Macromolecules

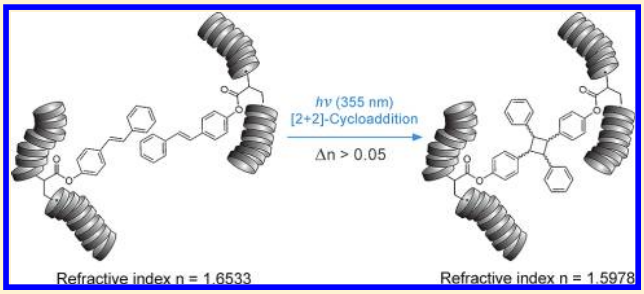
ARTICLE

pubs.acs.org/Macromolecules

# Selective [2 + 2]-Cycloaddition in Methacrylic Stilbene Polymers without Interference from *E*/*Z*-Isomerization

Martin Schraub,[†] Helen Gray,[‡] and Norbert Hampp*[,†,§]

[†]Department of Chemistry, University of Marburg, Hans-Meerwein-Straße, Bld. H, 35032 Marburg, Germany
[‡]Imperial College London, South Kensington Campus, London SW7 2AZ, Great Britain
[§]Materials Science Center Marburg, Hans-Meerwein-Straße, 35032 Marburg, Germany



**ABSTRACT:** Stilbene is known to undergo two different reactions upon photochemical excitation. The first is an *E*/*Z* isomerization and the second is a [2 + 2]-cycloaddition of two stilbene molecules. Because both reactions occur in parallel their use is limited. Here we report on photorefractive polymers with a methacrylate backbone and covalently attached 4-hydroxy-(*E*)-stilbene or 3,5-dimethoxy-4-hydroxy-(*E*)-stilbene units in the side chain which show [2 + 2]-cycloaddition only. Both polymers, poly(4-methacryloyloxy-(*E*)-stilbene) (PMAES) and poly(4-methacryloyloxy-3,5-dimethoxy-(*E*)-stilbene) (PMADMES), show very high initial refractive indices of 1.6533 for PMAES and 1.6288 for PMADMES. The photochemical reaction upon laser irradiation with 355 nm was monitored by UV/vis, fluorescence, and IR spectroscopy. The light-induced changes of the refractive index at 633 nm measured by surface plasmon resonance (SPR) were found to be $\Delta n > 0.05$ for PMAES and $\Delta n > 0.04$ for PMADMES. The sensitivity of PMADMES is enhanced compared to PMAES due to the electron donating groups (EDG) as the direct comparison of both polymers shows. Both polymers are useful for optical devices because they do not show any absorption in the visible range and are noncrystalline as determined by wide-angle X-ray scattering (WAXS) and differential scanning calorimetry (DSC).

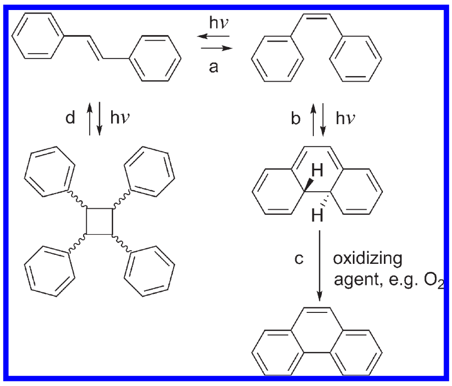
## ■ INTRODUCTION

Over the past decades the development of photoresponsive polymers gained significant attention as may be seen from the increasing number of publications and applications per year. The fields of interests for photorefractive polymers range from optical waveguides[1] over switching devices[2] to photo-cross-linkable polymers.[3]

There are several synthetic pathways to synthesize photoresponsive polymers, among them integration of a light sensitive compound into the backbone of a polymer,[4] or in the side chain (pendant group),[5] or simply by using it as an additive to a polymer.[6] In general there are two types of refractive index change materials; refraction-increase materials[7,8] and refraction-decrease materials.[9,10] Typical values for refractive index changes are in the range of $\Delta n$ 0.001−0.1.[1] Light sensitive compounds may be coumarins,[11] cinnamic acids,[12] stilbenes,[13] chalcones,[14] and others.[15] Stilbenes are one of the best examined substance classes from the mechanistic as well as from the preparative photochemistry point of view.

One of the photochemical pathways of stilbene, the dimerization of *E*-stilbene, was first discovered by Ciamician and Silber at the beginning of the 20th century.[16] The structural analysis of the dimer by Fulton and Dunitz followed in 1945.[17] The second photochemical pathway, the *E*/*Z*-isomerization, was described first in 1909 by Störmer[18] and finally a third photochemical step, the photocyclization via oxidative dehydrogenation of dihydrophenanthrene was found by Smakula in 1934[19] (Scheme 1).

**Scheme 1. Photochemical Pathways of (*E*)-Stilbene: (a) *E*/*Z* Isomerization, (b) Conrotatory Electrocyclic 6-π Photochemical Cyclization, (c) Oxidation, and (d) Photochemical Cycloaddition**

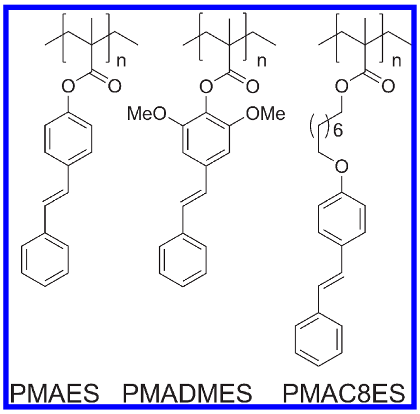


The $[\pi^2 s + \pi^2 s]$-cycloaddition occurs between the first excited singlet state $S_1$ of an *E*-stilbene and a second *E*-stilbene in the ground state $S_0$[5] under formation of a cyclobutane ring. Only

**Received:** July 7, 2011
**Revised:** October 4, 2011
**Published:** November 01, 2011

dx.doi.org/10.1021/ma2015485 | *Macromolecules* 2011, 44, 8755–8762

Scheme 2. Structure of the Synthesized Polymers[a]



[a] Key: (left) poly(4-methacryloyloxy-(*E*)-stilbene) (PMAES), (middle) poly(4-methacryloyloxy-3,5-dimethoxy-(*E*)-stilbene) (PMADMES), and (right) poly(8-methacryloyl-octyl-4-oxy-(*E*)-stilbene) (PMAC8ES).

*E*-stilbene shows dimerization because the lifetime of the $S_1$ state of *Z*-stilbene is too short to contribute effectively to the reaction. Neither does *Z*-stilbene take part in the ground state as part of the exiplex.[20] It is noteworthy that photochemical cycloaddition does not occur in highly diluted solutions. Because the $S_1$-lifetime of the molecules is too short to find a dimerization partner by diffusion[5] only isomerization is observed. If *Z*-stilbene is exposed to light of appropriate wavelength it undergoes isomerization as well as conrotatory, electrocyclic 6-$\pi$ photochemical cyclization to form dihydrophenanthrene (DHP). DHP accumulates over time and in the presence of mild oxidizing agents, e.g., oxygen or iodine, it undergoes an irreversible oxidation to phenanthrene.[21]

Polymers containing stilbene either as part of the backbone or in the side chain, were studied and physical and mechanical property changes in dependence on the *E*/*Z* isomerization in condensed matter, e.g. conductivity,[22] solubility,[23] change in volume,[24] and shape,[25] were analyzed. Only little attention has been payed to the irradiation dependent refractive index changes so far.

