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# Photoresponsive Adhesives Based on Arylazoisoxazoles-Containing Polymers

Ruggero Rossi, Antonella Salvini, Benedetto Pizzo, Marco Frediani, Diederik Sybolt Wiersma, Camilla Parmeggiani, and Daniele Martella\*

Adhesives exist in many forms and are essential in the daily life, in industrial processes, and in healthcare, calling for continuous improvements in terms of application fields, strength, biocompatibility, recyclability, and reversibility. Regarding the last two points, embedding photoresponsive molecules into the adhesive allows the use of light to attach or detach reversibly different surfaces. Photoresponsive adhesives can be removed without the use of high temperature or solvents, which is ideal for delicate environments. To date, azobenzenes are the most explored chromophore to prepare smart adhesive formulations. Here, the synthesis of polymer containing arylazoisoxazoles (AIZs) — azobenzene analogs containing a heterocycle — and their application as adhesives is described. Mechanical tests demonstrate an enhancement of the adhesion strength from 0.39 to 2.79 MPa, passing from low molecular weight monomer to selected AIZs acrylate polymer. Irradiation with UV induces the formation of the *cis* isomer with a consequent drop of more than 70% in the adhesion strength. The different compounds result as possible candidates as adhesives on the basis of the increased load that can be held, together with the possibility to obtain joints that can be either stable or detachable under light irradiation.

adhesives.<sup>[4]</sup> Adhesives are ubiquitous in products, their use by humans dates back as far as the period of the Neanderthals, ranging from industrial to domestic use.<sup>[5]</sup> Their design has to face many aspects depending on the material interface to join, the load to be supported, and the resistance over time. One of the most challenging aspects in their development is related to their easy application and removal without sacrificing adhesion efficiency, and trying to avoid the use of solvents or high-temperature treatment. Introduction of photoswitches in their formulation allowed to process the different joint formation steps by remote irradiation. Light can be used to prepare the joint, to detach the surfaces, to strengthen a material after joint formation, and eventually to allow the material recycling.<sup>[6]</sup> Even if this technology requires at least one transparent surface for light transport, it opens the way for new solutions for the adhesion of fragile object (such as thin glasses) or in delicate environments (such as underwater or in biological samples).

## 1. Introduction

Macroscopic system properties can be easily controlled by light using photoswitches.<sup>[1,2]</sup> These compounds undergo changes in their molecular structure under light irradiation, and can be interconverted in at least two different states presenting different chemical and physical properties.<sup>[3]</sup> Research on such molecules is now moving toward daily life products, and, among these,

Photoresponsive adhesives have been produced using different photoswitches, such as azobenzenes, spiropyrans, donor-acceptor Stenhouse adducts, and even exploiting the photoinduced phase transition in hydrogels or liquid crystalline elastomers.<sup>[7–10]</sup> However, the most studied and promising systems are those based on the *trans*–*cis* isomerization of azobenzene.<sup>[6]</sup> This molecule presents very different properties between the two isomers, especially regarding their shape

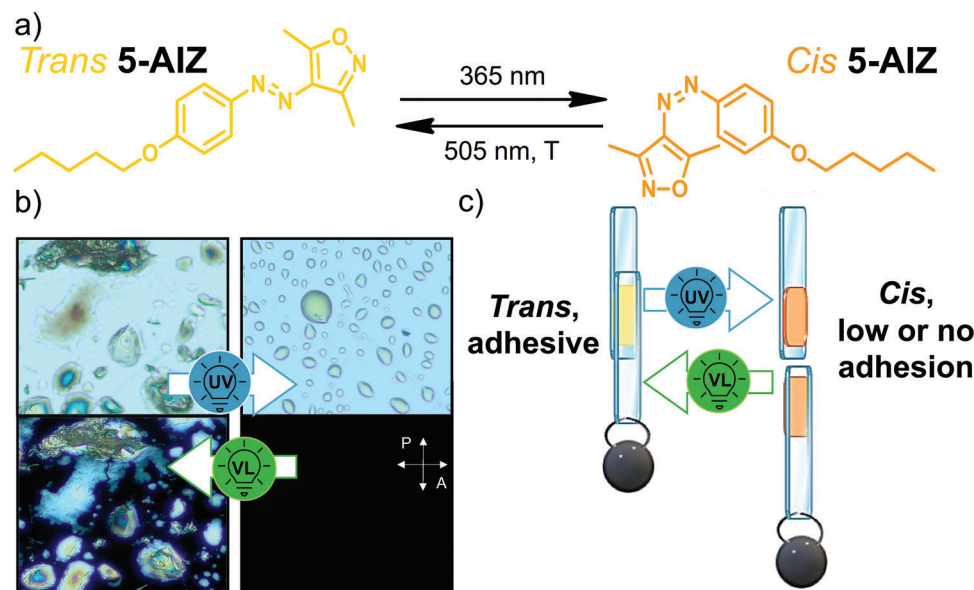
R. Rossi, D. S. Wiersma, C. Parmeggiani, D. Martella  
 European Laboratory for Non-Linear Spectroscopy (LENS)  
 via Nello Carrara, 1, Sesto Fiorentino 50019, Italy  
 E-mail: martella@lens.unifi.it

