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Article

Measurement of the Transition Temperature Governing the Photoinduced Reversible Solid-to-Liquid Transition of Azobenzene-Containing Polymers

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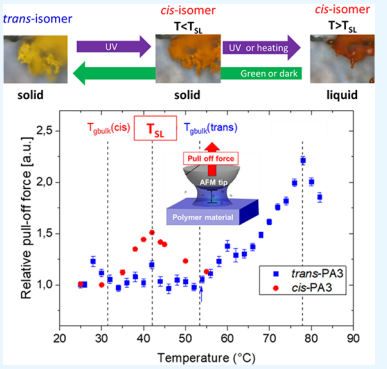
ABSTRACT: The ability to observe photoinduced reversible solid-to-liquid transitions for some polymers bearing photo-active azobenzene groups (azopolymers) has become a competitive research field in materials science and technology because of their potential applications in photocontrolled adhesives, photohealable materials, or soft lithography. Unfortunately, methods to accurately characterize this transition are scarce and mainly qualitative, which limits the understanding of the parameters governing it. In the first part of this paper, we will show that the photoinduced reversible solid-to-liquid transition can be associated to a transition temperature (named T_{SL}). This transition temperature can be accurately measured using a scanning probe microscopy-based method. Then, the measurement of T_{SL} on azopolymers with different chemical structures will allow us to understand why the experimental irradiation conditions to observe the solid-to-liquid transition were different. With the possibility to accurately characterize the photoinduced solid-to-liquid transition, we believe that this work paves the way to the optimization of azopolymer design for a better photocontrol of their mechanical properties.



KEYWORDS: *azobenzene, photoreversible solid-to-liquid transition, azopolymer, AFM, force spectroscopy, nano-dynamic mechanical analysis*

INTRODUCTION

Despite their first synthesis in 1834, it was only in 1937 that Hartley first reported the reversible *trans* (*E*) to *cis* (Z) photoisomerization of azobenzene molecules. Since then, azobenzene molecules have been associated with a multitude of materials to control their properties by light.[1] The photoresponsive characteristics of azomolecule-containing polymers (azopolymers) and their subsequent applications have been intensively studied in the past decades.[2,3] Among them, since its first mention in 2017,[4] the ability to observe a photoreversible solid-to-liquid transition has become a competitive research field in materials science and technology because of its potential applications in photocontrolled adhesives,[3,5] photohealable materials,[4] or soft lithography.[6] Despite numerous publications on the application of the photoreversible solid-to-liquid transitions, to our knowledge, the only proposed mechanism hypothesizes that the photoreversible solid-to-liquid transition is due to a glass temperature variation during the *trans*-to-*cis* photoisomerization.[7] The transition may occur when the temperature of the azopolymer is between the glass transition temperature (*i.e.*, T_g) of the *cis* form and that of the *trans* one.[7] This hypothesis is widely used[1,3,8,9] to explain the properties of azopolymers exhibiting a reversible phase transition. However, since T_g is known to be a transition between a vitreous and a viscoelastic state, it seems probable that T_g *cis* or *trans* is not the real transition temperature governing the solid-to-liquid transition. As a consequence, it is still unclear how the isomerization of azobenzene is coupled with the chain dynamics of azopolymers, which is critical for applications like the photoinduced solid-to-liquid transition.[10] The lack of study probably lies in the fact that the detection of this transition is made in almost all situations in a qualitative way. Indeed, for bulk materials, optical microscopy is usually used.[3,6,11] Although easy to set up, this method is not satisfactory if one wants to accurately determine the transition conditions. Indeed, the "appearance" of droplets under the microscope depends on the objective magnification, the size of the material grain, etc. In addition, the obtained transition time depends on the illumination conditions (*i.e.*, light intensity).[12]

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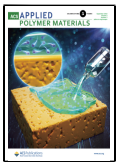


