Electrically induced concentration profiles of nanoparticles in a MMA-Silane matrix: A New method to obtain GRIN-lenses.

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ABSTRACT

A new technique to produce a radial gradient in the refractive index (r-GRIN) in organic-inorganic nanocomposite materials using sol-gel techniques in combination with electrophoretically induced concentration profiles of oxide nanoparticles is presented. The composite material is based on methacryloxylpropyl trimethoxysilane (MPTS), zirconium n-propoxide (ZR), Methacrylic acid (MA) and tetraethyleneglycol dimethacrylate (TEGDMA). Irgacure 184 was used as a photosensitive initiator. The surface of these particles is enriched with MA which is linked by a chelating complex to the initial ZR component. The TEGDMA component is used to introduce more flexibility in the organic inorganic network and to reduce polymerization stresses. Electric charges on the ZrO_2 nanoparticle surface force the particles to diffuse in the gel state by electric fields employed by appropriate electrodes in presence of an electric field. The movement and interdiffusion of the Zr-nanoparticles in the matrix were measured by zeta-potential measurements and by photon-correlation spectroscopy (PCS). In the performed experiments, a radial electric field amplitude of 200 V/cm was used and held for 5 hours keeping the material in the gel state. The variation of refractive index in real time was measured by Mach-Zehnder interferometry. After the electrophoretic process, a polymerization step was carried out to immobilize the Δn gradient. Δn was measured by ellipsometry and the value of 0.07 was obtained for a sample of 1 cm in diameter. The form of the concentration profile and hence from the index profile was detected by EDX (Energy Dispersive X-ray analysis) measurements.

Keywords: GRIN-lens, nanocomposite, electrophoresis, sol-gel, nanoparticles

1.INTRODUCTION

Glass GRIN-Lenses have been applied to many optical systems for communication devices and consumer electronic equipments. Gradient lenses have become a key optical component for photocopiers, facsimile, medical imaging systems and optical printers. Many different techniques such as ion-exchange [1], chemical vapor deposition (CVD) [2] and molecular stuffing [3] have been used and intensifly investigated. Most of the radial-GRIN lenses in glass are fabricated by ion-exchange methods. Nippon Sheet Glass (NSG) Corporation has fabricated lenses form 1 to 3 mm in diameter with the trade name SELFOC micro-lens. Limitations of ion exchange techniques include small size of the lenses and limited variety of optical characteristics such as index profile and base index of refraction [4-8].

Problems with the economical fabrication of large diameter GRIN elements (> 5 mm), as well as the limitation of variation of the refractive index and the time consuming fabrication process (7 days) by ion exchange impede the applications of these developments. Another alternative to glass GRIN-lenses are GRIN-lenses made from organic polymers by diffusive exchange of low refractive index monomers into a high refractive index polymeric gel [9] . The refractive index change of such lens is between 0.01 to 0.05 and the lents diameter of 3,4 mm (commercially available very recently from Mitsubishi Rayon Company [10]. In order to obtain GRIN lenses with diameters larger than 10 mm with high refractive index variations ($\Delta n>0.05$) and short fabrication times, chemical nanotechnologies were used and first results using contactless electrodes will be described and discussed in this paper.

Chemical nanotechnologies offer a wide range of material tailoring for optical applications: nanoparticles can be used to change the refractive index of thin films [11] and of bulk lenses made from organic-inorganic nanocomposites [12] scattering losses due to Rayleigh-scattering in case of refractive index mismatch between the particles and the matrix can widly be reduced using nanoparticles with particle diameters < 10 nm [13], the Colburn-Haines [14] effect allows the formation of a gradient of concentration of nanoparticles inducing a gradient of refraction index with a very good signal/noise ratio (450/1) and subsequent photopolymerisation of the matrix and fixation of the gradient [15-17] and surface charged nanoparticles can be forced to diffuse unidirectionally in a electrical potential difference.

In this paper, a combination of these features will be presented using an electrophoretical cell. The local variation of the electric potential initiates a concentric concentration variation of nanoparticles by up-diffusion of the particles in the potential and fixed well defined GRIN-structures are obtained after a photocuring process.

