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Classification

Physics Abstracts

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Second harmonic generation in a liquid-crystalline elastomer

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Summary. — A liquid-crystalline elastomer with NLO active nitrogroups bonded covalently to a siloxane network has been investigated. By means of polarizing microscopy, X-ray diffraction and UV-VIS spectroscopy it was found that the elastomer exhibits a S_A phase and is macroscopically ordered. The elastomer is transparent for wavelengths above 450 nm and the anisotropy of refractive index at room temperature is about 0.1. Applying an external electric poling field breaks centrosymmetry and second harmonic generation similar to crystals can be observed. The poling process is single exponential with an activation energy of 190 kJ/mol and is identified as a δ -process. In contrast to low molar mass liquid crystals no director reorientation is observed by the laser field strength. From Maker fringe experiments in the liquid crystalline phase at room temperature the second-order susceptibilities are $\chi_{zzz} = 0.92$ pm/V and $\chi_{zxx} = 0.06$ pm/V for a poling field of 19 V/ μ m.

1. Introduction.

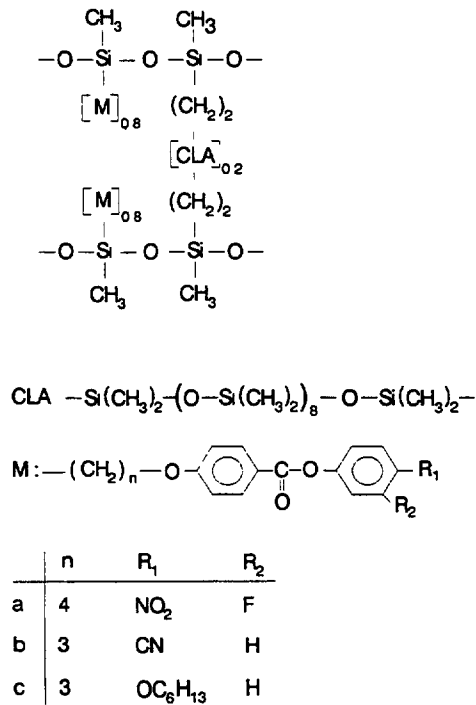
Apart from organic and inorganic crystals, polymers have been intensively investigated with respect to their non-linear optical properties [1, 2]. Two approaches are generally used to obtain polymeric materials containing NLO active chromophores: the first approach is to swell a polymer matrix with the chromophores. This procedure is often limited by the poor solubility of chromophores in the matrix. To overcome this problem the second approach is to covalently link the chromophores to the polymer matrix. With this procedure materials with high non-linear susceptibilities are available. However, not only the chemical structure of the chromophores but also the degree of order of the matrix strongly influences the non-linear susceptibilities. Theoretical considerations show that the value of the susceptibilities is smaller for an isotropic medium than for the limiting case of an Ising medium [3]. Considering liquid crystals their state of order is between the perfect order of the crystalline state and the disorder of an isotropic medium. This fact makes liquid crystals very interesting materials for non-linear optics because in the lc state the molecules can be easily macroscopically aligned with respect to the long molecular axis (director) by applying external electric or magnetic fields. For polymeric liquid crystals, however, a perfect alignment of the director often fails in the electric or magnetic field and defect structures remain in the samples. These defects cause high optical damping which prevents their applicability. To overcome these problems we

choose a new way. Detailed investigations on crosslinked l.c. side chain polymers (l.c. elastomers) proved, that uniform orientation of the director can be obtained by applying a mechanical field. The effect of the mechanical field strongly exceeds magnetic and electric field [4]. In this way l.c. elastomer films can be prepared whose optical properties are similar to the optical properties of anisotropic single crystals. Furthermore the optical damping of these elastomer films is very low in the range of 1-2 dB/cm [5].

In this paper we investigate a liquid crystalline elastomer where the NLO active chromophores (e.g. nitrogroups) are covalently bonded to the polymer network. The phase structure, the poling behaviour and the second-order optical susceptibilities will be reported.

2. Experimental.

2.1 SYNTHESIS OF THE ELASTOMER. — It is well known that materials containing highly polar end-groups (e.g. $-\text{NO}_2$ groups) are ideal materials to observe second harmonic generation [6]. Therefore we choose an elastomer with a chemical structure shown in figure 1. The liquid crystalline siloxane network with the mesogenic side chains M is synthesized by a Pt-catalyzed addition reaction of the liquid crystalline molecules and the crosslinker CLA to a linear polyhydrogensiloxane, according to a well known synthesis route [7]. Elastomer films of 100-200 μm thickness are prepared by spin casting technique. For purification the elastomer is extracted by swelling in toluene and deswelling in petrolether. The elastomer is characterized by a glass transition at $T_g = 258 \text{ K}$ with a change of specific heat $\Delta C_p = 0.21 \text{ J/gK}$ and a first order transformation at $T = 373 \text{ K}$ (Onset) with an enthalpy change of $\Delta H = 4 \text{ J/g}$. Above



$$a \cdot b \cdot c = 0.3 \cdot 0.05 \cdot 0.65$$

Fig 1 — Chemical structure of the elastomer (M Mesogen, CLA Crosslinking agent)

this temperature the elastomer displays an isotropic phase. The values for ΔC_p and ΔH indicate the existence of a smectic A or a smectic C phase. The elastomers are completely transparent and do not absorb above 450 nm