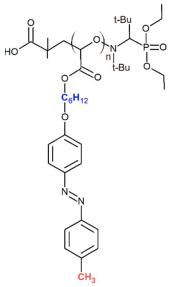
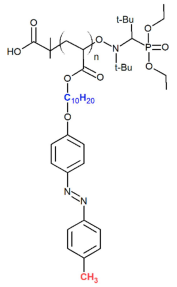
Differential scanning calorimetry (DSC) is the technique of choice for measuring transitions in polymeric materials. Its use for azopolymers allows the measurements of glass transition temperature, *cis*-to-*trans* isomerization, and liquid crystalline phase transitions for both *trans* and *cis* isomers.[4] However, to our knowledge, the solid-to-liquid transition was never detected with this technique. Dynamic mechanical analysis (DMA) has been used to study the viscoelastic properties of azopolymers. Zhang *et al.* mentioned a flow temperature (T_f) "a few degrees higher than the T_g" but no direct relationship was made with the solid-to-liquid transition and the way to determine the value of this flow temperature is imprecise.[11] For many applications such as photohealable coating, reversible adhesive..., the azopolymer has to be used as a coating, but all the abovementioned techniques are not applicable due to the small quantity of available material.

To accurately detect the solid-to-liquid transition of azopolymer coatings, we have developed a new method based on atomic force microscopy (AFM). This method consists in measuring the force needed to detach an AFM tip from the film surface after a contact with a controlled load (*i.e.*, pull-off force). The pull-off force is known to be influenced by the wetting properties of the polymer surface and the polymer viscoelastic properties.[13] We have shown in the past that when performed as a function of the sample temperature, the measurement of the pull-off force allowed the detection of subtle thermomechanical transition in polymer materials such as surface or bulk glass transition temperature and even for polymer thin films with thicknesses down to 7 nm.[14] In this work, we will demonstrate that the solid-to-liquid transition can be associated to a transition temperature called solid-to-liquid temperature (T_{SL}) that can be, for the first time, effectively measured. We also used AFM in the recently nano-dynamic mechanical analysis (nano-DMA) mode to quantify the viscoelastic properties of the studied thin films (see below).

EXPERIMENTAL SECTION

Azopolymer Synthesis. The chemical formula and properties of the two azopolymers (PA3 and PB1) used in this study are presented in Table 1. The azopolymers were synthetized using nitroxide-mediated polymerization (NMP) following the procedure described by Pessoni *et al.*[12] The molecular weight and dispersity values of polymers were measured using size exclusion chromatography (SEC) using THF as an eluent. Number-average molar mass (M_n) values of the polymers were calculated from a calibration derived from polystyrene standards.

Table 1. Chemical Structures and Properties of the PA3 and PB1 Azopolymers

Azopolymer name	PA3	PB1
Formula		
Mn (g/mol)[a] / Tg_{trans} (°C)[b]	5900 / 55	6000 / 54

[a]Measured by SEC. [b]Measured by DSC.

Azopolymer Coatings. Azopolymer thin films were prepared on UV-ozone cleaned microscopic glass slides by drop casting a solution of the azopolymer in CH_2Cl_2 (C = 10 g/L). The films were then dried under vacuum for 24 h. The resulting film thicknesses, measured by AFM after performing a scratch on the film, were close to 1.5 μm.

Differential Scanning Calorimetry. Glass transition temperature (T_g) and nematic-to-isotropic liquid crystalline transition (T_{NI}) were measured using a Differential Scanning Calorimetry (DSC) TA Instrument at 10 °C·min^{-1}. Two cycles of temperature containing a heating part, from −30 to 150 °C, and a cooling one to −30 °C were realized. The value of the T_g of the second cycle was chosen for the T_g of the *trans* isomer. DSC analysis on *cis* isomers was performed following the method described by Zhou *et al.*[4] *Trans* isomers were dissolved in CH_2Cl_2 and then illuminated with UV light under stirring. The solvent was removed under vacuum. ^{1}H NMR analysis of the photoisomerization in CD_2Cl_2 under the same irradiation conditions indicated *trans*-to-*cis* conversion rates above 73%. *Cis* isomers were finally studied by DSC between −30 and 70 °C at 20 °C·min^{-1}. TRIOS software version 5.0. was used for DSC treatment.

