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Optical switching behavior of azobenzene/PMMA blends with high chromophore concentration

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Abstract In this article, the authors will present a simple way to produce thin solid organic films, with a content of more than 60 wt% photoactive molecules dispersed in a polymeric matrix showing an almost complete and fully reversible photoisomerization. These high filling factors could be achieved by using branched side chains in the molecules, which prevent crystallization. The chromophores were codissolved with the polymer Polymethylmethacrylate (PMMA) of different M_w in toluene in various concentrations and spin casted onto the substrate. The effect of the M_w of PMMA on the switching kinetics and the agglomeration tendency of different molecule configurations were investigated.

Introduction

During the last years, many studies have been devoted to polymers containing photoswitchable chromophores [1–4]. Apart from fundamental interest, they are very interesting for various potential applications ranging from ophthalmic lenses [5] and optical data storage [6] to biomedical devices [7]. Among the available chromophores, azobenzene derivates are of particular interest because of the marked change in physical properties observed upon switching [8]. For example, in the ground state, the *trans* isomer of the azobenzene ether moiety (see Fig. 1) has a nearly flat geometry with a dipole moment of 0.5 D, whereas the *cis* isomer is roughly spherical with a dipole moment of 3 D. The research of azobenzene/polymer systems has also been driven by their high potential for applications in non-linear optics [8]. The chromophores can be incorporated into the polymer by covalent bonds [9], or they can be dissolved in the polymer matrix [10]. Covalent bonding either in the main backbone or in the side chain has many advantages and has been used extensively [11, 12]. The advantages are that the chromophore concentration is well defined that, the coupling of the chromophores to the polymer chains is very high and that aggregation of the chromophores is severely hindered. Furthermore, covalently bonded azobenzene units in the side chain give rise to higher stability in applications based on orientational alignment of the azobenzene units in holographic and/or surface relief gratings. Mainly push–pull azobenzenes have been used [13] but a similar stabilization effect has been observed recently for a grafted azobenzene of the non push–pull azobenzene type [14].

However, there are also disadvantages. The use of covalently attached chromophores requires a special and sometimes complicated synthesis for each chromophore/polymer combination.

Guest–host systems prepared by dissolution of the chromophores in the polymers on the other hand are attractive because of the easiness of their preparation and processing into thin films. Both, chromophore and polymer and their combination can be easily varied. The

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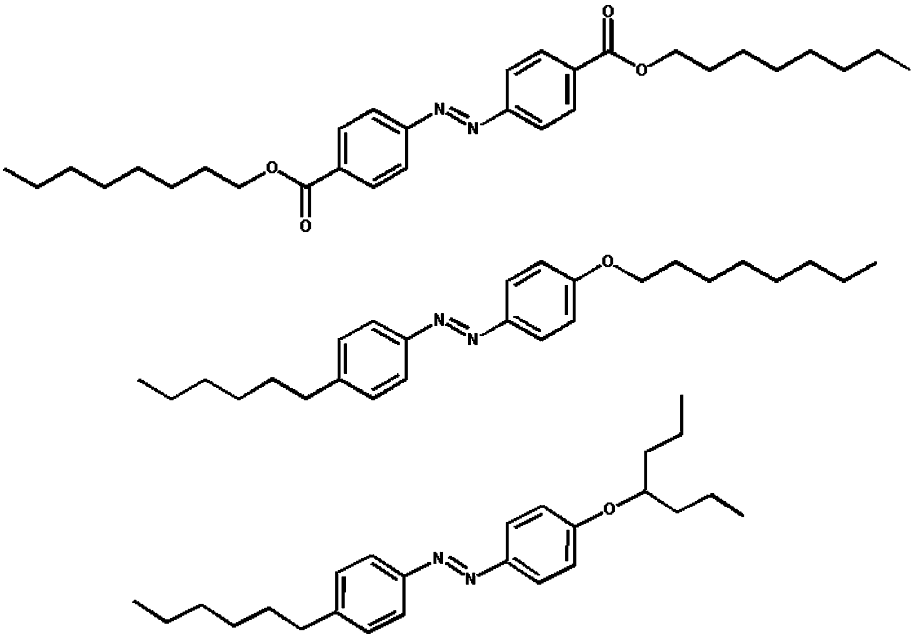

