a rule, in the studies mentioned above the decay of the potential was not measured simultaneously with the relaxation. Therefore, the suggestion of the influence of the captured charges on the characteristics of the relaxation processes are sufficiently justified, but are not proved.

VI. The influence of the captured charges on the characteristics of second harmonic generation and relaxation

The analysis of nonlinear optical characteristics of the polymeric materials presented above leads to the conclusion that a preferred orientation of the dipole chromophores is required to obtain noncentrosymmetrical structures in the optically transparent uniform polymeric films. The chromophores can be introduced in the polymeric chain or can be present as the side substituents in the macromolecule. Also, they can participate in the formation of a host–guest system as a low-molecular-weight additive to the polymeric matrix. The orientation of the chromophore groups results from the application of the poling electric field to the polymer film in the direction normal to its surface.

It is usually assumed that the contact polarisation method allows one to observe the nonlinear effects in the pure form, *i.e*., without the influence of the residual charge after the cut-off of the poling field. However, in the electrode poling the current is passing through the film, even if an additional dielectric layer of SiO_2 is deposited between the anode and the polymer, see above. This indicates unambiguously the charge penetration into the film.[33] Even in the absence of the external potential difference, the charge up to $\sim 10^{-8}$ C cm^{-2} is deposited on the surface of the dielectric polymeric film, when it comes in a contact with the metal owing to contact charging.[55, 56]

It is shown [33] that the SHG characteristics are independent of the film conductivity, if the charge carrier concentration is several orders of magnitude smaller than the concentration of the chromophore. For example, for the film PIBMA + 1 mass % of DANS these concentrations are 10^{10}–10^{15} and 5×10^{19} cm^{-3}, respectively. In addition, the residual solvent (chloroform) even after careful removal is retained in the film at a concentration of five molecules per one DANS molecule, which influences significantly the kinetic characteristics of the SH decay. If nonpolar toluene is used as a solvent, the effect of the solvent traces on the SHG characteristics in considerably less. It is assumed that the polar solvent affects significantly the local field factor, which is often estimated according to the Lorentz equation

$$f(\omega) = \frac{\varepsilon(\omega) + 2}{3}$$

or in a more accurate approximation through the Onsager equation

$$f(\omega) = \frac{(\varepsilon_\infty + 2)\varepsilon(\omega)}{\varepsilon_\infty + 2\varepsilon(\omega)}\,.$$

These expressions are strictly correct for a spherical symmetry and a continuum approximation for the dielectric medium surrounding the chromophore molecule. Thus, the decrease in the SH intensity is not necessarily associated with the change in the mean orientation of the chromophore molecules [see Eqn (7)]. However, the orientation can also be changed because of the change in the local electric field owing to molecular inhomogenity.[33] All together, this differs from the concepts according to which the decrease in the SH intensity after the cut-off of the poling field (usually the experiment is carried out in such a way) is related only to the change in the mean orientation of the chromophore. The authors' conclusion [33] is made on the basis of the fact that the decrease in the SH intensity was observed experimentally when the poling field was not switched off.

The study of the decay of the SH intensity after the cut-off of the poling electric field seems to be most interesting. The characteristic time of the SH decay determines the stability of the operation of the nonlinear optical element. The features of the SH decay kinetics allow one to obtain information on the relaxation processes of polymeric chains and low-molecular-weight additives oriented by the poling electric field. It has been mentioned above that the great variety of these decay features were found in different studies: the exponential with saturation,[33] the sum of two exponents [see Eqn (12)],[5, 40–42] the stretched exponent represented by the empirical function (14), the sum of two stretched exponents [see Eqn (14a)],[13, 57] *etc*.

