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Effects of Spacers on Photoinduced Reversible Solid-to-Liquid Transitions of Azobenzene-Containing Polymers

Philipp Weis,[b] Andreas Hess,[b] Gunnar Kircher,[b] Shilin Huang,[b] Günter K. Auernhammer,[b] Kaloian Koynov,[b] Hans-Jürgen Butt,[b] Si Wu*[a,b]

Abstract: Photoisomerization in some azobenzene-containing polymers (azopolymers) results in reversible solid-to-liquid transitions because *trans* and *cis* azopolymers have different glass transition temperature (T_g) values. This property enables photoinduced healing and processing of azopolymers with high spatiotemporal resolution. However, a general lack in knowledge about the influence of the polymer structure on photoinduced reversible solid-to-liquid transitions hinders the design of such novel polymers. Here, we demonstrate the synthesis and photoresponsive behaviors of new azopolymers with different lengths of spacers between the polymer backbone and the azobenzene group on the side chain. The azopolymers with no and 20 methylene spacer (P-0-Azo and P-20-Azo) did not show photoinduced solid-to-liquid transition. Azopolymers with 6 or 12 methylene spacer (P-6-Azo and P-12-Azo) showed photoinduced solid-to-liquid transition. This study demonstrated that spacer is essential for azopolymers for photoinduced reversible solid-to-liquid transitions and thus gives insight into how to design azopolymers for photoinduced healing and processing.

Introduction

Glass transition temperature (T_g) or melting temperature (T_m) of a chemical compound is highly dependent on its chemical structure.[1] To change a material from a solid to a liquid, the material is typically heated by rising the temperature. In some cases, it is advantageous to transfer a material from a solid to a liquid and vice versa isothermally using another external stimulus but not heat. The chemical structure of stimuli-responsive polymers can be changed using an external stimulus that can be exploited to change the materials properties like phase transition temperatures. External stimuli such as light have been used to switch polymer structures.[2] Light is a non-contact stimulus. It is clean and can be switched on and off fast. Photoswitchable polymers typically exhibit two states with different absorption spectra.[3] In this way, they can be transformed into each other by utilizing light with different wavelengths. Compared to heat induced solid-to-liquid transitions, photoinduced solid-to-liquid transitions have higher spatiotemporal resolution.

One of the most studied photoswitchable molecules is azobenzene.[4] Azobenzene has a thermodynamically stable *trans*-isomer with a rod-like shape. The metastable *cis*-isomer has a bent shape. *Trans*-to-*cis* isomerization is induced by UV irradiation. The *cis*-to-*trans* back isomerization can be induced by either visible light irradiation or heating. Azobenzene-containing small molecules show reversible photoinduced solid-to-liquid transition based on an isothermal crystal-to-melt transition.[5] However, most azobenzene-containing small molecules tend to crystallize, which restricts photoisomerization. In contrast, many azobenzene-containing polymers (azopolymers) show photoisomerization in solid state because coil structure of polymers give more free volumes for photoisomerization.[6] Photoirradiation of azopolymers has been exploited to fabricate healable coatings,[1a] photoswitchable adhesives,[7] photoactuators,[8] patterned surfaces,[9] deformable colloids[10] and solar thermal fuels.[11] Photoisomerization of some azopolymers leads to an isothermal solid-to-liquid transition of some azopolymers.[1a, 7, 12] Here, instead of heating the polymers above their T_g values, light was used to switch T_g of the polymers.[1a, 13] If T_g is lowered below the surrounding temperature, the material is liquefied. The adhesion of ABA-type triblock copolymers with azopolymer termini[12c] and azopolymers with different alkyl substitutions has been investigated.[7] It was found that the length of the alkyl chain has only minor influence on the adhesion strength. However, the solid-to-liquid transition based on photoswitchable T_g and other properties have not been investigated.

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[a] Prof. S. Wu
CAS Key Laboratory of Soft Matter Chemistry, Hefei National Laboratory for Physical Sciences at the Microscale, Department of Polymer Science and Engineering, University of Science and Technology of China, Jinzhai Road 96, Hefei 230026, China
E-mail: siwu@ustc.edu.cn
[b] Dr. P. Weis , A. Hess, G. Kircher, Dr. S. Huang, Dr. G. K. Auernhammer, Dr. K. Koynov, Prof. H.-J. Butt, Prof. S. Wu
Max Planck Institute for Polymer Research
Ackermannweg 10, 55128 Mainz, Germany
E-mail: wusi@mpip-mainz.mpg.de
Present Addresses: A.Hess: University of Potsdam, Institute of Chemistry, Karl-Liebknecht-Straße 24-25, 14476 Potsdam, Germany
Dr. S. Huang.: School of Materials Science and Engineering, Sun Yat-sen University, No. 135, Xingang Xi Road, Guangzhou, 510275, P. R. China
Dr. G.K.Auernhammer.: Leibniz-Institut für Polymerforschung, Hohe Str. 6, 01069 Dresden, Germany

