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PHOTO-INDUCED MASS TRANSPORT UNDER CONTINUOUS IRRADIATION IN NUCLEOBASE-MODIFIED AZOPOLYMERS

BY

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Abstract. This study investigates the influence of nucleobase functionalization–adenine and thymine–on the photo-induced mass transport behavior, surface-relief grating (SRG) formation, and long-term stability of azobenzene-containing polysiloxane films. Linear azopolysiloxanes with comparable azo-chromophore content but different nucleobase substitution degrees were synthesized and evaluated under identical optical-patterning conditions. The results show that both nucleobase type and substitution degree strongly influence polymer mobility. At comparable substitution levels, adenine-modified films exhibit higher mass-transport efficiency and stronger diffraction intensities. In contrast, thymine-functionalized materials show reduced surface modulation but improved stability, which is attributed to stronger hydrogen-bonding interactions. Film thickness also plays a critical role. Thicker layers enhance SRG amplitude in adenine and highly thymine-rich systems, whereas mobility remains limited in films with low thymine content. Overall, the study highlights a clear trade-off between mobility and stability: adenine enhances modulation and transport efficiency, whereas thymine improves long-term structural stability. These findings provide valuable design guidelines for nucleobase-modified azopolysiloxanes tailored for efficient surface patterning or durable nanostructured surfaces, offering design guidelines for robust, light-responsive polymer systems with tunable nanostructuring.

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1. Introduction

Azobenzene-containing polymers represent one of the most versatile classes of photoresponsive materials due to their ability to undergo reversible trans–cis isomerization, which can be exploited for holographic recording, surface-relief grating (SRG) formation, and nanoscale photofluidization (Hurduc *et al*. 2016; Hendrikx *et al*., 2017; Pawlik *et al*., 2019; Falcione *et al*., 2021; Kozanecka-Szmigiel *et al*., 2022). Under irradiation, the repeated cycling between isomers generates anisotropic molecular mobility that can lead to large-scale mass transport and surface deformation far exceeding molecular dimensions, a phenomenon documented across linear, crosslinked, and supramolecular azo-polymer architectures (Wang *et al*., 2016; Li *et al*., 2021).

Azopolysiloxanes represent a distinct subclass of azo-polymers whose flexible backbones, low glass-transition temperatures, and highly adaptable side-chain architecture render them excellent platforms for laser-driven surface structuring and photo-induced mass transport (Ene *et al*., 2008; Resmeriță *et al*., 2009; Păiuș *et al*., 2012; Hurduc *et al*., 2013, 2016).

Recent studies have expanded this concept further by functionalizing azopolysiloxanes with nucleobases such as adenine or thymine, creating hybrid materials where light-driven azo switching is modulated by hydrogen-bonding interactions (Hurduc *et al*., 2007; Epure *et al*., 2011). The presence of nucleobases introduces programmable H-bonding interactions that can either facilitate or restrict polymer mobility, depending on their strength, directionality, and density of crosslinking (Li *et al*., 2020). Van der Tol et al. (2023) demonstrated that strong hydrogen bonding can even drive light-induced solid ⇄ liquid transitions, revealing that H-bond networks may enhance or suppress photofluidization depending on how they reorganize during irradiation. Also, Zhang et al. (2022) highlighted that azobenzene-terminated polymers can exhibit light-controlled properties influenced by supramolecular interactions, including hydrogen bonding, providing a relevant framework for understanding how H-bond-mediated chain organization affects photo-induced mass transport and surface-relief formation in nucleobase-modified azopolysiloxanes.

Despite extensive studies on azobenzene-functionalized polymers with generic hydrogen-bonding motifs, investigations combining nucleobase-functionalized azopolysiloxanes remain limited. Consequently, the role of nucleobase-mediated hydrogen bonding in light-induced mass transport and photofluidization is still largely unexplored, highlighting the novelty and significance of the present study.

Preliminary investigations on nucleobase-modified azo-polysiloxanes reported distinct photoresponses for adenine- versus thymine-based systems:

adenine-functionalized films tended to show increased surface mobility and decreased roughness, while thymine-modified films exhibited roughness growth and more rigid supramolecular structuring (Hurduc *et al.*, 2007; Enea *et al.*, 2008). These differences were attributed to the higher stability of thymine-based hydrogen-bond networks, which resist breaking under optical excitation, whereas adenine forms weaker and more dynamic associations capable of supporting limited polymer flow. Such findings, together with more recent studies on nucleobase-directed assembly (Sikder *et al.*, 2022), highlight how hydrogen bonding and photoisomerization act cooperatively–or antagonistically–in dictating surface mobility and nanostructuring in these materials.

