

**RAFAŁ LEDZION¹, STEFAN KAROLCZAK²,
PIOTR GÓRSKI¹, WŁODZIMIERZ KUCHARCZYK¹**

¹Institute of Physics, Technical University of Łódź

Wólczańska 219, 90-924 Łódź, Poland. e-mail: rafal.ledzion@p.lodz.pl

²Institute of Applied Radiation Chemistry, Technical University of Łódź
Wróblewskiego 15, 93-590 Łódź, Poland. e-mail: skarol@mitr.p.lodz.pl

KERR CONSTANT OF FOMBLIN Z

The Kerr constant B of polyperfluoroethylenemethylene oxide Fomblin Z has been determined within the temperature range 295-323K. At 300K the constant B was found to be equal to $1.7 \cdot 10^{-15} \text{ m/V}^2$. The results obtained indicate usefulness of this oligomeric compound as an immersion liquid in measurements of the quadratic electrooptic effect and electrostriction in crystals.

Keywords: polyperfluoroethylenemethylene oxide Fomblin Z,
Kerr effect, quadratic electrooptic effect.

1. INTRODUCTION

In centrosymmetric crystals and liquids phenomena described by a third-rank polar tensor, like the linear electrooptic effect, are vetoed by symmetry and the lowest-order electrooptic effect is the quadratic one [1]. In liquids changes in the refractive index quadratic with electric field are often called as the Kerr effect. According to the frequency of involved electric field one can consider the electrooptic and optical Kerr effects for the static or low-frequency and optical frequency fields, respectively. The nature and, therefore, magnitude of nonlinear interactions responsible for the electrooptic and optical Kerr phenomena are very different. This work is devoted to measurements of the electrooptic Kerr effect.

The Kerr effect can be described in terms of various coefficients. In this work we follow the phenomenological theory of linear and quadratic electrooptic effects developed by Pockels [2] who introduced electrooptic coefficients defined in terms of changes in the optical impermeability tensor η_{ij}

which are induced by the low-frequency electric field \mathbf{E} . In a principal axes system the quadratic electrooptic coefficient is defined as

$$g_{ijk} = \frac{1}{2} \frac{\partial^2 \eta_{ii}}{\partial E_j \partial E_k}. \quad (1)$$

It follows from equation (1) that the changes in the refractive index due to the applied low-frequency field are given by [2]

$$\Delta n = \frac{1}{2} n^3 g_{ijk} E_j E_k. \quad (2)$$

Pockels coefficients are commonly employed in investigations of electrooptic properties of crystals. In liquids the induced birefringence Δn is usually described in terms of the factor B known as the Kerr constant

$$\Delta n = B \lambda E^2, \quad (3)$$

where λ is the light wavelength.

Up to now the linear electrooptic effect in many noncentrosymmetric crystals has been precisely measured. The quadratic electrooptic properties of the most crystals are, however, still not well recognized (see, e.g., [3-8]). This is despite the fact that the quadratic electrooptic effect in crystals attracts attention as related to numerous nonlinear phenomena (see, e.g., [3]).

Coefficients of the quadratic electrooptic effect in crystals usually need very sensitive experimental techniques to be determined. In some compounds the coefficients measured by different authors differ even by three orders of magnitude. For example, such spread can be observed for the quadratic electrooptic coefficients in the KH_2PO_4 (KDP) family of crystals. The reasons of the discrepancy have been discussed in [3,4], where a necessity of remeasurements of the quadratic electrooptic coefficients in many crystals, especially these which lack a center of inversion, have been shown.