Exposure of tetraphenylcyclobutane, the dimerization product of *E*-stilbene, to wavelengths shorter than 300 nm leads to cycloreversion.[26−28] With different wavelengths this reaction may be driven either toward cyclization or cycloreversion. The refractive index n of a material is depending on physical properties like density, molecular weight, molar refraction and relative permittivity. Indeed if one or more of these properties are changed the materials refractive index is changed too. The relation between the refractive index n and the relative permittivity $\varepsilon_r$ is given by the Maxwell equation.

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

During dimerization and cyclobutane formation the carbon−carbon double bond in stilbene is replaced by a carbon−carbon single bond and, caused by the loss of conjugation, the polarizability of the molecule, its relative permittivity $\varepsilon_r$, and in turn its refractive index are decreased.

In this study we present three photorefractive homopolymers, poly(4-methacryloyloxy-(*E*)-stilbene) (PMAES), poly(4-methacryloyloxy-3,5-dimethoxy-(*E*)-stilbene) (PMADMES) and poly(8-methacryloyl-octyl-4-oxy-(*E*)-stilbene) (PMAC8ES) which were synthesized by free radical polymerization (Scheme 2). Their photochemical behavior upon irradiation with 355 nm from a pulsed laser source and the influence of electron donating groups (EDG) on the photodimerization were investigated.

## ■ EXPERIMENTAL SECTION

The thermal characterization of the polymers was done using thermal gravimetric analysis (TGA) run on a thermo-balance TGA/SDTA 851$^e$ (Mettler Toledo) in open corundum crucibles under nitrogen atmosphere. Heating was at a rate of 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 25 to 230 °C at a rate of 10 K min$^{-1}$.

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

WAXS measurements were performed on a Siemens D5000 goniometer with nickel filtered CuK$_\alpha$-radiation (1.5404 Å) at room temperature.

Density measurements were performed using a 2 cm$^3$ pycnometer. Samples were heated to 150 °C under vacuum for 6 h before use for density measurement.

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

UV/vis spectra were measured on a Perkin-Elmer Lambda 35 with the UV-WinLab software. IR-measurements were performed on a Perkin-Elmer 1600 Series FTIR. Fluorescence spectra were taken on a Shimadzu spectrofluorophotometer model RF-1502.

Polymer films were cast onto quartz windows for UV/vis and fluorescence analysis, on NaCl plates for IR measurements, 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 Semiconducter Production Systems.

Polymer films were irradiated using a diode-pumped, Q-switched, frequency-tripled Nd:YAG laser (Avia) from Coherent at a wavelength of 355 nm and 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 $\mu$J.

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 ±0.001. For each refractive index value 4 randomly selected positions on a polymer sample were chosen.

Gel permeation chromatography (GPC) was performed on a Knauer System equipped with a PSS-SDV (10 $\mu$m) 300 × 8 mm$^2$ column and two columns 600 × 8 mm$^2$ at 25 °C with $CHCl_3$ 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.

Methacryloyl chloride (Lancaster) was distilled under reduced pressure prior to use. Benzyltriphenylphosphonium bromide (Acros, 97%), 8-bromooctan-1-ol (ABCR, 90%), *n*-butyl lithium (*n*-BuLi, Aldrich, 2 M solution in cyclohexane), 3,5-dimethoxy-4-hydroxybenzaldehyde (Acros, 98%), (*E*)-4-hydroxystilbene (Acros, 98%), Triethylamine (Acros, 99%) and solvents were used as received. Where necessary, the drying of solvents was performed according to standard protocols.[29]

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

**Syntheses.** *Synthesis of 3,5-dimethoxy-4-hydroxystilbene.* Benzyltriphenylphosphonium bromide (6.579 g, 15 mmol, 1 equiv) was suspended in 100 mL of dry THF. Once dissolved, the reaction mixture was cooled to 0 °C and *n*-BuLi (18.75 mL, 30.1 mmol, 2.1 equiv) was added dropwise to the stirred solution. After 0.5 h, 3,5-dimethoxy-4-hydroxybenzaldehyde (2.734 g, 15 mmol, 1 equiv) was added in aliquots to the deep red solution. The reaction mixture was stirred at room temperature for another 16 h. The yellow suspension was quenched with saturated $NH_4Cl$ solution (100 mL), extracted with dichloromethane (3 × 100 mL) and the combined organic phases were dried over $Na_2SO_4$. Evaporation of the solvent under reduced pressure yielded the crude product, which was purified by column chromatography (200:1 $CHCl_3$:MeOH). A pale yellow powder was obtained (2.98 g, 73% yield). $R_f$: 0.33 (200:1 $CHCl_3$:MeOH). $^1$H NMR (300 MHz, $CDCl_3$), $\delta$/ppm: 7.43 (d, 2H, $^3J$ = 7.1 Hz, $\mathrm{H_{arom}}$), 7.29 (m, 3H, $\mathrm{H_{arom}}$), 6.97 (d, 1H, $^3J$ = 16.3 Hz, $\mathrm{H_{olef}}$), 6.89 (d, 1H, $^3J$ = 16.1 Hz, $\mathrm{H_{olef}}$), 6.70 (s, 1H, $\mathrm{H_{arom}}$, ×2), 3.89 (s, 3H, O−$CH_3$, ×2), 3.61 (s, 1H, OH). $^{13}$C NMR (75 MHz, $CDCl_3$), $\delta$/ppm: 147.2 ($sp_2$, $C_q$, C−OH), 137.4 ($sp_2$, $C_q$), 134.9 ($sp_2$, $C_q$), 129.0 ($sp_2$, CH, $\mathrm{C_{arom}}$), 128.8 ($sp_2$, CH, $\mathrm{C_{arom}}$), 128.7 ($sp_2$, C-OMe, $\mathrm{C_{arom}}$, ×2), 127.3 ($sp_2$, $\mathrm{C_{olef}}$), 126.9 ($sp_2$, $\mathrm{C_{olef}}$), 126.3 ($sp_2$, CH, $\mathrm{C_{arom}}$), 103.4 ($sp_2$, CH, $\mathrm{C_{arom}}$), 56.3 ($sp_3$, O−$CH_3$, ×2). MS (EI, 70 eV), $m/z$ (%): 256 (100) [$M^+$], 209 (9), 195 (12), 181 (22), 165 (8), 152 (12), 141 (8), 69 (9). HRMS (EI): calcd for $C_{16}H_{16}O_3$ ($M^+$), 256.1099; found, 256.1094.