R. Rossi, A. Salvini, M. Frediani, C. Parmeggiani  
 Department of Chemistry “Ugo Schiff”  
 University of Florence  
 via della Lastruccia, 3–13, Sesto Fiorentino 50019, Italy  
 R. Rossi, B. Pizzo  
 Institute of Bioeconomy (CNR-IBE)  
 National Research Council (CNR)  
 via Madonna del Piano, 10 Sesto Fiorentino 50019, Italy  
 D. S. Wiersma  
 Physics and Astronomy Department  
 University of Florence  
 via G. Sansone, 1 Sesto Fiorentino 50019, Italy  
 D. S. Wiersma, C. Parmeggiani, D. Martella  
 Istituto Nazionale di Ricerca Metrologica (INRiM)  
 strada delle cacce, 91 Torino 10135, Italy

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/mame.202200504>

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**Figure 1.** AIZ photo-adhesion mechanism with a) molecular structure of 5-AIZ; b) images of *trans* and *cis* isomers observed at microscope with unpolarized (top panels) and polarized light (bottom panel, white lines indicate the polarizer direction); c) scheme of a photoresponsive adhesives working mechanism.

(from planar *trans* to angular 3D geometry of *cis*) and dipolar moment changes.<sup>[11]</sup> UV light induces the *trans*-to-*cis* isomerization that can be exploited to control several material properties when azobenzenes are used as a constituent, from the shape-change of artificial muscle to the wettability control, and – most interesting in adhesive applications – photo-softening.<sup>[12–14]</sup> Mechanical property changes due to UV irradiation can modulate surface adhesion strength and, in some cases, the isomerization to the *cis* state can cause an isothermal solid-to-liquid phase transition. On the other side, irradiation with visible light allows the recovery of the solid *trans* state.<sup>[15]</sup> In order to improve the adhesion strength of azobenzene derivatives, different multivalent systems based on sugar scaffolds, dendrimers, and polymers have been described.<sup>[16–18]</sup> Regarding the latter, very high adhesion has been demonstrated up to the MPa range that is consistent with those of many commercial adhesives.<sup>[19]</sup> In this case, adhesion can be tuned via the alkyl spacers, the polymerizable groups (acrylate or methacrylate), and the molecular weight of the product.<sup>[6,20]</sup>

The photochromic behavior of azobenzenes can be easily tuned also by substitution of one benzene ring with a heterocycle, thus maintaining the easy synthesis typical of azobenzenes while creating new chemical properties.<sup>[21]</sup> An interesting example in the field of adhesives is the use of arylazoisoxazoles (AIZs), which allow fast joint detaching under UV irradiation due to a solid-to-liquid phase transition.<sup>[22]</sup> The first report on the spectroscopic properties of this photoswitch has been published only in 2019, while few synthetic methods have been reported earlier.<sup>[23,24]</sup> AIZ adhesion can be triggered also by chemical stimuli, such as acidic conditions, to accelerate the *cis*-*trans* conversion.<sup>[25]</sup> However, the adhesive strength of these compounds is below 1 MPa and needs to be implemented to be really applied as adhesive.

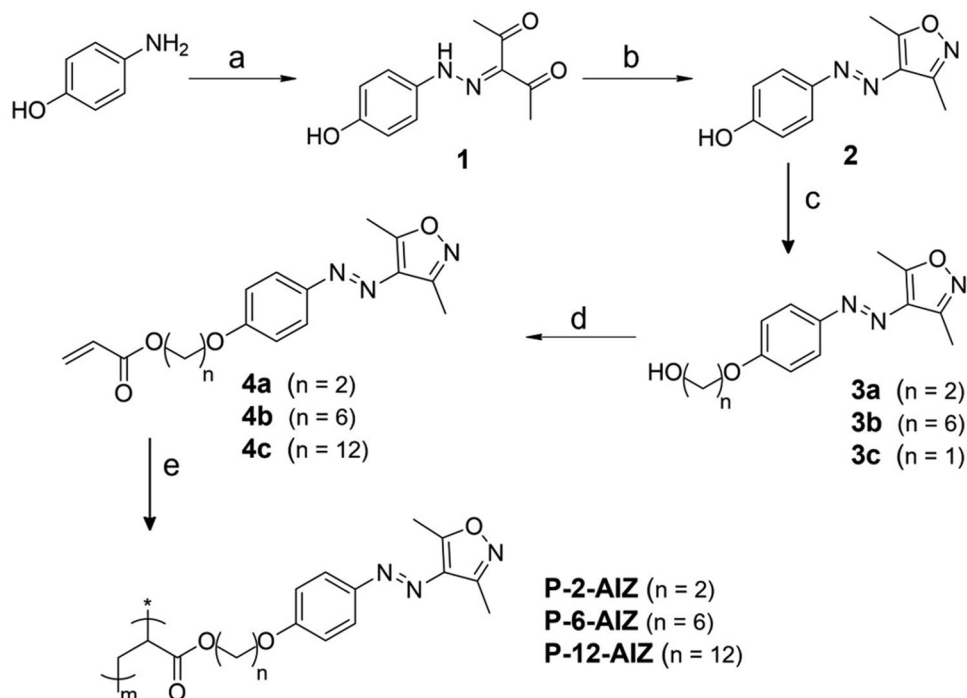
In this article, we report the first synthesis of polymeric AIZs adhesives by free radical polymerization of the corresponding acrylate-based dyes, to improve the performance of

these products as adhesives. The effect of the alkyl spacer in between the backbone and the chromophore was studied to modulate the spectroscopic and adhesive properties. Our results demonstrate how the insertion of AIZs in polymeric matrices allows to significantly improve the strength of the derived photoresponsive adhesives, leading to materials that support large weights and that can be photodetachable or photostable depending on the applied load. The same strategies could be applied to other low-molecular-weight azobenzene analogs used as adhesives to improve their strength.<sup>[26]</sup>