2.2 CHARACTERIZATION OF THE ELASTOMER — Thermodynamic properties were determined by differential scanning calorimetry (DSC-7, Perkin Elmer) and polarizing microscopy (Leitz-Ortholux 2 Pol BK). Structural investigations were performed by X-ray diffraction ($\text{CuK}\alpha = 0.154 \text{ nm}$) and recording of the scattered intensity on flat film plates. The refractive indices at $\lambda = 1.064 \text{ nm}$ (fundamental in SHG experiments) and $\lambda = 532 \text{ nm}$ (second harmonic) were calculated from measurements of the angle of total reflection.

2.3 SHG-EXPERIMENT — For the SHG experiment the elastomer film has to be poled to obtain the noncentrosymmetric structure. The film was sandwiched between two conductive glass plates (Balzers) which are connected to a DC source

The SHG experimental set-up is shown schematically in figure 2. A pulsed Nd-YAG Laser (DCR 3G, Spectra Physics, $\lambda = 1.064 \text{ nm}$, pulse width 8 ns, 10 pulses/s) with a Gaussian beam profile TEM_{00} is used. The sample is mounted on a temperature controlled rotation stage. The angle position of the sample is directed by a personal computer. The incident polarized light is focussed (lenses L) in the vicinity (4-5 cm) of the sample. After passing the sample the fundamental wave is blocked by a filter-element (Schott BG39) and a monochromator (filters). The intensity of the second harmonic beam is detected by a photomultiplier tube (PMT) and the signal is then passed after amplification (AMP) via a gated integrator and boxcar averager (BOXCAR) to a personal computer (PC). To avoid absolute measurements of the intensity of the fundamental wave a reference method was chosen using a quartz crystal (010 orientation, $\chi_{xxx} = 0.5 \text{ pm/V}$). The measured Maker fringe data are fitted with theoretical calculated curves to determine the second-order susceptibilities χ_{zzz} and χ_{zzx} .

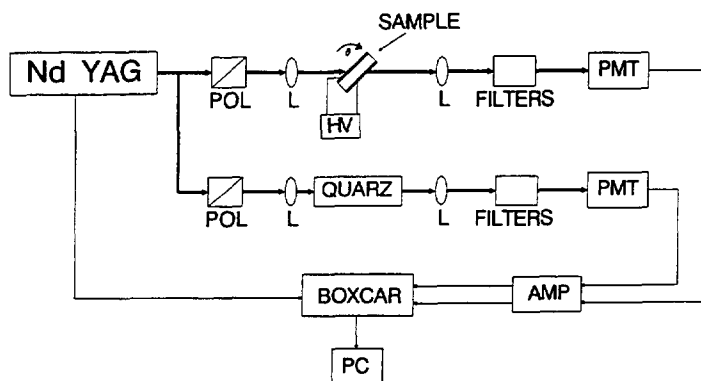


Fig. 2. — Experimental set-up for SHG experiments (Pol: Polarizer, L: Lens, HV: High voltage, PMT: Photomultiplier tube, AMP: Amplifier, BOXCAR: Gated integrator and boxcar averager, PC: Personal computer).

3. Results and discussion.

3.1 STRUCTURE. — For a quantitative description of the NLO properties of the synthesized elastomer, an analysis of the phase structure is required, because the polarization in a medium

caused by an incident light beam is directly connected to the symmetry class of this medium. In our case the type of smectic phase and the orientation of the director with respect to the macroscopic dimension of the sample has to be known for the second harmonic experiments [8]. Polarizing microscopic observation indicate a uniaxial phase structure, where the optical axis is parallel to the film normal. To decide whether the elastomer exhibits a smectic A phase or a two dimensionally ordered smectic phase, X-ray investigations were performed.

X-ray scattering diagrams were recorded at room temperature with the incident beam perpendicular and parallel to the film normal (Figs. 3a-c). Perpendicular to the film normal (Figs. 3a and 3b) the diagram is characterized by a diffuse wide angle reflection B ($d = 0.42$ nm) and several small angle reflections A corresponding to $d_1 = 3.3$ nm, $d_2 = 2.2$ nm, $d_3 = 1.2$ nm, $d_4 = 0.84$ nm, $d_5 = 0.65$ nm, where only the reflection corresponding to d_1 is sharp. Parallel to the film normal (Fig. 3c) the reflection B ($d = 0.42$ nm) and a reflection C ($d = 0.71$ nm) are observed as diffuse rings confirming the optical observation. With respect to the phase structure of the elastomer a positional long range order is only indicated in the sharp reflection corresponding to a layered structure with the periodicity d_1 . This is consistent with a smectic A phase. The layer thickness d_1 does not coincide with the