Diffusion of particles in a liquid medium is determined by a) the particle diameter and the viscosity of the suspension and b) in presence of an electric field determined additionally by the pH of the medium, the surface charge of the particles and the applied field itself. Cummins et al (1964) [18] verified that the spectrum of light scattered from a solution of polyestyrene

latex spheres is proportional to the diffusion coefficient of this spheres. In the same year Yeh and Cummins had shown that the Doppler-shifted spectrum is related to the velocity of the particles. Therefore the measurement of the Doppler-shifted spectra of nanoparticles in a solution give information on the diffusion coefficient and the velocity of the nanoparticles in the matrix. Ware and Flygare (1971) [18] first employed a combination of spectra of Rayleigh scattered light and the electrophoresis of charged macromolecules.
This concept using light scattering experiments to investigate diffusion phenomena in order to produce a defined graded refractive index was followed in this paper in order to understand in the involved precesses more detail and to correlate the obtained results and the experimental parameters.

2.THEORY

In a traditional diffusion experiment, two separate phases are allowed, at time t=0, to come to equilibrium. This macroscopic relaxation back to equilibrium is derived by Fick / / first low of diffusion

$$\frac{\partial c}{\partial t}(\vec{r},t) = -D_T \nabla(\vec{r},t) \qquad (1)$$

where r is a vector representing the spatial dependence of the concentration c and D_T is the translation diffusion coefficient given by Brownian temporal fluctuations. In a PCS (Photos Correlation Spectroscopy) experiment the fundamental quantity obtained from scattering at independent isotropic particles is the intensity autocorrelation function $G^2(t)$ of the scattered laser light. This has the form

$$G^2(t) = A + B\left|g^{(1)}(t)\right|^2 \qquad (2)$$

where A and B are instrumental constants and $g^{(1)}(t)$ is the electric field autocorrelation function which contains the information of interest. In case of mono disperse and non interacting particles the form of the electric field correlation function is

$$g^{(1)}(t) = \exp\left(\frac{t}{\tau_c}\right) \qquad (3)$$

with τ_c as the decay constant a relaxation time. The translation diffusion constant D_T is readily determined from τ_c using / /

$$\frac{1}{\tau_c} = q^2 D_T \qquad (4)$$

with $q = \frac{4\pi}{\lambda} n \sin(\theta)$ is the magnitude of the scattering vector, n is the refractive index of the medium and λ is the wavelength of the used laser. From equation 3 it is evident, that mono disperse particles should show a single exponential decay of the correlation function. In the presence of an electric field and an electric charge on the surface of the particles, particles in a colloidal systems will move by the influence of the electric field. The elecrophoretic velocity of the particles is determined by

$$V = U\vec{E} \qquad (5)$$

with E: electrical field strength, U: mobility of the particles. The mobility is directly correlated to the zeta-potential of the particles surface by

$$U = \frac{\varepsilon_l \xi}{6\pi\eta} \qquad (6)$$

ε_l: dielectric constant of the liquid
ξ:Zeta potential
η:viscosity of the colloidal system
Mobility of colloidal systems is usually measured in electrophoretic cells in combination with laser-Doppler techniques[ ]. In PCS experiment, the decay time τ_c is evaluated and reflects the decay of electric field autocorrelation function. In presence of an electric field, the PCS decay time is correlated to the mobility U of the particles by:

$$\frac{1}{E\tau_c} = U\frac{n}{\lambda}\sin\theta \qquad (7)$$

Determination of the decay time τ_c by PCS and calculation of the mobility allows to calculate the Zeta potential.

3.EXPERIMENTAL

The materials used to produce GRIN structures were synthesized from methacryloxypropyl trimethoxy silane (MPTS) methacrylic acid (MA) and zirconium-n-propoxide (ZR). A zirconium-n-propoxide/methacrylic acid complex was formed by reacting the alkoxide with methacrylic acid. After addiction of prehydrolysed silane (MPTS), hydrolyses and condensation[19] was performed by the addition of an appropriate amount of water. A detailed description of the synthesis procedure is described elsewhere [16] It is well known and described in literature that this syntheses route leads to ZrO_2-nanoparticles dispersed in an organic-inorganic matrix [20]

In order to enhance the chain flexibility and hence the mobility of diffusive nanoparticles the organic monomer tetraethylene glycol dimethacrylate, which acts simultanously as a network former during polymerisation of the C=C double bonds, was added. Irgacure 184 as a photoinitiator was added in concentration of 0.5 mol%/mol C=C and the material was photocured by illumination with a Hg-lamp.