## 2. Results and Discussion

The working mechanism of the photoresponsive adhesion of AIZ is depicted in **Figure 1**. In particular, the previously described pentyl derivative of the arylazo-3,5-dimethylisoxazole, 5-AIZ (Figure 1a), is able to undergo a reversible *trans*-*cis* isomerization under irradiation with UV and green light, respectively. The isomerization is accompanied by a solid-to-liquid isothermal phase transition (Figure 1b). Microscope images showed a different aspect of the product after UV irradiation, and the disappearance of birefringence during observation with polarized light, thus confirming the total absence of a crystalline structure in favor of an isotropic liquid in the *cis* state. This phase change can be used to obtain reversible adhesion (Figure 1c): the solid *trans* isomer can be used to connect the joint and, during illumination, it's melting in the liquid *cis*-state led to surface detaching.<sup>[22,23]</sup> Before focusing on the integration of this unit inside polymeric structures, the adhesive properties of 5-AIZ were characterized by a lap shear strength test.

To this aim, we prepared the joint by gluing two glasses with 5-AIZ and then we mounted it in a dynamometer. Application of a progressive tensile-mode shear stress on the joint allowed



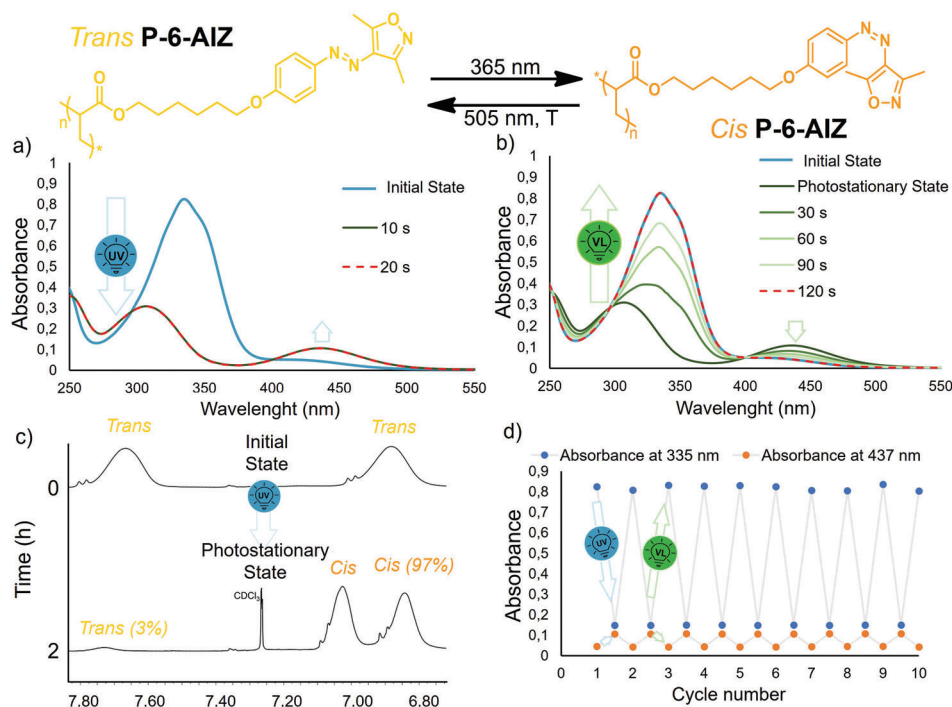
**Figure 2.** Synthesis of polymers containing AIZs. Reagent and conditions: a)  $\text{NaNO}_2$ ,  $0^\circ\text{C}$ , 1 h, 2,4-pentanedione,  $\text{NaOAc}$ ,  $\text{H}_2\text{O}$ , rt, 18 h, b)  $\text{NH}_2\text{OH}$   $\text{HCl}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{EtOH}$ , reflux, 18 h c) 2-bromo-1-ethanol (for 3a) or 6-chloro-1-hexanol (for 3b) or 12-bromo-dodecanol (for 3c),  $\text{K}_2\text{CO}_3$ ,  $\text{KI}$ ,  $\text{DMF}$ ,  $80^\circ\text{C}$ ; 18 h, d) acryloyl chloride,  $\text{TEA}$ ,  $\text{CH}_2\text{Cl}_2$ , rt; 2 h e)  $\text{AIBN}$ , toluene,  $80^\circ\text{C}$ ; 24 h.

to record the maximum stress at break that was used to calculate the adhesive strength. The same procedure has been applied afterward also to characterize the polymeric AIZs, and a more detailed scheme of adhesive testing is reported in Figures S1,S2 (Supporting Information).

