Photo-controlled alignment and helical organization in main-chain liquid crystalline alternating polymers

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Abstract
Materials with highly ordered nanoscale structures can translate molecular processes to macroscopic function. Here we report on the photo-controlled organization of achiral alternating copolymers composed of discrete length blocks showing well-defined sub-10 nm morphologies. These alternating copolymers consist of main-chain azobenzene building blocks alternating with discrete oDMS blocks of various precise lengths. Remarkably, we demonstrate the imprinting of a stable helical molecular arrangement in spin-casted thin films by irradiation with circularly polarized light, without chiral dopant or plasticizer required. By following the out-of-equilibrium photo-switching process over irradiation time, the mechanism of molecular reorganization is unraveled and rationalized with the nature of the morphology. Linear photo-organization is preferentially reached with flexible and symmetric cylindrical structures while helical photo-organization is most easily obtained with robust but rotatable lamella structures. These findings suggest that precision in the synthesis and assembly of alternating copolymers can lead to complete control over molecular organization and main-chain motion.

KEYWORDS
azobenzene, discrete oligomers, liquid crystalline copolymer, oligodimethylsiloxane, photo-alignment

1 INTRODUCTION

Translating the molecular transformation of photo-switches into controlled macroscopic function is a topic of major interest for photonic and energy applications.¹,² One of the most explored methods to mediate molecular motion is to embed the photo-active units into the ordered hierarchical assemblies of alternating copolymers or liquid crystal networks.³–⁹ Among photoactive molecules,¹⁰ azobenzenes are widely studied because of their well-known reversible photo-isomerization.¹¹,¹² Upon irradiation with linearly polarized light (LPL), azobenzenes align their transition dipole moment perpendicular to the electric vector (E) of the incoming light by continuous trans-cis-trans photo-isomerization.¹³–¹⁷ Using this technique, assemblies of alternating copolymers containing azobenzene moieties in the side chains can be linearly aligned when irradiated with LPL,¹⁴–¹⁹ and the photo-alignment process has been unraveled in time.²⁰–²² Based on the same principle, irradiation with
Circularly polarized light (CPL) has been used to imprint chiral organization into supramolecular structures.\textsuperscript{23–27} However, next to the plethora of examples reported of photo-responsive polymers with photo-active units in the side-chains, main-chain type azobenzene polymers display the greatest mechanical and electrical properties compared with side-chains azobenzene polymers. This is due to the higher local density of photoactive moieties and the large structural reorganization induced by the cooperative motion of the azobenzenes within the polymer chains. Main-chain azobenzene polymers offer the possibility of tuning the properties of the polymer dramatically using light.\textsuperscript{28–31} Yet, the photo-responsiveness of polymers containing azobenzene as part of the main chain is typically inefficient, particularly in thin film due to the restricted motion of the rigid polymer chains.\textsuperscript{32} To overcome this issue, next to the addition of plasticizers,\textsuperscript{31} flexible polydimethylsiloxane chains have been used to improve the segmental mobility of the main chain and facilitate the molecular reorientation of the chromophores by light.\textsuperscript{33–37} However, for these materials, the nanoscale organization is limited due to the polydispersity of the polydimethylsiloxane chains, which limits the cooperative motion of the photo-switches. Despite these promising results, design strategies to form flexible photo-responsive materials with highly ordered nanostructures are lacking.

Recently, to reach perfectly organized nanoscale structures, block co-oligomers with absence of molar mass dispersity ($D = 1.00$) have been exploited.\textsuperscript{38,39} Block co-oligomers with one block consisting of oligodimethylsiloxane (oDMS) of discrete length have been shown to assemble into well-defined phase-segregated structures with sub-10 nm feature sizes, due to the large Flory–Huggins interaction parameter ($\chi$) and low degrees of polymerization ($N$) of these systems.\textsuperscript{39} The introduction of azobenzene moieties in the rigid block has led to structures for sub-5 nm photopatterning,\textsuperscript{41} with fast thermal transitions\textsuperscript{42} triggered by the high degree of organization of the azobenzene units in spatially ordered domains. Hence, we envision that alternating copolymers combining azobenzene motifs and discrete oDMS blocks will allow the marriage of flexibility and nanoscale properties in polymeric materials.\textsuperscript{43}

Here, we explore the assembly and photo-responsive properties of alternating copolymers (BCPs) composed of alternating azobenzene and discrete oDMS blocks. We use linear polarized light (LPL) and CPL to imprint linear and chiral molecular organization into the bulk of the material. We demonstrate that photo-switching is possible without the use of plasticizer when the polymer is irradiated at a temperature close to its phase transition. Furthermore, we follow in time the out-of-equilibrium process of photo-organization in thin films and discuss on the relation between the nanostructures and the mechanism of photo-switching.