It should be noted that all effects connected to the SHG and observed upon multiple charging of the polymeric film, or upon changes in the solvent content in the sample, or after the cut-off of the poling field depend to a considerable degree, and sometimes crucially, on the value and kinetics of the surface charge relaxation. Thus, in order to obtain correct conclusions one should follow the change in the external electric field connected with the charges captured on the surface and in the bulk of the polymeric film and the SHG characteristics simultaneously. A simple relation exists between the surface potential, the external electric field $E(t)$ and the captured charge

$$E(t) = \frac{U(t)}{d}\,,$$

$$U(t) = \frac{d\sigma(t)}{\varepsilon\varepsilon_0} + \frac{1}{\varepsilon\varepsilon_0}\int_0^d (d-x)\rho(x,t)\mathrm{d}x\,, \qquad (18)$$

where d is the film thickness, $\sigma(t)$ is the charge density of the film surface, ε is the dielectric constant, ε_0 is the permittivity of free space, and $\rho(x,t)$ is the charge density of the same sign in the polymer bulk at a distance x from the surface.

Simultaneous measurement of the decay kinetics of the second-order susceptibility and the surface potential of a PMMA film containing 4 mass % of DANS after charging by the corona discharge was performed by Liu *et al*.[31] for the first time. It was established that at the temperatures of measurement higher and lower than T_g (T_g = 88 °C) the change in the relaxation of the normalised surface potential U/U_0 and normalised susceptibility χ/χ_0 are similar. The experimental results in the polymeric host–guest system studied could be explained if a

dynamic model that takes into account the Brown motion of the chromophores, the influence of the electric field, and the limitations imposed by the polymer matrix was used. The model contains four parameters, *viz*., D_{rot} (coefficient of the rotational diffusion); $a = \mu E/kT$; $b = v(g_1 - g_2)(E^2/kT)$, and θ_0 (the angle of the cone within which a chromophore molecule vibrates). Here, μ is the constant dipole moment of the chromophore, $v(g_1 - g_2)$ is the difference in the polarisability in the directions parallel and normal to the axis of the chromophore molecule. Small difference in the decay kinetics of U and $\chi^{(2)}$ is explained by the fact that the change in $\chi^{(2)}$ is more probably related not to the surface potential, but rather to the mean rotational moment $\langle T \rangle$ acting on the chromophore dipole in the external electric field,

$$\langle T \rangle = \int_0^{\pi} T(\theta) p(\theta, t) \sin\theta \, d\theta ,$$

where $T(\theta) = \mu E \sin\theta - E^2 \cos\theta \sin\theta \, v(g_1 - g_2)$.

The coincidence of the decay curves for $\chi^{(2)}$ and $\langle T \rangle$ hardly should be paid great attention as the parameter $v(g_1 - g_2)$ was obtained from the experimental $\chi^{(2)}$ values rather than from independent data. In any case, in the experiments considered the decay kinetics of $\chi^{(2)}$ were determined either directly or through $\langle T \rangle$ using the decrease in the surface potential. The problems of the reason for the decrease in U and of the mechanism of this phenomenon are discussed neither in the paper cited (see Ref. 31) nor in other publications.

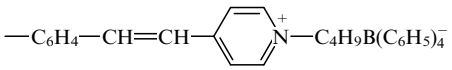
Practically, the main goals of the studies considered were the fabrication of the polymeric films with large values of $\chi^{(2)}$ that did not change with time and under the action of external factors. The decrease in $\chi^{(2)}$, fast or retarded, for different polymers at room temperature, indicates different thermal disordering of the chromophore orientation. Thus, it is possible to expect that the electric field results in the orientation of chromophores not only at high T_g, but at room temperature, as well. Consequently, it is possible to obtain polymeric films with nonlinear characteristics that can be manipulated by changing the external electric field in usual conditions. Using a simple system of PMMA + 2-methyl-4-nitroaniline (MNA) two components of the SHG response were registered at room temperature [58] when an alternating voltage of variable frequency was applied to the specimen comprising a film deposited on a glass substrate, and two metallic electrodes with a gap of 25 μm between them. The first component related to the orientation of the chromophore molecules is slow, and is observed up to 3×10^2 Hz. It lags in phase and decreases in the amplitude as the frequency of sinusoidal voltage increases. The second component, which seems to be caused by the third-order $\chi^{(3)}$ contribution into the SHG, is fast. This is characterised by the constant amplitude up to the maximum alternating field frequency 2×10^4 Hz and coincides with it in phase. The change in the slow component of the SH signal is determined by the rotational relaxation time of the oriented chromophores in the PMMA matrix, which is $\sim 10^{-2}$ s at room temperature.