Fig. 1 Chemical structures of the used azobenzene molecules in their *trans* conformation. From top to bottom: 4,4′-Azobenzoldicarbonsäuredioctylester, 4′-Hexyl-4-octoxyazobenzol (ether-1), and (4′-Hexyl-phenyl)-[4(propyl-butoxy)-phenyl]-diazene (ether-2)

concentration of the chromophores can be tuned over a broad range. Therefore, such systems have also been heavily used in the past [15–21]. The most severe problem of guest–host systems is the aggregation tendency of the molecules [20], but there are also strategies to overcome this problem, e.g., Priimagi et al. [22] used hydrogen bonding of the chromophores to the polymer to achieve high chromophore concentrations. Meerholz et al. [19] have shown that a eutectic mixture of isomeric chromophores can also effectively suppress crystallization. A very common approach is to modify the chromophores to enhance their solubility in the polymer [20, 21].

Most of the study done has focused on chromophores for non-linear optics or on azobenzene chromophores of the pseudo-stilbene type as classified by Rau [23]. There the bistable switching behavior of the chromophores in the polymeric matrix was not addressed. Here, the authors follow the common approach to enhance the solubility of the chromophore in the polymeric matrix, but with a focus on optimizing the bistable switching ability of the obtained material. The incorporation into the glassy polymer matrix causes a pronounced matrix effect, i.e., a strong slowing down of the isomerization dynamics compared to switching in solution [24].

It was shown that tails and branches can be used to enhance the solubility and to stabilize the molecules completely against crystallization. At the same time, it was demonstrated that the authors can obtain a large switching ratio at fairly short times for forward and backward switching upon illumination with light. The investigation of these azobenzene/polymer blend systems is partly motivated by the flexibility in the choice of chromophore and polymer matrix and to produce similar thin films by vapor phase deposition [25], or to combine these molecules into a variety of metal/polymer nanocomposites [26].

Experimental section

The authors have tested three different chromophores, an azobenzeneester (ester) as well as two different azobenzeneether (ether-1 and ether-2) molecules. The chemical structures are shown in Fig. 1. The ester-1 and the ether-1 molecules were self synthesized according to reference [27]. The ether-2 molecules were prepared via the following synthesis route: 2.4 g (8.5 mmol) 4-(4′-Hexylphenyl)diazophenol, 340 mg (8.5 mmol) Sodium hydroxide, 100 mL ethanol, and 4.7 mL (30 mmol) 4-Bromoheptane were refluxed over night or about 6 h. The solvent was evaporated in vacuum and the residue was solved in 80 mL ethyl acetate and 80 mL deionized water. After phase separation, the aqueous layer was extracted two times with 80 mL ethyl acetate. The combined organic phase were washed with 60 mL brine and 60 mL water, and then dried over magnesium sulfate. After evaporation of the solvent, the red–orange liquid was cleaned by column chromatography on silica gel with chloroform ($R_f = 0.88$).

The molecules are dissolved together with Polymethylmethacrylate (PMMA) powder in toluene, and mixtures with nominal contents from 10 to 60 wt% chromophores in the solid film were prepared. The authors used three different kinds of PMMA, a commercial one with a broad distribution in the chain lengths with an average molecular weight of 35 kg/mol from Scientific Polymer Products (PMMA-1) and two with uniform chain length molecular weights of 9.85 kg/mol (PMMA-2) and 161.5 kg/mol (PMMA-3), respectively from Polymer Source Inc. The ratio M_w/M_n of PMMA-2 and PMMA-3 was 1.09 and 1.06, respectively. For this study, the thickness of the films was in the range from 10 to 580 nm. This was achieved by a variation of the viscosity of the solution used for the spin-coating [28] simply by changing the amount of toluene solvent. The switching kinetic is influenced by the thickness of the films, i.e., thicker films show longer switching times. Similar samples were always prepared under similar conditions, thus only the change of the switching time is relevant in the present context, but not the absolute value of the switching time. Pure quartz was used as a substrate in order to minimize the UV absorption of the substrate. The thickness of the corresponding films has been determined by using a standard profilometer (DEKTAK 8000).

The films were analyzed with a UV–Vis spectrometer (Perkin Elmer Lamda 900) in the initial state and after each irradiation step with UV or visible light. The spectra background was corrected by subtraction of the spectrum of the quartz substrate.