\section{RESULTS AND DISCUSSION}

\subsection{Synthesis, thermal properties and morphological characterization}

The azobenzene-siloxane alternating copolymers (Azo-Si\textsubscript{n}, Figure 1) were synthesized by standard hydrosilylation between olefin-terminated azobenzenes and discrete oDMS dihydrides using Karstedt’s catalyst and were obtained as elastic orange solids (Figure S1). The polymers were characterized by NMR, MALDI-TOF and SEC (Table 1, Figures S1-S14).

The thermal transitions of the polymers were studied using differential scanning calorimetry (DSC) and polarized optical microscopy (POM) (Table 1, Figure 2, Figure S15). Upon heating, all alternating copolymers showed a glass transition ($T_g$) at temperatures below 20°C (Table 2). Sharp endothermic peaks at temperatures between 130 and 160°C ($T_c$) were observed, corresponding to a loss of birefringence in POM. In the cooling run of the DSC thermograms, all alternating copolymers showed a sharp exothermic transition ($T_x$) around 155°C (Azo-Si\textsubscript{8}) and 125°C (Azo-Si\textsubscript{16}, Azo-Si\textsubscript{24}). Going through this transition, the alternating copolymers changed into a birefringent solid. The enthalpic energies ($\Delta H_1 = 3.7–4.8$ kJ m\textsuperscript{ru} and $\Delta H_2 = 2.6–6.1$ kJ m\textsuperscript{ru}) of these transitions are relatively low, which point to order-disorder transitions similar to the clearing point of liquid crystals corresponding to melting of the azobenzenes crystalline domains. Therefore, the materials with discrete siloxane blocks behave like low molecular weight liquid crystals, with the flexible amorphous oDMS moieties acting as a bulk solvent and enabling the rigid azobenzene moieties to organize themselves easily in the solid. In contrast, the alternating copolymer Azo-Si\textsubscript{22} of disperse oDMS length did not show clear liquid

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{Chemical structures of azobenzene-siloxane alternating copolymers Azo-Si\textsubscript{n} (n = 8, 16, 24, and ~22). The disperse block is indicated with a tilde (~).}
\end{figure}
crystalline phase transitions in the DSC thermogram (Table 1, Figure 2) and did not show birefringence in POM (Figure S15d).

Small angle X-ray scattering (SAXS) measurements were conducted to investigate the nature of the structures formed. The morphology of the nanostructures varies depending on the length of oDMS moieties. Azo-Si₈ exhibits a lamellar morphology, Azo-Si₁₆ a hexagonal cylinder morphology, Azo-Si₂₄ a rectangular cylinder morphology and Azo-Si₂₂ a disordered hexagonal cylinder structure (Figure 3, Table S1, Figure S16). The disordered nanostructure of Azo-Si₂₂, together with the absence of an order–disorder transition and birefringence prove that the discrete length of the oDMS moieties is essential for forming well-defined nanoscale morphologies in these materials. The domain space lengths were smaller than 10 nm (Figure 3), giving feature sizes similar to those of low molecular weight liquid crystal molecules.⁴¹ For all alternating copolymers, a peak around 9 nm⁻¹ appears, representative for the amorphous siloxane halo and indicates the self-aggregation of the oDMS moieties in the solid state. For Azo-Si₈, the appearance of scattering peaks in the wide-angle region (q > 7 nm⁻¹) suggests the presence of π-stacking between the azobenzene moieties in the lamellar structure. In addition, variable temperature SAXS experiments confirmed