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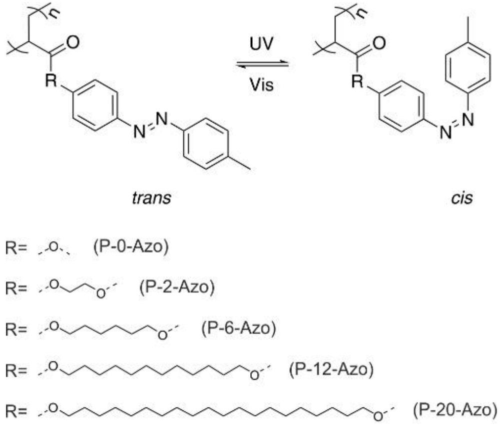
While our previous work has focused on demonstrating the proof-of-concept of photoswitchable T_g of azopolymers,[1a] here we focus on understanding the influence of the spacer between azopolymer backbone and azobenzene groups on the side chain. This variation of the spacer length is an important step towards a deeper understanding of photoinduced reversible solid-to-liquid transitions and the possibility for future applications such as healing and reprocessing hard polymers with light.



Scheme 1. Photoisomerization and chemical structures of P-n-Azo azopolymers with different spacer lengths ranging from 0 to 20.

Table 1. Some properties of P-n-Azo.

	Spacer Length (number of methylene units)	Mn / 10^3 g mol^{-1} (GPC)	PDI (GPC)	DP[a]	Photoinduced Solid-to-Liquid Transition
P-0-Azo	0	7.6	1.63	29	No
P-2-Azo	2	8.9	1.60	30	No
P-6-Azo	6	9.9	1.32	28	Yes
P-12-Azo	12	8.6	1.38	20	Yes
P-20-Azo	20	10.6	1.38	20	No

[a] Degree of polymerization calculated from GPC results.

Results and Discussion

Synthesis of P-n-Azo

First, the new azopolymers P-n-Azo were synthesized and characterized using NMR and GPC (Scheme S1 and Figures S1-S20). The synthesis of the azopolymers was according to our previous work with some modifications.[1a] In particular, we synthesized azopolymers with long and no spacers, which were not investigated in the previous work. After synthesizing the azobenzene molecule, methylene spacers of different sizes were attached to the azobenzene molecule, followed by an acrylate unit. The monomers were then polymerized by radical polymerization to get P-n-Azo. P-n-Azo are polyacrylates with different spacer lengths between the polymer backbone and the azobenzene unit (no spacer, 2, 6, 12 or 20 methylene units, Scheme 1). Number averaged molecular weights of P-n-Azo were 7.6, 8.9, 9.9, 8.6 and 10.6 × 10^3 g mol^{-1}, respectively (Table 1).

Photoinduced solid-to-liquid transition

All P-n-Azo in this study showed reversible *trans*-to-*cis* photoisomerization in solid state, which was demonstrated by UV-vis absorption spectroscopy of P-n-Azo films before and after light irradiation (Figure 1, left). Before irradiation all P-n-Azo exhibit a strong π-π* absorption band in the UV range and a weak n-π* band in the visible light range. UV light irradiation of P-n-Azo films decreased the π-π* band and increased the n-π* band, demonstrating *trans*-to-*cis* isomerization of P-n-Azo which is well known for azo chromophores. The *cis*-to-*trans* back isomerization was induced by visible light irradiation of the *cis* n-π* absorption band, enabling reversible photoisomerization. This reversible *trans*-to-*cis* isomerization was induced by light irradiation in several cycles (Figure 1, center). The absorbance of P-6-Azo and P-12-Azo films was lower before irradiation than after UV and visible light irradiation (Figure 1 and 2) because stacking and orientation of the chromophores changed.[1a,14] Azo groups preferentially orient perpendicular to the substrate before irradiation.[14] The degree of perpendicular oriented azo groups is reduced after UV and visible light irradiation and the absorption maxima and shape of P-12-Azo in THF solution and in film were different. The absorption band of the film was blue-shifted, indicating H-aggregation of azo groups.[15]

While photoinduced solid-to-liquid transition of P-0-Azo, P-2-Azo and P-20-Azo was not observed, P-6-Azo and P-12-Azo showed photoinduced solid-to-liquid transitions (Figure 1, right). P-2-Azo powders showed no distinct change under optical microscope and therefore P-2-Azo was not further investigated.

Photoinduced reversible solid-to-liquid transitions of P-12-Azo

First, we investigated why P-12-Azo showed photoinduced reversible solid-to-liquid transitions. Photoswitching *trans* P-12-Azo to *cis* P-12-Azo liquefied the sample. The liquid *cis* P-12-Azo was switched back to a solid P-12-Azo using green light (Figure 3a). While *cis* P-12-Azo was soft and stuck to a needle, *trans* P-12-Azo was hard and could be removed from the surface by scratching with a needle and blowing away with a stream of N_2. Accordingly, in piezo rheology measurements the moduli of P-12-Azo changed from low values for *cis* P-12-Azo to high values for *trans* P-12-Azo. (Figure 3b, c). For all tested frequencies, the fact that the storage modulus (G') of *cis* P-12-Azo was higher than its loss modulus (G'') evidenced that *cis* P-12-Azo was in a liquefied state (Figure 3 and S21).