The polymeric films of the type considered can be used for the elaboration of fast nonlinear optical devices of a new type controlled by the external electric field. In order to obtain stable SHG it is necessary to stabilise the oriented state of the chromophores because the process of the electric poling disturbs the equilibrium of the system, and after the cut-off of the corona discharge the dipole chromophores tend to disorder their orientation. This inevitably leads to the decrease in the second harmonic intensity, especially if a rapid decrease in the surface potential takes places. Several methods that allow one to minimise disordering of the chromophores are suggested.

1. The synthesis of polymers with high T_g, and consequently with small free volume at room temperature. This ensures low mobilities of the charged particles and prolonged preservation of the surface potential and nonlinear properties. Polyimides with $T_g > 200$ °C can be mentioned as an example. However, the necessity to use high temperature for the poling leads to the evaporation of the chromophore in the host–guest systems based on such polymers. In addition, in the host–guest systems the chromophore concentration is limited as it is crystalline and plasticises the polymer at high concentrations.

2. Chemical or photochemical cross-linking of a polymer containing the corresponding cross-linking groups in the macromolecule in the poling at T_g. The mechanism of the influence of cross-linking on the charge of the SHG characteristics is the same as in the former case. However, this method leads to an increase in optical losses because of nonuniformity of cross-linking reaction in the polymer bulk.

3. The synthesis of polymers the macromolecules of which contain chromophores and the groups that favour strong intermolecular interaction and consequently high rigidity of the system. The simultaneous investigation of the SHG and the surface potential in a polymeric system of the third type has been carried out.[59] A polyurethane (PU) $-[-1,3-C_6H_4(4\text{-}CH_3)-NH-CO-O-(CH_2)_2-NR-(CH_2)_2-O-CO-NH-]_n-$ was synthesised, where the side substituent R has the following structure



High chromophore group concentration (68 mass %) was the reason for high $\chi^{(2)}$ values: up to 200 pm V^{-1} (d_{33} = 100 pm V^{-1}, see Table 3). The formation of hydrogen bonds between neighbouring macromolecules favours an increase in the polymer hardness and the stabilisation of noncentrosymmetrical structure. In the corona discharge, $\chi^{(2)}$ and U are changed in the following way: at room temperature after the discharge is switched on, $\chi^{(2)}$ is increased sharply; $\chi^{(2)}$ and U remain constant as the temperature increases up to 145 °C (T_g = 121 °C), and at this temperature fast increase in $\chi^{(2)}$ is observed. Further heating to 190 °C leads to the decrease in the $\chi^{(2)}$ and U to zero, and the film becomes electroconducting. Subsequent cooling of the film starting from 170 °C to 145 °C is accompanied by the significant increase in the $\chi^{(2)}$ and U. In the process of cooling to room temperature, $\chi^{(2)}$ and U were little changed. At room temperature, after the switch-off of the corona discharge, the decrease in the surface potential to zero and the increase in the $\chi^{(2)}$ by $\sim 20\%$ were observed. The latter is possibly related to the noncolinearity of the dipole moment vector (that follows the direction of the electric field) and the largest component of the β tensor , which after the cut-off of the field can take the position corresponding to the increased value of $\chi^{(2)}$. After such treatment, the value of $\chi^{(2)}$ remained constant for at least 33 days. Consequently, strong intermolecular interaction providing for the system rigidity causes the preservation of the chromophore group orientation in the absence of the external electric field.