### Table 1 Molecular characterization and thermal properties of Azo-Siₙ polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Mₙ b [kg Mol⁻¹]</th>
<th>Mₚ b [kg Mol⁻¹]</th>
<th>Mₚ/Mₙ</th>
<th>DPₚ c</th>
<th>T₁ d [°C]</th>
<th>T₂ d [°C]</th>
<th>Tg d [°C]</th>
<th>ΔH₁ d [kJ mru⁻¹]</th>
<th>ΔH₂ d [kJ mru⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Azo-Si₈</td>
<td>30.5</td>
<td>104.6</td>
<td>3.42</td>
<td>92</td>
<td>158</td>
<td>154</td>
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<td>6.1</td>
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<tr>
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<td>315.6</td>
<td>6.76</td>
<td>182</td>
<td>132</td>
<td>122</td>
<td>3.8</td>
<td>3.7</td>
<td>2.6</td>
</tr>
<tr>
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<td>97.9</td>
<td>3.47</td>
<td>42</td>
<td>129</td>
<td>125</td>
<td>17.9</td>
<td>4.0</td>
<td>3.4</td>
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<td>36.5</td>
<td>167.6</td>
<td>5.42</td>
<td>77</td>
<td>n.o.</td>
<td>n.o.</td>
<td>14.0</td>
<td>n.o.</td>
<td>n.o.</td>
</tr>
</tbody>
</table>

aPolymers Azo-Siₙ as depicted in Scheme 1.
bNumber-average molecular weight (Mₙ) and weight-average molecular weight (Mₚ) were determined with SEC.
cAverage degree of polymerization.
dOrder–disorder temperature measured while heating (T₁), disorder–order temperature measured while cooling (T₂), glass transition temperature measured while heating (Tg), enthalpy change around T₁ measured while heating (ΔH₁) and enthalpy change around T₂ measured while cooling (ΔH₂) were determined with DSC using a heating and cooling rate of 10 K min⁻¹. Enthalpic values are per mole of repeating unit (mru) in order to highlight the discrete character of the blocks. n.o.: not observed.

**Figure 2** Differential scanning calorimetry traces (second heating and cooling run) of Azo-Siₙ polymers. A temperature ramp of 10 K min⁻¹ was used. Exothermic heat flows have a positive value.

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the morphological changes revealed by the DSC measurements (Figure S16). Upon heating above the order-disorder transition $T_g$, the profile changes from sharp reflection peaks at room temperature to a broad scattering peak at $160$–$200^\circ$C ($q^*$), showing an isotropization of the ordered morphology. Moreover, for Azo-Si$_8$, the scattering peak indicating the π-stacking between the azobenzene moieties disappears. These results point to a weakening of the azobenzene interaction and to the formation of a disordered structure above $T_g$. The broad peak that remains can be assigned to the correlation hole effect. Similarly, upon cooling below $T_g$, the profiles change from sharp reflection peaks at room temperature to broad scattering peak at $-30^\circ$C, indicating that the structures become less ordered in the glassy state, that is, below $T_g$. Most likely, this is due to the competition between phase segregation and "freezing" of the azobenzene units in the main chain of the polymer, resulting in a distorted structure.

To analyze the conformation of the azobenzenes units in the alternating copolymers, UV experiments were performed. In dichloromethane solution, Azo-Si$_8$ exhibits a maximum absorption at $333$ nm corresponding to the π−π* transition absorption band of the azobenzene trans isomers (Figure S17). On spin-casted thin films, the maximum absorption of Azo-Si$_8$ red-shifts to $335$ nm, indicating the formation of a J-type aggregated structure of the azobenzenes in the lamellar morphology. On the contrary, for thin films of Azo-Si$_{16}$ and Azo-Si$_{24}$, the absorption peak shows a blue shift to $330$ nm, indicating the formation of an H-type aggregated structure in the cylinder morphology. Besides, Azo-Si$_{12,22}$ thin films show a smaller blue shift, presumably due to the existence of less-ordered H-type assemblies.