Despite these insights, a comprehensive evaluation of mass-transport efficiency, nanostructuring potential, and long-term stability in nucleobase-functionalized azopolysiloxanes–especially in relation to nucleobase content and film thickness remains largely unexplored. Given the complex interplay between H-bonding, chain packing, and photoinduced mobility, understanding how these parameters modulate SRG formation is essential for designing reliable light-responsive materials.

The present work addresses this gap by evaluating adenine- and thymine-modified azopolysiloxane films with varying degrees of nucleobase substitution. We investigate their photo-induced mass transport, the dynamics of SRG formation, the influence of film thickness on modulation amplitude, and the dark-state stability of the resulting nanostructures. Through a comparative analysis of samples with different nucleobase substitution levels, we aim to elucidate the competing roles of azobenzene mobility and nucleobase-mediated supramolecular interactions in controlling surface patterning behavior.

Building upon these findings, this study focuses on three main objectives: (A) *the effect of nucleobase type and content,* to determine how adenine and thymine moieties in the polymer side chains influence the efficiency of photo-induced mass transport and surface-relief amplitude; (B) *the influence of polymer film thickness,* to examine the role of film thickness in modulation dynamics, diffraction intensity, and reproducibility of surface patterning; (C) *the temporal stability of nanostructured surfaces:* to evaluate the retention of surface-relief patterns over time under dark conditions, and correlate stability with nucleobase content and polymer chain conformation.

2. Experimental

2.1. Synthesis of azo-polysiloxanes containing nucleobase

Azo-polymers were synthesized through a sequential two-step process, beginning with a polysiloxane bearing chlorobenzyl (CBZ) side groups. During the first stage, a partial substitution with 4-hydroxyazobenzene was performed, resulting in approximately 50–55% of the CBZ groups being replaced. In the subsequent stage, the remaining unreacted CBZ moieties were modified with nucleobases. Details concerning the synthesis and characterization of these polymers were previously reported (Hurduc *et al*., 2007; Herghiligiu and Hurduc, 2022).

2.2. Measurement

Polymer solutions of varying concentrations were prepared in 1,1,2-trichloroethane and spin-coated onto silanized glass substrates, resulting in films with different thicknesses. Film thicknesses were measured using a Bruker Dektak XT profilometer and analyzed with Vision 64 software.

Surface patterning was performed using an interference setup generated by two laser beams incident at an angle θ, creating a sinusoidal intensity modulation along the film, with a spatial period $\Lambda = \lambda_L / (2 \sin \theta)$, where λ_L is the laser wavelength. A 488 nm diode laser was used within the azobenzene absorption band (intensity 180 $mW \cdot cm^{-2}$, beam p-polarized), while the pattern formation was monitored in real time with a He–Ne laser. This procedure has been described in detail previously (Hurduc et al., 2013; Rocha et al., 2014) and was applied here without modifications. The film topography was characterized by atomic force microscopy (AFM) using the Agilent Technologies 5100 AFM operated in tapping mode in air.

3. Results and Discutions

Linear polysiloxanes modified with 4-phenylazophenol and varying amounts of adenine and thymines (15–30% substitution) were synthesized. The polymers exhibited molecular weights (M_n) in the range of 13,000–15,000 and film thicknesses between 300 and 1000 nm. The main characteristics of the synthesized polymers are summarized in Table 1.

Table 1

Charecteristics of the synthetized polymers

Sample code	Substituient 1 Substituent 2	Gs (%)	Mn
CM 19	4-phenilazophenol adenine	53 15	14700
CM 13	4-phenilazophenol thymine	54 15	14600
CM 18	4-phenilazophenol thymine	45 30	14900

While similar samples have previously been investigated regarding surface modifications induced by aqueous environments in nucleobase-modified azo-polysiloxanic films (Herghiligiu and Hurduc, 2022), the present study focuses on their nanostructuring capabilities and long-term stability.

A. Effect of nucleobase type and content

To investigate the effect of nucleobase content in the side chains of azopolysiloxanes on photo-induced mass transport, three samples with similar azo-substitution degrees but different nucleobase contents–15% adenine, 15% thymine, and 30% thymine–were examined at a film thickness of approximately 500 nm.