To increase the accuracy of measurements of the quadratic electrooptic coefficients, or even sometimes to make them possible, it is necessary to apply to the sample the electric field of relatively high strength. This is often difficult to do. Many crystals under interest, are grown from solutions and are hygroscopic. To reduce the risk of electric breakdown the sample can be placed in a bath containing a liquid which does not solve the crystal (see, e.g., [3,5,9]). In measurements of electrooptic properties based on interferometric methods the use of two immersion media with different refractive indices makes also possible to evaluate changes in the optical path due to the electrostriction [9]. Any liquid is, however, a source of an additional contribution to the modulation of the light beam related to the fringing electric field and the Kerr constant of the liquid. When the Kerr constant is large enough, there appear difficulties in

distinguishing between contributions due to the modulation of the light by the crystal sample and that of the liquid. Usually the constant B lay in the range from 10^{-12} m/V² to 10^{-15} m/V². For example, the values of B determined at room temperature for nitrobenzene, water and metylosilicone oils are roughly; $2 \cdot 10^{-12}$ m/V², $5 \cdot 10^{-14}$ m/V² and $2 \cdot 10^{-15}$ m/V², respectively. By taking into account equations (2) and (3), the quadratic electrooptic coefficient as defined by Pockels may be related to the Kerr constant B by the relation

$$g = \frac{2\lambda B}{n^3}. \quad (4)$$

Thus, the values of B listed above correspond roughly to the Pockels quadratic electrooptic coefficient equal to $1 \cdot 10^{-18}$ m²/V², $3 \cdot 10^{-20}$ m²/V² and $1 \cdot 10^{-21}$ m²/V² for nitrobenzene, water and metylosilicone oils, respectively. One notes that despite the fact that metylosilicone oils are known for low electrooptic response, their quadratic electrooptic coefficients are close to that expected in KDP- type crystals [3-5].

The aim of this work is to test a possibility of application of polyperfluoroethylenemethylene oxide Fomblin Z as an immersion liquid to increase the sensitivity of measurements of quadratic electrooptic and electrostrictive coefficients in crystals. Investigations of electrooptic properties of crystals are often performed at different temperatures (see, e.g., [5]). Therefore, in our work we present the Kerr constant of the Fomblin Z as a function of the temperature as well.

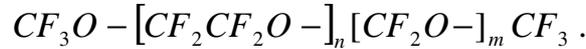
2. SOME PROPERTIES OF PERFLUOROPOLYETHERS

Perfluoropolyethers (PFPEs) are the family of polymers composed entirely of carbon, fluorine and oxygen atoms. These compounds are liquids over very wide temperature range (-100°C to 450°C) and posses high thermal oxidative stability, low volatility, non flammability, excellent lubrication properties, biological inertness, etc. [10-12]. Purified PFPEs are ultra-transparent materials and are promising media for optical lithography. They are employed in a number of diverse and demanding applications such as: high vacuum pump fluids, lubricants for jet-engines, turbines, nuclear reactor cooling pumps, satellite instrumentations as environmental coatings, electrical insulators and, recently, for magnetic recording media.

Optical properties of perfluoropolyethers have not been yet investigated in details. The refractive index of many PFPEs has been measured and found to increase with the molecular weight. The refractive index of the compounds is

only slightly sensitive to the oxygen/carbon ratio in the macromolecule. Perfluoropolyethers can be homopolymers or copolymers (linear or branched). The most common PFPEs are non polar and exhibit very low dielectric constant. The second generation of the polymers with terminating functional groups shows slightly increased polarity [10,11].

In the present work polyperfluoroethylenemethylene oxide Fomblin Z, product of Solvay Co. used as received, is investigated. The compound is a nonpolar linear copolymer with chemical structure :



3. EXPERIMENTAL

We have used the dynamic method the basis of which is the harmonic analysis of light modulated by an electric field $E(t) = E_0 \sin(\omega t)$. The intensity of the light passed through a cell containing a birefringent medium placed between the polarizer and analyzer is given by [12]

$$I = I_0 \left[\cos^2(\alpha) - \sin(2\rho) \sin[2(\rho - \alpha)] \sin^2\left(\frac{\Gamma}{2}\right) \right], \quad (5)$$

