



Photoinduced refractive index changes of 3-phenyl-coumarin containing polymers for ophthalmic applications



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ABSTRACT

A novel photorefractive polymer has been developed where 3-phenyl-coumarin (3PC) is attached via alkyl spacers to a methacrylate backbone. The 3PC is a fusion of the structural motives of coumarin and stilbene. In 3PC the *E/Z*-isomerization, known from stilbenes, is blocked and a more extended conjugated π -electron system than in coumarin is obtained. A methacrylate based polymeric material comprising 3PC in the side chain has been synthesized and its photorefractive properties have been studied. The initial refractive index is $n_{633}^0 = 1.613$ and the maximal light-induced change of the refractive index was found to be $\Delta n_{633} = -0.045$ in spin-coated thin films as well as in bulk material. The glass transition temperature of about 37 °C and the high lightfastness of the polymer make it a candidate material for intraocular lenses with photo-tunable refractive index properties.

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1. Introduction

About 45 years ago light-induced changes in the refractive index of a polymer material were reported first [1]. Since then numerous photorefractive polymers have been developed [2–6]. Their range of optical applications reaches from optical waveguides [7], microelectronics [8], optical 2D and 3D data storage [9], and recently to medical devices [10]. Photorefractive polymers may comprise embedded charge transport materials [11–13] or dispersed chromophores [14,15]. Another class are polymers with photoactive groups covalently attached to the polymer backbone [16,17]. Such photosensitive groups may be coumarins [18], cinnamic acids [19], stilbenes [20], chalcones [21], and others [22]. Among these functional groups the photochemistry of coumarin and its derivatives may be the one investigated best [23,24]. The photorefractive effect

in polymers containing coumarins is due to the photoinduced dimerization of the coumarin moieties [5].

In the course of dimerization cyclobutane derivatives are formed and the double bond in the lactone ring of the coumarin molecule is transformed to a single bond leading to a decrease in the extension of the conjugated system of the molecules which concomitantly reduces their polarizability (Fig. 1). A change in polarizability causes a change of the molecules' relative permittivity ϵ_r and in turn directly affects their refractive index n . The simple approximation $n = \sqrt{\epsilon_r}$ for the relation between a material's refractive index n and its relative permittivity ϵ_r is valid only for non-resonant frequency ranges of the electromagnetic spectrum. The relative permeability μ_r is taken as 1 for all organic polymers at visible wavelengths [25].

Recently we reported materials for refractive index change in intraocular lenses (IOLs) consisting of a poly(methacrylate) backbone with 7-hydroxycoumarin (umbelliferone) in the side chain [5] and a high refractive index change polymer containing stilbene in the side chain [25].

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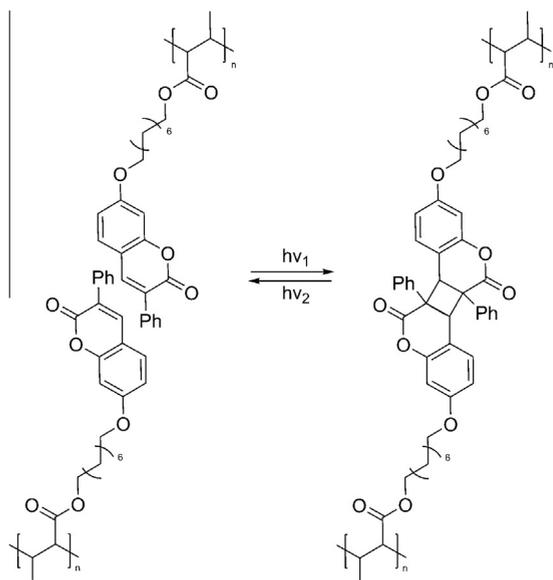


Fig. 1. Photochemistry of the synthesized 3-Phenyl-Coumarin (3PC) containing polymethacrylates.

In this study we present polymers, containing 3-phenylcoumarins in the side chain of acrylic polymers as photo-refractive polymers for novel IOLs with photo-tunable refractive index properties. The synthesized 7-hydroxy-3-phenylcoumarin (3PC) is a hybrid of 7-hydroxy-coumarin and stilbene. The structural relationship of this new chromophore to coumarin and stilbene is shown in Fig. 2. This novel material should combine the advantages of both coumarin and stilbene as it has a more extended π -electron system compared to coumarin and does not undergo *E/Z*-isomerization like stilbenes.