The relationship between kinetic parameters of the surface potential U and susceptibility $\chi^{(2)}$ was studied in the films of poly(vinyl acetate) (PVAC) doped with the chromophore DO3.[28,60] It was shown for this system [61–63] that the stepwise temperature decrease from T_g = 41.5 °C to 35 °C results in isothermal relaxation of the specific volume over 4 h. The decay of the normalised value of the second-order susceptibility after the cut-off of the corona discharge immediately after the temperature jump, and after 4 h is illustrated in the Figure 3. As is seen, the decay of $\chi^{(2)}$ in both cases is well approximated by the biexponential function

$$\left[\frac{I(-2\omega, t)}{I(0)}\right]^{0.5} = \varphi \exp\left(-\frac{t}{\tau_1}\right) + (1 - \varphi) \exp\left(-\frac{t}{\tau_2}\right) . \qquad (19)$$

Complete relaxation of the specific volume leads to the significant retardation of both fast and slow components: at 35 °C, in the case of nonrelaxed film the kinetic curves of the $\chi^{(2)}$ decay are characterised by the parameters $\varphi = 0.35 \pm 0.05$,

Table 3. Nonlinear second harmonic coefficients (d_{ZX}) in different media oriented at T_g. The measurements were performed after the cut-off of the constant electric field and the establishment of the steady-state characteristics.

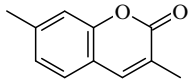
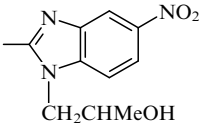
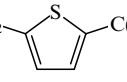
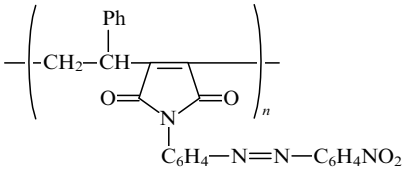
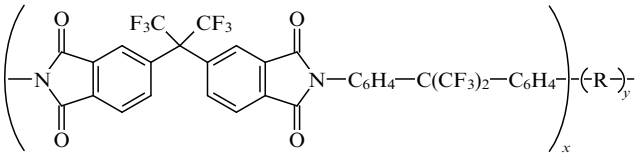
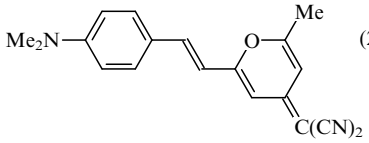
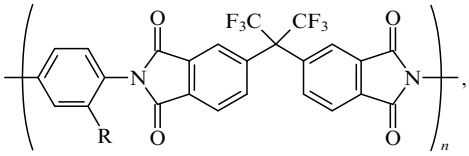
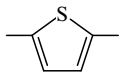
No.	Compound	λ /nm	d_{ZX} /pm V^{-1}	Ref.
1	α-Quartz	1064	d_{11} = 0.4–0.5	5, 70, 72–74
2	$BaTiO_3$	1064	d_{51} = 17	73
3	$LiTaO_3$	1064	d_{33} = 19	73
4	$LiNbO_3$	1064	41	73
5	Host — PMMA, guest — DANS (2 mass %)	1064	1	5
6	Host — spray-coated polytetrafluoroethylene, guest — DANS (10 mass %)	1064	6.2	75
7	Host — PMMA, guest — DO3	1064	5.8	5
8	Host [−O−C(O)−3-C_6H_3(OH)−5-C(O)−$(CH_2)_2$−NR−$(CH_2)_2$−]−, where R = $(C_6H_4SO_2(CF_2)_8F$; guest — chromophore NMePr−$C_6H_4SO_2C_8X_{17}$, where X = H (T_g = 80 °C), F (T_g = 83 °C)	1064	d_{33} = 3.4 3.0	77
9	Host — PMMA, guest — DR1	1064	d_{33} = 9	5
10	−[−CHR−CH_2−O−C_6H_4−CMe_2−C_6H_4−O−CH_2−CHR−CH_2−NR′−CH_2−]−, where R = −O−C(O)−CH=CHPh — pendent groups, NR′ — chromophore, R′ = −C_6H_4CN	1064	4.2	76
11	−[−CH_2−CHPh−]$_x$−[CH_2−CRMe−]$_y$−, where chromophore R = −C(O)−O−$(CH_2)_2$−C_6H_4−CH=N−C_6H_4−NMe_2	1064	d_{33} = 12.25	78
12	Copolymer of C(CO_2Me)Me=CH_2 and the chromophore $Et_2N-X-C(O)-NH-(CH_2)_2-O-C(O)-CMe=CH_2$, where −X− = 	1064	d_{33} = 13	79
13	PA	1542	d_{33} = 40	39
14	−[CH_2−CRMe−]$_n$, where R = −C(O)−O−$(CH_2)_2$−NEt−C_6H_4−N=N−C_6H_4  (T_g = 151 °C)	1064	d_{33} = 16.5	80
15	(*S*)-NPP-PHS (see text), *x* (%): 36 48 62 75 90	1064	d_{33} = 17.8 23.7 26.6 29.0 32.0	41
16	−[CH_2−CMeR−]$_x$−[CH_2−CMeR′−]$_y$−, where pendent chromophore is R = −C(O)−O−$(CH_2)_2$−NEt−C_6H_4−N=N−C_6H_3R″−NO_2, (a) R″ = H; R′ = −C(O)−OMe, x/y = 1; (b) R″ = −COOH; R′ = −C(O)−O−CH_2−CH(O)−CH_2−, *x*, %: 8 17 30	1320	d_{33} = 29 10.2 24.0 29.0	81
17	−CH_2−CMe_2−CRMe−C(O)−O−CH_2−CH(O)−CH_2−, where pendent chromophore is R = C(O)−O−CH_2−NMe−C_6H_4−N=N−C_6H_4−NO_2	1320	d_{33} = 47	82
18	−[CH_2−CMeR−]$_{0.9}$−[CH_2−CMe(COR′)−]$_{0.1}$− R = −C(O)−O−$(CH_2)_2$−NEt−C_6H_4−N=N−C_6H_4−NO_2, R′ = −NH−C_6H_3-3-$MeNO_2$	1064	d_{33} = 60	83
19	−[CH_2−CMe(CO_2Me)−]$_x$−[CH_2−CRMe−]$_y$−, where R = −C(O)−O−CH_2−C_6H_4−X=X−C_6H_4CN, −X=X− = −CH=CH−; *y* (%): 10.3 16.4 22.5 43.0 −X=X− = −N=N−; *y* (%): 11.9 16.4 31.5 44.0 49.0 71.7 100.0	1064	d_{33} = 8.8 11.5 12.0 12.0 5.2 21.0 68.0 45.0 32.0 31.0 26.0	84
20	Host — polyimide, guest — DANS	1300	d_{33} = 2.5	85
	or Et_2—C_6H_4—$(CH_2)_2$  C(CN)=C(CN)$_2$		40	