The samples were irradiated with UV-light either by illuminating the samples with a UV-lamp (Lambino 135 Spot Light) which has an intensity maximum at a wavelength of 365 nm with an energy of 63 mW/cm^2 or with a monochromized light source with a band width of 20 nm and an energy of 4.72 mW/cm^2 around a wavelength of 360 nm. For the back-switching, an intense visible light source of either a normal bulb which provided white light with an energy of 45 mW/cm^2 or a monochromized light source with an energy of 10.8 mW/cm^2 at a wavelength of 460 nm was used.

In order to check the miscibility of the molecules with the polymer matrix, an optical microscope (Polylite SC from Reichert-Jung) was used. It allows the detection of crystallites in the samples if they are formed, thus providing an upper limit of the chromophore concentration that can be dispersed in a certain polymer. All measurements were performed at room temperature.

Results and discussion

The switching behavior of all chromophores was tested in toluene solution before combining them with the polymer in a solid thin film. These measurements always showed complete reversible optical switching. In the solid, the azobenzene ester (see Fig. 1) showed for a sample containing 10 wt% of the molecule in PMMA-1, a small decrease of the *trans* band at 35 nm upon illumination with UV-light. Only a small fraction of chromophore molecules is transferred to the *cis* state in the solid phase, because of the strong aggregation and crystallization tendency of this molecule.

In order to enhance the switchable fraction of molecules inside the polymer matrix, the molecular structure was modified and an asymmetric substitution was chosen. Absorption spectra of 10 wt% ether-1 azobenzene molecule in PMMA-1 are shown in Fig. 2. Each series contains the spectrum of the as prepared film, i.e., the spectrum obtained after illumination with UV-light and the spectrum obtained after illumination with white light. The *trans* $\pi \rightarrow \pi^*$ band is reduced very much in intensity after UV illumination. It is noted that a large fraction of the remaining absorption intensity in the wavelength range of the *trans* absorption band originates from the $\pi \rightarrow \pi^*$ transition band of the *cis* state of the molecule with its absorption maximum located at 300 nm. A second proof for the conformational change of the molecules to the *cis* state is the appearance of a second band at around 450 nm. This band corresponds also to the $n \rightarrow \pi^*$ transition of the *cis*-conformation of the molecule. The backswitching process after white light illumination, indicated by the blue line, shows that complete reversibility to the *trans* state is achieved.

The authors also investigated the dependence of the switching behavior on the chromophore concentration. Absorption spectra from 10 to 70 wt% of the ether-1 molecules in PMMA and from 20 to 60 wt% of the ether-2 molecules are summarized in Fig. 3a, b. The authors observed an almost linear increase of the absorption intensity in case of ether-2 molecules with increasing amount of molecules, but this is observed only up to 25 wt% for the ether-1 molecules. Beyond this amount, the

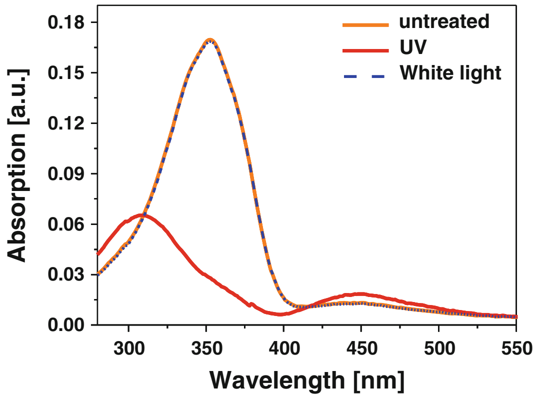

Fig. 2 Switching behavior of 10 wt% ether-1 molecules in PMMA matrix. The absorption spectra for the films after preparation, after UV and white light illumination are shown

