Vol. A53 (1978) ACTA PHYSICA POLONICA No 5

MACROMOLECULAR POLYDISPERSITY IN NONLINEAR ELECTRIC METHODS. STEADY STATE IN HOMOGENEOUS FIELD*

By W. Pyżuk and G. Bałakier

Laboratory of Nonlinear Optics and Chemical Physics, Institute of Fundamental Problems of Chemistry, University of Warsaw**

(Received August 2, 1977)

The formulas describing the nonlinear dielectric effect as well as nonlinear electrooptic effects in solution of polydisperse macromolecules are derived. The applications of these effects to the examination of macromolecular polydispersity are discussed, some of the results are tested experimentally.

1. *Introduction*

In the work on molecular structure, especially in biopolymer solutions, the best results are obtained with the parallel use of several research methods, e. g. [1]. Among them and of no little importance are the methods supplying some information about electric characteristics of macromolecules. It can be easily understood as in many cases macromolecules, compared with small molecules, possess rather unusual electric properties. In 1958 the giant dipole moment, c. 10^3 D, of synthetic polypeptides was discovered by Wada [2]. This fact let O'Konski et al. elaborate the theory of high electric field birefringence in macromolecular solutions [3]. Shah [4] and also Holcomb and Tinoco [5] have extended that to macromolecules of any symmetry and for other optical phenomena induced by the electric field. A theory of electric permittivity changes of macromolecular solutions subjected to the electric field has been given by Kielich [6].

All these field induced effects make it possible to compute the molecular factors responsible for the orientation of anisotropic solute molecules. On the basis of the relationship between the measured effect and the intensity of the applied field the dipole moment and the anisotropy of polarizability can be determined. Both these factors determine the mean degree of molecular orientation and in that way they limit the value of the effect.

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* Reported in part at the 2nd Summer School on "Application of Dielectric Methods to Organic Chemistry", Karpacz, Poland, September 16–20, 1975.

** Address: Instytut Podstawowych Problemów Chemii, Uniwersytet Warszawski, Żwirki i Wigury 101, 02-089 Warszawa, Poland.

The question of nonlinear electric effect (NEE) arises when a field induced effect ΔA being measured in an electric field of intensity E complies with the condition: $\lim_{E\to 0} (\partial \Delta A/\partial E) = 0$, as in the case of electrically induced birefringence, dichroism, electric permittivity changes, optical activity changes, etc.

The theories of these effects developed up to now concern dilute solutions of identical, rigid macromolecules, unchangeable in the electric field. In fact we rather have something to do with polydisperse specimens of macromolecules of the same kind, but polymerized to various degrees. Therefore it is of great importance to extend the NEE theories to that more real case. This problem has been put forward but not solved in the work of Holcomb and Tinoco [5], and recently in the work of Voitylov and Trusov [7] as well. On the other hand the information about the polydispersity of an examined sample, when obtained from the analysis of the NEE data, not only do characterise the specimen but can reveal for instance the polymerization mechanisms [8–9], association processes in solution and so on.

This paper is devoted mainly to the nonlinear dielectric effect (NDE). On the grounds of this effect other nonlinear electrooptic effects can be evaluated. Discussion will be limited to the condition of steady state arising in the solution under the influence of a homogeneous electric field. Other conditions, as well as the case of nonrigid molecules, changing their properties in the field, will be a subject of another paper.

2. *Theory*

2.1. Nonlinear dielectric effect

The NDE consists in the creation of the electric permittivity change $\Delta\varepsilon(E)$:

$$\Delta\varepsilon(E) = \varepsilon_{\parallel}(E) - \varepsilon(0) \tag{2.1}$$

under the action of a strong electric field of intensity E. This change is measured by a very small measuring field, usually parallel to $\vec{E}$, thus the subscript on ε will be hereafter omitted. The results of Kielich's NDE theory for axially symmetric macromolecules [6] is given here in a slightly changed notation:

$$\Delta\varepsilon = \frac{4\pi}{3}\frac{c_v}{v}\left(\pm 2|\Delta\alpha|R_\alpha - \frac{\mu^2}{kT}R_\mu\right). \tag{2.2a}$$

c_v denotes the volume fraction of macromolecules, the volume v, the dipole moment $\mu = \mu_1$ and the anisotropy of electric polarizability $\Delta\alpha = \alpha_{11} - \alpha_{22}$ are the molecular parameters (M). R_α and R_μ are the molecular orientation functions [6] depending on the electric field intensity via the orientation factors: $\beta = \mu E/kT$ — the dipolar one, and $\gamma = |\Delta\alpha|\,E^2/2kT$ — that of the anisotropy. The sign of $\Delta\alpha$ rules over the choice of the sign ± in all equations.