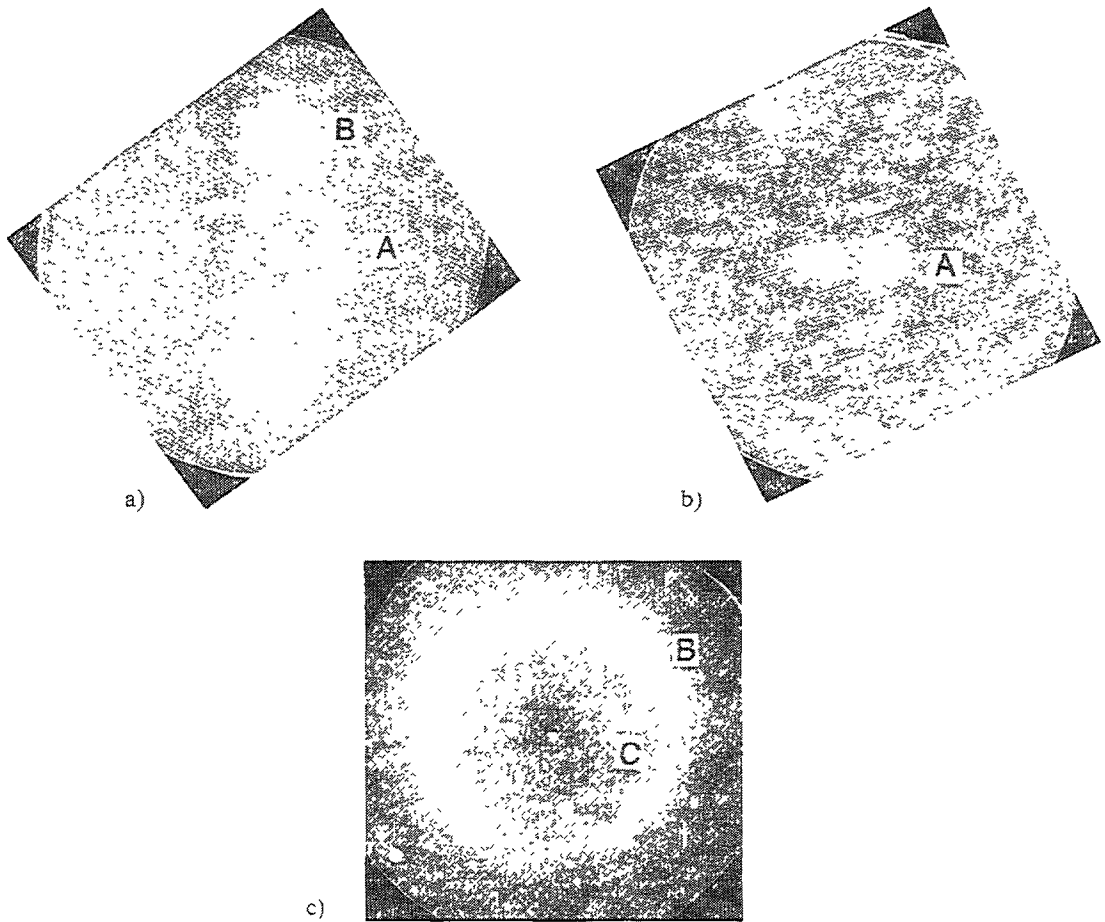


Fig 3 — X-Ray diagrams a) perpendicular to film normal (sample-film distance 7 cm), b) perpendicular to film normal (sample-film distance 17 cm), c) parallel to film normal (sample-film distance 7 cm).

length of the monomer units (2.0 nm for the —CN and —NO₂ substituted and 2.4 nm for the hexyloxy-substituted monomer unit) and a partially bilayer has to be assumed. The diffuse reflections corresponding to $d_2 - d_5$ characterize short range order. Reflection *B* is attributed to the mean distance between the side groups. Reflection *C* might be due to Si-Si correlations

3.2 THEORY OF SECOND HARMONIC GENERATION — It is known that a light wave travelling through a medium can excite higher harmonic waves in this medium depending on its intensity. The *i*-th component of the polarization P_i in the medium is then given by

$$P_i = \chi_{ij}^{(1)} E_j + \chi_{ijk}^{(2)} E_j E_k + \chi_{ijkl}^{(3)} E_j E_k E_l + \dots \tag{1}$$

where E_i denotes the *i*-th component of the laser field strength and the $\chi^{(n)}$ are the components of the susceptibility tensor [9]. The second term in equation (1) is responsible for the second harmonic, the third term for the third harmonic etc