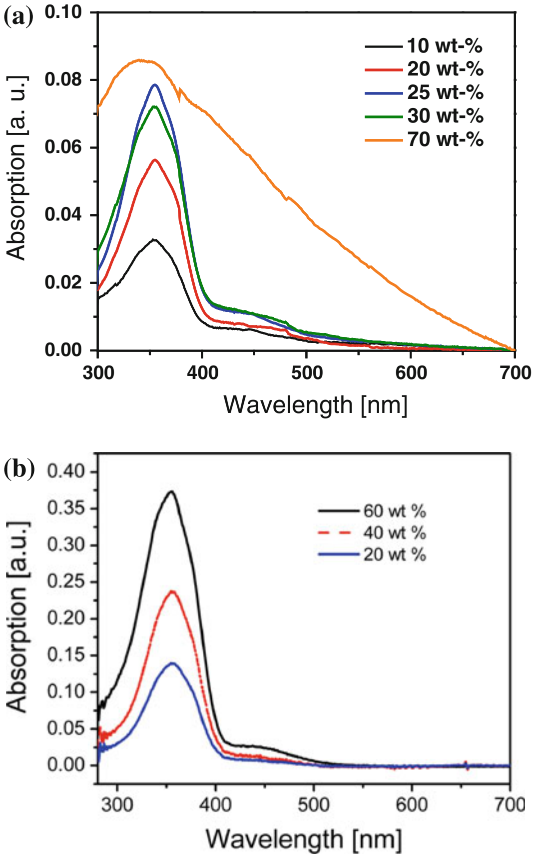

Fig. 3 **a** Absorption spectra of PMMA (35 kg/mol) films containing different amounts of ether-1 molecules from 10 to 70 wt%. Above 25 wt%, the expected trend of increasing intensity changes. **b** shows absorption spectra for PMMA (161.5 kg/mol) films containing 20 and 60 wt% ether-2 molecules and a PMMA (9.85 kg/mol) film containing 40 wt% ether-2 molecules. The absorption intensity increases nearly linear with the dye content

absorption intensity decreases without changing the peak form and with further increase of ether-1 azobenzene molecule, the peak broadens drastically. The optical microscopy pictures displayed in Fig. 4 show that at 25 wt% of ether-1 azobenzene molecules in PMMA-1, the molecules start to form optically visible crystallites. The degree of crystallization increases with increasing amount of molecules, which leads to the observed changes in the absorption behavior. AFM measurements showed for a sample with 70 wt% chromophores, the crystals have a height of around 300 nm, which is much larger than the total film thickness of around 50 nm. This means that the crystals grow even outside of the matrix. Additionally performed optical switching experiments confirmed that the *trans* to *cis* isomerization transition decreases significantly after crystallization sets in (see supplemental material).

It is well known that bulky side groups prevent the crystallization because of the steric hindrance. Therefore, the authors modified the chromophores accordingly and prepared the ether-2 molecules (see Fig. 1). The ether-2 molecules do not crystallize at room temperature, but form a liquid. Therefore, crystallization in the matrix does not occur even at large fractions of these azobenzene molecules in the PMMA matrix. Optical microscopy measurements showed that even with high fillings of 60 wt% ether-2, the films still appeared optically clear with no visible phase separation.

The optical switching experiments displayed in Fig. 5, show that even at 60 wt% a full and almost complete reversible switching occurs even in the high M_w-PMMA (PMMA-3). Thus, this molecule is well suitable to obtain large fractions of switchable molecules in a solid matrix.

For these molecules, the authors also studied the switching kinetics for both switching directions. The results are displayed in Fig. 6a, b which show the drop and the recovering of the *trans* absorption peak at 350 nm for the corresponding changes under illumination with UV-light (360 nm) and light with a wavelength of 460 nm, respectively for a composite of 40 wt% ether-2 in PMMA-2 and PMMA-3, respectively. The measurements were performed by illuminating the samples with a monochromatized light source. The wavelengths were selected based on an analysis of the switching behavior at different wavelengths. At 360 nm, the maximum concentration of *cis*-molecules is formed in the photoisomerization equilibrium. For both conformational changes, the switching processes follow an exponential behavior. The solid lines in the plots are the exponential fits. In General, an exponential behavior is observed, if the switching is not hindered [29]. In solution, this is always the case, but in many cases in polymeric matrices, a significant deviation from the exponential behavior has been observed because of the matrix effect [29]. Analysis of the data shows a true exponential behavior indicating only slightly disturbed switching behavior of the ether-2 molecules in the PMMA matrices. Quantitative analysis allows obtaining the characteristic switching times from the exponential fits. It is noted that the optical switching times are linearly dependent on the light intensities [29]. In our set-up, the light intensity in the visible region is higher than in the UV region and this partially explains the faster switching observed in the *cis* → *trans* direction.