The joints have been prepared with two different protocols. In the first case, 5-AIZ has been melted above  $100^\circ\text{C}$  and, after joining the two surfaces, the temperature has been lowered down to room temperature (with constant pressing) leading to the crystalline phase and to the stress-resistant assembly. In the second case, we employed light to prepare the joint: 5-AIZ has been converted by UV in the liquid *cis* isomer and, after pressure application, solidified with visible light. The adhesive strength measurements indicated stress values of  $0.17 \pm 0.02$  and  $0.39 \pm 0.12$  MPa (estimated from the load-displacement plots reported in Figure S3, Supporting Information) for the joint prepared with temperature or light activation, respectively. The increased adhesion due to irradiation during the joint formation has been already reported for other azobenzenes-based adhesives, and should be attributed to a different crystalline domain size during solidification with temperature or light.<sup>[6]</sup> Very interestingly, the recorded 5-AIZ adhesive strength perfectly matches with previously reported values, demonstrating the reproducibility of the method employed for adhesion characterization.<sup>[22]</sup> After irradiation of the joint, the *cis* isomer lost completely the adhesive properties (strength of 0 MPa) thanks to isomerization via an optical pathway. Thermal imaging confirmed a temperature increase of  $\approx 1^\circ\text{C}$  in our irradiation conditions, which was not sufficient to influence the standard thermal melting of the adhesive (Figure S4, Supporting Information).

To evaluate if greater molecular complexity can improve the adhesive strength, different polymers have been prepared incorporating the same chromophore of 5-AIZ inside their side-chain architecture. In particular, the chromophore has been functionalized with different alkyl chains bearing an acrylate group and then polymerized. The polymerization has been performed by a simple free radical process aiming to identify the simplest procedure for a possible easy and cheap scale-up of the formulation. The polymers have been called as P-*n*-AIZ, where *n* indicates the length of the alkyl spacer in the monomer (number of repeating  $-\text{CH}_2-$  units). The synthetic procedure is reported in Figure 2 and comprises the preparation of a single chromophore unit (2) bearing a free phenol moiety. This group has been used to insert directly the different alkyl chains starting from the same dye core.

The intermediate 2 has been prepared by coupling p-aminophenol with 2,4-pentanedione via diazonium salt formation (to give 1), followed by cyclization of the isoxazole by condensation of hydroxylamine with the 1,3-diketone moiety. The reactions occurred with a 94% yield, and without the need for chromatographic protocols for dye purification. In the following steps, the monomers have been prepared by adding the flexible spacer on the phenol group of 2 using different halogen-alcohols and a Williamson protocol (3a–c). Treatment with acryloyl chloride was performed to insert the polymerizable group at the end of the spacer. In this way, we prepared three monomers, having 2, 6, or 12 carbons in the alkyl chain (4a–c), that have been polymerized using 2,2'-azobis(isobutyronitrile) (AIBN) in toluene. The reactions proceeded at  $80^\circ\text{C}$  for 18 h leading to a conversion between 62% and 76%. The polymers have been purified by sequential dissolution in dichloromethane and precipitation



**Figure 3.** Light induced isomerization processes in polymers containing AIZs. a) absorption spectra of P-6-AIZ after UV light irradiation at different times; b) absorption spectra of *cis* P-6-AIZ after visible light irradiation at different times; c)  $^1\text{H-NMR}$  spectra of P-6-AIZ in the aromatic peak region (7.80–6.80 ppm) before and after UV irradiation; d) evolution of the absorbance at 335 nm and 437 nm of P-6-AIZ after 10 cycles of UV light/visible light irradiation.

by dropping the solution in ethanol. Polymer molecular structures have been characterized by NMR spectroscopy and gel permeation chromatography (GPC) (details can be found in Figures S5–S14, Supporting Information).

All compounds were initially studied in solution to investigate the isomerization process by UV-vis spectroscopy and  $^1\text{H-NMR}$ . All of them showed a very similar spectroscopic behavior as evident from the analysis of P-6-AIZ in **Figure 3** (and for 5-AIZ, P-2-AIZ and P-12-AIZ reported in Figures S15–S17, Supporting Information). The UV-vis spectrum of the *trans* isomer is characterized by two typical absorption bands. The first, with higher intensity, has a maximum  $\approx 335$  nm and corresponds to the  $\pi-\pi^*$  transition, while the second,  $\approx 330-370$  nm, indicates a  $n-\pi^*$  transition. During irradiation with UV light (365 nm), it was possible to monitor the isomerization process by the absorbance decrease in the first transition and the increase of the second absorption band as shown in **Figure 3a** for P-6-AIZ. To be noted that the complete isomerization has been obtained just after 10 s of irradiation and, after this time, a photostationary state was reached. The process was completely reversible, and by irradiating the solution with green light (505 nm) the opposite process occurred (increase of absorption band around 335 nm and decrease of that  $\approx 437$  nm as shown in **Figure 3b**). In our experimental condition, polymers presented a similar kinetic of photoisomerization (under both wavelengths) than those of the low molecular weight molecule 5-AIZ (**Figure S15**, Supporting Information). In particular, the photostationary state under UV was reached in less than 10 s for both P-6-AIZ and 5-AIZ. This observation is consistent with published data reported for monomers

and related polymer solution under irradiation demonstrated to behave in a comparable manner.<sup>[27]</sup>

Regarding the stability of the *cis* isomers, by monitoring the absorbance after UV irradiation we calculated its half-life time ( $t_{1/2}$ ) assuming the first-order kinetics as usual for this process in diluted solutions<sup>[27]</sup> (see **Figure S18**, Supporting Information). We observed a considerable improvement of the *cis* isomer stability in the polymeric structure, with a  $t_{1/2}$  that increased from 9 days for 5-AIZ to 18 days for P-6-AIZ. On the other hand, the alkyl spacer in the polymer plays a minor role in the stability of *cis* form and only small differences were observed between the 3 polymers (with  $t_{1/2}$  of 18 and 16 days for P-2-AIZ and P-12-AIZ, respectively).