The poled and therefore non-centrosymmetric structure of the elastomer under investigation is represented by a C_∞ symmetry. For the chosen beam geometry (Fig 4) with the electric poling field E_0 parallel to the *Z* axis the elements of the second-order polarization $\mathbf{p}_{NL} = (P_x, P_y, P_z)$ are given by [10]

$$P_x = 2 \chi_{zxx} E_x E_z \tag{2a}$$

$$P_y = 2 \chi_{zxx} E_y E_z \tag{2b}$$

$$P_z = \chi_{zxx} (E_x^2 + E_y^2) + \chi_{zzz} E_z^2 \tag{2c}$$

where χ_{zxx} and χ_{zzz} are the second-order susceptibilities. The second-order susceptibilities are related to the molecular hyperpolarizability element β_{zzz} by

$$\chi_{zzz} = N \beta_{zzz} F \langle \cos^3 \vartheta \rangle \tag{3a}$$

$$\chi_{zxx} = N \beta_{zzz} F (\langle \cos \vartheta \rangle - \langle \cos^3 \vartheta \rangle) / 2 \tag{3b}$$

where N is the number density, F includes local field factors and ϑ is the angle between the molecular axes of the single non-linear optical moieties and the external applied electric field E_0 . For the limiting cases of a poled isotropic medium and a poled Ising medium the following expressions have been derived from calculating equations (3a) and (3b) [3, 8]

Component	Poled isotropic medium	Poled Ising medium	(4)
χ_{zzz}	$\beta_{zzz} \mu E_0 / 5 kT$	$\beta_{zzz} \mu E_0 / kT$	
χ_{zxx}	$\beta_{zzz} \mu E_0 / 15 kT$	0	
χ_{zxx} / χ_{zzz}	1/3	0	

μ is the dipole moment of the molecule. Expressions (4) show a linear relationship between the non-linear susceptibility and the applied poling field E_0 . As the distribution function for a liquid crystalline material is intermediate between these two limits, the ratio of the second-order susceptibilities χ_{zxx} / χ_{zzz} should also lie in between

The dependence of the second harmonic power on the second-order polarization as a function of incident angle (Maker fringe experiment) has been calculated [11, 12]. For *s* polarization $\mathbf{E} = E(0, 1, 0)$ (see Fig 4) and from equation (2a-2c) follows

$$\mathbf{P}_{NL} = p^s(\vartheta) \begin{pmatrix} 0 \\ 0 \\ \chi_{zxx} E^2 \end{pmatrix} \tag{5a}$$

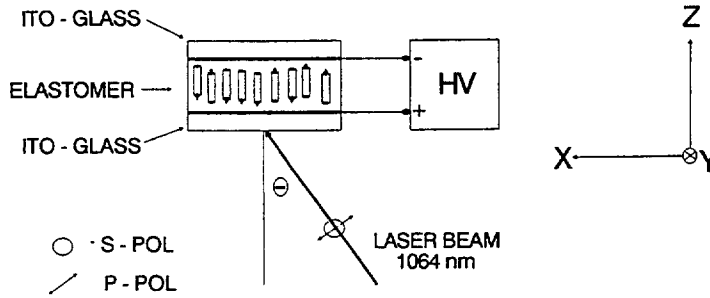


Fig 4 — Beam geometry for poling in SHG experiment (HV · High Voltage)

The intensity of the second harmonic is then given by

$$I(2\omega) = I(\omega)^2 P_{NL}^2 T^s(\Theta) \times 1/(n_w^2 - n_{2w}^2)^2 \times \sin^2(\Psi) \quad (5b)$$

$$\Psi = (\pi L/2)(4/\lambda)(n_w \cos \Theta_w - n_{2w} \cos \Theta_{2w}) . \quad (6)$$

For p polarization $\mathbf{E} = E(\cos \Theta_w, 0, \sin \Theta_w)$ (see Fig 4) and from equation (2a-2c) follows

$$\mathbf{P}_{NL} = p^p(\Theta) \begin{pmatrix} 2\chi_{zxx} E^2 \cos \Theta_w \sin \Theta_w \\ 0 \\ \chi_{zxx} E^2 \cos^2 \Theta_w + \chi_{zzz} E^2 \sin^2 \Theta_w \end{pmatrix} \quad (7a)$$

The intensity of the second harmonic is then given by

$$I(2\omega) = I(\omega)^2 P_{NL}^2 T^p(\Theta) \times 1/(n_w^2 - n_{2w}^2)^2 \times \sin^2(\Psi) \quad (7b)$$

Θ , Θ_w and Θ_{2w} denote the external and the internal angles of incidence, I_w is the intensity of the light wave at frequency ω , $T(\Theta)$ and $p(\Theta)$ are transmission factors resulting from boundary conditions, n_w and n_{2w} are the refractive indices at the fundamental respectively the second harmonic, and L is the thickness of the sample. The sinusoidal behaviour in equations (5b) and (7b) describes the interference of the second harmonics produced at different points in the medium.