where I_0 is the incident light intensity, α is the angle between the plane of polarization in polarizer and analyzer, ρ is the angle between the plane of polarization and the principal axis of the elliptical cross-section of the optical indicatrix. The induced birefringence which is due to the Kerr effect in liquids is of such symmetry that the directions of the principal axis of the cross-section of the indicatrix are parallel and perpendicular to the direction of the applied electric field. In equation (5) Γ is the phase difference between the ordinary and extraordinary beams

$$\Gamma = \Gamma_0 + kl\Delta n, \quad (6)$$

where Γ_0 is that part of Γ which is independent of the electric field, $k=2\pi/\lambda$ and l denotes the path length of the light beam in the liquid. In our measurements, the polarizers were crossed, i.e. $\alpha=\pi/2$ and oriented in such a way that $\rho=\pi/4$. A quarter-wave plate provided the optical bias $\Gamma_0=\pi/4$. For such optical bias equation (5) may be rewritten in the form

$$I = \frac{I_0}{2} (1 + \sin(kl\Delta n)). \quad (7)$$

By employing a lock-in technique, we determined the modulation index $m(2\omega)=I(2\omega)/I_0$, where I_0 is the constant component of the light intensity transmitted by the system and $I(2\omega)$ is the second harmonic of the emerging light intensity. A computer controlled data acquisition and processing system was used in our measurements. As in measurements performed for crystals (see, e.g., [6]), we employed the He-Ne laser ($\lambda=0.633 \mu\text{m}$) and the electric field of frequency 417 Hz was applied to the cell. As usually in the dynamic technique (see, e.g., [13]), the Kerr constant defined by equation (3) was determined by employing the following expression

$$B = \frac{m(2\omega)d^2}{\sqrt{2\pi}U^2l}, \quad (8)$$

where d is the distance between electrodes and l is the length of electrodes.

4. RESULTS AND DISCUSSION

The dependence of the modulation index $m(2\omega)$ and the Kerr constant on the temperature and the square of rms modulating voltage is shown in Fig. 1 and Fig. 2, respectively. The results obtained indicate that the Kerr constant decreases slightly with temperature. Such behavior, i.e. the decrease in B with temperature is typical for many liquids.

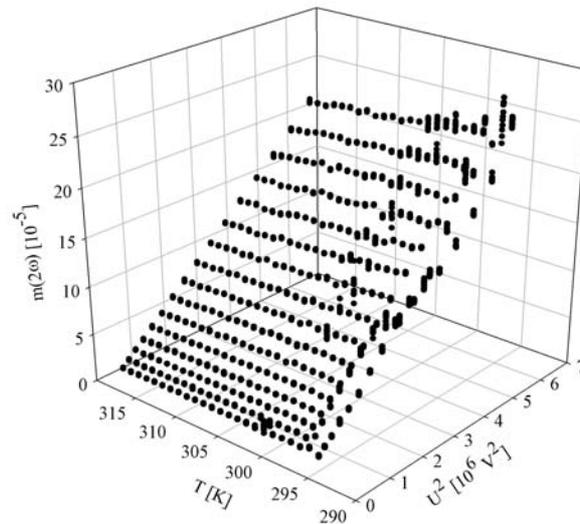


Fig. 1. The modulation index $m(2\omega)$ in polyperfluoroethylenemethylene oxide Fomblin Z plotted against the square of rms modulating voltage U^2 and temperature T

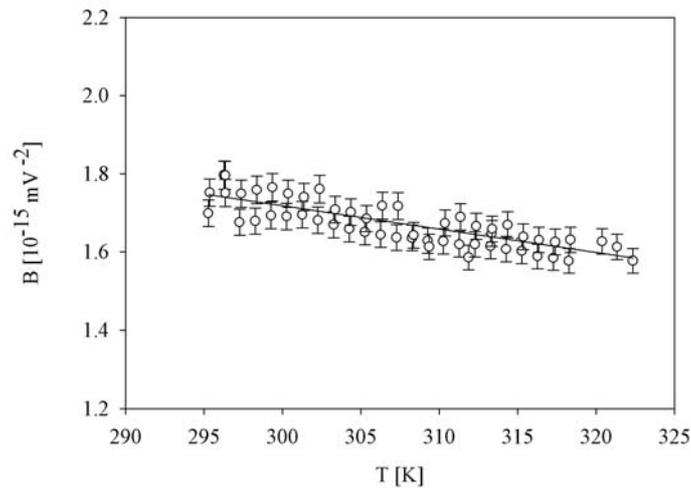


Fig. 2. The temperature dependence of the Kerr constant B in polyperfluoroethylenemethylene oxide Fomblin Z