To investigate the photostationary state composition,  $^1\text{H-NMR}$  spectra have been recorded on the irradiated solution as reported in **Figure 3c** (see **Figures S15–S17**, Supporting Information, for the same test on other compounds). In the time zero spectra, the signals of the aromatic benzene ring gave two peaks  $\approx 7.76-7.57$  and  $6.97-6.88$  ppm (**Figure 3c**). During the irradiation, a decrease in the intensity of these signals was observed with the appearance of *cis* peaks  $\approx 7.10-6.96$  and  $6.90-6.78$  ppm, clearly separated by the *trans* isomer. By the integration of the different signals, we estimated a composition of 97% of the *cis* isomer in the photostationary state after UV treatment and 3% of the *trans* isomer after green irradiation (**Figure 3c**). This overall characterization demonstrated a good interconversion in between the two isomers that are essential to develop light-responsive materials. The effect of following cycles of UV and green light irradiation on the same solution demonstrated the stability and the fatigue

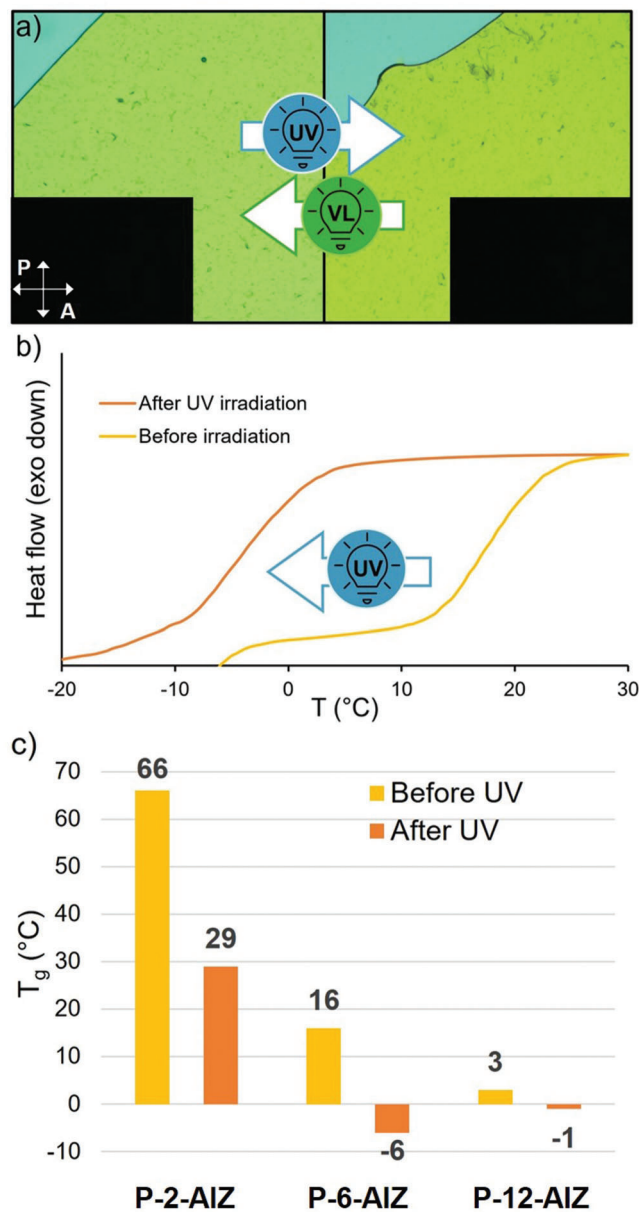


resistance, without decreasing the initial absorbance value after several cycles of irradiation of the photoswitches (Figure 3d).

A comparable analysis was also performed on dry polymer films and reported in Figure S19 (Supporting Information). The first data collected demonstrated the possibility to obtain both isomerization processes (with UV and visible light) even if longer irradiation times, with respect to the polymer in solution, are needed to reach the photostationary state, e.g., 100 s of UV light (Figure S19a, Supporting Information). This time is also dependent on material thickness and light intensity. Another interesting difference with the polymer solution has been observed for the thermal-back relaxation of the *cis* isomer. Indeed, in our experiments the thermal-back isomerization of all polymers presents an initial deviation from the first-order kinetics (see Figure S19c, Supporting Information). The thermal isomerization can be described as a two phase process, a faster relaxation phase (lasting in less than the first day, which corresponds to an estimated 5% of the initial absorbance recovery at 369 nm for P-6-AIZ) and a slower predominant one (which can be described by a first-order kinetic, Figure S19c,d, Supporting Information). All the kinetics parameters are reported in table S1 (Supporting Information), also showing a general increase of the *cis* isomers stability in the solid state. For example,  $t_{1/2}$  (calculated for the second part of the process) changed from 18 to 32 days in P-6-AIZ passing from the diluted solution to the dry film.

This behavior was already observed for some solid samples containing azobenzenes, both dispersed in a polymeric matrix or covalently linked to a polymer chain.<sup>[28–30]</sup> Some of these examples also reported a *cis-trans* isomerization initially faster than the samples in solution that later become slower.<sup>[31]</sup> Furthermore, this behavior could be also related to the glass transition temperature, and interpreted on the basis of rotational and translational relaxation processes of the chain segments.<sup>[32]</sup> In our polymers, such relation with the glass transition temperature was not observed.