3.3 DYNAMICS — Poling of an elastomer in an external electric field yields a relaxation of the molecules from a centrosymmetric to a non-centrosymmetric structure [13]. To determine absolute values of the non-linear susceptibilities it is important to be in an equilibrium state. Therefore it is necessary to know the relaxation of the molecules as a function of temperature. The relaxation of the molecules from the poled non-centrosymmetric to the centrosymmetric structure is directly indicated by the disappearance of the second harmonic intensity. The intensity of the second harmonic as a function of time when applying or removing an electric DC field was measured. Due to the low glass transition temperature of the elastomer the relaxation times are below the resolution of the experimental set-up in a temperature interval near room temperature. To obtain information about the relaxation mechanism, we analysed a corresponding elastomer which contains only the NO_2 -substituted mesogenic side chains. For this elastomer T_g is elevated by approximately 15 K causing a slowing down of the relaxation in the investigated temperature regime. The diagram of these measurements (Figs. 5a and 5b) show that the relaxation behaviour is single exponential reaching an equilibrium state with the same relaxation times for rise and decay of the intensity. From an

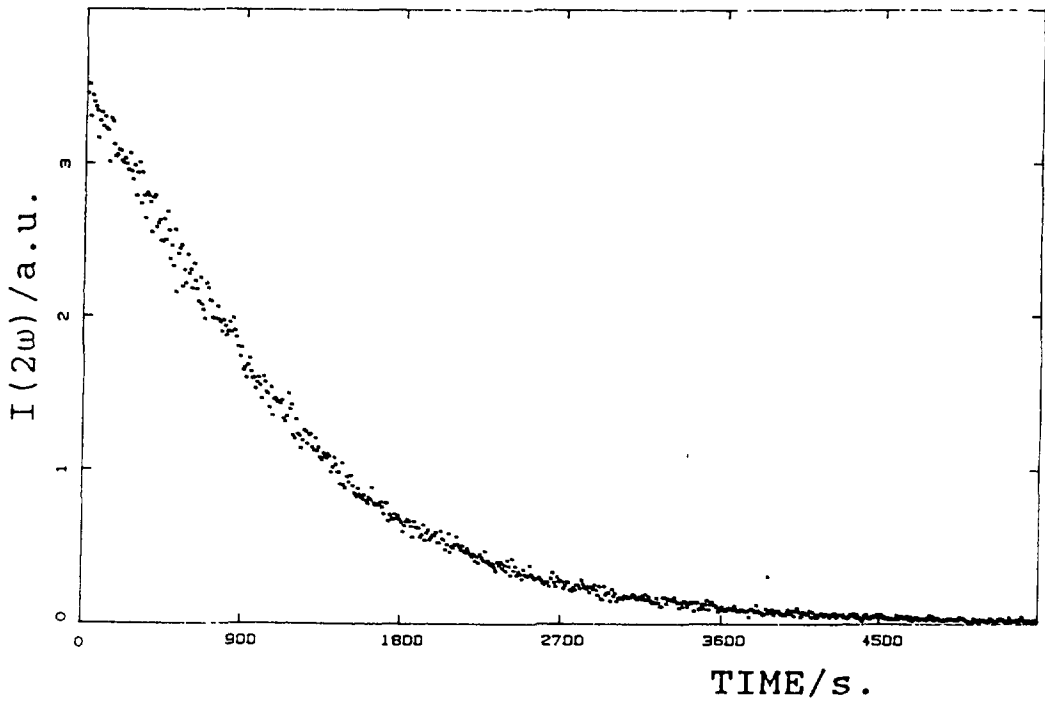
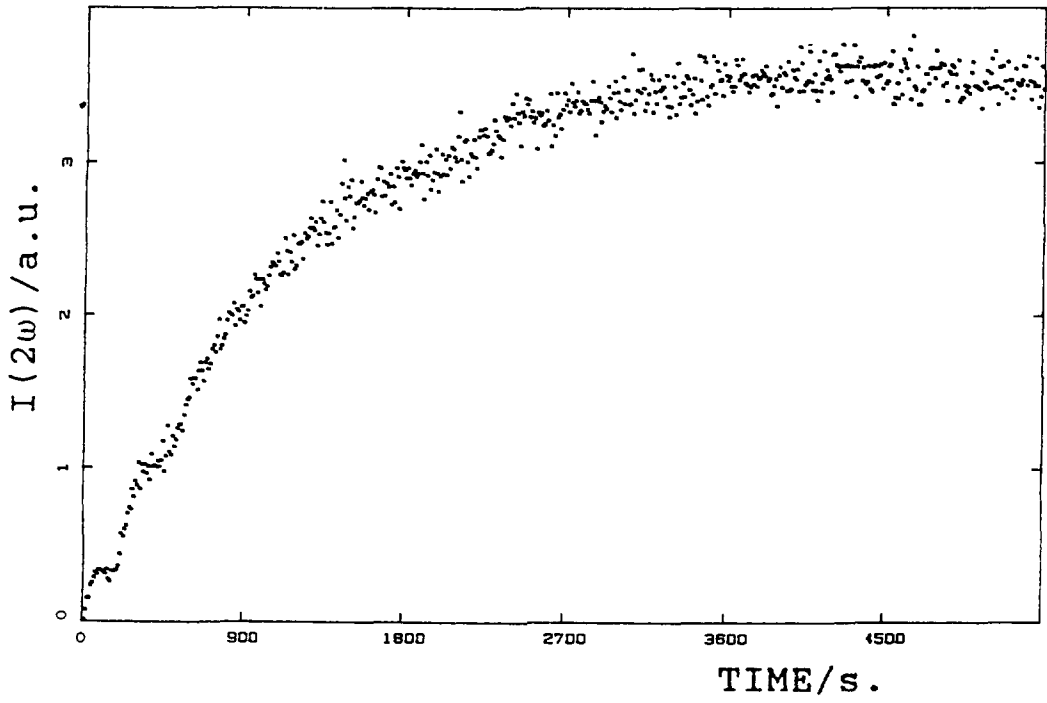