Table 3 (continued).

No.	Compound	λ /nm	d_{ZX} /pm V^{-1}	Ref.
21	 (T_g = 137 °C)	1338 1542	d_{31} = 23 15	86
22	Host —  (R is the group, which undergoes cross-linking upon photochemical or thermal action), guest —  (20 mass %)	1064	d_{33} = 13	87, 88
23	P1 P2 P3 (see text)	1064	d_{33} = 30 90 100	46
24	,	1064		
	where R = $-O-(CH_2)_2-NEt-C_6H_4-CH=CH-C_6H_4-SO_2Me$ (T_g = 240 °C); $-O-(CH_2)_2-NEt-C_6H_4-X-C_6H_4-NO_2$, where		d_{33} = 51	89
	$-X-$ =  (T_g = 227°C)		103	90
	$-X-$ = $-CH=CH-$ (T_g = 229°C)		146	90, 91
	$-X-$ = $-N=N-$ (T_g = 235°C)		169	90
25	Linear polyurethane with chromophores directed normally to the main chain	1064	d_{33} = 67	92
26	PU (see text)	1064	100	59
27	PU [$-O-(CH_2)_2-NR-(CH_2)_2-O-C(O)-NH-C(O)-]_n$, where R = $-C_6H_3(Me-N=N-C_6H_3Me-NO_2$	1064	140 – 223	93
28	Langmuir – Blodgett films of 2,4-bis[4-(*N*,*N*-dibutylamino)phenyl]squaraine $(C_4H_9)_2N-C_6H_4-C_4O_2-C_6N_4-N(C_4H_9)_2$	1064	d_{33} = 125	94

$\tau_1 = 0.6\pm0.1$ min, $\tau_2 = 8\pm0.5$ min, while for the relaxed film $\varphi = 0.35\pm0.05$, $\tau_1 = 2\pm0.3$ min, $\tau_2 = 28\pm2$ min.