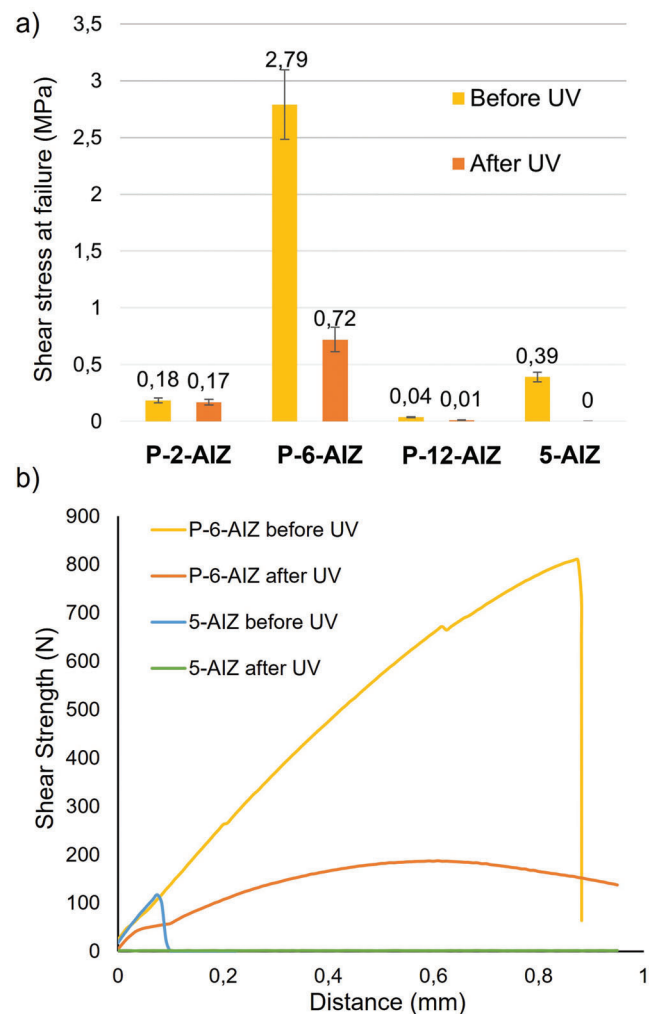
Before testing the adhesion, we investigated the bulk macroscopic properties of the solid material under light irradiation. In the first analysis, microscope observation has been performed with and without polarized light. Despite 5-AIZ, in this case we did not observe a solid-to-liquid phase transition following the isomerization in any polymer evaluated that remained amorphous, both before and after irradiation (see Figure 4a). However, differential scanning calorimetry (DSC) analysis revealed light to efficiently modify the polymer thermal properties. For all polymers, we measured the glass transition temperature ( $T_g$ ) and its variations after illumination caused by the *cis* content, as already reported for other azobenzene polymers.<sup>[33]</sup> As expected,  $T_g$  decreased by increasing the length of the alkyl chain as reported in Figure 4c. DSC performed after irradiation highlighted how  $T_g$  decreased due to the *cis* isomer formation (Figure 4b; Figure S20, Supporting Information). Also, in this case, a strong dependence of the variation of the  $T_g$  in dependence of the length of the alkyl chain was observed, with a greater variation for the shorter chain in the side group. For the *cis* polymers, an exothermic peak was observed in between 70 and 135 °C indicating the thermal *cis-trans* isomerization (see Figure S21, Supporting Information). Despite photoinduced solid-liquid phase transition being suppressed by the polymer chain, the macroscopic thermal properties of the systems were still modified under irradiation



**Figure 4.** Effect of UV irradiation on solid photoresponsive polymers with a) optical image of P-6-AIZ film before and after UV irradiation (in the inset the observation with polarized light, white lines indicate the polarizer direction), b) DSC trace (20 °C min<sup>-1</sup>) during the heating cycle for P-6-AIZ before and after UV irradiation. c) Glass transition temperature of the three synthesized polymers. Values are determined from the midpoint of the baseline jump in the DSC trace.

with photo-softening effect verified by  $T_g$  variation, leading to possible differences in the adhesives properties.

For the evaluation of the adhesion strength, all compounds were tested with a single lap shear strength test, as already described for 5-AIZ (Figure 5a). Data reported were obtained on joints made by heating at 70 °C the polymers (to increase their fluidity) homogeneously distributed in between the two glasses. In fact, these compounds do not liquefy by irradiation, and the



**Figure 5.** Adhesive strength measurements with a) histograms reporting the adhesive strength of the initial joints and after UV irradiation; b) stress-displacement curves of joints prepared by 5-AIZ or P-6-AIZ.

joint formation can be obtained only by heating (and not by light such as for 5-AIZ).

Very interestingly, the adhesion strength was strongly influenced by the alkyl chain length, although in a non-obvious way. Both P-2-AIZ and P-12-AIZ presented adhesive strength lower than the lower molecular weight 5-AIZ (<0.20 MPa for P-2-AIZ and P-12-AIZ, and  $0.39 \pm 0.02$  MPa for 5-AIZ, Figure 5a), while P-6-AIZ has a much higher adhesive strength.

For this polymer, the stress at rupture was  $2.79 \pm 0.32$  MPa, thus demonstrating that the insertion of the AIZ in a polymeric backbone could be used to improve the mechanical performances of the chromophore. However, no correlation between the adhesive strength and the alkyl chain length (and therefore  $T_g$ ) was highlighted within the series.