Fig 5 — Second harmonic intensity *versus* time at 293 K for a) poling field on b) poling field off

Arrhenius plot of the logarithm of the relaxation frequency *versus* the reciprocal temperature in the liquid crystalline phase close to T_g (Fig. 6) we achieve an activation energy of 190 kJ/mol. This value is only slightly higher than the activation energy of the δ -process found for liquid crystalline side chain polymers [14]. From these results we can conclude that due to the single exponential relaxation behaviour and the magnitude of the activation energy, the poling process is determined by the δ -process of the mesogenic moieties. The δ -process is due to a rotation of the side group around the main chain in the direction of the applied electric poling field. All following experiments were performed in the equilibrium state which is reached when switching on the poling field.

3.4 STATIC SHG PROPERTIES — In equations (4), (5b) and (7b) a linear relationship between non-linear susceptibilities and applied poling field and a quadratic relationship between second harmonic intensity and applied poling field is predicted. From low molar mass systems it is known that the intensity of the laser field can influence the orientation of the director. Depending on the laser field strength a director reorientation can occur which can be easily recognized if the predictions made in equations (4), (5b) and (7b) are not fulfilled [15]. To verify whether director reorientation occurs in the elastomer the behaviour of the second harmonic as a function of the incident laser power respectively as a function of the applied poling field was investigated. Figures 7 and 8 indicate a quadratic dependence of the second harmonic on the incident laser power as well as on the electric poling field strength. This is in agreement with the prediction in equations (5b) and (7b) and proves that no director reorientation processes occur. The elastomer behaves similar to a conventional organic material in the crystalline state.