It is appropriate to express the permittivity change $\Delta\varepsilon$ measured in a polydisperse mixture by the formula

$$\Delta\varepsilon = \frac{4\pi}{3}\frac{c_v}{{}^m v}\left(\pm 2\,{}^m|\Delta\alpha|\,{}^m R_\alpha - \frac{{}^m\mu^2}{kT}\,{}^m R_\mu\right), \tag{2.2b}$$

analogical to Eq. (2.2a). Here "m"-denoted functions relating to the mixture are introduced instead of molecular parameters and molecular orientation functions. These functions can be obtained in the subsequent procedure.

In a dilute polydisperse solution of noninteracting macromolecules the value of $\Delta\varepsilon$ is the sum of contributions made by all the mixture components. Later on the summation will be replaced by integration over all the degrees of polymerization p as it is generally accepted for considering the macromolecular polydispersity [8–10]. It is not correct only in the case of oligomers being excluded in the following from our interest. Introducing the distribution function $q(p)$ as the number-fraction of p-mers and assuming that the density of macromolecules does not depend significantly on p, we can express the concentration $c_v(p)$ of the p-mers by the total concentration c_v:

$$c_v(p) = \frac{p}{\langle p\rangle} q(p)c_v, \tag{2.3}$$

where bracketed functions here, as well as in all the following, denote

$$\langle\ldots\rangle = \int_0^\infty \ldots(p)q(p)dp. \tag{2.4}$$

By the summation of all the molecular contributions $\Delta\varepsilon(p)$ given by Eqs. (2.2a) and (2.3) the total effect $\Delta\varepsilon$ can be expressed in the form

$$\begin{aligned}\Delta\varepsilon &= \int_0^\infty \Delta\varepsilon(p)dp \\ &= \frac{4\pi}{3} c_v \left\langle \frac{1}{v}\left(\pm 2|\Delta\alpha|R_\alpha - \frac{\mu^2}{kT} R_\mu\right) p\right\rangle \frac{1}{\langle p\rangle}.\end{aligned} \tag{2.5}$$

For the transformation of Eq. (2.5) into Eq. (2.2b) it is necessary to accept the relation between the degree of polymerization and molecular parameters:

$$v = v_0 p, \qquad \mu = \mu_0 m(p), \qquad |\Delta\alpha| = |\Delta\alpha_0|\, a(p), \tag{2.6}$$

where the subscript "0" concerns the mer. Inserting Eqs. (2.6) into Eq. (2.5) and profiting from the independence on p of all the "0"-indexed parameters we have

$$\begin{aligned}\Delta\varepsilon &= \frac{4\pi}{3} \frac{c_v}{v_0\langle p\rangle}\left(\pm 2|\Delta\alpha_0|\,\langle aR_\alpha\rangle - \frac{\mu_0^2}{kT}\langle m^2 R_\mu\rangle\right) \\ &= \frac{4\pi}{3} \frac{c_v}{\langle v\rangle}\left(\pm 2\langle|\Delta\alpha|\rangle \frac{\langle aR_\alpha\rangle}{\langle a\rangle} - \frac{\langle\mu^2\rangle}{kT} \frac{\langle m^2 R_\mu\rangle}{\langle m^2\rangle}\right).\end{aligned} \tag{2.7}$$

Here the field dependent averages $\langle aR_\alpha\rangle$ and $\langle m^2 R_\mu\rangle$ were divided by $\langle a\rangle$ and $\langle m^2\rangle$ to become the orientation functions ${}^mR_\alpha$ and ${}^mR_\mu$. These functions are subjected in that way to the normalising condition: $\lim_{E\to\infty} R = k$, where $k = (1\pm 3)/4$. Now ${}^mv$, ${}^m|\Delta\alpha|$ and ${}^m\mu^2$ from Eq. (2.2b) are identical to $\langle v\rangle$, $\langle|\Delta\alpha|\rangle$ and $\langle\mu^2\rangle$ from Eq. (2.7). It is evident that no arbitrary assumptions are required in relating equivocally the polydisperse functions to the averaged molecular parameters.