To better understand why P-12-Azo was liquefied at room temperature by UV light irradiation, we performed differential scanning calorimetry (DSC) measurements (Figure 3d, e). P-12-Azo was stable at least up to 200 °C (Figure S22). DSC curve of *trans* P-12-Azo was measured and compared to the DSC curve of *cis* P-12-Azo. *Trans* P-12-Azo showed a T_g at 45 °C (Figure 3e and S23b) and a phase transition at 120 °C. P-12-Azo was

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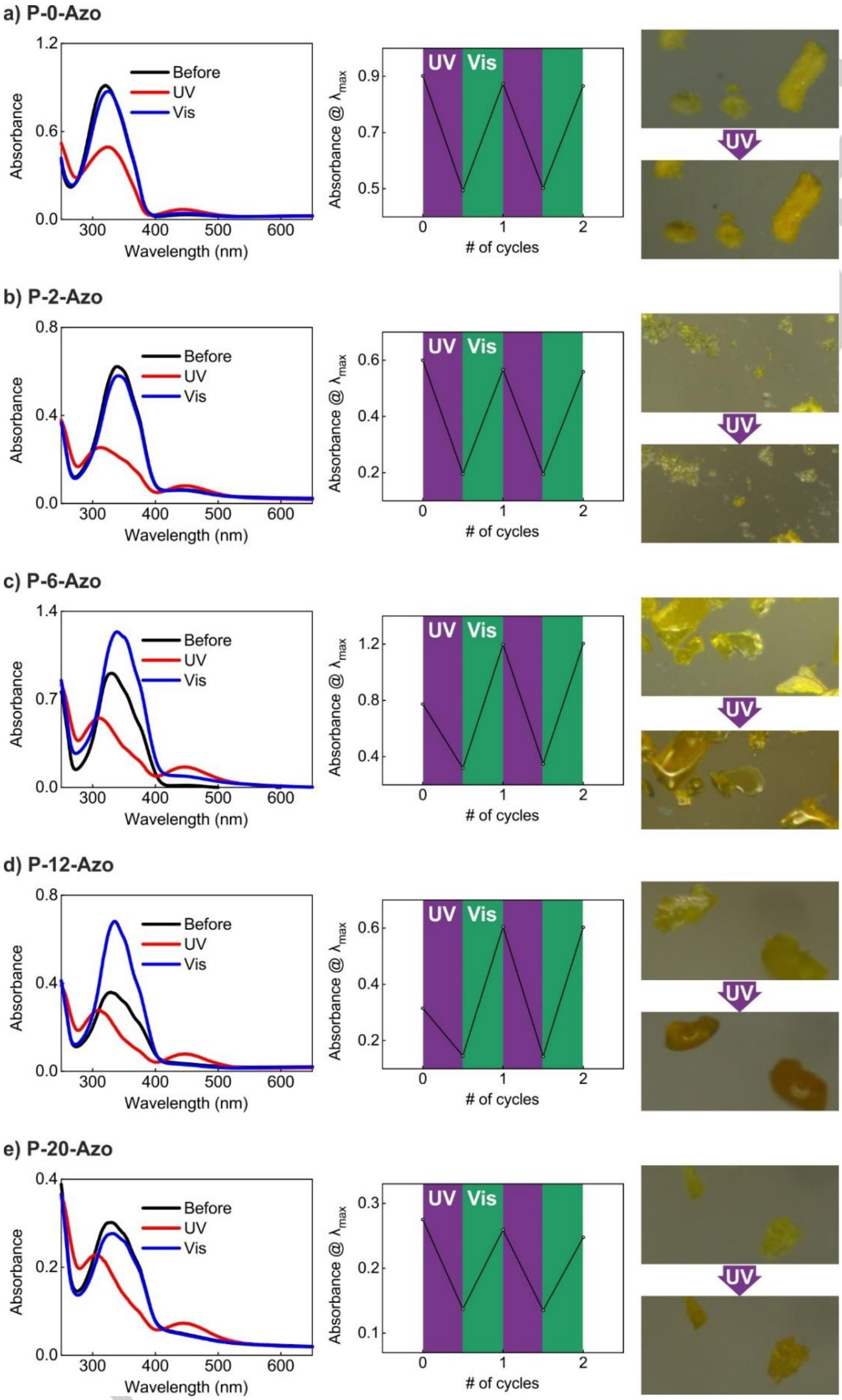

Figure 1. Photoisomerization of P-n-Azo (n = 0, 2, 6, 12, 20). Left: UV-vis absorption spectra of P-n-Azo films before irradiation (black line), after UV irradiation (365 nm, 10 min, 45 mW cm^{-2}) (red line) and after subsequent green light irradiation (blue line) (530 nm, 2 min, 50 mW cm^{-2}). Center: Value of absorbance maximum after repeated UV and green light irradiation demonstrating switching cycles. Right: Optical microscopy images of P-n-Azo powders before and after UV light irradiation (365 nm, 8 min, 20 mW cm^{-2}). Image size: 260 µm × 130 µm.