*Synthesis of (E)-8-(4-styrylphenoxy)octan-1-ol.* 4-Hydroxystilbene (3 g, 15 mmol, 1 equiv), 8-bromooctan-1-ol (4.06 g, 19.5 mmol, 1.3 equiv) and potassium carbonate (8.25 g, 60 mmol, 4 equiv) were refluxed under stirring for 24 h in acetone. The solid was filtered off, washed with hot acetone and the solvent of the combined organic phases was evaporated under reduced pressure. The crude product was purified by column chromatography (100:1 $CHCl_3$:MeOH). A colorless powder was obtained (4.17 g, 84% yield), (*E*)-8-(4-styrylphenoxy)octan-1-ol (C8ES). $R_f$: 0.30 (100:1 $CHCl_3$:MeOH). $^1$H NMR (300 MHz, $CDCl_3$), $\delta$/ppm: 7.47 (dd, 4H, $^3J$ = 8.0 Hz, $^3J$ = 13.9 Hz, $\mathrm{H_{arom}}$), 7.34 (t, 2H, $^3J$ = 7.5 Hz, $\mathrm{H_{arom}}$), 7.22 (td, 1H, $^4J$ = 1.6 Hz, $^4J$ = 2.4 Hz), 7.02 (q, 2H, $^3J$ = 16.3 Hz, $\mathrm{H_{olef}}$), 6.89 (d, 2H, $^3J$ = 8.8 Hz, $\mathrm{H_{arom}}$), 3.97 (t, 2H, $^3J$ = 6.5 Hz, −O−$CH_2$), 3.65 (t, 2H, $^3J$ = 6.6 Hz, −O−$CH_2$), 1.79 (m, 2H, $\mathrm{H_{aliph}}$), 1.57 (m, 2H, $\mathrm{H_{aliph}}$), 1.44 (m, 8H, $\mathrm{H_{aliph}}$). $^{13}$C NMR (75 MHz, $CDCl_3$), $\delta$/ppm: 158.8 ($sp_2$, $C_q$), 137.7 ($sp_2$, $C_q$), 129.9 ($sp_2$, CH, $\mathrm{C_{arom}}$), 128.6 ($sp_2$, CH, $\mathrm{C_{arom}}$), 128.2 ($sp_2$, CH, $\mathrm{C_{arom}}$), 127.6 ($sp_2$, $\mathrm{C_{olef}}$), 127.1 ($sp_2$, $\mathrm{C_{olef}}$), 126.4 ($sp_2$, CH, $\mathrm{C_{arom}}$), 126.2 ($sp_2$, CH, $\mathrm{C_{arom}}$), 114.7 ($sp_2$, CH, $\mathrm{C_{arom}}$), 68.0 ($sp_3$,−O−$CH_2$−, $\mathrm{C_{aliph}}$), 63.0 ($sp_3$,−O−$CH_2$−, $\mathrm{C_{aliph}}$), 32.7 ($sp_3$, −$CH_2$−, $\mathrm{C_{aliph}}$), 29.3 ($sp_3$, −$CH_2$−, $\mathrm{C_{aliph}}$, ×2), 29.2 ($sp_3$, −$CH_2$−, $\mathrm{C_{aliph}}$, ×2), 25.9 ($sp_3$, −$CH_2$−, $\mathrm{C_{aliph}}$, ×2), 25.6 ($sp_3$, −$CH_2$−, $\mathrm{C_{aliph}}$). MS (EI, 70 eV), $m/z$ (%): 324 (78) [$M^+$], 196 (47). 165 (9), 130 (17), 69 (78).