In many cases it is reasonable to consider the NDE constant defined as $\Delta\varepsilon/E^2$, and called also Piekara factor [11]. That constant approaches a finite value for low fields, therefore it is useful in describing small field effects. For polydisperse systems the NDE constant can be obtained again by the summation of all the molecular contributions $\Delta\varepsilon(p)/E^2$ and by presenting the result in a form convenient for dipolar macromolecules:

$$\frac{\Delta\varepsilon}{E^2} = \frac{4\pi}{3}\frac{c_v}{{}^m v}\left\{\pm 2\,{}^m|\Delta\alpha|\frac{{}^m\mu^2}{k^2T^2}\,g\,{}^m(R_\alpha/\beta^2) - \frac{{}^m\mu^4}{k^3T^3}\,{}^m(R_\mu/\beta^2)\right\}, \tag{2.8}$$

where the factor $g = \langle am^2\rangle/\langle a\rangle\langle m^2\rangle$ results from the transformation of ${}^m(|\Delta\alpha|\mu^2)$ into ${}^m|\Delta\alpha|{}^m\mu^2$. We do not discuss here nondipolar macromolecules, because it is not possible to observe their extremely small NDE in dilute solutions.

The functions related to the polydisperse system occurring in Eqs. (2.2) and (2.8) are given for molecular parameters M by

$${}^mM^i = \langle M^i\rangle, \tag{2.9a}$$

and for the field dependent functions by

$${}^mR_\mu = \langle r_{02}R_\mu\rangle, \quad {}^m(R_\mu/\beta^2) = \langle r_{04}R_\mu/\beta^2\rangle,$$

$${}^mR_\alpha = \langle r_{10}R_\alpha\rangle, \quad {}^m(R_\alpha/\beta^2) = \langle r_{12}R_\alpha/\beta^2\rangle, \tag{2.9b}$$

where $r_{ij} = a^im^j/\langle a^im^j\rangle$. These formulas enable the calculation of $\Delta\varepsilon$ and $\Delta\varepsilon/E^2$ in a macromolecular mixture of known composition $q(p)$ and of a given relation $M(p)$ between molecular parameters and the degree of polymerization.

2.2. Nonlinear electrooptic effects

There are two ways to measure the ΔA effects induced by an electric field. Firstly, we can measure, in a given direction the change of any physical property due to the action of a strong field. For instance, in addition to the NDE, the changes in refractivity index n defined by Eqs. (2.10a, b) can be measured by interferometric methods [12]. Secondly, we can measure the difference of a physical property in two directions, usually parallel and perpendicular to the inducing field. The example is the birefringence defined by Eq. (2.10c) and measured in the Kerr effect [13],

$$\Delta n_{\parallel}(E) = n_{\parallel}(E) - n(0) \tag{2.10a}$$

$$\Delta n_{\perp}(E) = n_{\perp}(E) - n(0) \tag{2.10b}$$

$$\Delta n(E) = n_{\parallel}(E) - n_{\perp}(E). \tag{2.10c}$$

The Havelock formula [13]: $\Delta n_{\parallel}/\Delta n_{\perp} = -2$ proves that the two above mentioned ways are equivalent, for

$$\Delta n = \tfrac{3}{2}\Delta n_{\parallel} = -3\Delta n_{\perp}. \tag{2.11}$$

Similar relationship can be derived for other physical properties: electric permittivity, optical absorption, optical activity and so on [5]. The experimental way chosen depends then on the conveniency of procedure.

The easiest to observe electrooptical effect is the birefringence Δn related to the Kerr constant $B = \Delta n/\lambda E^2$, where λ is the wave-length. The dipole moment and the anisotropy of electric polarizability contribute to the molecular orientation process enforcing the anisotropy of a liquid, measured here as Δn. The reorientation of dipoles, depending on frequency, shows dispersion. Thus only the reorientation of polarizability ellipsoid contributes to the effect detected by the very frequently changeable optical field. In this way for all the nonlinear electrooptic effects, or more generally, for all the electric effects measured above the dipole dispersion frequency region we have

$$\Delta A = \Delta A^s R_\alpha^0/k, \tag{2.12}$$

where ΔA^s is the value of the effect ΔA in an extremely strong electric field and where the orientation function R_α^0 is given explicitly in part 3.