Switching times have been determined as 6.2 ± 0.2 s for the *trans* → *cis* transition and 4.4 ± 0.3 s for the *cis* → *trans* transition in the PMMA-2 matrix. The values are about 15–30% higher in the higher M_w PMMA-3 matrix. This increase in the switching time must be related to the difference in molecular weight, which is 9.85 kg/mol for PMMA-2 and 161.5 kg/mol for PMMA-3. Higher molecular weight leads to a lower chain mobility (higher glass transition temperature) and therefore, on an average

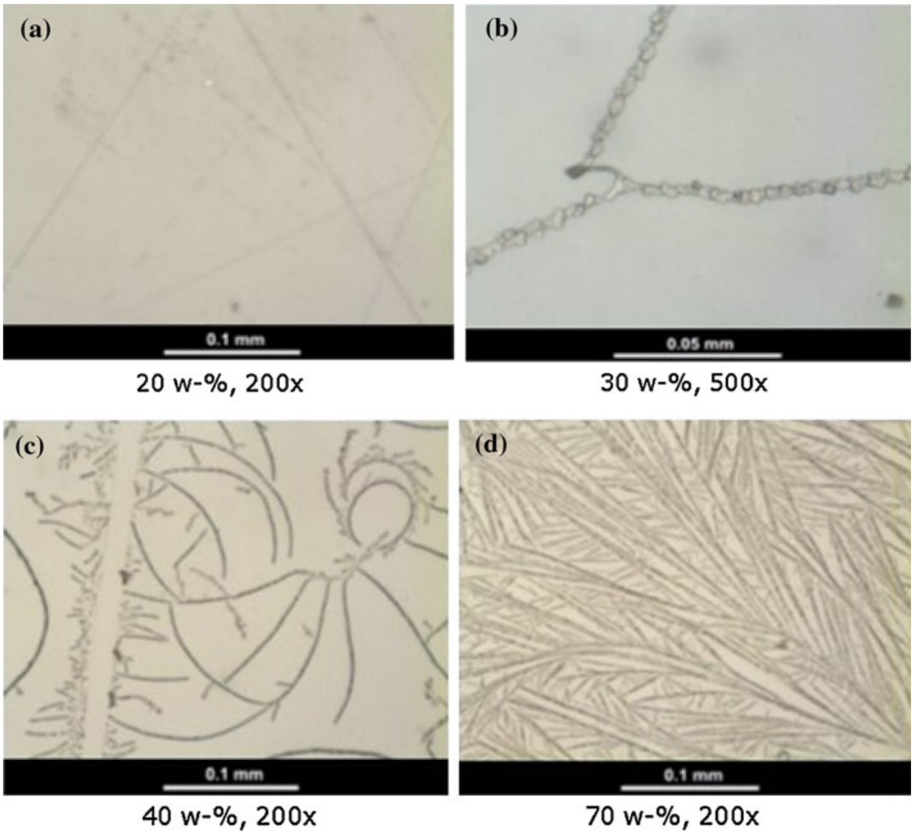

Fig. 4 Optical microscope pictures of different samples with changing amount of ether-1 in PMMA (35 kg/mol). Starting from 30 wt% crystallization sets in, which is increasing with increasing amount of the azobenzene ether molecule

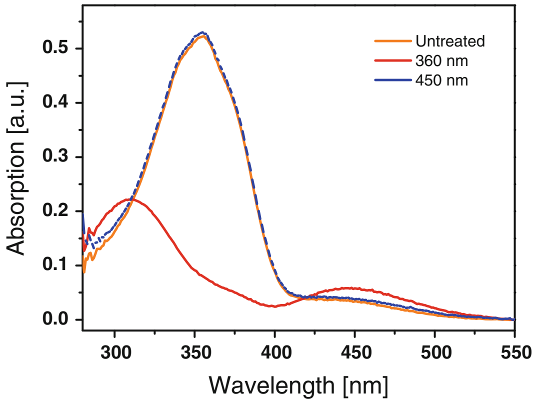

Fig. 5 Switching behavior of a PMMA-3 film (161.5 kg/mol) containing 60 wt% ether-2. One can clearly see that the isomerization process is fully reversible. This can be attributed to the plasticization of the polymer matrix by incorporation of the azobenzene molecules

to a higher mechanical resistance of the matrix against the conformational changes of the dispersed molecules. It should be noted that the dispersed ether-2 molecules have a strong plasticizing effect on the PMMA matrix, lowering the glass transition temperature. The glass transition temperature of the PMMA blend with 40 wt% azobenzene ether moieties was determined by independent DSC measurements with a heating rate of 10 K/min. The resulting T_g onset of 39 °C is much below the T_g of 105 °C measured by DSC for the pure PMMA polymer.