The measurement of the decay kinetic curves for $\chi^{(2)}$ and U at 23 °C (Fig. 4) have practically have shown their virtually complete identity; $\varphi = 0.3\pm0.05$, $\tau_1 = 2.1\pm0.3$ min, and $\tau_2 = 110\pm5$ min. Consequently, the SHG in the PVAC + DO3 films is completely governed by the surface potential, *i.e.*, by the charges deposited on the films by the corona discharge in the range from T_g to 23 °C. A direct proof of this conclusion was obtained using an effective method for the removal of the surface charge: the film was immersed for 15 s in a saturated aqueous NaCl solution, which led to the disappearance of SHG and the surface potential (see Fig. 4, points on the x axis). Preliminary experiments have shown[29] that other known methods of the surface potential removal, namely, keeping in a moist atmosphere, contact with the grounded metallic electrode, *etc.*, are ineffective. With a PMMA + DO3 film non-swelling in water as an example it was shown that the disappearance of the surface charge is not connected to the swelling and plasticisation of the PVAC immersed for a short time in an aqueous solution. The SHG behaviour of this film after the removal of the surface charge is similar to that in the PVA + DO3 film (see Fig. 4).[64] For the latter system, it was sufficient to use even distilled water, *i.e.*, the charged particles are water-soluble; the cycles 'discharge in water – charging by the corona discharge' can be repeated many times without change of nonlinear optical and electrical characteristics; the charged film retains constant surface potential and $\chi^{(2)}$ for several months (time of observation) while kept in ordinary conditions. The unambiguous conclusion can be made on the basis of these results that all charge is concentrated on the film surface. In such a case, the surface potential is determined by the first term in Eqn (18).

Charging the film by the negative corona discharge results in predominant deposition of the CO_3^- ions onto the surface (see Refs 65, 66). The subsequent fate of the deposited ions depends on the characteristics of the polymeric system. First, the existence of

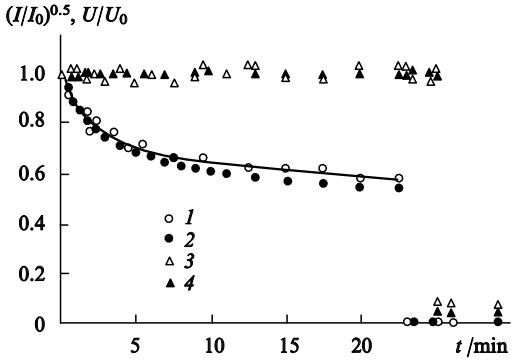


Figure 4. The kinetics of the decay of the second harmonic intensity and the surface potential. PVAC + 2 mass % of DO3 (*1*). PMMA + 5 mass % DO3 (*2*).
(*1*) second harmonic signal for PVAC + 2 mass % of DO3, keeping at 43 °C for 5 min, then charging by the corona discharge for 2 min at 23 °C; (*2*) surface potential for PMMA + 5 mass % DO3, charging by the corona discharge for 10 min at 23 °C, measurement at 23 °C; (*3*) second harmonic signal; (*4*) surface potential. the curve is plotted according to equation (19) with parameters $\varphi = 0.3$, $\tau_1 = 2.3$ min, $\tau_2 = 115$ min.

the electronic conductivity can not be assumed in the films. Even if we consider that the chromophores can serve as the electron-transport centres, their concentration (2 mass % – 5 mass %) is definitely insufficient for the effective electron (or hole) transport through the film as the mean distance between neighbouring transport centres should not be exceed ~ 15 Å.[67] In addition, penetration of ions into the bulk of the film should possibly be excluded. This is supported by the fact that after the polymer film treatment in the electrolyte solution the surface charges are practically completely removed (see Fig. 4).