*Esterification of 4-Hydroxystilbene Compounds.* The stilbene compound (15 mmol, 1 equiv) was dissolved in 60 mL of dry THF. Triethylamine (75 mmol, 5 equiv) was added at once and the reaction mixture was left to stir at room temperature for 1 h. Methacryloyl chloride (18 mmol, 1.2 equiv) was added dropwise over a period of 15 min and the reaction mixture was left to stir at room temperature for additional 16 h. The precipitated ammonium chloride salts were filtered off and after evaporation of the solvent under reduced pressure the crude product was purified by column chromatography (3:1 pentane:diethyl ether). A colorless powder was obtained (75% yield), 4-methacryloyloxy-(*E*)-stilbene (MAES). $R_f$: 0.27 (3:1 pentane:diethyl ether). $^1$H NMR (300 MHz, $CDCl_3$), $\delta$/ppm: 7.45 (d, 2H, $^3J$ = 7.2 Hz, $\mathrm{H_{arom}}$), 7.30 (t, 2H, $^3J$ = 7.4 Hz, $\mathrm{H_{arom}}$), 7.21 (d, 2H, $^3J$ = 10.2 Hz, $\mathrm{H_{arom}}$), 7.19 (s, 2H, $\mathrm{H_{arom}}$), 6.99 (s,1H, $\mathrm{H_{arom}}$), 6.70 (s, 2H, $\mathrm{H_{olef}}$), 6.29 (s, 1H, $\mathrm{H_{arom}}$), 5.69 (s, 1H, $\mathrm{H_{arom}}$), 2.02 (s 3H, $CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$), $\delta$/ppm: 165.76 ($sp_2$, C═O), 150.36 ($sp_2$, Cq, $\mathrm{C_{arom}}$), 136.93 ($sp_2$, CH, $\mathrm{C_{olef}}$), 135.81 ($sp_2$, CH, $\mathrm{C_{olef}}$), 129.2 ($sp_2$, $C_q$, $\mathrm{C_{arom}}$, C−OCO), 128.69 ($sp_2$, CH, $\mathrm{C_{arom}}$, x4), 127.74 ($sp_2$, CH, $\mathrm{C_{arom}}$, ×2), 127.68 ($sp_2$, CH, $\mathrm{C_{arom}}$, ×2), 127.40 ($sp_2$, CH, $\mathrm{C_{arom}}$, ×2), 123.50 ($sp_2$, $CH_2$, $\mathrm{C_{arom}}$, ×2), 18.38 ($sp_3$, $CH_3$). MS (EI, 70 eV), $m/z$ (%): 264 (68) [$M^+$], 196 (52), 177 (8), 167 (8), 165 (12), 152 (9), 119 (5), 69 (98), 44 (16), 41 (32). HRMS (EI): calcd for $C_{18}H_{16}O_2$ ($M^+$), 264.1150; found, 264.1145. A similar procedure yielded 4-methacryloyloxy-3,5-dimethoxy-(*E*)-stilbene (MADMES). $R_f$: 0.23 (pentane:diethyl ether 3:1). $^1$H NMR: (300 MHz, $CDCl_3$), $\delta$/ppm: 7.52 (d, 2H, $^3J$ = 7.1 Hz, $\mathrm{H_{arom}}$), 7.37 (t, 2H, $^3J$ = 7.4 Hz, $\mathrm{H_{arom}}$), 7.28 (d, 2H, $^3J$ = 7.3 Hz, $\mathrm{H_{arom}}$), 7.06 (s, 2H, $\mathrm{H_{arom}}$), 6.78 (s, 2H, $\mathrm{H_{olef}}$), 6.70 (s, 1H, $\mathrm{H_{arom}}$, ×2), 6.41 (s, 1H, $\mathrm{H_{olef}}$) 5.76 (s, 1H, $\mathrm{H_{olef}}$) 3.87 (s, 3H, O−$CH_3$, ×2), 2.10 (s, 3H, $CH_3$). $^{13}$C NMR: (75 MHz, $CDCl_3$), $\delta$/ppm: 165.2 ($sp_2$, C═O), 152.4 ($sp_2$, $C_q$, $\mathrm{C_{arom}}$, ×2), 137.0 ($sp_2$, Cq, $\mathrm{C_{arom}}$), 135.7 ($sp_2$, $C_q$, $\mathrm{C_{arom}}$), 135.5 ($sp_2$, CH, $\mathrm{C_{olef}}$), 129.0 ($sp_2$, $C_q$, $\mathrm{C_{arom}}$, C−OCO), 128.7 ($sp_2$, CH, $\mathrm{C_{arom}}$, ×2), 128.6 ($sp_2$, CH, $\mathrm{C_{arom}}$), 128.5 ($sp_2$, CH, $\mathrm{C_{arom}}$), 127.7 ($sp_2$, CH, $\mathrm{C_{olef}}$), 127.1 ($sp_2$, $CH_2$, $\mathrm{C_{arom}}$, ×2), 126.5 ($sp_2$, $CH_2$, $\mathrm{C_{arom}}$), 103.3 ($sp_2$, CH, $\mathrm{C_{arom}}$, ×2), 56.2 ($sp_3$, O−$CH_3$, ×2), 18.5 ($sp_3$, $CH_3$). MS (EI, 70 eV), $m/z$ (%): 324 (92) [$M^+$], 255 (98), 195 (16), 181 (14), 167 (12), 152 (9), 141 (8), 113 (6), 86 (36), 69 (92), 41 (52). HRMS (EI): calcd for $C_{20}H_{20}O_4$ ($M^+$), 324.1362; found, 324.1369. A similar procedure yielded (*E*)-8-(4-styrylphenoxy)octyl methacrylate (MAC8ES). $R_f$: 0.38 (pentane:diethyl ether 3:1). $^1$H NMR (300 MHz, $CDCl_3$), $\delta$/ppm: 7.47 (dd, 4H, $^3J$ = 8.0 Hz, $J$ = 13.9 Hz, $\mathrm{H_{arom}}$), 7.34 (t, 2H, $^3J$ = 7.5 Hz, $\mathrm{H_{arom}}$), 7.22 (td, 1H, $^4J$ = 1.6 Hz, $^4J$ = 2.4 Hz. $\mathrm{H_{arom}}$), 7.02 (q, 2H, $^3J$ = 16.3 Hz, $\mathrm{H_{olef}}$), 6.89 (d, 2H, $^3J$ = 8.8 Hz, $\mathrm{H_{arom}}$), 6.10 (dd, 1H, $^4J$ = 0.9 Hz, $^4J$ = 1.7 Hz, $\mathrm{H_{olef}}$), 5.55 (dd, 1H, $^4J$ = 0.9 Hz, $^4J$ = 1.6 Hz, $\mathrm{H_{olef}}$), 4.15 (t, 2H, $^3J$ = 6.7 Hz, −O−$CH_2$), 3.97 (t, 2H, $^3J$ = 6.5 Hz, −O−$CH_2$), 1.95 (dd, 3H, $^4J$ = 1.0 Hz, $^4J$ = 1.4 Hz, −$CH_3$), 1.78 (m, 2H, $\mathrm{H_{aliph}}$), 1.67 (m, 2H, $\mathrm{H_{aliph}}$), 1.45 (m, 8H, $\mathrm{H_{aliph}}$). $^{13}$C NMR (75 MHz, $CDCl_3$), $\delta$/ppm: 167.5 ($sp_2$, C═O), 158.8 ($sp_2$, Cq, $\mathrm{C_{arom}}$), 137.7 ($sp_2$, $C_q$), 129.9 ($sp_2$, CH, $\mathrm{C_{arom}}$), 128.6 ($sp_2$, CH, $\mathrm{C_{arom}}$), 128.2 ($sp_2$, CH, $\mathrm{C_{arom}}$), 127.6 ($sp_2$, $\mathrm{C_{olef}}$), 127.1 ($sp_2$, $\mathrm{C_{olef}}$), 126.4 ($sp_2$, $\mathrm{C_{olef}}$), 126.2 ($sp_2$, $\mathrm{C_{olef}}$), 125.1 ($sp_2$, CH, $\mathrm{C_{arom}}$), 114.7 ($sp_2$, CH, $\mathrm{C_{arom}}$), 68.0 ($sp_3$, −O−$CH_2$−, $\mathrm{C_{aliph}}$), 64.7 ($sp_3$,−O−$CH_2$−, $\mathrm{C_{aliph}}$), 29.2 ($sp_3$, −$CH_2$−, $\mathrm{C_{aliph}}$, ×2), 29.1 ($sp_3$, −$CH_2$−, $\mathrm{C_{aliph}}$, ×2), 28.6 ($sp_3$, −$CH_2$−, $\mathrm{C_{aliph}}$), 25.9 ($sp_3$, −$CH_2$−, $\mathrm{C_{aliph}}$), 25.8 ($sp_3$, −$CH_2$−, $\mathrm{C_{aliph}}$), 25.7 ($sp_3$, −$CH_2$−, $\mathrm{C_{aliph}}$). MS (EI, 70 eV), $m/z$ (%): 392 (47) [$M^+$], 324 (34), 264 (36), 196 (63), 152 (7), 130 (12). 69 (82), 44 (15), 41 (27).

*Polymerization in Solution.* For a typical reaction, 0.658 g of MADMES (2.25 mmol, 1 equiv) or 0.710 g of MAES (2.69 mmol, 1 equiv) was dissolved in 7 mL of DMF. AIBN (2.4 mg, 8 $\mu$mol, 0.01 equiv) was added and the solutions were degassed by three freeze−pump−thaw cycles each, flushing with argon after each cycle. The reaction mixtures were stirred under heating at 70 °C for 72 h. After cooling, the reaction mixtures were added dropwise into ice cold methanol (1.25 L), upon which precipitation of the polymers as colorless threads occurred. After filtration, the polymers were redissolved in DMF and once again precipitated into ice cold methanol. After filtration, the colorless polymers were left to dry under vacuum for 48 h, yielding poly(4-methacryloyloxy-(*E*)-stilbene) (PMAES): GPC: $M_n$ 75 690 g mol$^{-1}$; $M_w$ 32 500 g mol$^{-1}$. TGA: $T_{5\%}$: 288.9 °C. DSC: $T_g$: 143.0 °C. IR: 3026, 2950, 1950, 1892, 1748, 1674, 1596, 1506, 1448, 1414, 1388, 1266, 1198, 1164, 1102, 1014, 960, 940, 884, 806, 750, 710, 690, 666, 534. A similar procedure yielded poly(4-methacryloyloxy-3,5-dimethoxy-(*E*)-stilbene) (PMADMES). GPC: $M_n$ 47 690 g mol$^{-1}$; $M_w$ 23 510 g mol$^{-1}$. TGA: $T_{5\%}$: 284.9 °C. DSC: $T_g$: 140 °C. IR: 3058, 3026, 2998, 2938, 2840, 1960, 1800, 1754, 1674, 1592, 1504, 1456, 1418, 1348, 1326, 1260, 1240, 1204, 1130, 1084, 1022, 988, 956, 864, 812, 750, 692, 666, 622, 570, 520. A similar procedure yielded poly(8-methacryloyl-octyl-4-oxy-(*E*)-stilbene) (PMAC8ES). GPC: $M_n$ 27 390 g mol$^{-1}$; $M_w$: 12 540 g mol$^{-1}$. TGA: $T_{5\%}$ = 283.5 °C. DSC: $T_g$ not detectable.