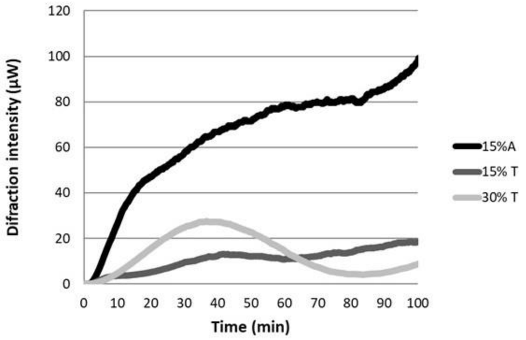


Fig. 1 – Modulation dynamics of the samples with film thickness around 500 nm (A-adenine; T-Thymine).

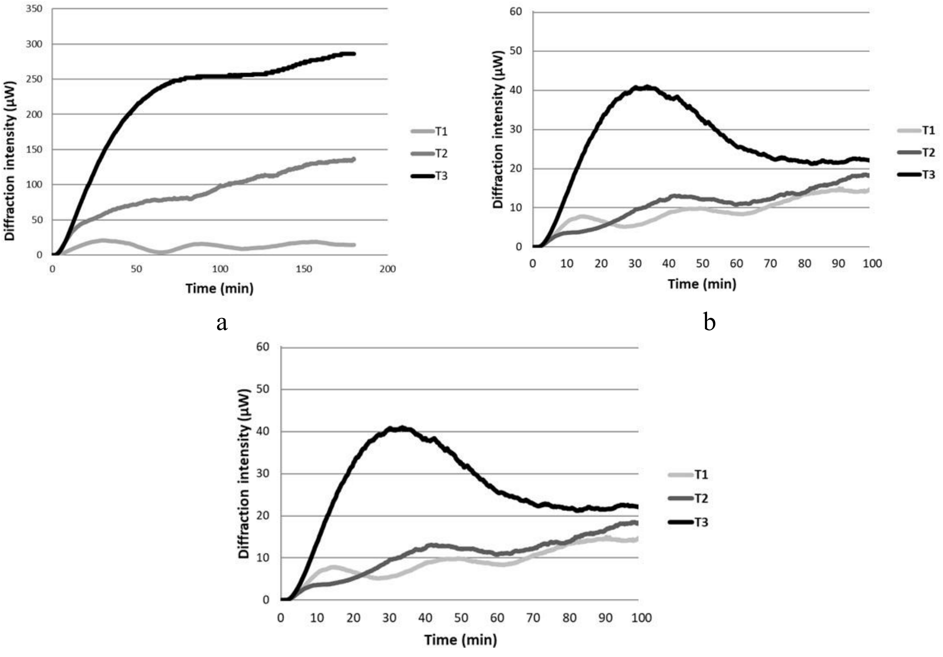
The sample containing 15% adenine exhibited the highest diffraction intensities throughout irradiation, indicating the most efficient mass-transport response among the tested materials. In contrast, the sample with 15% thymine showed substantially lower diffraction intensities, reflecting reduced mass-transport efficiency, likely due to stronger hydrogen-bonding interactions that limit chain mobility. Increasing the thymine content to 30% resulted in a further decrease in modulation efficiency, although the diffraction signal remained more stable over time (Fig. 1). These results demonstrate that both the type and the percentage of nucleobase incorporated in the polymer side chains strongly influence the photo-induced mass transport, with adenine promoting higher mobility and thymine contributing to reduced but more stable responses.

B. Influence of polymer film thickness

Film thickness was evaluated to determine how the height of the polymer layer influences photo-induced mass transport and surface-relief amplitude. Since the magnitude of material displacement depends not only on chromophore mobility but also on the available volume for polymer-chain rearrangement under irradiation, comparing films of different thicknesses allows us to identify thickness-dependent limitations or enhancements in SRG formation.

Analysis of the three tested film-thickness ranges–T1 (300–350 nm), T2 (500–570 nm), and T3 (900–1000 nm)–reveals that thickness has a pronounced and sample-dependent effect on the diffraction-intensity dynamics and thus on SRG formation.

