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Multistage Reversible T_g Photo-Modulation and Hardening of Hydrazone-Containing Polymers

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ABSTRACT: A series of poly(methyl acrylate)- and poly(methyl methacrylate)-based polymers containing bistable hydrazone photoswitch pendants were synthesized by reversible addition-fragmentation chain-transfer polymerization. An increase in the polymers' glass transition temperature (T_g) was observed upon $Z \rightarrow E$ photoisomerization, resulting in the photo-hardening of the polymeric network. This effect was corroborated using nanoindentation measurements that show increase in hardness (18%) and modulus (7.5%) upon photoswitching. The bistability of the switch allowed for the indefinite locking-in of the properties of the *E*-rich polymer at ambient temperature. Moreover, and unlike in other photoswitchable polymers, the photo engineered T_g was sustained even at elevated temperatures of up to 150 °C. This unique property allowed us to dial-in multiple T_g values in the same polymeric material as a function of the hydrazones switch's Z/E isomer ratio, which is unprecedented. The reported strategy presents a new opportunity for the post-synthetic photo-tuning of the physical properties of polymers.

The temperature at which a polymer transitions from a hard and glassy state into a soft rubbery one is termed the glass transition temperature (T_g). This physical property defines the mechanical characteristics of a polymer, how it can be applied, and whether it is re-processable and healable at ambient temperatures.[1,2] In most cases the T_g of a polymer, and hence its associated properties, is difficult to change once the polymer is made. Post-synthetic modification of T_g values typically requires the addition of plasticizers, which, while cheap and effective in reducing the T_g, may compromise other physical properties of the material, reduce its shelf-life, and cause pollution.[3,4] Alternatively, photo-melting,[5-10] induced by the *trans*/*cis* isomerization of azobenzene,[11] can be used to change the T_g value, though this process is far less explored and understood. This strategy is promising for post-synthetic polymer property engineering, and having a better understanding and control over it will result in various applications in photolithography, self-healable devices, actuators, etc.[5-10, 12 - 16] However, there exists a significant drawback in this approach as the metastability of the *cis* form of azobenzene prevents effective locking-in of the photo-engineered T_g values, and hence, properties.[5-10,17]

We recently reported on a new family of bistable photochromic hydrazones[18 - 24] having thermal isomerization (*i.e.*, $E \rightarrow Z$) half-lives of thousands of years.[19] This unusual property in the context of configurational switches was subsequently used in the kinetic trapping of i) different shapes of a liquid-crystalline elastomer strip,[25] and ii) self-assembled helical structures of liquid crystals,[26] and hence their photophysical properties. In both cases, the hydrazone switching resulted in a novel order-to-order transition in the bulk system (vs. the order-to-disorder transition observed in azobenzene-based systems[27-36]). We postulated that the bistability of the hydrazones combined with the order-to-order transition they induce would allow us to design and lock-in innovative polymeric functions and properties that are not possible with the photochromic compounds currently in the literature, especially azobenzene.

Herein, we verify this hypothesis by incorporating the hydrazone photoswitches into polyacrylate- and polymethacrylate-based polymers as side chains and studied how photoisomerization and nature of the polymer affect the T_g value and difference in T_g value (ΔT_g) upon isomerization. We show that the photoswitching results in photo-hardening of the polymers, *i.e.*, the T_g value increases as a function of light irradiation, as opposed to the photo-melting. We ascribe this result to the order-to-order transition that hydrazones induce in bulk material, allowing for stronger interactions between the polymer chains. This behavior is similar to what is observed in heat-stiffening polymer composites.[37 - 39] We also carried structure property analysis to lower the initial T_g value to ambient and

physiologically relevant temperatures to enable their future use in 3D printing[40] or bioimplants.[41] The end goal here is the development of polymers that can be induced to undergo liquid-to-solid phase transitions, with properties that can be precisely controlled and dialed-in. Finally, the bistability of the hydrazone switches allowed us to lock-in different T_g values for the same polymer as a function of irradiation wavelength, *i.e.*, the *Z*/*E* isomer ratio at the photostationary state (PSS), a feat that has not been accomplished before. This photo-hardening strategy presents a new avenue for the post-synthetic manipulation of adaptable, healable,[3-4] and shape-memory[42,43] polymers among other applications.[5-10]