The index of refraction of the different compositions was measured by ellipsometry. The Zeta potential of the nanoparticles in a selected composite system was first measured in an electrophoretic cell (ESA-SAMPLE SSP-1 MATEC). In order to change the pH of the sol, HCl or NaOH was added. The viscosity was measured by a Physicer-Viscosimeter (UM-MC200). Particles size and size distribution were measured by PCS (ALV-5000 Multiple Tau Digital correlator-ALV- Laser mbh) and high resolution transition electron microscopy (Phillips CM 200 FEG). The concentration profile of Zr in the photocured bulk material was measured by Enery Dispersive X-Ray (EDX). The experimental setup to measure relaxation times and hence mobility of the particles locally in presence of an electric field is shown in figure 1. The cylindrical electrophoretic cell with a diameter of 10 mm was made from polyethylene (PE). The front and back window of the cell were made both from fused silica. The center electrode and the circular electrodes were made from metal.

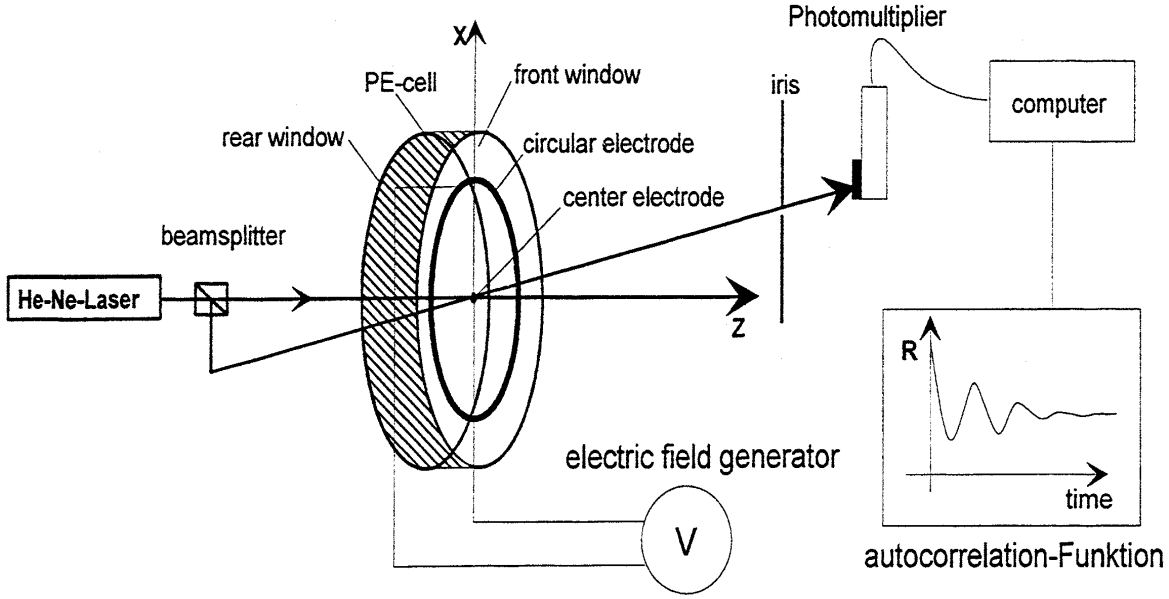


Figure 1: Scheme of the experimental setup to obtain the autocorrelation function in presence of an electric field. Electrophoretic cell material polyethylene (PE), electrode material Platinum, window material fused silica.

Density and concentration fluctuations in the sol result in frequency shifts of a coherent light source (He-Ne Laser λ=362,8 nm, 30 mW). This time dependent light intensity fluctuations are detected thorough a pin hole at an angle of 64^0 with a photomultiplier. The signal of the photo multiplier is transferred to a computer in well defined time delays and the autocorrelation function, which reflects the dynamics of diffuse species in the sample, is calculated. In order to apply an electric potential, a center and circular electrode were fixed on the front and back window of the electrophoreic cell and conected to an electric source. With regard to the production GRIN-lenses, a special design of the electrodes was calculated to obtain a well defined field distribution over the whole electrophoretic cell.

Several circular electrodes were fixed at different diameters of from the center on the fused silica windows. Additionally a center electrode was installed. The wires of the front and rear window were connected each other. The center electrodes of the front and back window were connected.