## ■ RESULTS AND DISCUSSION

**Synthesis of (*E*)-3,5-Dimethoxy-4-hydroxystilbene.** It is known that stilbene synthesis is not restricted to a single reaction type.[30] In this study, we have chosen the Wittig reaction to achieve the desired stilbene derivative. The aldehyde component has a phenolic hydroxyl group, which, if added to the ylide, would reprotonate the ylide and no reaction would take part. We choose to use two equivalents of base to prevent the protonation of the ylide instead of using a protection−deprotection procedure for the phenolic hydroxyl group which would increase the number of synthesis steps by two. The desired (*E*)-3,5-dimethoxy-4-

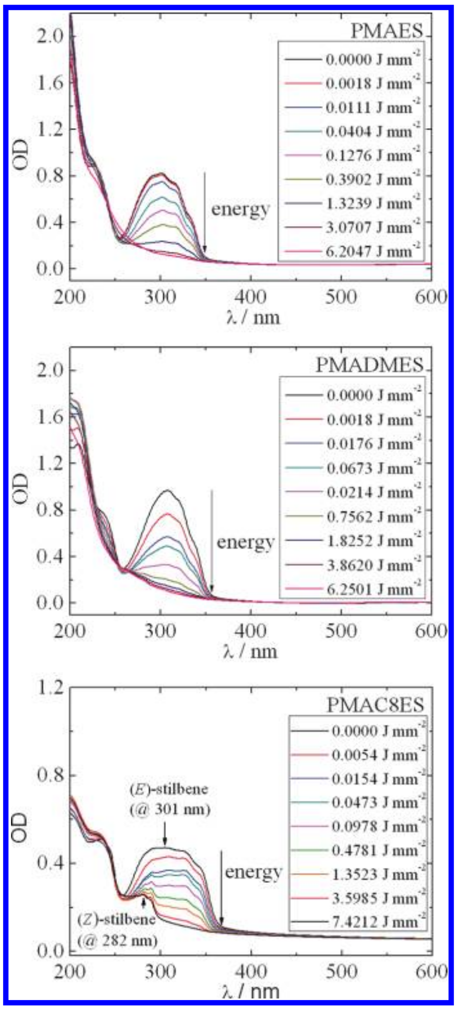


**Figure 1.** Photoinduced absorption changes of the polymers PMAES, PMADMES and PMAC8ES induced by excitation with 355 nm light. The $\pi \rightarrow \pi^*$ absorption at about 300 nm decreases as a result of photochemical $[2\pi + 2\pi]$ cycloaddition. Identical energy doses cause larger absorption changes in PMADMES than in PMAES. In PMAC8ES, both photodimerization as well as photoinduced *E*/*Z* isomerization takes place. This is indicated by the appearance of the new absorption at 282 nm.

hydroxystilbene was received in good yields (73%). The product was clearly defined by $^1$H and $^{13}$C NMR, MS, and HRMS.

**Synthesis of (*E*)-8-(4-styrylphenoxy)octan-1-ol.** A typical Williamson ether synthesis was performed to obtain the desired alkylated stilbene derivate. The yield of 81% is in the typical range of such reactions. The product (*E*)-8-(4-styrylphenoxy)octan-1-ol was clearly identified by $^1$H and $^{13}$C NMR and MS.

**Synthesis of Methacrylates Containing Stilbene Units.** The monomers were synthesized according to a standard esterification reaction starting from (*E*)-4-hydroxystilbene and (*E*)-3,5-dimethoxy-4-hydroxystilbene and (*E*)-8-(4-styrylphenoxy)octan-1-ol, respectively. Under alkaline conditions esterification with methacyrloyl chloride takes place and 4-methacryloyloxy-(*E*)-stilbene (MAES) was obtained with 81% yield, 4-methacryloyloxy-3,5-dimethoxy-(*E*)-stilbene (MADMES) with 78% yield, and (*E*)-8-(4-styrylphenoxy)octyl methacrylate (MAC8ES) with 80% yield, respectively. The products were clearly defined by $^1$H NMR, $^{13}$C NMR, MS, and HRMS.

The extinction coefficients of the monomers MAES and MADMES were determined from chloroform solutions (0.01–0.05 mmol L$^{-1}$) and for MAES an extinction coefficient of $\varepsilon_{301}$ = 24 454 L mol$^{-1}$ cm$^{-1}$ and for MADMES of $\varepsilon_{308}$ = 31 977 L mol$^{-1}$ cm$^{-1}$ was found. These finds correlate with the electron donating effect of the methoxy groups on the conjugated π-system.

**Synthesis of the Polymers.** Poly(4-methacryloyloxy-(*E*)-stilbene) (PMAES), poly(4-methacryloyloxy-3,5-dimethoxy-(*E*)-stilbene) (PMADMES), and poly(8-methacryloyl-octyl-4-oxy-(*E*)-stilbene) (PMAC8ES) were obtained by free radical polymerization of the monomers using AIBN as an initiator in DMF at 60 °C for 72 h. PMAES was obtained as a colorless powder with $M_n$ = 75 690 g mol$^{-1}$ in 90% yield, PMADMES as a colorless powder with $M_n$ = 47 690 g mol$^{-1}$ in 88% yield and PMAC8ES as a colorless powder with $M_n$ = 27 390 g mol$^{-1}$ in 90% yield.

**Photochemical Dimerization with UV Light.** The photochemical properties of the synthesized polymers under UV radiation were investigated. Stilbene and its derivatives are known to undergo several photochemical reactions when irradiated with ultraviolet light.[20] In a previous study it was shown that a copolymer containing MAES shows photoisomerization when irradiated with ultraviolet light.[2] In this study we report on an exclusive photodimerization when thin films of PMAES and PMADMES were irradiated with ultraviolet light from a frequency tripled Nd:YAG laser (355 nm). In contrast to PMAES and PMADMES the third polymer PMAC8ES shows both, photodimerization as well as photo induced *E*/*Z* isomerization (Figure 1, bottom).

Stilbene and its derivates show characteristic UV/vis absorption spectra (Figure 1). Absorption maxima around 300 nm correspond to the π–π* electronic transition of the *E*-stilbene moiety, while absorption maxima around 280 nm correspond to *Z*-stilbene.[5] Absorption maxima found for both PMAES and PMAC8ES were 301 and 308 nm for PMADMES. The slight bathochromic shift in absorption maximum arises from the electron donating methoxy groups which expand the conjugated π-system and therefore lower the energy needed for the π–π* transition. The absorption band seen at around 230 nm is due to a n-π* transition occurring in the PMA-backbone ester linkage. Obviously there is no absorption in the visible (400 nm and higher) as it is required for a polymer to be applied in optical devices.