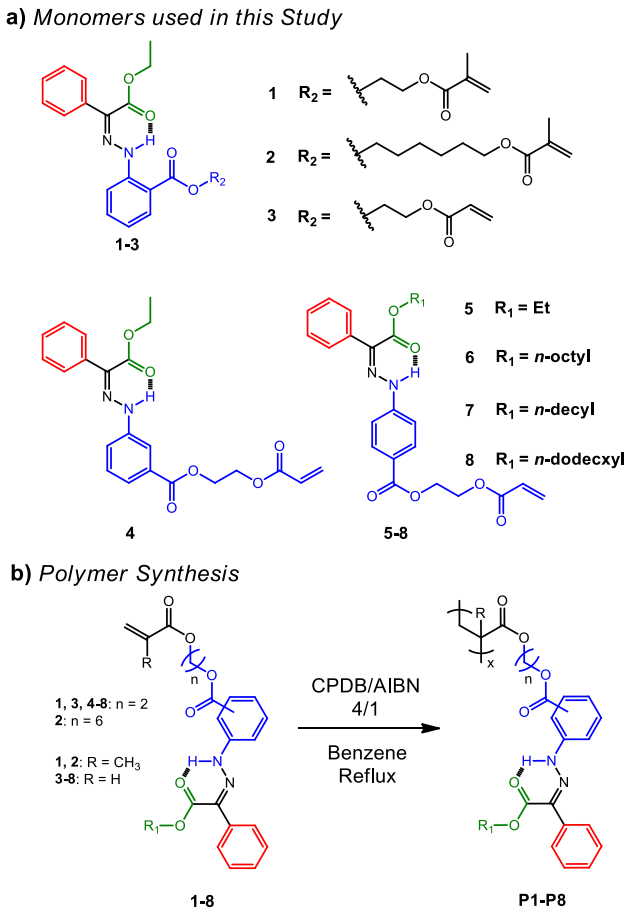

Figure 1. a) The monomers (**1**-**8**) used in this study; and b) Synthesis of polymers **P1**-**P8** via reversible addition-fragmentation chain-transfer polymerization.

The hydrazone monomers **1-8** (Figure 1a) were synthesized in 57-87% yield by following earlier established protocols (Scheme S1 and S3).[25] The hydrazones were characterized using NMR spectroscopy (Figure S2-S17) and ESI mass spectroscopy. The monomers were then (Figure 1b) subjected to reversible addition-fragmentation chain-transfer polymerization conditions with a target degree of polymerization of 150 to give polymers **P1**-**P8** in reasonable yields (41-85%). The polymers were characterized using ^{1}H NMR spectroscopy (Figure S18-S25), and their molecular weights (Figure S1 and Table S1) determined using gel permeation chromatography. The photoswitching properties of the polymers, namely their *Z*/*E* isomerization, in both solution and as thin films, were investigated by UV/vis spectroscopy (Figures S42-S57), and their PSSs at particular wavelengths were determined using ^{1}H NMR spectroscopy. In general, a solution of *Z*-enriched polymer (pristine state, >99 % *Z*) in CD_2Cl_2 was irradiated with 410 nm light until the photostationary state (PSS_{410}) was reached. The PSS_{410} consisted of >94 % of the *E* isomer as observed by ^{1}H NMR spectroscopy. Back-isomerization from the *E* to *Z* isomer was achieved by irradiation of an *E*-enriched solution with 340 nm light to yield 68-83% of the *Z* isomer (Figures S58-S64 and S92). The switching cycle of **P5** (Figure 2a) is given here as an example: the pristine polymer has a maximum absorption (λ_{max}) at 368 nm, which shifts to 338 nm (Figure 2b) upon irradiation with 410 nm light (PSS_{410} consisting of 97% *E* isomer (Figure S83)). The reverse process is induced by irradiation of the *E*-enriched sample with 340 nm light, resulting in a red shift of the λ_{max} to 364 nm, and a PSS_{340} consisting of 83% *Z* isomer.