As it is normally considered that polymers having higher  $T_g$  also present better mechanical characteristics, to be sure that these results were not related to the experimental condition of joint formation, we prepared the joint using P-2-AIZ and P-6-AIZ by heating at  $100^\circ\text{C}$ , far from both polymer  $T_g$ . Tests showed only

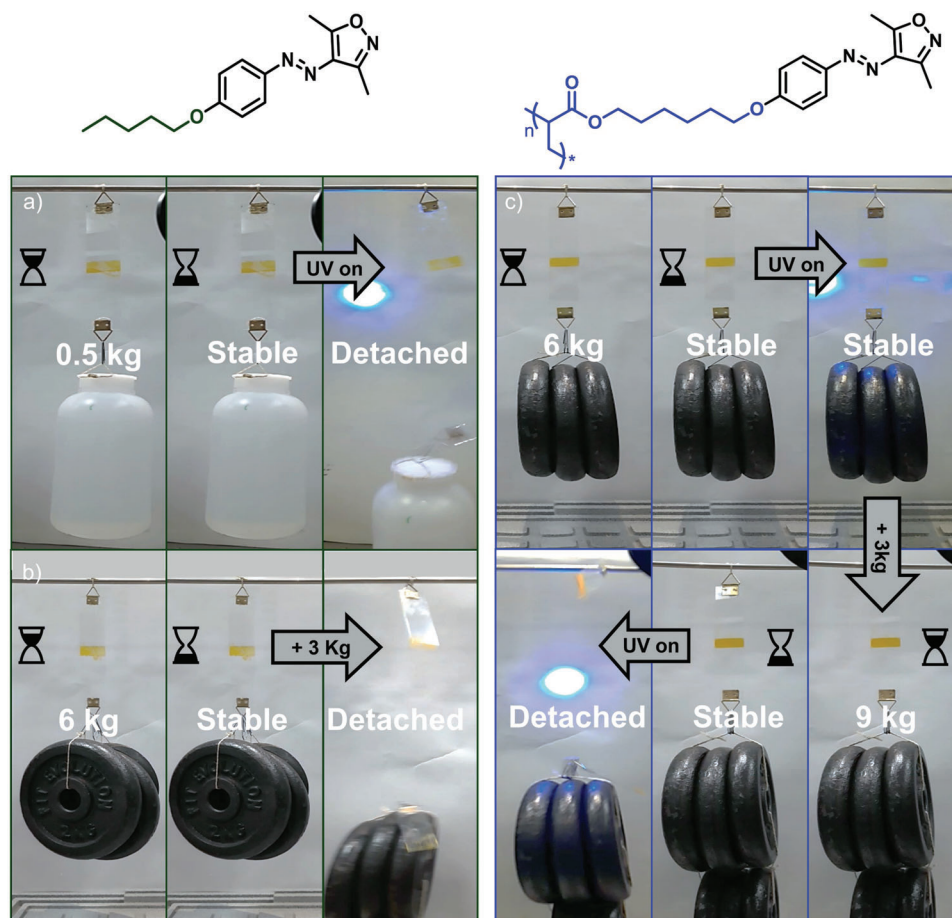
a moderate increase of the strength for the polymer with a shorter alkyl chain (shear stress at failure of 0.26 MPa with respect to 0.18 MPa reported in Figure 5a) with value still lower than that of 5-AIZ, whereas no beneficial effect was observed for P-6-AIZ. Therefore, it has been confirmed that there is an optimal value in the structure of the polymer that enables it to develop its best adhesion properties. This optimal value for this series corresponds to a length of 6 units of  $-\text{CH}_2-$  groups as spacers.

An additional test has been performed with P-6-AIZ. Even if polymers were already demonstrated not undergoing the solid-to-liquid phase transition after isomerization, we assessed the possibility to form the joint by light using a cycle of UV irradiation – joint formation – green light irradiation (as already discussed for 5-AIZ). The measured stress at rupture was  $0.70 \pm 0.13$  MPa, well below that obtained by forming the joint by heating the polymer at  $70^\circ\text{C}$  ( $2.79 \pm 0.02$  MPa). Interestingly, the value obtained by joint formation with light was still higher than the value from 5-AIZ ( $0.39 \pm 0.02$  MPa, Figure 5a). Furthermore, unlike other azobenzene compounds, a cycle of UV and visible light irradiation on the thermally melted joint did not result in any additional increase in adhesive strength.

Finally, strength tests were performed on joints made using the three polymers after irradiation with visible light to cause the *cis* isomer formation (Figure 5a). Although P-6-AIZ does not liquefy by irradiation, it still preserves the possibility to control the adhesion by light with a drop of 74% in the adhesive strength after UV irradiation (shear stress at failure  $0.72 \pm 0.13$  MPa, Figure 5a). This change in adhesion can be attributed to a variety of factors; among these are the dipolar moment change of the chromophore and the photo-softening effect. From the load-displacement curve, the stiffness of polymers was retrieved as shown in Figure S22 (Supporting Information). We observed that by increasing the alkyl spacer on the chromophore, stiffness exhibited the same trend as the adhesive strength. Moreover, and more important, UV irradiation reduced the stiffness of P-6-AIZ by 14% (photo-softening effect).