The electric field variation in the electrophoretic cell was measured with a 100 µm metallic point probe. The refractive index profiles were measured by Mach-Zehnder interferometer setup (figure 2) using a He-Ne laser (wavelength=632,8 nm) as a

coherent light source. The variation of the refractive index can be measured in real time analysing the interference pattern produced by the superposition of a planar reference wave and the wavefront generated by a GRIN structure. The change of the refractive index Δn between two adjacent fringes is given by $\Delta n = \lambda / d$, where λ is the wavelength of the used light source and d is the thickness of the GRIN-rod.

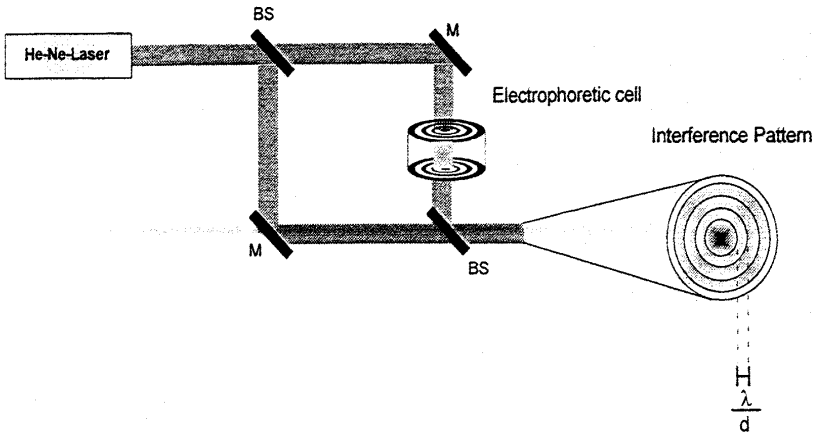


Figure 2: Real time refractive index measurement by Mach-Zehnder interferometry, M: mirror, B.S beam splitter. λ/d is the refractive index variation between two lines of the interference pattern.

4.RERULTS AND DISCUSSION

In a first experiment, the index of refraction of photocured composites of different Zr-concentrations for the material system MPTS/ZR/MA/TEGDMA was investigated. Results obtained by ellipsometric measurements on bulk samples are shown in figure 3.

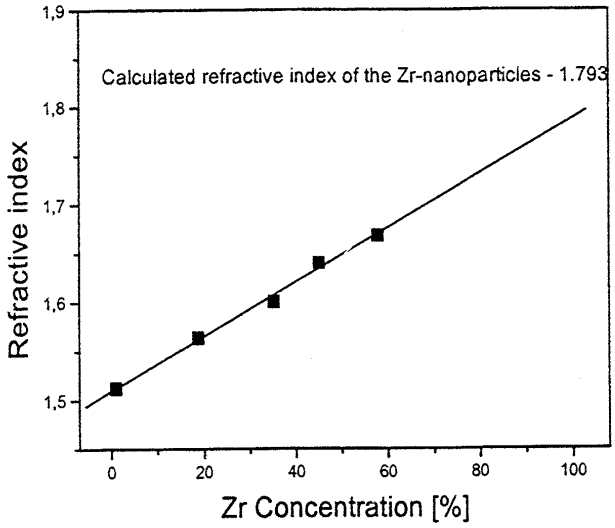


Figure 3: Refractive index n_e of photopolymerised MPTS/ZR/MA/TEGDMA bulk samples in dependence of the Zr-concentration.

In case of a local up-concentration of Zr, high initial Zr-concentrations will result in very high index modulations, but light scattering losses due to the up-concentration of high index ZrO_2 in a matrix with low refractive index is no more negligible for bulks samples. To avoid this problem, a moderate starting concentration of Zr was chosen and the following experiments were carried out with a composition MPTS/ZR/MA/TEGDMA (5/1/1/5 in mol%, corresponding to a bulk refractive index of 1.52). Results of PCS-measurements of the uncured material and a HTEM micrograph of the polymerised composite showing the particle size and the size distribution of the in-situ generated ZrO2-nanoparticles are given in figure 4a and b.