Accordingly, softening of the polymer matrix further should also lead to faster switching times. To test this hypothesis, the authors investigated the change in the isomerization kinetics by exposure of the polymer matrix to organic solvent vapors. The solvent induced swelling leads to a further plasticization of the PMMA and thus, to a softer matrix. In these experiments, the switching times were indeed reduced in both switching directions. Besides the optically induced switching also thermal back switching of the molecules has become much faster, so that even at room temperature a large fraction of molecules is transferred back to the *trans* state within a few seconds after UV-illumination. This effect could be important for application for the adjustment of switching speeds.

Finally, the thermal backswitching of the azobenzene molecules in the polymer matrix was studied. The thermal backswitching limits the time that the composite can be used as a bistable optical switch. The rate is very temperature dependent. Our measurements showed that for a film of a PMMA-2 matrix containing 40 wt% ether-2 molecules the complete recovery of the pristine state is reached at room temperature (about 25 °C) in the dark roughly after 2 h with a half-life time of roughly 30 min. These times are still large compared to optical switching times achieved

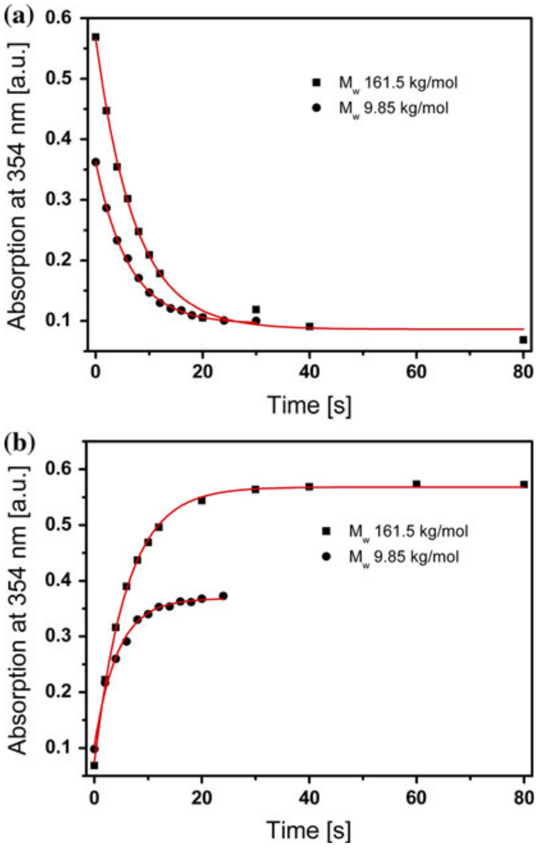

Fig. 6 Time dependence of the conformational changes of 40 wt% ether-2 molecules in different molecular weight PMMAs. **a** shows the *trans* to *cis* transition in PMMA-2 and 3. **b** the corresponding measurements for the *cis* to *trans* transition. The *solid lines* represent an exponential fit through the data points. The time constants for the transition in PMMA-2 are 6.2 ± 0.2 and 4.4 ± 0.3 s for **a** and **b**, respectively. The time constants in PMMA-3 are 15–30% higher

under white light illumination. It can be neglected in applications with a sufficiently high frequency of switching events, but on the other hand it excludes application where the composite needs to be stored in the *cis* state for a prolonged time, i.e., in the range of hours or even longer. However, strategies have been reported in the literature to stabilize azobenzene molecules in the *cis* state for much longer times, but usually this has a detrimental effect on the switching rate that can be achieved.

Conclusion

The authors have shown a simple and fast method to create optically switchable thin organic films with a high content of more than 60 wt% of dissolved azobenzene derivatives in a polymer matrix. It was shown that crystallization of the azobenzene molecules already affects the absorption of UV-light and has to be prevented to obtain well switchable systems. The high filling factors could be achieved by using branched side chains in the molecules, which prevent crystallization. In addition, the authors have shown that the polymer matrix also has a big influence on the switching times for the change from the *cis* to the *trans* state due to the average mobility of the polymer chains in the blend.

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