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isotropic above 120 °C and anisotropic below 120 °C (Figure S24). After UV light irradiation, *trans* P-12-Azo was transformed into *cis* P-12-Azo (Figure S25). *Cis* P-12-Azo showed a T_g below room temperature (-9 °C) and thus acted as a liquid at room temperature. During the first DSC heating, *cis* P-12-Azo started to thermally transform back to *trans* P-12-Azo at 50 °C and was completely switched to *trans* P-12-Azo after the first heating. In the second heating the DSC curve was the same as that for the solid *trans* P-12-Azo. It can be concluded that the T_g difference of *cis* and *trans* P-12-Azo leads to the photoinduced solid-to-liquid transition.

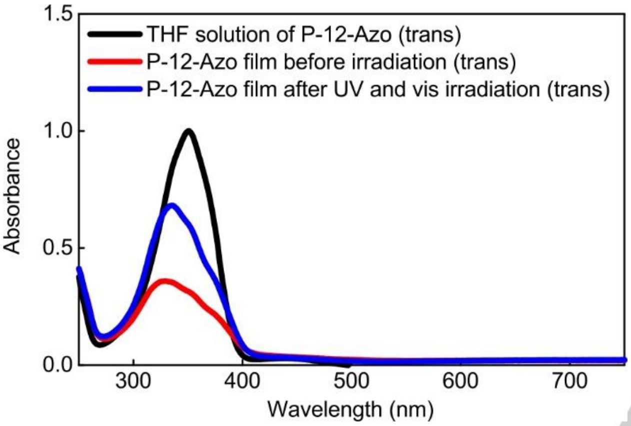

Figure 2. UV-vis absorption spectra of P-12-Azo in THF solution (black) in comparison to P-12-Azo film before irradiation (red) and after UV (365 nm, 45 mW cm^{-2}, 10 min) and visible light irradiation (530 nm, 88 mW cm^{-2}, 2 min) (blue). The absorption spectra of P-12-Azo film before and after irradiation were different because orientation and stacking of azo groups in the film were different before and after irradiation.

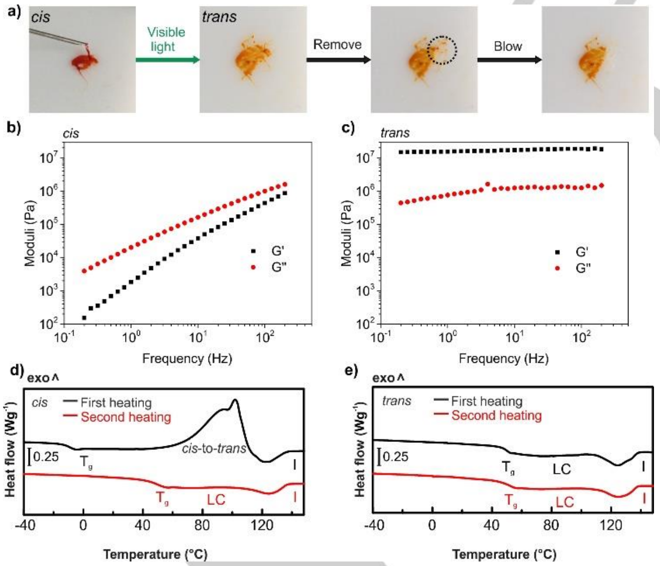

Figure 3. Photoinduced liquid-to-solid transition of P-12-Azo. a) Photographs of liquid *cis* P-12-Azo and solid *trans* P-12-Azo. First, the liquid stuck to a needle. After visible light irradiation, the liquid turned into a solid and was scratched from the substrate with a needle (dashed circle). The powder was removed by blowing with a nitrogen gun. b) *G'* = storage modulus; *G"* = loss modulus of *cis* P-12-Azo and c) after it was switched back to *trans* P-12-Azo using green light irradiation. Measurements were conducted at 18 °C. d) DSC first and second heating curves of *cis* P-12-Azo. During first heating the *cis* form switched back to the *trans* form thermally, demonstrated by the exothermic peak around 100 °C. The second heating curve was similar to the *trans* heating curves in e), demonstrating the *cis* form was completely switched back to *trans* by heating. LC: liquid crystalline phase; I: isotropic phase.