Atomic Force Microscopy (AFM). All force−distance AFM measurements were performed with an Agilent 5500 AFM equipped with an environmental chamber. Temperature control was monitored by a PID controller (Lakeshore) connected to a heat stage allowing heating from T = 20 to 250 °C with an accuracy of 0.1 °C. The controller was calibrated with standard fusion point solids (azobenzene (T_f = 68 °C) and acetanilide (T_f = 114.5 °C)). Force−distance curves were recorded using the same CP-FM-SiO-B tip equipped with a silica sphere (R = 3.5 μm) with a spring constant of 0.92 N·m^{-1} (measured by the thermal noise method).[15] A calibrated z-close loop scanner was used to carefully control the indentation depth, and a maximum load (100 nN) was fixed to prevent any critical indentation of the film. All the force−distance curves were conducted at 1 Hz. Pull-off force values were measured from the retraction force−distance curve as the difference between the minimum force and the force at large distances.[14] For each temperature, a 4 × 4 pixel mapping on a 2 × 2 μm^2 surface (with each pixel containing 10 force−distance curves) was averaged to give the pull-off force intensities and uncertainties. Picoview software from Agilent and Atomic J freeware version 2.0[16] were used to analyze and extract pull-off forces and Young's moduli (JKR model, Poisson ratio = 0.33).

Nano-Dynamic Mechanical Analysis. AFM nano-DMA is a recently developed AFM mode to quantify the viscoelastic properties at the nanoscale.[17] It has been performed on a wide range of samples, from biological samples to heterogenous nanocomposites. The "measurement process" is similar to force−distance curve measurement, except that when the tip is in contact with the studied sample, the load is maintained and a frequency modulation is applied to the tip.[18] The difference of phase between the dynamic solicitation and the cantilever deflection, coupled with the force−curves analysis, gives access to local rheological parameters of the sample, such as storage modulus (E'), loss modulus (E''), and damping factor (tan δ).

AFM nano-DMA has two modes. The first is an imaging mode where the frequency modulation is fixed and the tip scans the surface, providing quantitative mapping of viscoelastic properties. The second is a spectroscopic mode where the position of the tip is fixed while a ramp script of discrete frequencies is applied, providing the evolution of rheological properties as a function of those frequencies.

All nano-DMA measurements were performed on a Dimension Icon AFM (Bruker Corp.). Temperature control was monitored by a PID controller (Lakeshore) connected to a heat stage inside the AFM device. The probes used are pre-calibrated RTESPA 300-30 cantilevers from Bruker Corp. with a spring constant around 40 Nm^{-1} and a tip radius of 30 nm.

All measurements were done in spectroscopic mode with frequencies randomly chosen within the range from 1 to 160 Hz. For each temperature, a series of 3 × 3 grid acquisitions over a 1 μm^2

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area were collected. The homogeneity in terms of morphology and mechanical properties (adhesion, Young's modulus, and indentation) of those areas where previously checked by peak force tapping mode. Nanoscope Analysis 3.0 was used to analyze and extract data.

RESULTS AND DISCUSSION

Figure 1 shows the evolution of the normalized pull-off force (*i.e.*, pull-off force measured at temperature T divided by pull-off force at T = 25 °C) with temperature for the PA3 film before (*trans*-PA3) and after UV irradiation (*cis*-PA3). For *trans*-PA3, we observe for T < 50 °C a domain where the pull-off force remains almost constant, indicating no major change of the adhesion properties. From T = 55 °C, an increase in the pull-off force is observed until a maximum value is reached for T_{max} = 78 °C. After this point, the pull-off force decreases progressively. Based on our previous study,[14] the transition temperature between 50 and 55 °C can be associated with the glass temperature (T_g) of the *trans*-PA3, which was confirmed by DSC on the bulk polymer (Figure S1). When a similar experiment is performed on *cis*-PA3, the pull-off force vs temperature curve is translated toward lower temperatures. Indeed, T_g *cis* is measured between 30 and 35 °C and the temperature of maximum pull-off force is measured at T_{max} = 42 °C, which is also confirmed by a small decrease in the heat flow on the DSC chart (Figure S1). The reversibility of the process is demonstrated by performing the *cis* to *trans* back isomerization (*i.e.*, irradiating the *cis*-PA3 with green light or keeping in the dark for 24 h) and by obtaining a pull-off vs temperature curve similar to that of the *trans*-PA3 (Figure S2).