The polymers were dissolved at a concentration of 1% (w/w) in chloroform solution and spin-coated onto quartz plates. When the stilbene unit in the polymer is photochemically excited and undergoes [2 + 2] cycloaddition the π–π* absorption band decreases with increasing energy and irradiation time, respectively. Figure 1 shows the decreasing absorbance of PMAES and of PMADMES as a function of total applied energy at 355 nm. In both cases an isosbestic point is observed indicating that only two states are involved. Like mentioned earlier PMAC8ES shows photodimerization as well as photo induced *E*/*Z* isomerization. This is due to the alkyl spacer, which increases the space between two stilbene molecules and in turn lowers the probability that two stilbene molecules react with each other. As the photochemistry of PMAC8ES is a mixture of isomerization and photodimerization, this material is not useful for optical applications. It serves as a reference to proof that PMAES and PMADMES show exclusive dimerization.

As the number of monomeric stilbene units decreases with increasing irradiation time the photochemical dimerization decelerates and finally stops (Figure 2). The decrease in absorbance

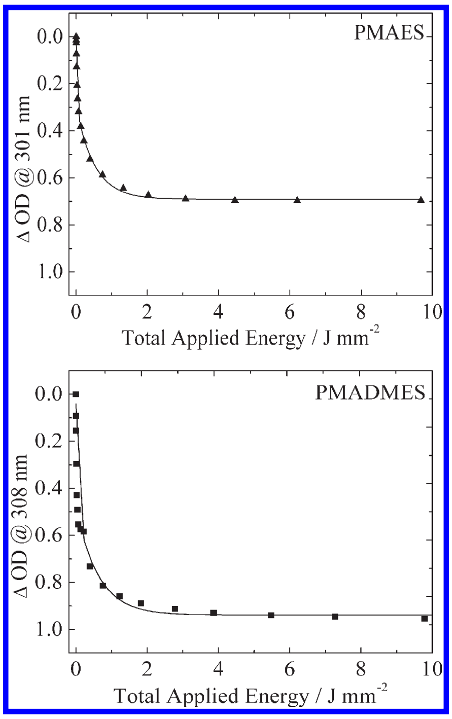


**Figure 2.** Optical density changes (ΔOD) in dependence on cumulative energy exposure for PMAES and PMADMES. The initially fast dimerzation reaction slows down as the number of reactive monomeric stilbene units decreases and reaches an equilibrium at about 2 J $\mathrm{mm}^{-2}$, but at significantly different levels.

of PMADMES progresses faster and with a greater change than the decrease observed with PMAES. This observation is due to the fact that the methoxy groups increase the conjugated system and therefore the probability that a light quantum is absorbed is increased.

Because of the about 30% higher extinction coefficient of the disubstituted MADMES over the "reference" MAES, PMADMES will have more excited molecules in the $S_1$ state compared to PMAES at comparable light intensities. This in turn enhances the dimerization rate and PMADMES appears to be more light sensitive than PMAES and at the same exposure a faster refractive index change occurs.

To ensure the decrease in absorbance is due to photodimerization and not due to photoisomerization, like it was reported in a previous study,[2] we analyzed the photoreaction in the polymer with several complementary methods. In the case that *E*/*Z*-isomerization would be contributing to the overall changes observed, phenanthrene formation should be detectable, caused by oxidation through air. Thin polymer films were irradiated with a 355 nm laser and the fluorescence was analyzed. Phenanthrene formation was neither monitored by UV/vis nor by the more sensitive fluorescence spectroscopy in PMAES and PMADES. In no case an increase of the phenanthrene typical absorption at 345 nm could be detected and the fluorescence spectra did not show any incidence for the typical emission spectrum of phenanthrene (Figure 3).

FT-IR measurements were used to trace the photochemistry of PMAES and PMADMES. Polymer films were cast on NaCl plates and dried in an oven at 60 °C for 48 h. The FT-IR spectra (Figure 4) show the typical absorptions for stilbenes and for the methacrylate backbone. With progressing irradiation time, the typical C—H deformation vibration at 950—970 $\mathrm{cm}^{-1}$ is decreasing and concomitantly no other absorption increase in the fingerprint region was observed. At 2931 $\mathrm{cm}^{-1}$ an absorbance peak is detected, which refers to tetracyclobutane.[31]

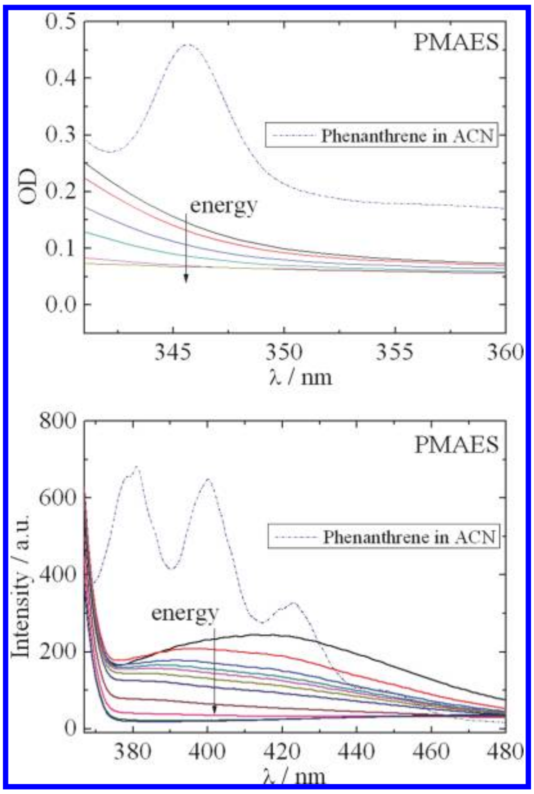


**Figure 3.** Absence of phenanthrene formation. (Top) UV/vis spectrum of a PMAES film in the vicinity of 345 nm, which is a characteristic peak for phenanthrene (see absorption spectrum, dashed line), as a function of energy dose. No increase in absorbance is detectable which rules out phenanthrene formation. (Bottom) Fluorescence spectra of a PMAES film prepared on a quartz window plate (excitation wavelength is 345 nm) after certain irradiation times at 355 nm. Typical fluorescence maxima for phenanthrene (see fluorescence spectrum, dashed line) were not observed.[2]

**Photo-Induced Refractive Index Changes.** One of the key parameters for photorefractive polymers are the refractive index changes obtained upon irradiation. Polymer films were prepared by spin coating solutions of the polymer in chloroform at a concentration of 6% (w/w) onto silicon wafers. The refractive index of PMAES was determined to be $n_{633}$ = 1.6533 and the thickness of a typical film to be 1.5231 μm. The corresponding values for PMADMES films were a refractive index of $n_{633}$ = 1.6288 and a typical film thickness of 1.5116 μm and for PMAC8ES films $n_{633}$ = 1.5930 and a typical film thickness of 2.2985 μm, respectively.

