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High refractive index coumarin-based photorefractive polysiloxanes

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ABSTRACT

In the past decades the development of photorefractive devices evolved rapidly as can be seen by the increasing number of publications and numerous applications. There is still need of innovative materials which are suitable for a broad range of applications through tailored properties. We present photorefractive linear and crosslinked polysiloxanes with refractive indices of up to $n = 1.603$ which may be tuned in their refractive index in a range of up to $\Delta n = 0.04$ photochemically. The polysiloxanes, more commonly named silicones, have side chains containing coumarin which are attached to the polymer backbone via different spacers ranging in length from 3 to 9 methyl groups. The coumarins undergo wavelength-dependent photodimerization and photocleavage in the polymer which cause the desired refractive index changes. The polysiloxanes have low glass transition temperatures ranging from −2 °C to 35 °C and show a high thermal stability ($T_{5\%} > 410$ °C). These properties make these materials promising candidates for the manufacture of photo tunable polymers, e.g. for the use as optical data storage materials, alignment of liquid crystals, and photorefractive intraocular lenses.

1. Introduction

The very first use of photo tunable polymers dates back to the Babylonians about 3500 BC. which used asphalt oil to waterproof their boats. Through photocrosslinking in sunlight of the monomeric asphalt oil a solid and waterproof polymer film was generated [1]. One of the first systematic approaches to synthesize photo tunable polymers was reported by Minsk et al. in 1959 where the photochemical dimerization of poly(vinyl cinnamate) under irradiation with light of appropriate wavelength was described [2–4].

Meanwhile photorefractive polymers have received great interest in a large variety of scientific fields, such as microelectronics [5–7], optoelectronic materials [8–10] and medical devices [11–13]. Several photoresponsive systems were evaluated including anthracene [14–16], cinnamic esters [17–19], coumarin [20,21], and others [22,23]. Among these systems coumarin and its derivatives are one of the best studied systems (Fig. 1) [24,25].

We recently reported a system consisting of a poly(methacrylate)-backbone with coumarin moieties in the side chains as a photorefractive material for IOLs [26]. The change in refractive index is induced through the photochemical dimerization of the coumarin moieties. Over the course of dimerization cyclobutane derivatives are formed and the double bond in the lactone ring of the coumarin molecule is replaced by a single bond leading to a decrease in the molecules conjugated system which concomitantly reduces the molecules polarizability. As a change in polarizability causes a change of the molecules relative permittivity ε_r this directly influences the refractive index n. The simple approximation

$$n = \sqrt{\varepsilon_r} \quad (1)$$

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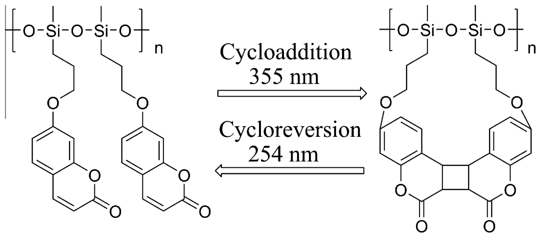

Fig. 1. Photochemistry of polymer bound coumarins, e.g. via a C_3-spacer. Cycloaddition under irradiation with light $\lambda > 300$ nm leads to the formation of coumarin dimers. Irradiation with light <300 nm leads to cycloreversion.

for the relation between a materials refractive index n and its relative permittivity ε_r is valid only for a small frequency range of the electromagnetic spectrum. The relative permeability μ_r is taken as 1 for all organic polymers at these frequencies [27].

Taking the aforementioned considerations into account we believe that silicones comprising coumarin side chains (see Fig. 1) are promising photo tunable polymers for a large variety of applications such as optical data storage, aligned membranes for LC displays, and for photorefractive intraocular lenses.

2. Experimental section

The thermal characterization of the polymers by Thermal Gravimetric Analysis (TGA) was performed using a thermo-balance TGA/SDTA 851^e (Mettler Toledo) in open corundum crucibles under nitrogen atmosphere. The linear temperature ramp was from 25 °C to 800 °C at a rate of 10 K min^{-1}. DSC measurements were performed on a DSC 821^e (Mettler Toledo) under nitrogen atmosphere in a temperature range from 25 °C to 230 °C at a rate of 10 K min^{-1}.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV-300 A (300 MHz) and on a Bruker AV-300 B (75 MHz) spectrometer using $CDCl_3$ and acetone-d_6 as solvents. The δ chemical shift scale was expressed in ppm and calibrated using the residual solvent peak.