For CM 19 (15% adenine), thicker films (T3) exhibit the fastest and highest diffraction-intensity growth, reaching ~300 μW, indicating highly efficient mass transport (Fig. 2a). Decreasing the thickness to T2 significantly reduces both the growth rate and maximum intensity, and T1 shows only marginal modulation. This suggests that medium-to-thick films (T2 and T3) promote more efficient SRG formation, while thinner films (T1) are less responsive.



a b

c

Fig. 2 – Modulation dynamics of CM 19 (a), CM 13 (b) and CM 18 (c) as a function of film thickness (T1:300–350 nm, T2: 500–570 nm, and T3: 900–1000 nm).

In contrast, CM 13 (15% thymine) shows an overall lower modulation capability across all thicknesses (Fig. 2b). Even in the thicker regime (T3), the diffraction intensity peaks are around 40 μW and subsequently decreases, indicating partial relaxation during inscription. For T1 and T2, the intensities remain below ~15–20 μW, with reduced modulations and slower dynamics.

This reinforces that thymine's stronger hydrogen bonding limits polymer-chain mobility regardless of thickness; thus, increasing thickness further restricts the already hindered mass transport.

Interestingly, when the amount of thymine on the side chain was doubled, contrarily to all information, reinforced until now, the behavior is different from both CM 19 and CM 13. For sample CM 18 (30% thymine) the thickest films (T3) show a diffraction intensity exceeding 400 µW (Fig. 2c). Meanwhile, the thinner films (T1, T2) produce only minimal modulation. This reversal indicates that in highly thymine-rich materials, thicker films accumulate sufficient photo-induced stress to overcome the strong intermolecular interactions, enabling more pronounced material transport. In thin films, these interactions dominate, suppressing flow almost entirely. These results demonstrate that increasing film thickness generally enhances SRG geometry, although the maximum achievable relief also depends on the degree of nucleobase incorporated into the side chain of the azopolysiloxane.

C. Temporal stability of nanostructured surfaces

The temporal stability of the nanostructured surfaces was assessed by monitoring the diffraction intensity over time under dark conditions at 21°C.

For CM 19, containing 15% adenine, the diffraction intensity exhibited a pronounced decreased over time, corresponding to a 50–70% reduction in surface modulation amplitude, depending on the initial relief (Fig. 3). This behavior confirms that adenine-modified films, although highly efficient in mass transport, produce surface patterns that relax more rapidly once irradiation ceases. In contrast, CM 13 (containing 15% thymine) showed significantly improved temporal stability with only ~25% decrease in diffraction intensity after 72 hours, as supported by AFM measurements included in the dataset (Fig. 4). Results confirmed that thymine-based hydrogen bonding stabilizes the laser-induced surface geometry and restricts chain mobility during relaxation, which is consistent with previous findings (Hurduc *et al.*, 2017).

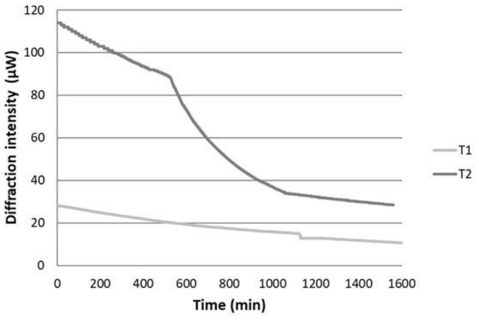
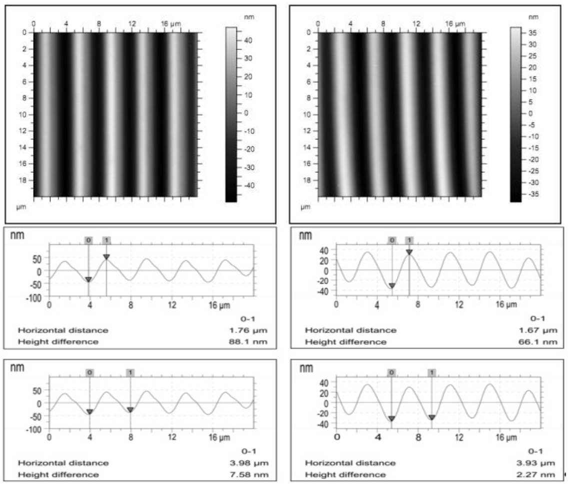


Fig. 3 – Time-dependent stability of the nanostructured surface of sample CM 9.



a b

Fig. 4 – AFM image and surface-relief geometry of sample CM 13 – G1 – 650 nm immediately after irradiation (a) and after 72 hours in dark conditions (b).