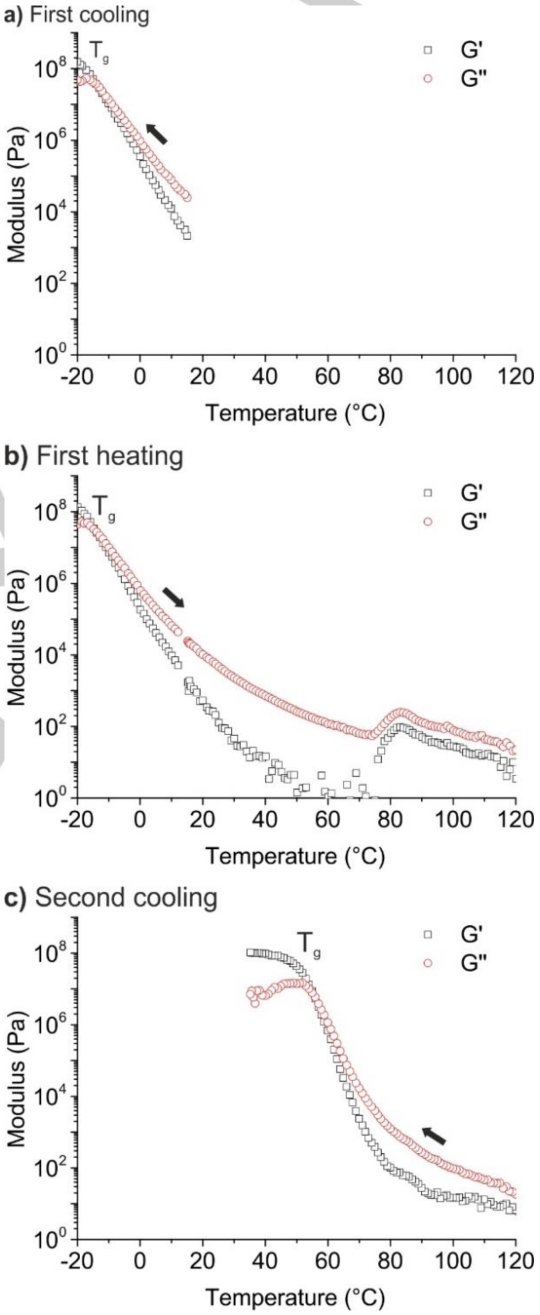

Figure 4. DMA data of *cis* P-12-Azo. *G'* = storage modulus; *G"* = loss modulus. From the maximum of *G"* the glass transition temperatures were determined. a) *Cis* P-12-Azo was cooled from room temperature to -20 °C. T_g was -14 °C. b) *Cis* P-12-Azo was then heated from -20 to 120 °C. T_g was -14 °C. During the heating, the *cis* P-12-Azo was switched to *trans* P-12-Azo thermally. c) Then, the sample was cooled towards room temperature. T_g was 48 °C, which

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confirms that *cis* P-12-Azo was a liquid at room temperature, while *trans* P-12-Azo was a solid at room temperature.

Photoswitchable T_g of P-12-Azo was confirmed by dynamic mechanical analysis (DMA) measurements (Figure 4): *Cis* P-12-Azo was cooled from room temperature to -20 °C where *G”* had a maximum at -14 °C. During heating *G”* still had a maximum at -14 °C. This showed that T_g (-14 °C) of *Cis* P-12-Azo is below room temperature. *Cis* P-12-Azo thermally switched back to *trans* P-12-Azo during the first heating. During the second cooling *G”* had a maximum at 48 °C, which was in accordance with T_g of *trans* P-12-Azo measured by DSC. This experiment confirmed that *cis* P-12-Azo was a liquid and *trans* P-12-Azo was a solid. P-12-Azo has switchable T_g because of *trans*-*cis* isomerization.

In the *trans* state, P-12-Azo showed anisotropic structures. UV light irradiation changed the anisotropic *trans* state to an isotropic *cis* state (Figure 5 and S26). However, the loss of the anisotropic structure was not the reason for the solid-to-liquid transition. By quenching *trans* P-12-Azo from the isotropic state at high temperature, amorphous *trans* P-12-Azo was prepared, which also showed the photoinduced solid-to-liquid transition (Figure S27). P-12-Azo, which had a slightly longer methylene spacer between the backbone and the chromophore than P-6-Azo, showed similar behavior to P-6-Azo.[1a]

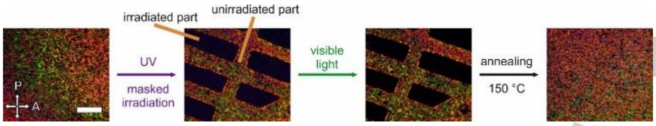

Figure 5. Polarized optical microscopy (POM) images of P-12-Azo before irradiation, after UV irradiation (365 nm, 65 mW cm^{-2}) through a mask, green light irradiation (530 nm, 12 mW cm^{-2}) and annealing at 150°C. The scale bar is 250 µm. P: polarizer; A: analyzer. *Trans* azo groups exhibited liquid crystalline order. UV irradiation transformed azo groups from an anisotropic *trans* to an isotropic *cis* state. Visible light irradiation switches *cis* azo groups back to *trans* azo groups. The resulting *trans* state was amorphous. The anisotropic order was regenerated by annealing at 150 °C and cooling down to room temperature.