The process of the surface potential decrease consisting of relatively fast (hundreds of seconds) and slow steps is well known. This was observed for different polymeric films without low-molecular-weight chromophores charged by the corona discharge (see Ref. 30 and references therein). For different polymers, the magnitude of the surface potential at the fast step varies from several to dozens percent relative to the initial value. It is assumed that the fast decay is connected with the drift of ions and their capture near the film surface by the polarisation and structural traps. The slow exponential decay seems to be related to the discharge of the captured charge because of the intrinsic bulk electric conductivity of the film. The rate of this decay is determined by the dielectric relaxation time (τ_M). Polymeric films always possess some ionic conductivity due to the residual solvent or ionic dissociation of the polar groups in macromolecules.[30, 68] Thus, the decay of the surface potential is expressed by equation

$$U = U_0\left[\varphi\exp\left(-\frac{t}{\tau}\right)+(1-\varphi)\exp\left(-\frac{t}{\tau_M}\right)\right],$$

where $\tau = (v_t N\sigma)^{-1}$, $\tau_M = \varepsilon\varepsilon_0/e n\mu$, v_t is the thermal velocity of ions, N is the concentration of the capture centres, σ is the charge capture cross-section, e is the electron charge, n and μ are the concentration and the mobility of the free charge carriers in the polymer bulk.

Retardation of the decay kinetics of $\chi^{(2)}$ upon physical ageing of a polymer can be explained by the decrease in the polymer free volume. The diffusion coefficient of molecules D in an amorphous phase at $T < T_g$ is linked to the free volume by Eqn (16). Taking into account the Einstein relation

$$\frac{\mu_d}{D} = \frac{e}{kT},$$

where μ_d is the mobility, we obtain that the decrease in $V_{fr}(T)$ leads to the increase in τ_M.

VII. The second harmonic electrooptical coefficient and nonlinear coefficient

The idea of using light for information transmission has become a reality after the invention in the 50 – 60s of coherent radiation sources in UV, visible, and IR ranges, as these allow one to increase substantially the capacity of the transmitting optical systems and to multiply the capacity of systems in the millimetre range. However, in addition to the coherent light sources it was necessary to develop transmitting media, active optical elements, materials for recording, storage and reproduction of optical information that would be cheap, technological, highly efficient, and compatible with modern microelectronic devices. Nowadays, organic polymeric materials of different chemical structure meet these requirements entirely. Polymeric nonlinear optical systems are promising for their utilisation as the light beam modulators, fibre optic switches, the laser radiation harmonic generators for enhanced capacity of recording, photorefractive media for the reversible recording of the holograms with the diffractional efficiency close to 100%, *etc.*[69–71] The main parameter, which characterises an electroptical material is the electrooptical coefficient r. For example, r is 1.43 pm V^{-1} for AsGa, and 30 pm V^{-1} for $LiNbO_3$, it increases considerably (up to 100 pm V^{-1}) for polymers.[70]

On the one hand the electrooptical coefficient relates the change in the refractive index Δn of a polymer to the magnitude of the external electric field E: $\Delta n = -0.5n^3 rE$. On the other hand, the electrooptical coefficient is connected with the second-order susceptibility, which determines the intensity of the second harmonic

$$r = -\frac{2\chi^{(2)}}{n^2\varepsilon}, \qquad (20)$$

If r directly characterises the effects of modulation and switching of light fluxes and also the efficiency of the hologram recording on polymeric photorefractive materials, $\chi^{(2)}$ determines the efficiency of the laser radiation frequency transformation. Generally, the quantities r and $\chi^{(2)}$ are of equal value for the characterisation of the electrooptical properties of the material, however, in this review more numerous and detailed studies on the second harmonic generation are analysed. In addition, the relation of $\chi^{(2)}$ to the molecular motions in a polymeric matrix is direct and more obvious.