The saturation values ΔA^s are related to the anisotropy of molecules. In particular, the high frequency dielectric saturation $\Delta\varepsilon^s$ and the birefringence saturation Δn^s can be found from Eqs. (2.2) and (2.11) using the relation $\varepsilon = n^2$:

$$\Delta\varepsilon^s = \pm k\frac{8\pi}{3}c_v\frac{{}^m|\Delta\alpha|}{{}^m v}, \quad \Delta n^s = \pm k\frac{2\pi}{n}c_v\frac{{}^m|\Delta\alpha^0|}{{}^m v} \tag{2.13}$$

$\Delta\alpha^0 = \alpha_{11}^0 - \alpha_{22}^0$ denotes the optical anisotropy, otherwise the anisotropy of electronic polarizability α^0. In general it differs from the electric polarizability α as it is the sum of the electronic and atomic polarizabilities.

Formally the saturation effects should be always positive because $k = (1 \pm 3)/4$ depends on the sign of molecular anisotropy. Nevertheless, a negative Δn^s has been observed for macromolecules of $\beta \gg \gamma$ [14]. In point of fact for dipolar molecules of negative anisotropy the electric fields applied in practice are enough to orient fully the dipole moment (which corresponds to $k = 1$) but not to enforced the reorientation via the greatest induced dipole moment of an oblate ellipsoid of polarizability (which corresponds to $k = -1/2$). Thus only the first value of k should be applied in Eq. (2.13) apart from the sign of molecular anisotropy.

3. *Applications*

3.1. General remarks

The dependence of field induced effects on field intensity and even the appearance of full saturation has been observed in many macromolecular solutions [13]. The media of interest divide into two classes: polyelectrolytes in water-like solutions and rigid, inert macromolecules in organic solvents. Polyelectrolytes are of limited use for testing the theories of nonlinear effects. The high anisotropy of electric polarizability causing their easy orientation in an electric field is not a purely molecular parameter, since it greatly depends on the molecular concentration, addition of salts etc.

On the contrary synthetic polypeptides of a helical structure in solution are suitable media for testing the theoretical consideration. It is possible to prepare nearly monodisperse samples with a narrow distribution in the degrees of polymerization (d. p.) concentrated around the mean value fixed in advance [9]. The high dipole moment of helices can be simply interpreted as a sum of identically directed dipole moments of all the mers of the molecule. The dipole moment of ideal helices as well as the polarizability increase then proportionally to the d. p., that is:

$$a(p) = p, \qquad a^0(p) = p, \qquad m(p) = p \tag{3.1}$$

according to the notation used in Eq. (2.6). This information enables one to investigate the properties of samples consisting of nearly identical macromolecules of known electrical properties as well as to prepare the mixtures of a given composition, modelling on the polydisperse systems.

In the following the case of macromolecules with the dipole mechanism of nonlinear effect enforcement, when $\beta \gg \gamma$, will be discussed. The orientation functions for monodisperse systems are then of the form [15]

$$R_\mu = 3\mathscr{L}^2(\beta)+6\mathscr{L}(\beta)/\beta-2, \quad R_\alpha^0 = 1-3\mathscr{L}(\beta)/\beta, \quad R_\mu^0 = 0, \tag{3.2}$$

where $\mathscr{L}(\beta) = \operatorname{cth}\beta-1/\beta$, resulting from Kielich's general formulas [6]. Here the first equation concerns the effect measured at frequencies below the dipole dispersion region and the remaining ones refer to the effects measured above these frequencies. Functions for polydisperse systems can be obtained from Eqs. (3.2) and (2.9)

$$^{m}R_\alpha^0 = 1-3\langle a^0\mathscr{L}(\beta)/\beta\rangle/\langle a^0\rangle$$

$$^{m}R_\mu = 3\langle m^2\mathscr{L}^2(\beta)\rangle/\langle m^2\rangle-2(1-3\langle m^2\mathscr{L}(\beta)/\beta\rangle/\langle m^2\rangle). \tag{3.3}$$

The form of the functions $^{m}(R_\alpha^0/\beta^2)$ and $^{m}(R_\mu/\beta^2)$ describing the dependence of nonlinear effect constants $\Delta A/E^2$ on field intensity can also be easily given.