Photoresponsiveness of P-0-Azo

Photoinduced solid-to-liquid transition of P-0-Azo was not observed (Figure 1). *Trans* P-0-Azo has a T_g at ~100 °C (Figure 6 and Figure S23a). Anisotropic phases of P-0-Azo could not be observed because the temperature for P-0-Azo to become isotropic is close to the decomposition temperature of P-0-Azo. When the polymer was switched to *cis*, a T_g shift was not observed. T_g of *trans* P-0-Azo is in the same temperature range of the broad exothermic peak of the thermal *cis*-to-*trans* back reaction. T_g of *cis* P-0-Azo could overlap with the *cis*-to-*trans* peak. Additionally, the step in DSC which is considered as T_g was small. After preparation for DSC measurements, *cis* P-0-Azo was a fine powder (Figure 6), in contrast to *cis* P-12-Azo, which was a liquid (Figure 3a). Typically, a spacer is used between the azo chromophore and the polymer backbone to provide enough space and freedom for the motions of azo chromophores.[15a, 16] Our results demonstrated that the spacer is essential for photoinduced solid-to-liquid transition of azopolymers.

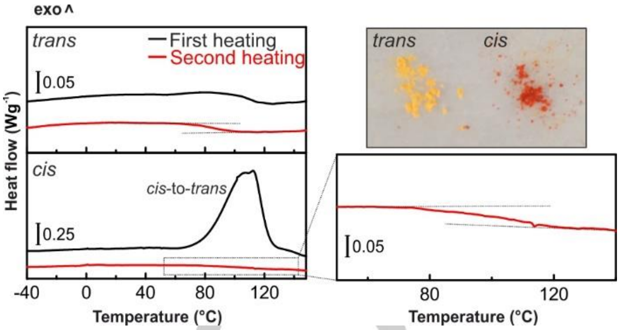

Figure 6. First and second heating DSC curves of *trans* and *cis* P-0-Azo. Note: the y-axis of the *trans* and *cis* DSC curves have different ranges because of the large exothermic *cis*-to-*trans* peak in the first heating of the *cis* DSC curve. The zoomed-in *cis* DSC curve has the same y axis range as the *trans* curve to demonstrate similarity of second heating curves of P-0-Azo. Dotted lines are guides for the eye to see the step which corresponds to T_g. Photographs show solid *trans* (yellow) and *cis* (red) P-0-Azo powders.

Photoresponsiveness of P-20-Azo

Photoinduced solid-to-liquid transition of P-20-Azo was not observed at room temperature (Figure 1). *Trans* P-20-Azo showed two phase transitions at ~80 °C and ~110 °C (Figure 7a and S24). Above 125 °C, P-20-Azo was isotropic; below 125 °C, P-20-Azo was anisotropic. After UV irradiation, *trans* P-20-Azo was transformed to *cis* P-20-Azo and showed a phase transition at ~40 °C. Even though *cis* P-20-Azo had a lower phase transition than *trans* P-20-Azo, *cis* P-20-Azo was not a liquid at room temperature because the phase transition temperature was above room temperature. However, when *trans* P-20-Azo was irradiated using UV light at 50 °C, liquefaction occurred (Figure 7b). These results showed that *cis* P-20-Azo was liquid at 50 °C and *trans* P-20-Azo was solid at 50 °C. Photoinduced solid-to-liquid transition was achieved at 50 °C. Also, *cis* P-20-Azo was isotropic at 60 °C, while it was anisotropic at 36 °C and could be reversibly switched between the two states (Figure 7c).

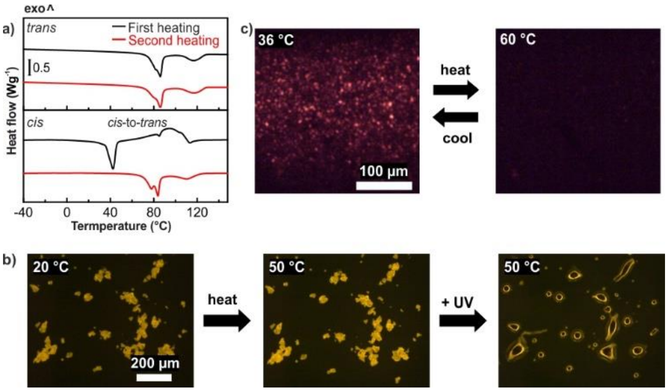

Figure 7. a) DSC first and second heating curves of *trans* and *cis* P-20-Azo. b) Optical microscopy of *trans* P-20-Azo powders at 20 °C, after heating to 50 °C and after UV light irradiation at 50 °C. c) POM images of a *cis* P-20-Azo film losing anisotropy after heating to 60 °C and recovers it after cooling to 36 °C.

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Azopolymers typically exhibit liquid crystalline phases.[17] Switching *trans* azobenzene groups in polymer side chains to *cis* azobenzene disrupts the anisotropic phase because in contrast to the rigid *trans* azobenzene, *cis* azobenzene is a bent molecule.[18] Longer spacer increases the interaction of polymer side chains. When the azobenzene at the end of the long side chain is switched from *trans* to *cis*, there are interactions between the long alkyl side chains. Crystallization of P-20-Azo is similar to polyethylene or polyacrylates with long side chains but without azobenzene,[19] which explains why a phase transition at ~40 °C was observed for *cis* P-20-Azo.