It is also worth noticing that, after rupture, in all tested samples an adhesive layer was visible on both glass surfaces (Figure S23, Supporting Information), denoting a cohesive failure for the joints. This demonstrated that also after irradiation with UV light the joint breaking had not to be attributed mainly to a decreased interaction between glass and polymer due to isomerization, but rather to photsoftening, which is usually accompanied by a decreased material cohesion.

The overall picture of our mechanical tests suggested the need of different adhesives depending on the desired joint strength and therefore on the weight to be loaded. Examples of light responsive joints sensitive to different loads are reported in **Figure 6** and in Movies S1 and S2 (Supporting Information). All joints were prepared using 3 mg of 5-AIZ or P-6-AIZ as adhesives showing different behaviors when different loads were attached to the substrates, and the samples were irradiated with light. In the first test (Figure 6), a small load (500 g) was applied to the sample containing 5-AIZ and, after 30 seconds of irradiation with UV light, it was detached (photoresponsive adhesive, Figure 6a). The joint made with 5-AIZ, without irradiation, was stable also when loaded with 6 kg, while it broke with a 9 kg load (Figure 6b). On the other hand, P-6-AIZ gives a photostable joint under UV irradiation with a 6 kg load, as reported in Figure 6c.



**Figure 6.** Photoresponsive adhesive supporting different weights with a) 5-AIZ joint breaks after UV irradiation (30 s) with a small load of 0.5 kg, b) 5-AIZ joint breaks when loaded with 9 kg c) P-6-AIZ joint is photostable when loaded with 6 kg, it breaks after UV irradiation (3 min) with a load of 9 kg.

In the last example, for high weight (9 kg, Figure 6c), P-6-AIZ behaves as photoresponsive adhesive showing detachment under irradiation. As a result, the inability of P-6-AIZ to undergo liquefaction during the *trans*-to-*cis* transition, and thus to completely lose its adhesive properties after irradiation, became an opportunity to develop load-sensitive photoresponsive adhesives.

A last consideration to be done is related to the velocity of joint detachment under illumination. In a previous report, 5-AIZ allowed very fast detaching (time scale of seconds) under UV light (radiant flux 1.2 W, increase of temperature up to 7 °C).<sup>[23]</sup> However, in our examples, we observed a longer detaching time. This effect is mainly attributed to the low power of our lamp, thus leading to slow *cis* conversion and limited light penetration. Detachment under light exposure resulted faster for 5-AIZ than for P-6-AIZ, even if the photoconversion in solution was demonstrated slower for the low molecular weight compound 5-AIZ.

### 3. Conclusion

Arylazoisoxazoles have been introduced inside acrylate-based polymers, demonstrating how the macromolecular structure affected both the physical and mechanical properties of the sys-

tems. Regarding the first aspect, we observed a fast photoisomerization process for the polymers in solution, allowing for almost quantitative formation of *cis* and *trans* isomers under UV and green light irradiation, respectively. While the low molecular weight 5-AIZ is able to undergo a reversible solid-to-liquid phase transition under irradiation with UV, the same property was not maintained for the polymers. However, changes in thermal properties have been detected, e.g. variation of the glass transition temperature, therefore making the polymerization an interesting route to modulate adhesive properties. The alkyl chain between the polymeric backbone and the chromophore plays a fundamental role in the adhesion properties, and only P-6-AIZ presented higher adhesive strength if compared to 5-AIZ. Under irradiation, the polymer also allows the detachment of joints when heavy loads are applied (which cannot be supported by 5-AIZ), a behavior that can broaden the fields of application of these adhesives. This research could be expanded by performing adhesion tests on different materials and optimizing the procedure for joint preparation that, now, follows a heating protocol. Toward real application, also the possibility to use exclusively visible light for both isomerization processes deserves to be investigated to allow adhesion control in biological materials, where UV light should generally be avoided.



## 4. Experimental Section

**General Materials and Methods:** The reagents used are commercially available (Merck) and were used as received. Details of instruments for material characterization by NMR and UV-vis spectroscopy, GPC, and DSC are reported in Supporting Information.

**Polymer Synthesis:** Synthesis of 5-AIZ and acrylate-based monomers is reported in Supporting Information together with their NMR spectra (Figures S5–S11, Supporting Information). The polymers P-2-AIZ, P-6-AIZ, and P-12-AIZ were obtained by free radical polymerization using AIBN as radical initiator. Briefly, monomer and AIBN (5% in weight) were placed in a Sovirel tube under a nitrogen atmosphere using the Schlenk technique. Anhydrous toluene (1.5 mL mg<sup>-1</sup>) was added, then the mixture was stirred for 18 h at 80 °C. Toluene was removed at reduced pressure and the polymer was purified by precipitation. In particular, the polymer was dissolved again in dichloromethane and dropped in ethanol to cause the precipitation. The solid product was recovered by centrifugation and the procedure was repeated 3 times. <sup>1</sup>H-NMR spectra of the polymers are reported in Figures S12–S14 (Supporting Information).

**Adhesion Strength Characterization:** The adhesion tests were carried out on a dynamometer for uniaxial tensile tests INSTRON 5567. The tests were performed with a tensile speed of 0.5 mm min<sup>-1</sup>. Details on specimen preparation are described in Supporting Information (Figures S1–S3, Supporting Information).

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.;

## Keywords

adhesives, arylazoisoxazoles, photoresponsive polymers, photoswitches, smart materials

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