The huge and somewhat unexpected difference in initial refractive index between PMAES and PMADMES is astonishing as the disubstituted polymer should have, according to Maxwell's eq 1, a higher refractive index than the nonsubstituted. However, the refractive index is also linearly related to the density of a material according to the Lorentz—Lorenz equation. The density of both polymers was measured by a pycnometer and found to be 1.283 for PMAES and 1.253 for PMADMES respectively. On one hand the electron donating methoxy groups increase the relative permittivity $\varepsilon_r$ and therefore the refractive index $n$ is increased,

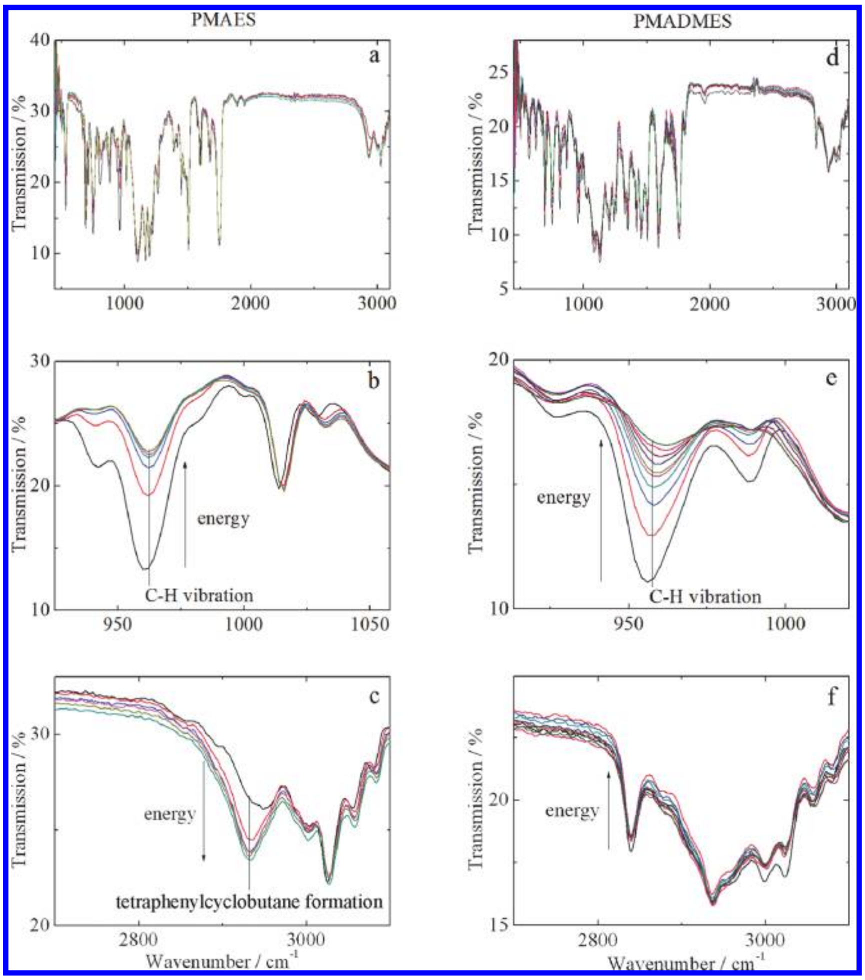


**Figure 4.** Molecular changes resulting from light exposure at 355 nm in PMAES and PMADMES. (a and d) FT-IR spectra of PMAES/PMADMES after various energy doses of irradiation. (b and e) C—H vibration regime enlarged. (c and f) cyclobutane regime enlarged. Decrease of C—H and appearance of cyclobutane vibration indicates the dimerzation process.

but on the other hand, the methoxy groups require space and therefore the number of molecules per unit volume is decreased resulting in a lower density which finally becomes the overwhelming effect that decreases the refractive index. The lower initial refractive index of PMAC8ES compared to PMAES and PMADMES is in accordance with the theory, because the number of stilbene molecules per unit volume is the lowest of the three synthesized polymers.

The refractive index was measured as an absolute value and after each irradiation dose the value of the polymer sample was analyzed on four randomly chosen positions. The refractive index change $\Delta n_{633}$ compared to the nonirradiated polymer is plotted in Figure 5 for PMAES, PMADMES, and PMAC8ES. The change in absorption (Figures 1 and 2) is directly related to the refractive index change. The gradient of the curve is remarkably steep in the beginning. In fact for all polymers, almost the full refractive index change $\Delta n$ is observed after only 0.4 J mm$^{-2}$ have been applied. The reaction is almost completed after application of 2.5 J mm$^{-2}$.

Whereas the maximal refractive index change obtainable is important from a fundamental point of view, in an application the full range probably never will be used. From a more practical point of view there is a figure-of-merit for the required refractive index change. In many cases a $\Delta n$ = 0.02 is such a value. The question is, how much energy is needed to obtain this value, the lower the better. A refractive index change of $\Delta n$ = 0.02 is obtained at an energy of 0.26 J mm$^{-2}$ for PMAES and 0.03 J mm$^{-2}$ for PMADMES. This clearly shows that the disubstituted polymer is significantly more photosensitive than the unsubstituted polymer as less than one-eighth of energy is required only. As shown in the UV/vis spectra PMAC8ES shows a different behavior than PMAES and PMADMES. At the very beginning of the irradiation the decrease in refractive index of PMAC8ES up to a refractive index change of $\Delta n$ = 0.02 is almost the same as for PMAES. After an energy dose of 0.25 J mm$^{-2}$ the change in refractive index becomes very small. This behavior is typical also for other refractive index change polymers which show photoisomerization.[1] This result indicates, that in PMAC8ES photodimerization takes place before photoisomerization happens. A more detailed description of the kinetics of PMAC8ES will be part of future work.

Thickness changes of the polymer films related to irradiation and the resulting dimerization reaction were not observed (Figure 6). This is important in all cases where the polymers are used for optical devices. In this case the refractive index is decoupled from any change in density potentially induced by the dimerization process.

Finally a clear material free of any opaqueness etc. is desired. We used WAXS (Figure 7) as well as DSC to prove that the

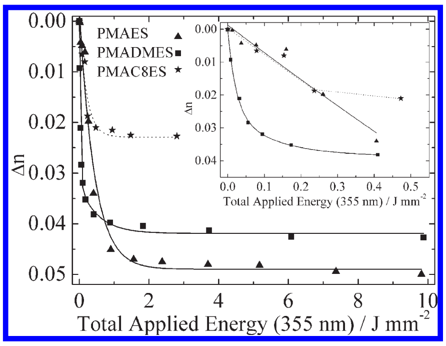


**Figure 5.** Change of refractive index Δ*n* in dependence on the cumulative energy applied at 355 nm for PMAES, PMADMES, and PMAC8ES films on silicon wafer. Analogue to the decrease in optical density the change of refractive index slows down and finally stops as the number of monomeric stilbene units decreases.