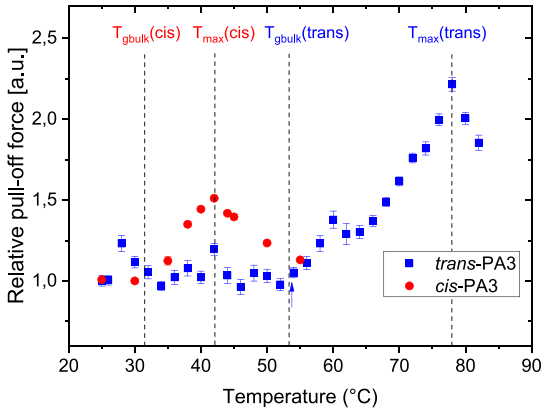

Figure 1. Evolution of the normalized pull-off force as a function of temperature for the PA3 azopolymer before (*trans*-PA3) and after UV irradiation (*cis*-PA3) (λ_{max} = 365 nm, E_e = 300 mW·cm^{-2}, T = 30s).

During the pull-off force measurement, the Young's modulus can also be measured. Figure 2 shows the evolution of the Young modulus with temperature for both *trans*- and *cis*-PA3. Figure 2 is similar to those already observed for azopolymers.[11] At room temperature, both isomers have a modulus close to 0.1 GPa, characteristic of the hard glassy behavior of a polymer with low molecular mass (M_n). As expected, increasing the temperature close to the T_g of the polymer led to a decrease in the Young's modulus. Only for *trans*-PA3 that a short rubber plateau, typical of polymers with entangled or cross-linked chains, can be observed between T = 57 °C and T = 64 °C. Since the theoretical critical entanglement molecular weight of PA3 (M_c = 68 kDa)[19] is much higher than its M_n (5.9 kDa), there is no chain entanglement for PA3.

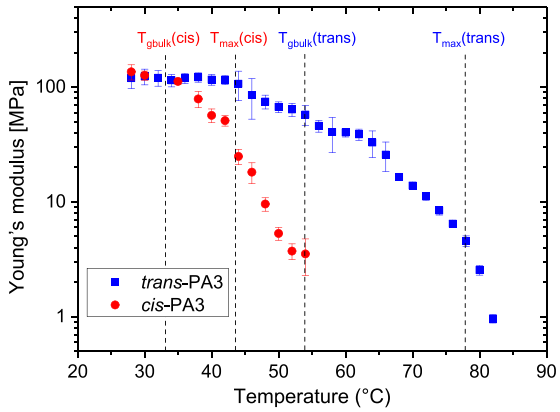

Figure 2. Evolution of the Young's modulus as a function of temperature for the PA3 azopolymer before (*trans*-PA3) and after UV irradiation (*cis*-PA3) (λ_{max} = 365 nm, E_e = 300 mW·cm^{-2}, t = 30 s).

Consequently, the presence of a plateau may reflect the existence of strong interchain interactions for this temperature range. For both polymers, the measured T_{max} by the pull-off force experiment is not clearly visible on the Young's modulus versus temperature curve, indicating that the temperature of maximum adhesion is probably fairly little linked to the elastic properties of the polymer.

The presence of a maximum in the pull-off force vs temperature curve was already observed by our team for thin PS films.[14] Kim *et al.* also detected this maximum for PMMA using a tribometer[20] when undulations, known as Saffman–Taylor instabilities,[21] formed at the periphery of the contact between the rigid probe and the polymer material. The occurrence of Saffman–Taylor instabilities indicates that the polymer material is in a viscous flow state in this temperature range.[22] The shape of the force–distance curves (Figure 3) obtained by AFM below and above T_{max} for *trans*-PA3 confirms the change in the mechanical properties of the material at T_{max}. Indeed, in contrast to the force–distance curves obtained at T = 65 °C, a high hysteresis between the approach and retraction curves, a high pull-off force, and a high separation distance(D) (*i.e.*, the distance between the point of maximum adhesion and the full detachment of the AFM tip) are observed for T = 80 °C. These changes are characteristic of a transition between an elastic behavior and a behavior where energy dissipation is intense, confirming the appearance of a viscous behavior at $T > T_{max}$. For *cis*-PA3, the change of behavior at $T > T_{max}$ is subtler, but it is clearly observable with the increase in D and the rounder shape of the retraction curve.