In conclusion, the Kerr constant B of Fomblin Z of the order of magnitude 10^{-15} m/V^2 along with its high electric strength allows to use the perfluoropolyether as the immersion liquid in measurements of the quadratic electrooptic effect in crystals. The electrooptic response of Fomblin Z is of the same order of magnitude as that observed in transformer mineral and silicon oils employed previously as immersion liquids [14]. Moreover, the fact that the refractive index of Fomblin is close to 1.3, i.e. is much lower than the refractive index of the oils, indicates a possibility of making use of the perfluoropolyether in interferometric measurements of electrostriction in transmission in crystals.

REFERENCES

- [1] **Kerr J.**, *Phil. Mag. Ser. 5*, **50** (1880) 157.
- [2] **Pockels F.**, *Lehrbuch der Kristallogoptik*, Teubner, Leipzig 1906; English Translation in **I.P. Kaminov** *An Introduction to Electrooptic Devices* Academic Press, New York 1974.
- [3] **Gunning M.J., Raab R.E., Kucharczyk W.**, *J. Opt. Soc. Am. B* **18** (2001) 1092.
- [4] **Izdebski M., Kucharczyk W., Raab R.E.**, *J. Opt. Soc. Am. A* **19** (2002) 1417.
- [5] **Ledzion R., Górski P., Kucharczyk W.**, *J. Phys. Chem. Solids* **68** (2007) 1965.

- [6] **Melnichuk M., Wood L.T.**, J. Opt. Soc. Am. A **22** (2005) 377; errata J. Opt. Soc. Am. A **24** (2007) 2843.
- [7] **Melnichuk M., Wood L.T.**, J. Opt. Soc. Am. A **23** (2006) 1236.
- [8] **Izdebski M., Kucharczyk W.**, J. Opt. Soc. Am. B **25** (2008) 149.
- [9] **Gunning M.J., Raab R.E., Kucharczyk W.**, Ferroelectric Lett. **24** (2001) 93.
- [10] **Scheirs J.**, Perfluoropolyethers, in: **Scheirs J.**, (Ed.), Modern Fluoropolymers, Wiley, New York 1997.
- [11] **Marachioni G., Ajrodi G., Pezzin G.**, Structure-properties Relationships in Perfluoropolyethers: a Family of Polymeric Oils, in **Aggarwal S.L., Russo S.**, (Eds), Comprehensive Polymers Science, Pergamon Press, London 1997.
- [12] **Born M., Wolf E.**, Principles of Optics, Pergamon, Oxford 1975.
- [13] **Ledzion R., Bondarczuk K., Górski P., Kucharczyk W.**, Cryst. Res. Technol. **34** (1999) 745.
- [14] **Ledzion R., Bondarczuk K., Górski P., Kucharczyk W.**, Quant. Electronics **34** (1999) 745.

This project was partially supported financially by project No 204 057 31/1485 from the Ministry of Science and Higher Education of Poland.

STAŁA KERRA FOMBLINU Z

Streszczenie

Zmierzono stałą Kerr B polimeru Fomblin Z w zakresie temperatur 295-323 K. Otrzymane wyniki pokazują, że ze względu na małą wartość stałej B, rzędu 10^{-15} m/V², związek ten może być wykorzystany jako ciecz immersyjna w pomiarach współczynników kwadratowego efektu elektrooptycznego oraz elektrostrykcji w kryształach.