The steady-state values of the second harmonic nonlinear coefficient ($d_{33} = 0.5\chi^{(2)}_{ZZZ}$) measured (mainly at 20 °C) after the orientation of the chromophores in a constant electric field at the glass transition temperature for different polymeric systems are listed in Table 3. Despite different conditions corresponding to the measurement of this characteristic, some general features may be found. As is seen, the host – guest systems with small rotational diffusion times are characterised by low d_{33} values. The nonlinear coefficient in polyesters with chromophores in the pendent substituents (entries 17 – 19) is close to the d_{33} values in inorganic crystals and is increased markedly upon replacement of the stilbene-containing chromophores by the diazo groups. In the polymer 19 (where $-X=X-$ is $-N=N-$), the increase in the concentration of the chromophore groups first results in the increase of d_{33}, then it passes through a maximum (with one third of the repeating units containing the chromophores), and then gradually decreases. The decrease is related to the change in the polymer conformation at high chromophore content. The d_{33} values of polyimides (entry 24) with the high glass transition temperatures and, consequently, low polymeric chain mobility at room temperature exceeding remarkably those in inorganic crystals. Polyurethanes (entry 27), which acquire rigid structure after

the orientation due to the presence of intermolecular hydrogen bonds, possess the highest d_{33} values ($\geqslant 200$ pm V^{-1}).

Polyesters with the pendent chromophore groups that alternate with the cinnamate groups $(-(CH=CH)-)_n-R$ (R is alkyl), are used for the creation of a rigid polymeric matrix following UV radiation.[95] It is known that UV light induces [2 + 2]-cycloaddition involving of the double bonds and results in cross-linking of the neighbouring side groups. The polymers 16b and 17 contain the epoxy groups which are cross-linked in the course of the orientation in the constant field at the temperature above 70°C. The absence of the effect of the epoxy groups (see entries 16a and 16b) is explained by the fact that the cross-linking proceeds faster than orientation, which becomes ineffective in the rigid cross-linked matrix. It should be added that in polydiacetylenes [96, 97] the stable oriented state is achieved even in the absence of the external electric field, namely, upon radiation-chemical or thermal synthesis from substituted diacetylene leading to the formation of a cross-linked three-dimensional structure. The polymer obtained in this synthesis had $d_{33} = 5.57$ pm V^{-1}.

All systems considered above contain chromophores with intramolecular electron transfer. Significant effects can be expected in polymeric systems with intermolecular donor-acceptor complexes. This followed from the fact that self-organised Langmuir – Blodgett films [94] consisting of centrosymmetrical molecules of 2,4-bis[4-(*N*,*N*-dibutylamino)-phenyl]squaraine $(C_4H_9)_2N-C_6H_4-C_4O_2-C_6H_4-N(C_4H_9)_2$ possessed high second-order susceptibility $\chi^{(2)}_{ef} = 250$ pm V^{-1} ($d_{ef} = 125$, see Table 3, entry 28). The effect is due to the formation of the noncentrosymmetrical intermolecular donor-acceptor T-shape complexes, where the donor amino group of one molecule is oriented towards the central four-membered acceptor ring $(-C_4O_2-)$ of another molecule.

As regards practical application of polymeric materials with stable nonlinear second-order properties, for example, as optical switches or modulators, the absence of optical absorption at the wavelength of the second harmonic and photochemical stability of the chromophore groups and molecules with respect to the atmospheric oxygen are of significant importnance.[98] The former demand can be met by the synthesis of appropriate chemical structures, and the latter is achieved by the introduction of oxygen acceptors into the working layer and the use of protective layers. In all cases, low electric conductivity of polymeric nonlinear optical systems is a must.

VIII. Conclusion

In polymeric host – guest NLO systems in ordinary conditions (room temperature or temperature up to T_g, the range of characteristic time from ~ 0.1 s to ∞) the decay kinetics of the SH intensity is determined entirely by the kinetics of the change in the surface potential. This phenomenon is explained by the fact that the characteristic times of the rotational diffusion of chromophores are shorter than the times of flight of the charged particles through the polymeric films. The reasons for the decrease in the surface potential and the features of this process are not sufficiently studied to date. In polymeric systems where chromophores are chemically linked to the polymer chain (pendent substituents) or they are the fragments of the main chain, at the temperatures below T_g the behaviour of the SH is determined by the dynamic characteristics of the polymeric matrix. For example, the formation of a polymeric network or strong intermolecular interaction due to the formation of the hydrogen bonds or the presence of the charged groups determine the SH stability with time, which is not connected with the presence of an external electric field.

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