To confirm the viscoelastic nature of the transition observed at T_{max}, we performed nano-DMA measurements. This recent SPM-based technique[17] makes it possible, by oscillating the sample at a given frequency, to access both the storage modulus (E') and loss modulus (E'') as a function of frequency or temperature. The measurements carried out on *trans*- and *cis*-PA3 show a decrease in both E' and E'' with temperature (Figure S3) as expected for low mass polymers.[23] Tan δ is commonly referred to as the loss factor and conveniently describes the viscoelastic behavior of the material as a ratio between the energy loss and stored during deformation (*i.e.*, E''/E'). Figure 4 shows the evolution of tan δ for *trans*- and *cis*-PA3 as a function of temperature and for three different frequencies. For *trans*-PA3, if a very slight maximum at T = 50 °C (close to T_g) is only observable at a low frequency (*i.e.*, 1

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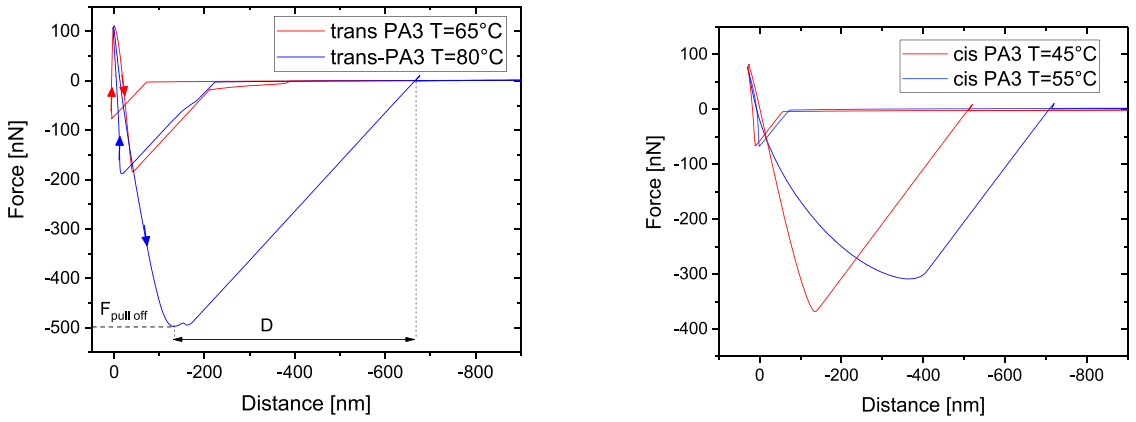

Figure 3. Approach and retraction force−distance curves obtained for the *trans*-PA3 and *cis*-PA3 below and above their respective T_{max}. On the *trans*-PA3, $F_{pull\text{-}off}$ and D indicate, respectively, the intensity of the pull-off force and the distance needed to detach the AFM tip from the surface.