Mass spectra were measured after electron impact ionization using either a CH7 (Varian) or a MAT95 (Finnigan) for high resolution mass spectra (HR-MS).

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

Polymer films were cast onto quartz windows for UV/Vis analysis and on silicon wafers for refractive index measurements. Thin films of the polymers were obtained by spin coating (Spin 150-v3 spin coater from Semiconducter Production Systems) from chloroform solutions (HPLC grade) of the polymers.

Photodimerization in the polymer films was accomplished by 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 265 µJ was chosen.

Photocleavage of the polymer-bound coumarin dimers were obtained by irradiation with 254 nm light from a Philips low pressure mercury lamp with an output of 9 W.

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 were chosen and the results were averaged.

Gel permeation chromatography (GPC) was performed on a Knauer System equipped with a PSS-SDV (10 µm) 300×8 mm^2 column and two columns 600×8 mm^2 at 25 °C with THF as the eluent at a flow rate of 1.0 mL min^{-1} followed by a differential refractometer (Knauer) and a UV detector (Knauer). Polystyrene (PS) standards were used for calibration.

2.1. Chemicals

Chemicals were used as received. Amberlyst 15 (Sigma Aldrich), dec-9-en-1-ol (Fluka, 99%), diisopropylazodicarboxylat (DIAD) (Acros, 94%), dimethoxy-methyl-silane (TCI, >97%), 7-hydroxycoumarin (Acros, 99%), potassium carbonate (Merck, 99%), Karstedt catalyst (Sigma, 2% Pt in xylene), methyl-triethoxy-silane (Fluka, 99%), pent-4-en-1-ol (Fluka, 99%), phosphazen base P4-t-Bu (Sigma Aldrich, purum), poly-(methylhydrosiloxane) (Sigma Aldrich), conc. sulphuric acid (Riedel-de Häen, 96%), tetraethoxy-silane (Sigma Aldrich, 99%), tetramethoxy-silane (Fluka, 99%), toluene (Sigma Aldrich, 99.8%), triethoxy-silane (Fluka, 98%), triethylamine (Fisher scientific, 99%), trifluoromethanesulphonic acid (Sigma Aldrich, 99%), triphenylphosphine (Sigma Aldrich, 99%).

2.2. Synthesis of 7-(allyloxy)coumarin

7-Hydroxycoumarin (2.43 g, 15 mmol, 1.0 eq) and potassium carbonate (6.22 g, 45 mmol, 3.0 eq) were dispersed in acetone (75 ml). Allylbromide (1.56 ml, 18 mmol, 1.2 eq) was added dropwise and the reaction mixture was stirred at 60 °C for 5 h. The potassium carbonate was filtered off and the solvent was evaporated at reduced pressure. The yellowish crude material was crystallized from methanol.

2.2.1. 7-(allyloxy)coumarin (C_3O-Cou): yield 79%, colourless needles

^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.63 (d, 1H, J = 9.4 Hz); 7.36 (d, 1H, J = 8.5 Hz); 6.84 (m, 2H); 6.24 (dd, 1H, J = 9.4 Hz, J = 1.3 Hz); 6.03 (m, 1H); 5.38 (m, 2H); 4.59 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ/ppm = 161.8; 161.1; 155.8; 143.3; 132.1; 128.7; 118.4; 113.2; 113.1; 112.6; 101.7; 69.2.

2.3. Mitsunobu alkylation of 7-hydroxycoumarin

7-Hydroxycoumarin (9.41 g, 56.9 mmol, 1.0 eq) was dissolved in absolute THF and triphenylphosphine (14.92 g, 56.9 mmol, 1.0 eq) and pent-4-en-1-ol (5.95 ml, 56.9 mmol, 1.0 eq) were added, same stoichiometric amounts for the reaction of non-8-en-1-ol respectively. The stirred solution was cooled to 0 °C and DIAD (12.0 ml, 56.9 mmol, 1.0 eq) was added dropwise. The reaction mixture was stirred at room temperature for an-