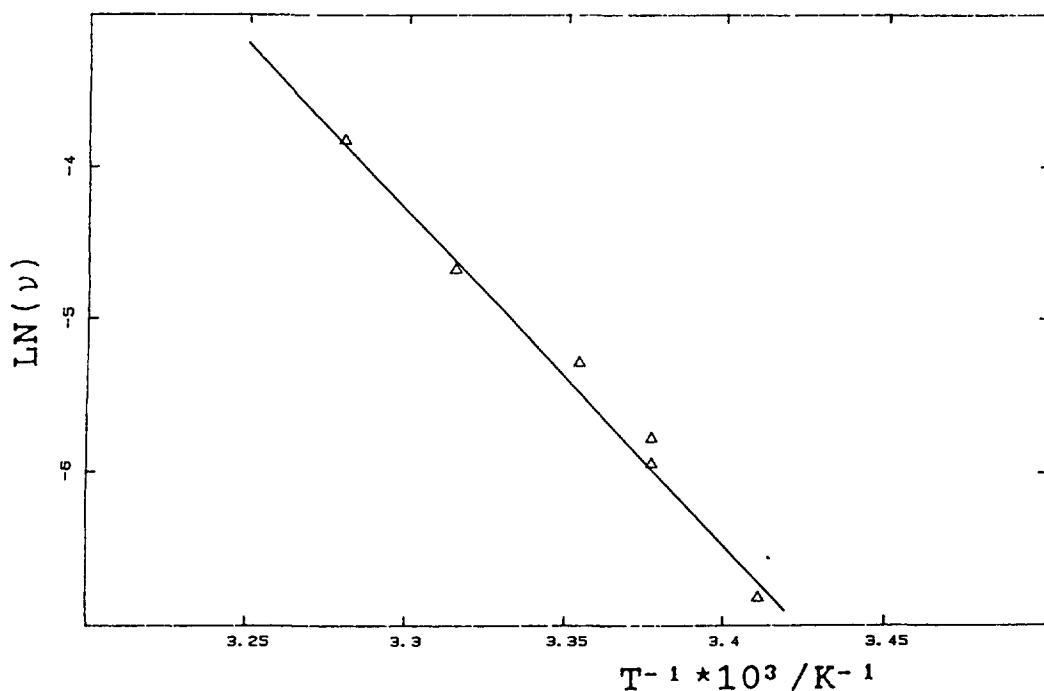


Fig 6 — Activation diagram from second harmonic intensity *versus* time

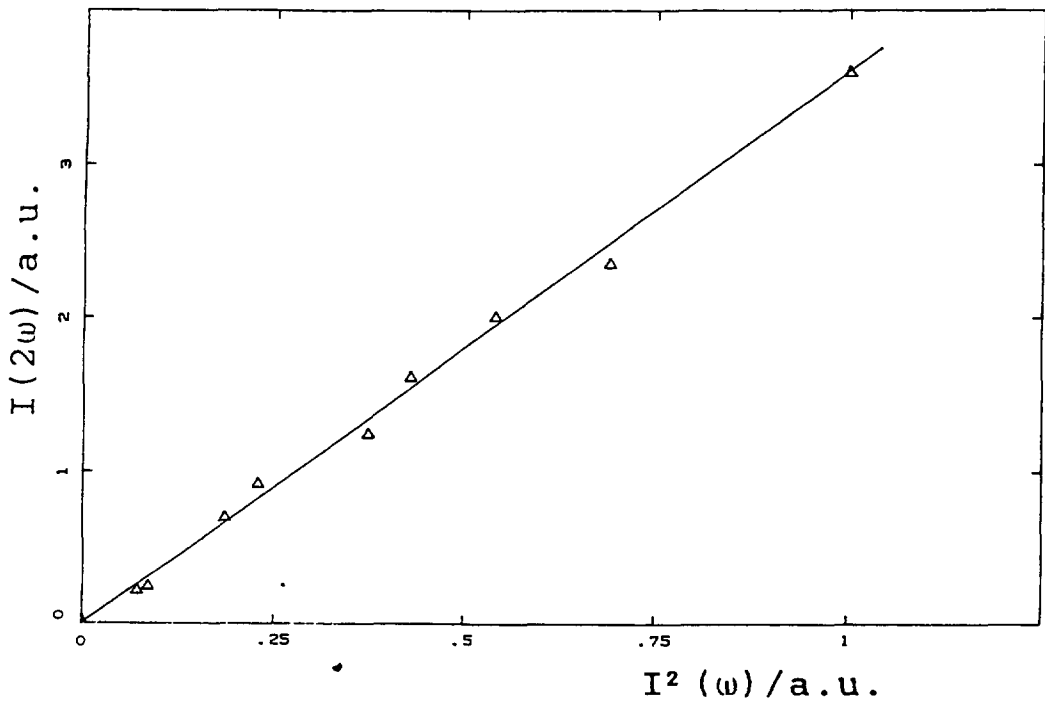


Fig. 7 — Second harmonic intensity *versus* square intensity of incident light ; (Δ) measured points, (—) linear fit

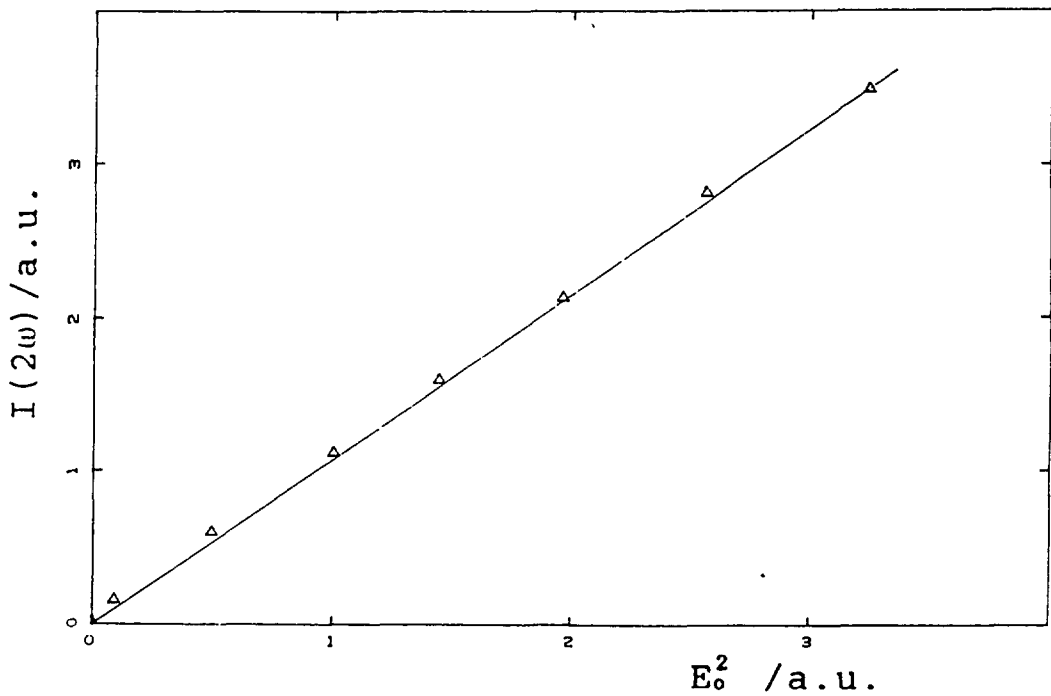


Fig. 8 — Second harmonic intensity *versus* square of electric poling field , (Δ) measured points, (—) linear fit