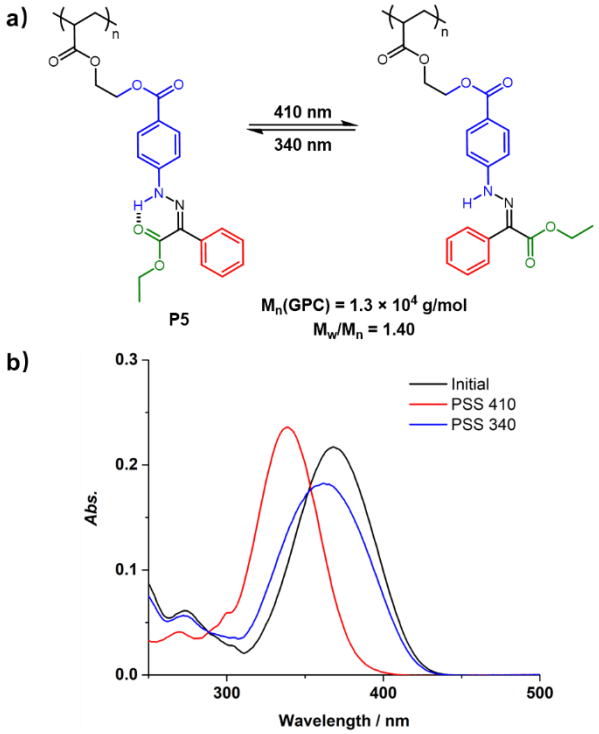

Figure 2. a) Light-activated photoisomerization of **P5**; and b) its UV/Vis spectra in CH_2Cl_2 (4 µg/mL) before (black) and after irradiation with 410 nm light (red), followed by irradiation with 340 nm light (blue).

The T_g values (Table 1), determined from second heating of the polymers, were measured using a heat/cool/heat program cycling (35→150→0→150 °C) at a rate of 10 °C min^{-1}. Samples (~ 6-10 mg) were prepared in aluminum Tzero pans and were either pristine precipitates (>99 % *Z* by ^{1}H NMR) or *E*-enriched (*via* irradiation to PSS). For more details, please see the Supporting Information.

The modularity of the hydrazones enabled us to use structure property analysis to assess how substitution patterns and length of alkyl linkers modulate the T_g and ΔT_g values (Table 1). We started the study with the polymethacrylate polymers **P1** and **P2**. Polymer **P1** has a pristine T_g of

86 °C which increases to 103 °C upon photoisomerization to an *E*-enriched state, resulting in a ΔT_g of 17 °C. Polymer **P2** has a pristine T_g of 41 °C and a ΔT_g of 7 °C, indicating that the lengthening of the alkyl tether attaching the hydrazone to the polymer backbone enhances the free volume in the polymer (lowering T_g) while mitigating the change in free volume upon photoisomerization (lowering ΔT_g). This result suggests that achieving large ΔT_g requires the photoswitch to be in relatively close proximity to the polymer backbone. These preliminary results were considered in the development of hydrazone polymers **P3**-**P8**. The objectives with the design of these polymers were to i) lower the initial T_g value to ambient temperatures, and ii) maximize the ΔT_g value to achieve a wider range of T_g tunability.

Table 1. Summary of the T_g's of P1-P8 before and after isomerization

Polymer	T_g Pristine (°C) (*Z* > 99 %)	T_g PSS_{410} (°C) (*E* %)	ΔT_g (°C) [a]
P1	86	103 (94 %)	+17
P2	41	48 (95 %)	+7
P3	68	79 (95 %)	+11
P4	64	73 (98 %)	+9
P5	75	97 (97 %)	+22
P6	28	42 (98 %)	+14
P7	20	35 (98 %)	+15
P8	21	37 (98 %)	+16

a. $\Delta T_g = T_g$ PSS410 - T_g pristine

With these goals in mind, we switched to a polyacrylate backbone, which inherently has a lower T_g than its polymethacrylate counterpart. **P3** was designed as the polyacrylate equivalent of **P1**, and as expected it has lower pristine and switched (i.e., *E*-enriched) T_g values (68 and 79 °C, respectively). It also, however, has a slightly lower ΔT_g value of 11 °C as opposed to 17 °C for **P1**, indicating that the change in free volume is smaller upon switching. To address this issue and study the effect of the substitution pattern on the polymer properties, we synthesized polymers **P4** and **P5**, which have the acrylate group attached at the *meta* and *para* positions of the stator phenyl group (blue, Figure 1a), respectively, instead of the *ortho* one as in **P1**/**P3**. **P4** yielded a smaller ΔT_g value (9 °C) than **P1**, while **P5** yielded the large ΔT_g value (22 °C) in the whole series. These results indicate that pristine **P5,** which also has the highest T_g value in the acrylate series, has the best molecular packing among the three substitution positions in both pristine and irradiated states.

We retained the *para* substitution pattern in our next designs and moved our focus to lowering the overall T_g value near to ambient temperature. We hypothesized that extending the alkyl chain length attached to the rotor ester group (green, Figure 1a) would add free volume to the polymer, thus lowering the T_g. Hence, polymers **P6** – **P8** were synthesized having octyl, decyl and dodecyl chains attached to the ester group, respectively. This design motif successfully lowered the T_g values of the polymers to the range of 20 to 42 °C (Table 1). Moreover, a relatively large ΔT_g value was consistently maintained ($\Delta T_g \approx +15$ °C) in all three polymers. The difference in T_g of **P7** and **P8** was minimal indicating that we reached the limit of the extended alkyl group approach. More importantly the pristine T_g values of **P6**-**P8** are now at ambient and even physiologically relevant temperatures, indicating that our structure property analysis driven approach for tuning the T_g and ΔT_g values was successful.