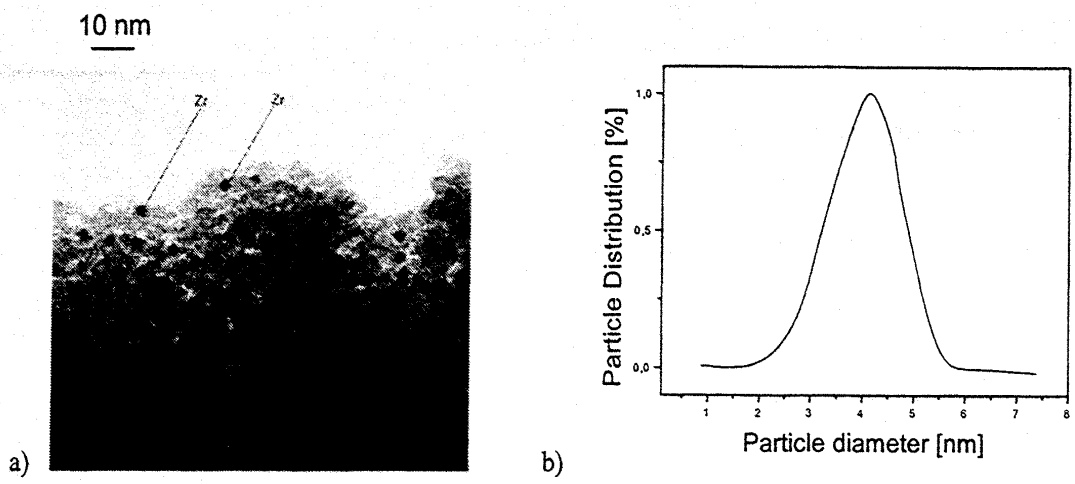


Figure 4: a)HTEM picture showing the particles of ZrO_2 produced „in situ" from zirconium-n-propoxide/methacrylic acid complex (1/1 mol%) in a (MPTS)/ TEGDMA jmatrix (5/5 mol %). b) Particle size distribution of ZrO_2 in the sol used to prepare the bulk sample of figure 4a.

From figure 4a and 4b it is evident, that the mean particle diameter of 4 nm determined by PCS and HTEM is uneffected by the photopolymerisation process (figure 4a).
The self-diffusion coefficient of the ZrO_2-Particles in the liquid uncured organic-inorganic matrix was measured with a commercial PCS-equipment and a value of D_f=6,82*10^{-9} cm^2/s was obtained. The investigation of the mobility of the nanoparticles in different positions of the cell (and hence to the time dependent up-concentration of nanoparticles) were performed with the setup shown in figure 1. This setup represents a combination of classical PCS and zeta-potential determination and gives high spacial and temporal resolution in an electrophoretic cell.
The single exponential correlation function obtained with this experimental setup (no electric field applied) is shown in figure 5. The calculated self-diffusion coefficient (equation 1) gave a value of D_f=6.53*10^{-9} cm^2/s (±0.2*10^{-9} cm^2/s), which is in very good agreement to the value obtained with the commercial PCS-equipment.

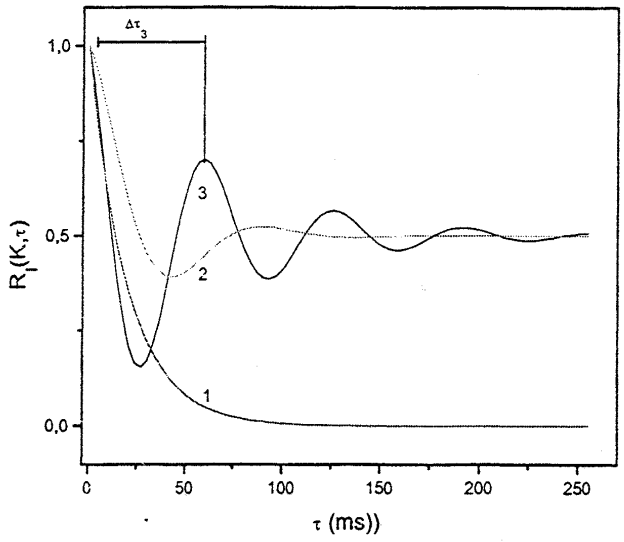


Figure 5: Calculated auto correlation function 1) whitout electric field 2) 75V/cm and 3) 100 V/cm of uncured MPTS/ZR/MA/TEGDMA (5/1/1/5 mol%) measured at 64° degrees, T= 25 °C, viscosity=160 mPas.s.

Application of an electric potential results in periodical modulations of the the correlation function. The frequency of these modulations is proportional to the mobility of the ZrO_2 nanoparticles (equation 7). The calculated auto correlation function measured for the material system MPTS/ZR/MS/TEGDMA (5/1/1/5 in mol%; scattering angle 64°; T=25 °C, viscosity of the suspension=160 mPas.s, pH=4) in presence of an electric field of 150V/cm and 200 V/cm is also shown in figure 5.