3.5 MAKER FRINGE EXPERIMENT. — To prove whether the second harmonic can be described completely by equations (5b) and (7b) and to determine the second-order susceptibilities χ_{zzz} and χ_{zxx} the intensity of the second harmonic wave was measured as a function of the incident angle (Maker fringe experiment). The experiment was performed for s- and p-polarized incident light at room temperature for a definite applied poling field. Figure 9 shows a diagram for p-polarized incident light. A symmetric increase of second harmonic intensity is observed starting from the 0 deg. position. At higher angles fringes occur resulting from the phase mismatch, because refractive indices $n_{2\omega}$, n_{ω} and optical path length change continuously by rotating the sample. Interestingly, sharp fringes are observed, which indicates the uniform director orientation. For samples having lower order, only the envelope of this curve is observed. To check whether the measured values can be fitted by applying equations (5b) and (7b) the refractive indices of the fundamental and second harmonic wave in the elastomer have to be known. Table I shows the measured refractive indices. The birefringence is 0.1 at room temperature. With these values and equations (5b) and (7b) the experimental results of figure 9 can be reproduced. The calculated curve is indicated by the solid line in figure 9. On the basis of this fitted curve and measurements of the absolute intensity of the second harmonic with the quartz reference, the second-order susceptibilities are determined. For a poling field of $19 \text{ V}/\mu\text{m}$ we found $\chi_{zzz} = 0.92 \text{ pm/V}$ and $\chi_{zxx} = 0.06 \text{ pm/V}$. The ratio of χ_{zxx}/χ_{zzz} is about $1/15.3$ indicating that the state of order of the elastomer is within the limiting cases of an isotropic poled and an Ising poled field system (Eqs (4)). The value is in good agreement with the values found for doped polymer films in a smectic A phase [12].

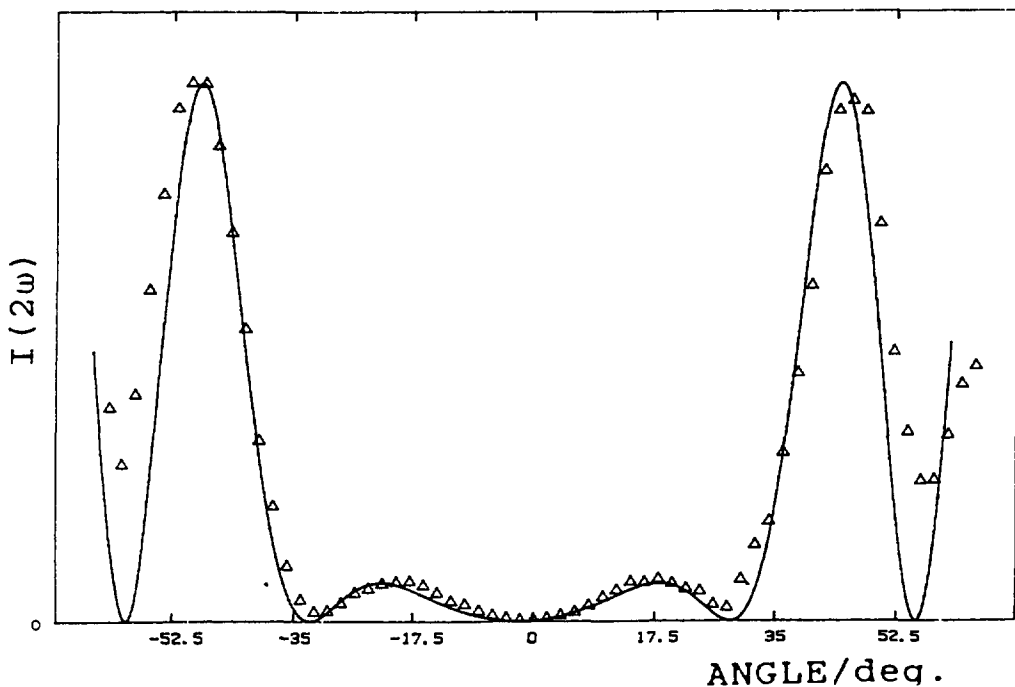


Fig 9 — Maker fringe diagram for p-polarized incident light ; (Δ) measured points, (—) calculated curve

Table I. — *Refractive indices as calculated from measurements of the angle of total reflection for different wavelengths of light*

λ/nm	n_e	n_o
532	1.608	1.494
632.8	1.598	1.485
1 064	1.580	1.478

4. Conclusion.

We have shown that liquid crystalline elastomers are suitable materials for non-linear optics. A uniform director orientation can be easily achieved by a simple mechanical deformation of the elastomer avoiding defect structures which normally appear in low molar mass liquid crystals and liquid crystalline side chain polymers. Although the elastomers are not in a solid state but in a liquid-crystalline state, the behaviour is comparable to solid bodies. The network prevents any director reorientation by the laser field strength. On the one hand the non-linear susceptibilities can be enhanced by variation of the chemical structure. On the other hand ferroelectric l.c. elastomers should allow to observe second harmonic generation without any external poling field.

Acknowledgements.

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