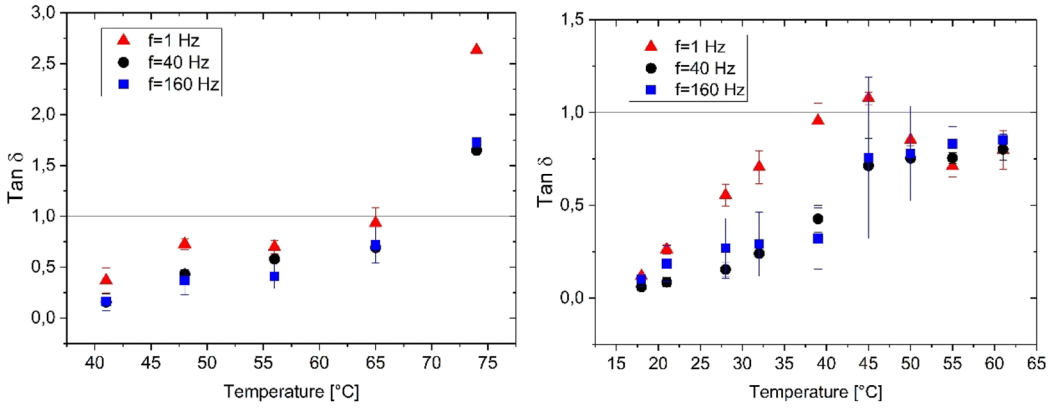

Figure 4. Evolution of tan δ with temperature for *trans*-PA3 (left) and *cis*-PA3 (right) measured by nano-DMA for three frequencies.

Hz), a strong increase in tan δ up to the temperature of 75 °C (close to T_{max}) is observed for all frequencies. The strong increase in tan δ is characteristic of strong dissipation and confirms the viscous character of the material at a temperature very close to T_{max}. Unfortunately, for higher temperatures, the tip−sample interaction was too strong to allow the measurement of the mechanical properties. For *cis*-PA3, no maximum is clearly detected at the temperature corresponding to the T_g (*cis*) but a maximum is observed at a low frequency for $T = T_{max}$. Again, the viscous character of the transition observed at T_{max} is confirmed. The tan δ peak at T_{max} is only visible for frequencies below 50 Hz (Figure 4), which may indicate that the characteristic time of the transition is close above 0.2 ms. Even if the understanding of the link between measurement of pull-off force and measurement of tan δ is beyond the scope of this article, it is interesting to notice the similarity in the shapes of the tan δ curves (*trans*- and *cis*-PA3) obtained with both techniques at a frequency of 1 Hz.

With these results, we can now assert with confidence that the temperature where the maximum pull-off force is detected (T_{max}) for both *trans* and *cis* isomers can be associated to a solid-like to liquid-like transition temperature.

To link the measured T_{max} and the photoinduced solid-to-liquid transition observed in azopolymers, we made an experiment consisting in observing under a microscope small grains (average diameter = 20 μm) of PA3 (Figure 5). At room temperature, without irradiation, pristine yellow solid grains (*trans*-PA3) can be observed. Then, the sample was irradiated on a Peltier stage to keep the sample temperature at 25 °C. As

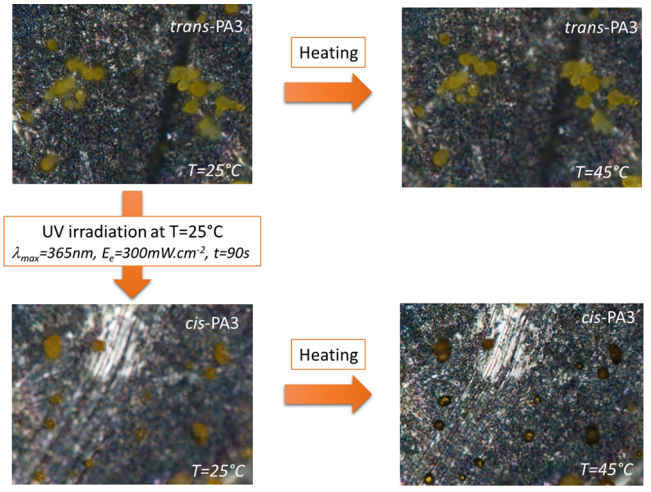

Figure 5. Optical microscopy pictures (350 × 264 μm) of PA3 grains as a function of substrate temperature for *trans*-PA3 and *cis*-PA3.

shown on Figure 5, a change of color (yellow to orange) characteristic of the *trans*-to-*cis* isomerization is observed but the grains remain solid. The solid-to-liquid phase transition is only observed when the grains are heated above $T = T_{max}$(*cis*) = 42 °C.

Our results clearly demonstrate that the reversible photoinduced solid-to-liquid transition interesting for numerous applications can be associated to a transition temperature named T_{SL} that can be measured by AFM as the maximum of

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the pull-off force vs temperature curve of the *cis* isomer ($=T_{max}(cis)$).