Further increasing the thymine substitution to 30% (sample CM 6) resulted in an even greater stability, where nanostructured features remain visible after one month (Fig. 5). These observations demonstrate a strong stabilizing effect associated with higher thymine substitution levels. Overall, these findings demonstrate that both the nucleobase type and its substitution level in the azopolysiloxane significantly influence the dark-state stability of the resulting SRG. Adenine (15%) promotes high mass-transport efficiency but lower temporal stability, whereas thymine (15–30%) confers enhanced structural stability, particularly at higher substitution degrees, thereby supporting long-term preservation of SRG.

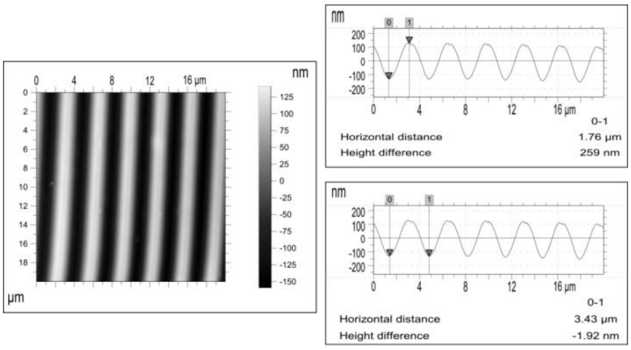


Fig. 5 – AFM image and surface geometry of the nanostructured surface of sample CM 6 (T2) recorded 30 days after irradiation.

4. Conclusions

This study shows that nucleobase type, substitution degree, and film thickness collectively govern the photo-induced mass transport, surface-relief grating (SRG) formation, and stability of azobenzene-containing polysiloxane films. The results highlight a controllable balance between polymer mobility and structural retention mediated by nucleobase-driven supramolecular interactions.

At comparable substitution levels, adenine-functionalized films display higher mass-transport efficiency and stronger diffraction responses, indicating enhanced photo-induced mobility. In contrast, thymine-functionalized materials exhibit reduced modulation efficiency but improved stability of the surface relief, consistent with the formation of stronger hydrogen-bonding networks. Film thickness further modulates these effects: thin layers limit material displacement, while thicker films favor SRG development, particularly enabling highly thymine-rich systems to combine substantial surface modulation with excellent stability.

Overall, the findings demonstrate that the photoresponsive behavior of nucleobase-modified azopolysiloxanes can be finely tuned by adjusting molecular composition and film thickness. This work provides concise design guidelines for developing light-responsive polymer systems optimized either for efficient surface patterning or for durable nanostructured surfaces with long-term stability.

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COMPORTAMENTUL AZOPOLIMERILOR MODIFICAȚI CU NUCLEOBAZE LA IRADIERE ÎN REGIM CONTINUU

(Rezumat)

Acest studiu investighează influența nucleobazelor (adenină și timină) grefate pe lanțurile azopolisiloxanice asupra comportamentului de transport de masă fotoindus, a formării reliefului de suprafață (SRG) și a stabilității pe termen lung a nanostructurilor obținute. Au fost sintetizați și evaluați, în condiții identice de structurare optică, polisiloxani liniari cu azobenzen, având un conținut comparabil de cromofor azo, dar cu grade diferite de substituție cu nucleobaze. Rezultatele arată că atât tipul de nucleobază, cât și gradul de substituție modulează semnificativ mobilitatea polimerului: la substituții comparabile, filmele modificate cu adenină prezintă cea mai ridicată eficiență a transportului de masă și intensități de difracție superioare, în timp ce materialele funcționalizate cu timină prezintă o modulație a suprafeței mai redusă, dar considerabil mai stabilă, datorită interacțiunilor mai puternice de tip legături de hidrogen. Grosimea filmului joacă, de asemenea, un rol esențial, filmele mai groase amplificând amplitudinea SRG în sistemele funcționalizate cu adenină și în cele cu un conținut ridicat de timină. Rezultatele studiului evidențiază un compromis clar între mobilitate și stabilitate: adenina favorizează eficiența procesului de modulare și transport, în timp ce timina contribuie la îmbunătățirea stabilității structurale pe termen lung. Aceste constatări oferă direcții valoroase de proiectare pentru azopolisiloxanii modificați cu nucleobaze, optimizați fie pentru modelarea eficientă a suprafeței, fie pentru obținerea unor structuri nanometrice durabile, contribuind la dezvoltarea unor sisteme polimerice robuste, fotosensibile, cu nanostructurare reglabilă.