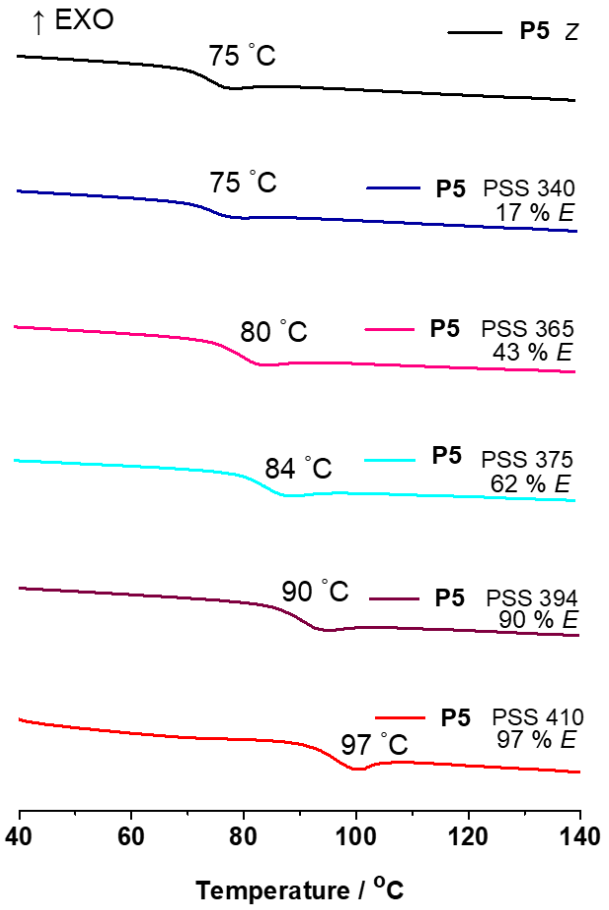

Figure 3. Second cycle DSC curves at the different PSSs of **P5** as obtained by irradiation using wavelengths of light between 340 and 410 nm.

To take full advantage of the intrinsic bistability of the hydrazones, we demonstrated that the T_g of the polymers can be manipulated not only in a binary manner between the *Z* and *E* forms, but also incrementally as a function of wavelength-dependent PSS, *i.e.*, isomer ratio. We decided to use **P5** for this demonstration as it has the largest ΔT_g value. As can be seen in Figure 3 various T_g values between 75 and 97 °C can be locked in by controlling the PSS. The *Z*/*E* isomer ratios at the different PSS values were measured using ^{1}H NMR spectroscopy after irradiation with 340, 365, 375, 394, and 410 nm light. Moving from PSS_{365} to

PSS_{410} steps of 4–7 °C difference in T_g values are obtained, which correspond to the increase in the *E* isomer ratio in the polymer. Moreover, the lack of a difference between the first and second heating cycle traces in the DSC measurements confirms that each of these T_g values can be locked in place (Figure 3). This premise is true even at temperatures as high as 150 °C as no exothermic peak,[6,17] which is indicative of $E \rightarrow Z$ thermal isomerization is observed during the heating cycles (Figure S93). This observation confirms the stability of the *E* isomer within the temperature bounds evaluated and demonstrates the benefit of using bistable hydrazone photoswitches in controlling the T_g values of polymers.[17]