Expanding the above functions in a power series of field strength, the birefringence saturation and the dielectric saturation at very high fields can be computed for $E^{-1} \to 0$:

$$\Delta n = \pm\frac{2\pi}{n}\frac{c_v}{\langle v\rangle}\langle|\Delta\alpha^0|\rangle\left\{1-\frac{3}{\langle\mu\rangle}\frac{kT}{E}+\dots\right\},$$

$$\Delta\varepsilon = -\frac{4\pi}{3}\frac{c_v}{\langle v\rangle}\frac{\langle\mu^2\rangle}{kT}\left\{1-\frac{3}{\langle\mu^2\rangle}\left(\frac{kT}{E}\right)^2+\dots\right\}, \tag{3.4}$$

where $c_v/\langle v\rangle = N$ is the number of macromolecules per unit volume.
The corresponding result for $\Delta\varepsilon$ in monodisperse systems has been obtained formerly [16]. On the other hand both the effect constants at very low fields, where $E^2 \to 0$, are

$$B = \pm\frac{2\pi}{15n\lambda}\frac{c_v}{\langle v\rangle}\langle|\Delta\alpha^0|\rangle\frac{\langle\mu^3\rangle}{\langle\mu\rangle}\frac{1}{k^2T^2}\left\{1-\tfrac{2}{21}\frac{\langle\mu^5\rangle}{\langle\mu^3\rangle}\left(\frac{E}{kT}\right)^2+\dots\right\}$$

$$\frac{\Delta\varepsilon}{E^2} = -\frac{4\pi}{15}\frac{c_v}{\langle v\rangle}\frac{\langle\mu^4\rangle}{k^3T^3}\left\{1-\tfrac{10}{63}\frac{\langle\mu^6\rangle}{\langle\mu^4\rangle}\left(\frac{E}{kT}\right)^2+\dots\right\}. \tag{3.5}$$

As it follows from Eqs. (3.4) and (3.5) the calculation of those values by extrapolation procedure allows one to determine the i-th order dipole moment defined as

$$\mu_i = \langle \mu^i \rangle^{1/i} \tag{3.6}$$

for $i = 1, 2, 3, 4, 5, 6$. The comparison of the mean values of different orders is a useful method to detect the polydispersity in macromolecular systems [8–9].

We have compared some of the above results with the experimental data of the birefringence induced in polydisperse solutions of synthetic polypeptides.

3.2. Experimental

The arrangement and the technique of measurement are described elsewhere [17]. The Kerr constant was determined with standard error varying from 3% for the lowest applied fields of intensity 5 kV/cm, to 1% for the highest ones, up to 40 kV/cm. The polydisperse mixture was made up by mixing 1 : 1 two poly-γ-benzyl-L-glutamate (PBLG) solutions of the same concentration $c_v = 2.2 \times 10^{-4}$ (0.29 g/l). PBLG of the mol. wt. 75.000 (Miles-Yeda, Lot Gl 112) and PBLG of the mol. wt. 125.000 (Schwarz-Mann, Lot Y3633) were dissolved in 1,2-dichloroethane with 1% mol N,N-dimethylformamide added to prevent molecular association. The results were corrected for the birefringence of the solvent.

In Fig. 1 the points representing the normalized Kerr constant of the examined solutions are shown. For the original solutions the theoretical data $B(E^2)/B(0)$ described by the function $15 R_\alpha^0/\beta^2$ are drawn as the two extreme continuous lines. The dipole moments of components were obtained, according to Eq. (3.2), by the best fitting of those curves to the experimental points. The middle curve, showing the function of $15^m(R_\alpha^0/\beta^2)$, was calculated for the known concentrations and for the known dipole moments of the components. The broken line representing a hypothetical monodisperse sample of the same dipole