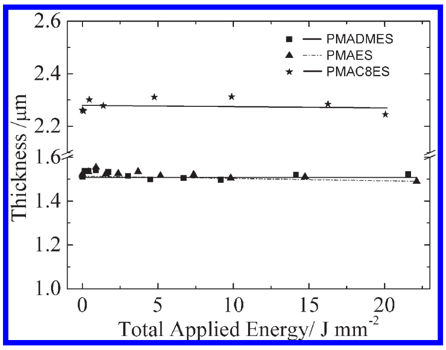


**Figure 6.** Thickness changes of PMAES, PMADMES and PMAC8ES polymer films upon irradiation with 355 nm light. The thicknesses of the samples were 1.5231 $\mu$m for PMAES, 1.5116 $\mu$m for PMADMES, and 2.2985 $\mu$m for PMAC8ES.

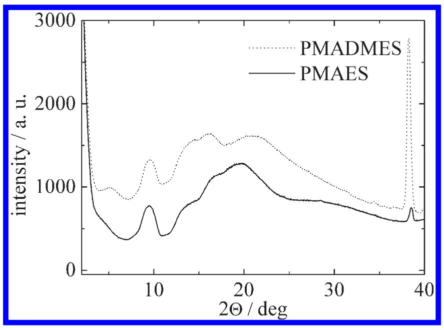


**Figure 7.** WAXS spectra of PMAES and PMADMES proving that both polymers do not show microcrystallinity.

polymers prepared are amorphous and do not show any phase transitions at ambient temperatures. No Bragg reflexes indicating crystalline domains were observed, but there are signs for near field effects arising from $\pi$-stacking of the stilbene units in the polymer. This probably supports the dimerization and is responsible for the suppression of *E*/*Z*-isomerization.

## ■ CONCLUSION

We reported on refractive index change materials consisting of a PMA backbone and (*E*)-stilbene or (*E*)-3,5-dimethoxystilbene units covalently attached in the side chain of the polymer. In polymer films of PMAES and PMADMES no side reactions like *E*/*Z* isomerization or phenanthrene formation are observed during photoinduced dimerization with 355 nm light from a pulsed laser source. This finding is analytical supported by UV/vis, fluorescence, and FT-IR spectroscopy. The polymer PMAC8ES, which was synthetized as a reference, shows photodimerization as well as photoisomerization, which was shown by UV/vis and refractive index measurements. The two polymers PMAES and PMADMES with a well-defined photochemistry are noncrystalline, are highly transparent in the visible wavelength regime, show a high initial refractive index ($n$ > 1.6) and high photoinduced refractive index changes of up to $\Delta n$ = 0.05. The combination of these attractive properties make these photorefractive polymers potentially interesting for optical devices and applications in optical data storage. Future work will deal with 2-photon cleavage of the tetraphenylcyclobutane to show the reversibility of the photorefractive polymers PMAES and PMADMES.

## ■ AUTHOR INFORMATION

### Corresponding Author

*E-mail: hampp@staff.uni-marburg.de.

## ■ ACKNOWLEDGMENT

This work was financially supported by the Federal Ministry of Education and Research (BMBF) under Grant FKZ 13N8978.

## ■ REFERENCES

(1) Kudo, H.; Yamamoto, M.; Nishikubo, T. *Macromolecules* **2006**, *39*, 1759.

(2) Tsai, F.-J.; Torkelson, J. M.; Lewis, F. D.; Holman, B. *Macromolecules* **1990**, *23*, 1487.

(3) Träger, J.; Heinzer, J.; Kim, H.-C.; Hampp, N. *Macromol. Biosci.* **2008**, *8*, 177.

(4) Osado, Y.; Katsumura, E.; Inoue, K. *Makromol. Chem. Rapid Commun.* **1981**, *2*, 411.

(5) Meier, H. *Angew. Chem.* **1992**, *104*, 1425.

(6) Stuber, F. A.; Ulrich, H.; Rao, D. V.; Sayigh, A. A. R. *J. Appl. Polym. Sci.* **1969**, *13*, 2247.

(7) Höfler, T.; Grießer, T.; Gstrein, X.; Trimmel, G.; Jakopic, G.; Kern, W. *Polymer* **2007**, *48*, 1930.

(8) Zhang, Y.; Burzynski, R.; Ghosal, S.; Casstevens, M. K. *Adv. Mater.* **1995**, *8*, 111.

(9) Horie, K.; Murase, S.; Takahashi, S.; Teramoto, M.; Furukawa, K. *Macromol. Symp.* **2003**, *195*, 201.

(10) Zhao, C.; Park, C.-K.; Prasad, P. N. *Chem. Mater.* **1995**, *7*, 1237.

(11) Kim, H.-C.; Kreiling, S.; Greiner, A.; Hampp, N. *Chem. Phys. Lett.* **2003**, *372*, 899.

(12) Bernstein, H. I.; Quimby, W. C. *J. Am. Chem. Soc.* **1943**, *65*, 1845.

(13) Ulrich, H.; Rao, D. V.; Stuber, F. A.; Sayigh, A. A. R. *J. Org. Chem.* **1970**, *35*, 1121.

(14) Stobbe, H.; Hensel, A. *Chem. Ber.* **1926**, *59*, 2254.

(15) Sharma, L.; Matsuoka, T.; Kimura, T.; Matsuda, H. *Polym. Adv. Technol.* **2002**, *13*, 481.

(16) Ciamician, G.; Silber, P. *Chem. Ber.* **1902**, *35*, 4128.

(17) Fulton, J. D.; Dunitz, J. D. *Nature* **1947**, *160*, 161.

(18) Störmer, R. *Ber. Dtsch. Chem. Ges.* **1909**, *42*, 4865.

(19) Smakula, A. *Z. Phys. Chem. Abt. B* **1934**, *25*, 90.

(20) Lewis, F. D.; Wu, T.; Burch, E. L.; Bassani, D. M.; Yang, J.-S.; Schneider, S.; Jäger, R. L. *J. Am. Chem. Soc.* **1995**, *117*, 8785.

(21) Maeda, H.; Nishimura, K.; Mizuno, K.; Yamaji, M.; Oshima, J.; Tobita, S. *J. Org. Chem.* **2005**, *70*, 9693.

(22) Irie, M.; Hirano, Y.; Hashimoto, S.; Hayashi, K. *Macromolecules* **1981**, *14*, 262.

(23) Fissi, A.; Pieroni, O. *Macromolecules* **1989**, *22*, 1115.
(24) Blair, H. S.; Law, T. K. *Polymer* **1980**, *21*, 1475.
(25) Stille, J. K.; Zimmermann., E. K. *Macromolecules* **1985**, *18*, 321.
(26) Frings, R. B.; Schnabel, W. *J. Photochem.* **1983**, *23*, 265.
(27) Buckup, T.; Dorn, J.; Hauer, J.; Härtner, S.; Hampp, N.; Motzkus, M. *Chem. Phys. Lett.* **2007**, *439*, 308.
(28) Härtner, S.; Kim, H.-C.; Hampp, N. *J. Polym. Sci. A: Polym. Chem.* **2007**, *45*, 2443.
(29) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 4th ed.; Butterworth-Heinemann: Oxford, U.K., 2000.
(30) Hilt, G. *J. Org. Chem.* **2007**, *72*, 7337.
(31) Lüttke, W. *Eur. J. Org. Chem.* **1963**, *668*, 184.