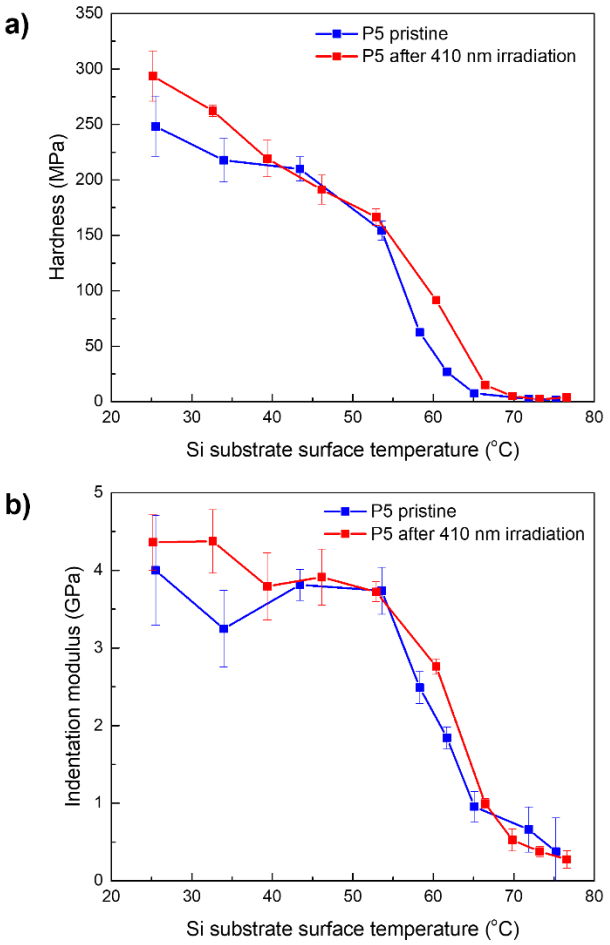

Figure 4. a) Indentation hardness and b) modulus **P5** before and after 410 nm irradiation.

Finally, to verify the improved molecular packing upon $Z \rightarrow E$ photoisomerization,[44] we performed variable-temperature nanoindentation studies[45] to investigate the photo-induced changes in the hardness and modulus of the hydrazone polymers (Figure 4; Details are in the Supporting Information). Alike to the gradual T_g control experiments (Figure 3), **P5** was our polymer of choice for this experiment, rationalized by its large ΔT_g value. Because of the difficulty in measuring the polymer film surface temperature accurately, the temperature of the silicon substrate onto which the films were deposited on has been reported instead. At room temperature, the hardness increases from 248 to 294 MPa, *i.e.*, by 18 %, upon light irradiation. At increased temperature, the hardness systematically decreases and becomes immeasurable once the T_g is reached. While the photo-hardening is more difficult to detect at elevated temperatures, the general trend seems to prevail (Figure 4a). The light-induced change in modulus (from 4 GPa to 4.4 GPa) is less drastic (7.5%) than the change in hardness. We hypothesize that this stems from the elastic influence of the underlying non-photoswitched material within the 30 µm thick polymer film used in these experiments, of which only the top layer can be converted to an *E*-rich PSS. The indentation modulus is more severely influenced by the non-photoconverted film fraction in comparison to hardness for equivalent indentation depths for graded materials and thin films.[46] The nanoindentation results further pinpoint the unique role the bistable hydrazone photoswitches play in the photochemical control over the thermomechanical properties of polymers: both azobenzene-containing amorphous polymers[47-49] and liquid crystalline polymer networks[50-52] typically soften upon photoirradiation. Moreover, in these examples, the *cis*-state of azobenzene prevails for hours at most and in the case of fast-switching azobenzenes, photothermal heating is likely to contribute to the photo-softening. Hence the lock-in of the photoinduced changes, as reported here, is unachievable with azobenzenes.

In conclusion, a correlation between Z/E isomer ratio and T_g value was observed in a series of polyacrylate- and polymethacrylate-based polymers having bistable hydrazone photoswitches as pendants. As the amount of *E* isomer propagates in the polymer, an obvious increase in T_g – up to 22 °C – is observed. We attribute this observation to an increase in order that the hydrazones induce upon $Z \rightarrow E$ photoisomerization, resulting in hitherto unreported photo-hardening effect. Variable-temperature nanoindentation studies show that this effect is taking place on the surface of the bulk material. The bistability of the hydrazones allows for the dialing-in and locking-in of various T_g values as a function of *E* isomer ratio even after several heating cycles. Further analysis of these effects will be geared towards testing whether this behavior can be extended to tuning the physical (*e.g.*, density)[25], or thermal (*e.g.*, thermal conductivity)[53] properties of polymer.

ASSOCIATED CONTENT

Supporting Information. General methods, experimental procedures, NMR spectra, photoisomerization and kinetic studies, DSC measurements. (PDF)
This material is available free of charge via the Internet at http://pubs.acs.org

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Notes

The authors declare no competing financial interest.

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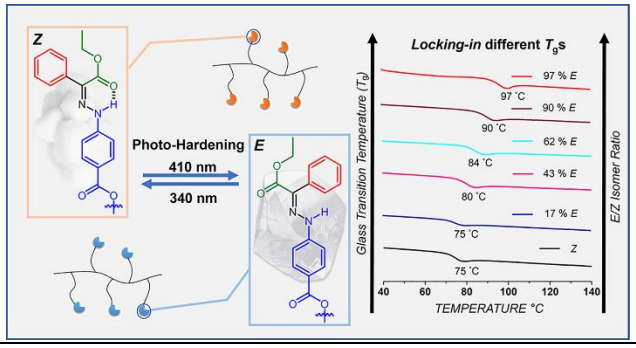
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