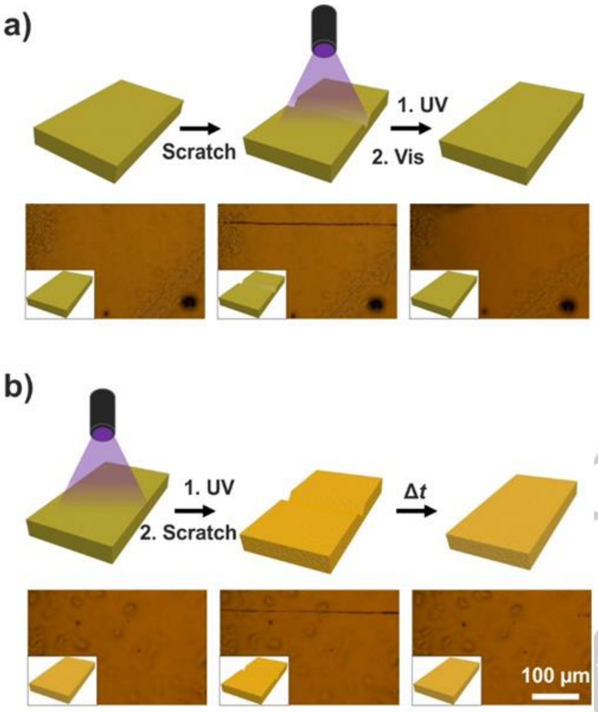

Figure 8. a) Scheme and optical microscopy images of a *trans* P-12-Azo film before scratching, after scratching and healed after UV and visible light irradiation. b) Scheme and optical microscopy images of a *cis* rich film before scratching, after scratching and healed after 10 s. Characteristic areas of the films were used to find exactly the same position on the films after irradiation.

Flowing and healing of P-12-Azo induced by light

Inspired by the photoinduced reversible solid-to-liquid transitions of P-12-Azo, the polymer was used for photo-healable coatings. Spin-coated films of P-12-Azo were scratched with an AFM tip attached to a micromanipulator at characteristic spots to demonstrate the same area is used for all measurements. After UV light irradiation and subsequent visible light irradiation, the scratch was healed because *cis* P-12-Azo was a liquid and can flow to fill the gap of the scratch (Figure 8). Visible light switched back the liquid *cis* to a solid *trans* film.

The flowing of the material on a *cis* P-12-Azo surface was also studied under an optical microscope. To demonstrate healing of *cis* P-12-Azo a film was irradiated with UV light (6 min, 65 mW cm^{-2}) to obtain a *cis* rich film. After irradiation, P-12-Azo was in a *cis* rich state and the film was liquid. Then, the film surface was scratched with an AFM tip attached to a micromanipulator. Immediately the polymer flowed to fill the gap of the scratch after 10 s (Figure 8b and Movie 1).

To neglect any heating effect during irradiation several control experiments were performed.

1. There were 30 min between irradiation and scratching. The film was still healed.
2. A thermal imager was used to detect the temperature of the polymer film during irradiation. The temperature of the film did not rise above 25 °C (Figure S28), which was below T_g of the *trans* polymer.
3. Irradiating the film with visible light for 30 s to transform the liquid *cis* film back to the solid *trans* film immediately stopped the flow (Figure S29a and Movie 2).
4. Heating the film to 35 °C for 10 min did not liquefy the film (Figure S29b and Movie 3). After that the same film was irradiated with UV light again (365 nm, 65 mW cm^{-2}, 6 min) to obtain a *cis* rich film and the scratches on it was immediately healed again (Figure S30 and Movie 4).

All these experiments clearly showed that the flow and healing were because of photoisomerization but not a photothermal effect.

Conclusions

Side-chain type azopolymers with different spacer lengths were synthesized and their photoresponsive properties were studied. For P-6-Azo and P-12-Azo, photoswitchable T_g and photoinduced reversible solid-to-liquid transitions were observed. For azopolymers with a short or long spacer between the azobenzene group and the polymer backbone, photoinduced solid-to-liquid transitions at room temperature were not observed. P-0-Azo did not show photoinduced solid-to-liquid transition because its T_g did not show significant decrease after irradiation. P-20-Azo did not show photoinduced solid-to-liquid transition at room temperature, but it showed the transition at 50 °C because the phase transition temperature was decreased to ~40 °C. Its side chain is so long that interactions among the side chains enable crystallization of the polymer in solid state. However, the phase transition of *cis* P-20-Azo was above room temperature and photoinduced solid-to-liquid transitions cannot be observed at room temperature. When *cis* P-20-Azo was heated to 50 °C, a photoinduced solid-to-liquid transition was achieved. P-12-Azo showed similar behavior to P-6-Azo. Using P-12-Azo, we demonstrated photoinduced healing at real time for the first time. We expect that this kind of photoresponsive polymers can be used as smart materials for printing and microstructure preparation. By UV light irradiation, the polymer can flow or be processed. After the desired structure is formed, the polymer can be solidified by visible light irradiation to obtain a tough material for different applications.