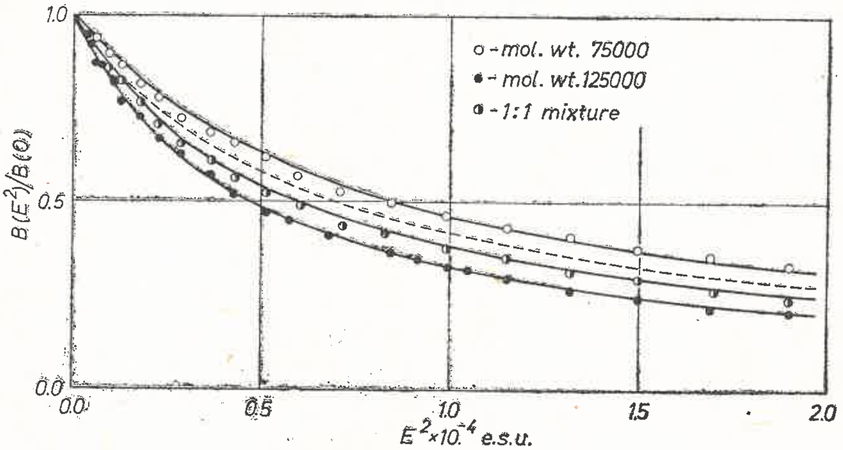

Fig. 1. Normalized Kerr constant $B(E^2)/B(0)$ vs. the square of the electric field intensity E^2 for three PBLG samples. Dashed line refers to a monodisperse sample of the same dipole moment $\langle \mu \rangle$ as that of the mixture

moment as the first order mean moment dipole of the mixture is also shown for comparison.

The PBLG 125.000 sample, within the range of experimental error, behaves like a monodisperse of the intrinsic anisotropy $\Delta\alpha^0/v = 4.35 \times 10^{-3}$. This value was assumed for the second, a slightly polydisperse sample and for the mixture. From the value of $B(0)$ obtained by extrapolation, and from the initial slope of $B(E^2)/B(0)$ vs E^2 the mean dipole moments of the samples were computed according to Eq. (3.5). The results are listed in Table I. Again we find satisfactory agreement between the experimental data and that expected for the mixture.

TABLE I

Normalized dipole moments of the three PBLG samples

Composition of sample in molar fractions $f_{75\cdot000}:f_{125\cdot000}$	Normalized dipole moments $\times 10^2$ in e. s. u.		
	$\frac{1}{kT}\langle\mu\rangle$	$\frac{1}{kT}\left(\frac{\langle\mu^3\rangle}{\langle\mu\rangle}\right)^{1/2}$	$\frac{1}{kT}\left(\frac{\langle\mu^5\rangle}{\langle\mu^3\rangle}\right)^{1/2}$
1.000 : 0.000	3.58 ± 0.15 [a]	3.64 ± 0.04	3.75 ± 0.15
0.000 : 1.000	4.89 ± 0.05 [a]	4.89 ± 0.05	4.87 ± 0.10
0.622 : 0.378	— 4.07 [b]	4.23 ± 0.05 4.22 [b]	4.46 ± 0.10 4.42 [b]

[a] estimated from data for all the fields used; [b] expected on the basis of (a) data.

4. *Discussion*

Besides the possibility of calculating of several of the mean dipole moments, exemplified in part 3, there are some other applications of NEE to macromolecular polydispersity research. The parameters of an assumed distribution $q(p)$ can be evaluated by obtaining a best fit of the calculated NEE-field strength curves to the experimental data.

Up to now we have dealt with a rather simple problem of adding the contributions from the particular degrees of polymerization (d. p.) just to compute the properties of a polydisperse system. The inverse problem [10, 18], consisting in finding a $q(p)$ distribution based on the measured properties of the system, is more difficult. Apart from the mathematical difficulties the problem reduces itself to knowing the molecular parameters $M(p)$ as a function of d.p. It seems that various applications of this relationship can be useful for further investigation of macromolecules, e. g. dipole moments as well as molecular anisotropies depend on the rigidity of helical structures in relation to the degree of polymerization. The measurement of NEE carried out in strongly polydisperse samples of a given composition is necessary for this purpose.

Such investigation can concern not only rod-likehelical polypeptides but also dipolar macromolecules of a worm-like chain configuration and even those of a random coil.

However, to get the right advantage from applying the NEE to the determination of the functions $q(p)$ or $M(p)$ a very high experimental accuracy is necessary as well as the possibility of using the electric field within as wide range of strengths as possible. At present it excludes all the nonlinear effects, except the Kerr effect, from our field of interest. The successful application of NDE requires higher sensitivity of measurement performed in weak fields. Other nonlinear effects, e. g. nonlinear optical activity [19], are barely observed.

The authors are greatly indebted to Professor A. Piekara and Doc. Dr. T. Krupkowski for helpful discussions.

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