Now that we have an accurate method to detect the photoinduced solid-to-liquid transition, we can compare different azopolymers to understand which parameters may influence this transition. We have studied another azopolymer (named PB1) with a similar M_n (6000 g/mol) but with a different chemical composition (Table 1). For PB1, whereas the same para-substituent ($-CH_3$) of the azobenzene group is present, the linker chain possesses a longer length than PA3 ($C_{10}H_{20}$ for PB1 and C_6H_{12} for PA3). AFM pull-off force vs temperature was performed on both *trans*- and *cis*-PB1 (Figure S4), and transition temperatures were extracted from these curves (Table 2).

Table 2. Transition Temperatures (in °C) Measured by AFM for PA3 and PB1 Azopolymers

	PA3		PB1	
	trans	*cis*	*trans*	*cis*
T_g	52 (2)	32 (2)	55 (2)	0 (2)
T_{max}	78 (2)	42 (2) = T_{SL}	70 (2)	15 (2) = T_{SL}

On the one hand, PA3 and PB1 show similar T_g and T_{max} values for the *trans* isomers. On the other hand, a decrease of 30 °C is observed for both $T_g(cis)$ and $T_{max}(cis)$ (*i.e.*, T_{SL}) between PA3 and PB1. These results may indicate that like T_g, the T_{SL} is influenced by the polymer chain dynamics. The decrease in these two temperatures may be explained by the presence of a longer and therefore more flexible linker for PB1, which facilitates the movements of the polymer chains. This effect seems to be more important for the *cis* form than for the *trans* for which the transition temperatures have similar values. These differences probably lie in the fact that the bent *cis*-azomolecule impacts the dynamics of the chains more than the *trans* with its rod-like shape.

The comparison of the two polymers properties allows us to better understand why, despite comparable *trans*-to-*cis* isomerization kinetics,[24] the PA3 photoinduced solid-to-liquid transition needed a longer irradiation duration (45 s against 30 s at 365 nm and 340 mW·cm^{-2}) than PB1 to be observable. Indeed, under UV irradiation, the *trans*-to-*cis* isomerization leads to a modification of the thermomechanical properties of the azopolymer, characterized by a reduction of both T_g and T_{max}. We have seen previously that the photoinduced solid-to-liquid transition occurs only if the sample temperature is above T_{SL} ($T_{max}(cis)$). Since the T_{SL} of PB1 is lower that the T_{SL} of PA3 (Table 1), the T_{SL} of the PA3 sample is reached by increasing the irradiation time. As shown for PA3 on Figure 5, this temperature may have been reached with the same irradiation time of PB1 but with the help of an external heating source. The difference in irradiation duration to reach the photoinduced solid-to-liquid transition can now be simply explained by the difference in T_{SL} value.

CONCLUSIONS

In this work, we have demonstrated that measurement by AFM of the pull-off force vs temperature is an effective way to detect the photoinduced solid-to-liquid transition of azopolymers. Indeed, we have shown that this transition occurs at a temperature called T_{SL} corresponding to the temperature where the pull-off force on the *cis*-azopolymer reaches a maximum value.

By comparing two azopolymers with azobenzene groups with different chemical natures, we have shown that the difference in irradiation duration needed to observe the solid-to-liquid transition can be explained by a difference in T_{SL}. With the possibility to accurately characterize the photoinduced solid-to-liquid transition, we believe that the opportunity is given to the community to study the physical parameters (chemical structure, polymer backbone...) that can influence this transition and thus to be able to design polymers with a T_{SL} compatible with the application domain (*i.e.*, photohealable material, photoreversible adhesive...). The influence of the azopolymer molecular weight and the chemical structure of the azo group on the values of T_g and T_{SL} will be presented in an upcoming paper.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsapm.3c01256.

DSC charts of the PA3-azopolymer, demonstration of the reversibility of the pull-off force vs temperature measurements, evolution of E' and E'' measured by nano-DMA, and evolution of the normalized pull-off force as a function of temperature for PB1-azopolymer (PDF)

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Notes

The authors declare no competing financial interest.

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