Calculating the mobility of the nanoparticles (equation 7) gives U=7,98*10^{-6} cm^2/sV and using equation 6, a zetapotential of 28 mV is obtained.
The comparison of results obtained with this PCS-electrophoretic cell and of results obtained with a commercial equipment for the measurement of the zeta potential of particles (in dependence of the pH of the suspension) is shown in figure 6. An excellent agreement of the results for both techniques can be concluded.

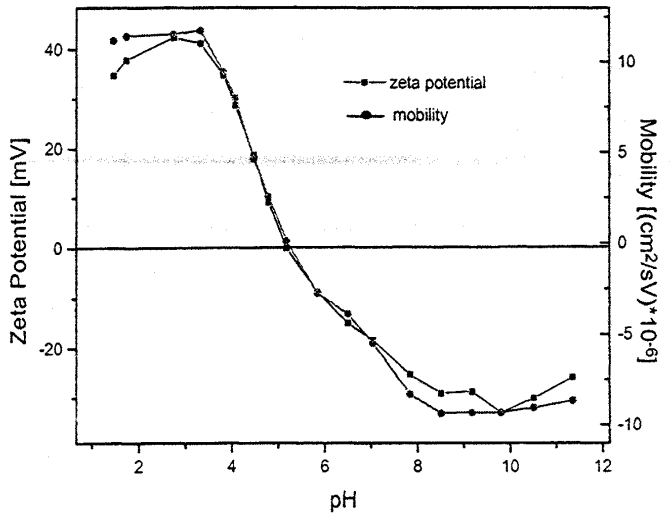


Figure 6: MPTS/ZR/MS/TEGDMA-system (5/1/1/5 mol%): ▪ measurement of the pH dependent Zeta potential (in isopropanol, commercial equipment) of the ZrO_2 nanoparticles and ● measurement of the pH dependent mobility of the ZrO_2 nanoparticles (without any additional solvent, PCS-optical setup developed in our lab).

In the Zeta potential zero point at pH=5.18, the mobility of the particles is zero and due to the lack of repulsing electrical forces, the particles tend to agglomerate and segregate. The decay of the Zeta potential and mobility at high and low pH-values (pH<3 and pH>9) can be contributed to a dissolution of the particles in the suspension. At high and low pH-values no more scattered light is detectable indicating that particles, which act as scattering centers, are vanished. figure 6 also explains, why experiments shown in figure 5 were made at a pH of 4, where highest mobility of the nanoparticles without dissolution effect is found. All following experiments relevant for the production of GRIN-lenses with the material system MPTS/Zr/MS/TEGDMA (5/1/1/5 in mol%) were made at a pH of 4.
A homogeneous electric field of well defined shape inside the electrophoretic cell can be obtained by the optimization of the position of the electrodes and the implied charge in every electrode. The variation of the local electric field potential φ in any segment of the cell is given by the dielectric constant of the uncured material, the charge of the circular wires on the front window and rear window and the thickness of the cell. The calculated potential profile and the potential profile obtained experimentally with the metallic 100 µm point probe is shown in figure 7. The fit is excellent and indicates, that is a very good tool to tailor potential profiles inside the cell.

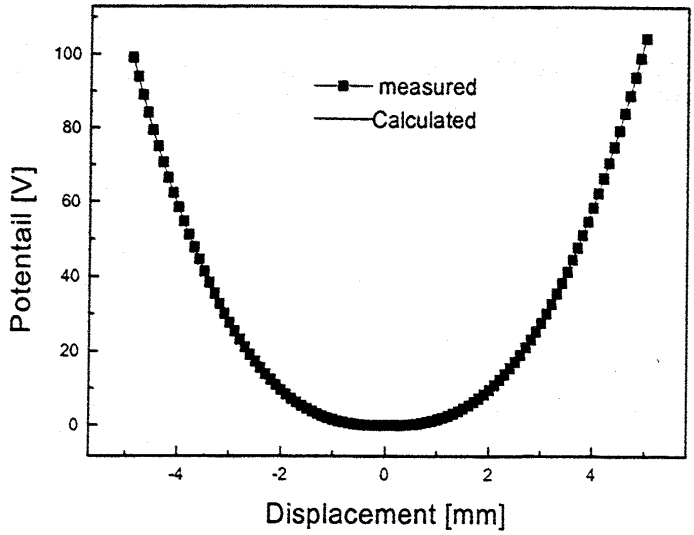
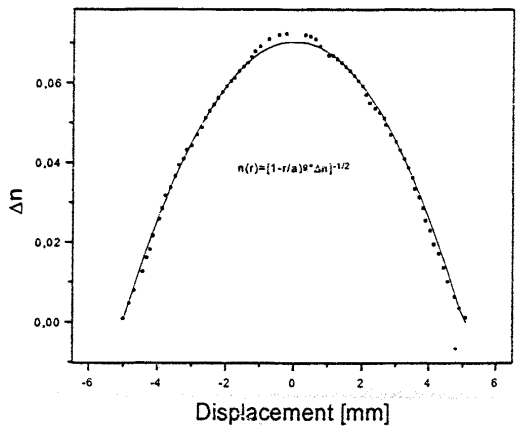