Experimental Section

Materials: Phenol (>99%), p-toluidine (99%), acryloyl chloride (97%), reactants and solvents were purchased from Sigma Aldrich and used without further purification. 12-Bromo-1-dodecanol (>98%) was purchased from TCI. Dimethyl icosanedioate (>95%) was purchased from TCI. 2,2'-Azobisisobutyronitrile (AIBN) (98%) was purchased from Sigma Aldrich and was recrystallized from ethanol before use. Milli-Q water was provided by a Sartorius Arium 611 VF Purification System.

Synthesis: The synthesis route of the P-n-Azo polymers is shown in Scheme S1. Details of syntheses and characterization of the azopolymers are provided in the Supporting Information (Figures S1-S20).

Methods: Proton and carbon nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 250 MHz, 300 MHz or 500 MHz spectrometer. Mass spectra (MS) were obtained using a VG instrument ZAB 2-SE-FPD. The molecular weights and molecular weight distributions of P-n-Azo were determined using an Agilent Technologies 1260 Infinity PSS SECurity GPC (pump: 1260 IsoPump) equipped with UV and RI detectors running in tetrahydrofuran (THF) at 30 °C and a PLgel MIXED-B column (dimension: 0.8 × 30 cm, particle size: 10 µm) with a polystyrene standard. UV-vis absorption spectra were recorded on a Perkin Elmer Lambda 900 spectrometer. Baselines were corrected and spectra were normalized using OriginPro software. Optical microscopy images were captured on a Zeiss optical microscope equipped with a CCD camera. Thermogravimetric analysis (TGA) was carried out on a Mettler Toledo TGA-851 under nitrogen atmosphere with a heating rate of 10 °C min^{-1}. DSC data were collected using a Mettler Toledo DSC-822 under nitrogen atmosphere. The polymers were measured with a heating or cooling rate of 10 °C min^{-1}. The shear moduli were measured using a homemade piezo-rheometer in shear mode at 18 °C.[20] A *cis* azopolymer sample with a thickness of 100 µm was sandwiched between two quartz plates that were used as transparent sample holders. Firstly, the shear moduli of *cis* azopolymers were measured in a dark environment to prevent possible light-induced transitions. Subsequently, *cis* azopolymers between the quartz plates were converted to *trans* azopolymers by 530 nm light irradiation. *Trans* azopolymers were measured by the piezo-rheometer under the same conditions. DMA was conducted on an Advanced Rheometric Expansion System (ARES, Rheometric Scientific Company). Shear deformation was applied under conditions of controlled deformation amplitude, which was kept in the range of the linear viscoelastic response of the studied samples. Plate-plate geometry was used with plate diameters of 6 mm. The experiments were conducted under dry nitrogen atmosphere at a heating rate of 3 °C min^{-1} and a constant deformation frequency of 1 or 10 rad s^{-1}. Photoisomerization was induced by LEDs with wavelengths of 365 nm, 470 nm and 530 nm (Mightex Systems, device types LCS-0365-07-22, LCS-0470-03-22 and LCS-0530-15-22, respectively). The output intensities were controlled by an LED controller (Mightex Systems, device type SLC-MA04-MU), calibrated by an optical powermeter (Spectra-Physics Corporation, Model 407A). Preparation of *cis* polymers for DSC and DMA measurements was described in our previous paper.[1a] An MMO-203 hydraulic micromanipulator (Narishige, Tokyo, Japan) equipped with an AFM cantilever was used to scratch polymer films.

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Keywords: azobenzene • photoisomerization • photoresponsive • polymers • self-healing

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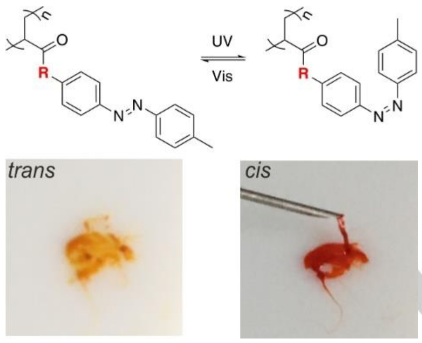
Entry for the Table of Contents

FULL PAPER

The influence of the spacer (R in the TOC figure) on photoinduced solid-to-liquid transitions of azopolymers is investigated. While azopolymers with moderate spacer length exhibit photoinduced solid-to-liquid transitions, azopolymers with short and long spacer do not. Healing scratches by light is demonstrated on hard coatings made from azopolymers and followed at real time.



*Philipp Weis, Andreas Hess, Gunnar Kircher, Shilin Huang, Günter K. Auernhammer, Kaloian Koynov, Hans-Jürgen Butt, Si Wu**

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Effects of Spacers on Photoinduced Reversible Solid-to-Liquid Transitions of Azobenzene-Containing Polymers