2. Experimental

The thermal characterization of the polymers was done running thermal gravimetric analysis (TGA) on a thermobalance TGA/SDTA 851^e (Mettler Toledo) in open corundum crucibles under nitrogen atmosphere. Heating rate was 10 K min⁻¹ in the range from 25 to 800 °C.

Differential scanning calorimetry (DSC) measurements were performed on a DSC 821^e (Mettler Toledo) under nitrogen atmosphere in a temperature range from -50 °C to 250 °C at a rate of 10 K min⁻¹.

¹H NMR and ¹³C NMR spectra were recorded on Bruker AV-300 A (300 MHz) and on Bruker AV-300 B (75 MHz)

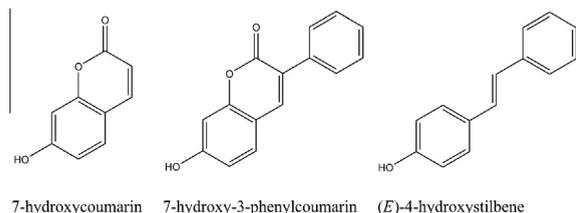


Fig. 2. Structural relationship of 7-hydroxycoumarin (left), 7-hydroxy-3-phenylcoumarin (middle), (*E*)-4-hydroxystilbene (right).

spectrometers using CDCl₃ or DMSO-d₆ as a solvent. The δ chemical shift scale is expressed in ppm and calibrated using the residual solvent peak.

Mass spectra were measured using a CH7 (Varian) with electron impact ionization (EI) or a LCQ-Duo (Thermo) using electrospray ionization (ESI).

UV/Vis spectra were measured on a Perkin Elmer Lambda 35 with the UV-WinLab software.

Polymer films were cast onto quartz windows for UV/Vis spectroscopy and on silicon wafers for refractive index measurements. Solutions of identical concentrations of the polymers in chloroform (HPLC grade) were prepared using a Spin 150-v3 spin coater from Semiconductor Production Systems.

Polymer films were irradiated using a diode-pumped, Q-switched, frequency-tripled Nd:YAG laser (Avia) from Coherent operating at 355 nm with a pulse length of 25 ns. For the described experiments the pulse rate was set to 10 kHz and a pulse energy of approximately 260 μ J was used.

The refractive indices as well as the thickness of the polymer films were determined using a Metricon Model 2010 prism coupler. The refractive indices were measured at 632.8 nm with an accuracy of ± 0.001 . For each refractive index value 4 randomly selected positions on a polymer sample were chosen and the mean value was calculated.

Gel permeation chromatography (GPC) was performed on a Knauer System equipped with a PSS-SDV (10 μ m) 300 \times 8 mm² column and two columns 600 \times 8 mm² at 25 °C with CHCl₃ as the eluent at a flow rate of 1.0 mL/min equipped with a differential refractometer (Knauer) and a UV detector (Knauer). Polystyrene (PS) standards were used for calibration.

Photostability studies were carried out using an Atlas Suntest XLS + solar simulator.

Topographical surface characterization of intraocular lenses was done using a Cyber Technologies CT100 optical profilometer. For the evaluation of the surface roughness parameter the Scan CT8 software was used.

All chemical reactions were carried out in dried glassware under argon atmosphere.

2.1. Chemicals

Methacrylic acid (Sigma Aldrich, >98%), 2,2'-azobisisobutyronitrile (Sigma Aldrich), DCC (Sigma Aldrich, 99%), DMAP (Merck, 99%), sulfuric acid (Riedel-de Haën, 96%), potassium carbonate (Merck, 99%), 2,4-Dihydroxy-benzaldehyde (Sigma Aldrich, 98%), camphor chinone (Sigma Aldrich, 97%), dimethylaminobenzoat (Sigma Aldrich 99+%), EGDMA (Acros, 98%) phenyl acetic acid (Sigma Aldrich, 99%), 8-bromooctan-1-ol (ABCR, 90%), 10-bromodecan-1-ol (Sigma Aldrich, 90%), acetic anhydride (Fluka, 99%), pyridine (Acros, water <50 ppm) and solvents were used as received. Where necessary, the drying of solvents was done according to standard protocol.

2.2. Synthesis of 3-Phenyl-7-hydroxycoumarin

2,4-Dihydroxy-benzaldehyde (14.09 g, 100 mmol, 1.0 eq) and phenyl acetic acid (113.75 g, 1.0 eq) were

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