Figure 7: Potential gradient of the electric field produced by a circular electrode: ___ calculated and measured in the uncured MPTS/ZR/MA/TEGDMA-system (5/1/1/5 mol%) inside the electrophoretic cell.

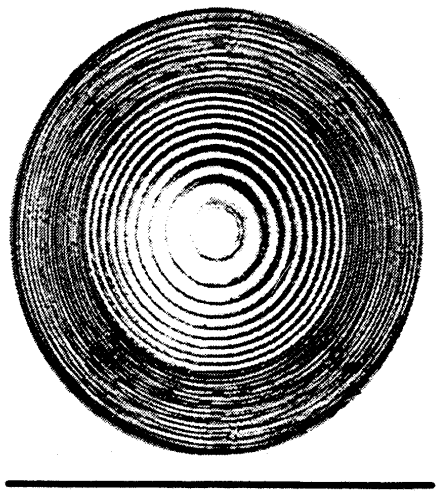
The GRIN-lens was realized applying an electric field of 100 V. After 5 h, the material was photopolymerized by the Hg-light source (50 J/cm^2) and the fixed radial gradient of the refractive index was measured with a Mach-Zehnder interferometer. A photograph of the obtained interference pattern is shown in figure 8b. The calculated radial variation of the refractive index from figure 8b is shown in figure 8a. Fitting the experimentally obtained curve of figure 8a by equation 9 allows to determine the exact shape of the index profile.

$$n(r) = \sqrt{1 - \left(\frac{r}{a}\right)^g \Delta n} \qquad (8)$$

n(r) is the variation of refractive function in dependence of the radius (r in cylindrical coordinates), a is the radius of the lens, Δn is the amplitude of the refractive index change and g is a constant. For g=0, n(r) is a constant, for g=1 the n(r) -function has a triangle form, for g=2 the n(r) -function has a parabolic form. For practical applications of GRIN-lenses, a parabolic variation of the refractive index is mostly desired. The fitted n(r) -function from figure 9a has g=1.96, which is very close to the ideal value for a parabolic variation of the refractive index.



a)



b)

Figure 8: a)- Radial variation of the refractive index measure by Mach-Zehnder interferometry in the material system MPTS/ZR/MA/TEGDMA (5/1/1/5 mol%) after electrophoresis and photocuring, ___ curve fitted by equation 9, g=1.98, b) interference pattern of the bulk GRIN-lens obtained in the Mach-Zehnder interferometer.

The refractive index shows a linear relationship to the concentration of the nanoparticles (see figure 3), and this linear relationship allows a direct comparison of the local refractive index measured by interferometry and the local concentration of the ZrO_2 measured by EDX (figure 10). The calculated Δn of 0.07 is far over the state of the art for organic polymer GRIN-lenses and reveals the high potential of chemical nanotechnologies to produce GRIN lenses of defined index gradient. Only a slight disagreement between the EDX and interferometer results in the center of the GRIN structure is visible. Investigations to optimize the parabolic shape of the index profile using different, transparent electrode materials are in progress.

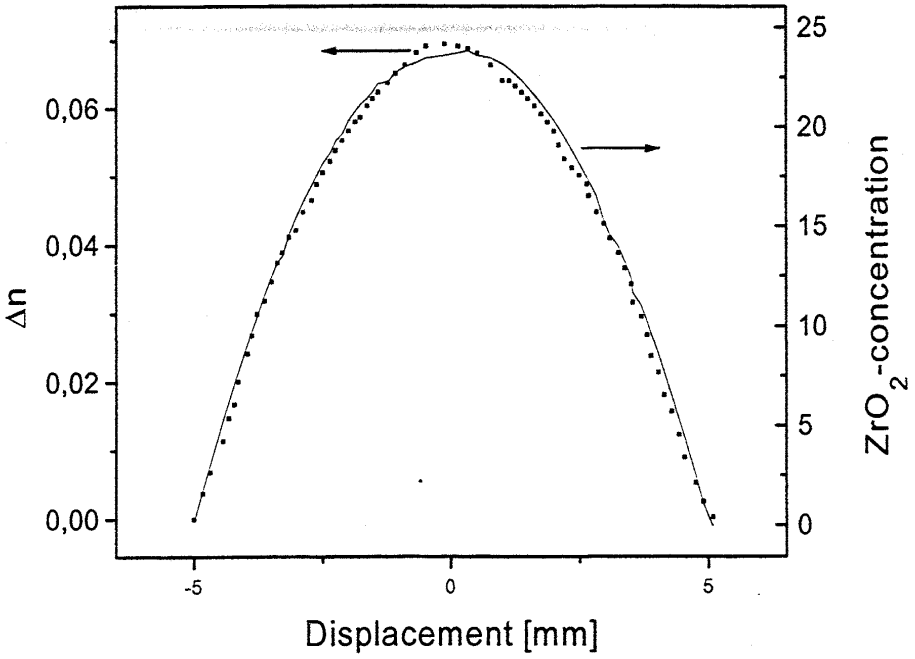


Figure 10: EDX-measurement of the concentration profile of ZrO_2-nanoparticles in MPTS/Zr/MS/TEGDMA (5/1/1/5) after applying 100 V for 5 hours and a subsequent photopolymerisation step (right) and the measured Δn from figure 9a (left)

The so called pitch length of the GRIN profile form figure 10 is given by equation 10

$$L_p = \frac{2\pi a}{\sqrt{2\Delta n}} \qquad (9)$$

where a is the lens radius and Δn is the refractive index amplitude. The first phase mode is completed at L_p= 8.39 cm and the focus distance $d_f = \frac{L_p}{2\pi}$ is 1.33 cm. The relative short mode period length (L_p) is due to the high amplitude of the refractive index modulation of 0.07, which allows decreasing the optical path of a lens system for example in photograph cameras. figure 11 shows the GRIN-effect produced electrophoretically by a parabolic radial up concentration of ZrO_2 nanoparticels in the material system MPTS/Zr/MS/TEGDMA after fixation of the concentration profile by photopolymerization. The overall production time to realize this GRIN-lens was less than 6 h.

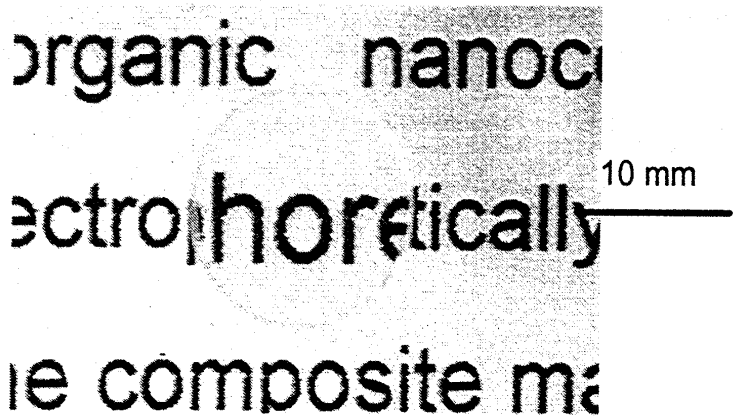


Figure 11: GRIN-lens (diameter=10 mm and thickness=13 mm) made in the material system MPTS/Zr/MS/TEGDMA (5/1/1/5 in mol%) by electrophoretically controlled diffusion of the ZrO_2 nanoparticels after fixation of the index porfile by photopolymerization.

5.CONCLUSION

Electrophoresis of nanoparticles in organic-inorganic matrices by application of well defined electric fields allows to produce GRIN-lenses with a high amplitute of the refractive index modulation. Not only parabolic refractive index curves but almost any distributions of the index of refraction may be possible. The presented work reveals that chemical nanotechnologies in combination with skilled process engineering allows to produce GRIN materials with a high application potential for optical equipments.

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