### 2.2 Reversible supramolecular organization induced by light

The resemblance of these materials to low molecular weight liquid-crystal behavior prompted us to investigate their photo-induced organization. We explored the linear photo-orientation of the alternating copolymers with LPL. Spin-casted thin films of Azo-Si$_n$ polymers were illuminated with $405$ nm LPL while cooling from the isotropic to the ordered phase (about $5$ K min$^{-1}$). Under the POM, an LPL-irradiated Azo-Si$_{16}$ film showed brighter birefringence and larger domain sizes than before irradiation (Figures S19–S20). The LD spectra of the obtained films exhibit a strong signal centred at $330$ nm (Figure 4). In polarized UV–vis spectroscopy measurements, an LPL-irradiated Azo-Si$_{16}$ thin film showed highly anisotropic absorbance with a dichroic ratio ($A_{⊥}/A_{∥}$) of $5.18$ and an order-parameter ($((A_{⊥}-A_{∥})/(A_{⊥}+2A_{∥}))$ of $0.58$ at $350$ nm. Maximum absorbance is observed perpendicular to $E$ of the LPL, indicating an orthogonal orientation of the azobenzene moieties to $E$ (Figure S21).

To further confirm the anisotropic organization of the LPL-aligned thin films, grazing-incidence small-angle scattering (GISAXS) measurements were carried out. The results confirm the appearance of highly ordered Azo-Si$_{16}$ cylinders oriented parallel on the glass substrate, indicated by the bright spots at $q = \pm 1.6$ nm$^{-1}$ on the 2D pattern (Figure 5). Hence, the Azo-Si$_{16}$ nanostructured morphology in thin film is identical to the bulk nanostructure (Figure S3). The presence of a single spot in the 2D pattern when the sample is measured parallel to $E$ of the LPL indicates the orientation of the cylinders perpendicular to $E$ of the LPL (Figure 5(b)). In addition, the appearance of bright spots at azimuthal angles of $-30^\circ$ and $-150^\circ$ when the incident X-ray beam was oriented perpendicular to $E$ of the LPL confirms the orientation of the cylinders perpendicular to $E$ of the LPL (Figure 5(c)).

We then continued with CPL irradiation to imprint helical organization in the copolymer backbone. Initially, spin-casted thin films of achiral alternating copolymers were CD silent. They were irradiated with $405$ nm L-CPL (left-handed CPL) while cooling from the isotropic phase to the phase transition temperature $T_g$ for $1$ h. A positive CD signal of about $300$ mdeg was measured at $348$ nm.

![Figure 3](image-url)
for *Azo-Si*$_8$ and of about 100 mdeg at around 344 nm for *Azo-Si*$_{16}$ and *Azo-Si*$_{24}$ and no LD signal was observed, suggesting that a chiral supramolecular structure was induced by light (Figure 4, Figure S22). Irradiation with R-CPL (right-handed CPL) gave the mirror image CD signal, confirming that opposite CPL produced enantiomeric supramolecular structures. For *Azo-Si*$_8$ and *Azo-Si*$_{24}$, the differences of CD intensities between R-CPL and L-CPL irradiation are attributed to different starting morphologies after spin-casting of the samples. The dissymmetry factor for absorption of left and right CPL ($g_{abs} = 2 \times (A_L - A_R)/(A_L + A_R)$) in an *Azo-Si*$_8$ film
at 350 nm was about 0.03. Besides, a film-thickness dependence of $g_{\text{abs}}$ was observed, which suggests a cholesteric molecular arrangement of the polymer chains in the thin film.\textsuperscript{45} The changes of $g_{\text{abs}}$ with the thickness vary depending on the morphology of Azo-Si\textsubscript{16} (Figure S23). An increase in $g_{\text{abs}}$ as a function of film thickness is observed, and at thickness below 200 nm, only the Azo-Si\textsubscript{16} film presents a $g_{\text{abs}}$ value. This might be due to the difference in the pitch of the photo-induced helical structures (lamella, hexagonal and rectangular cylinders) and indicate that Azo-Si\textsubscript{16} film can form a helical structure of shorter pitch than Azo-Si\textsubscript{8} and Azo-Si\textsubscript{24}.

To confirm the structures formed, the samples were further analyzed by UV spectroscopy and GiSAXS. In GiSAXS measurements, a CPL-irradiated Azo-Si\textsubscript{16} thin film showed weaker scattering at azimuthal angles $\sim 30^\circ$ and $\sim 150^\circ$ than non-irradiated film (Figure 5(d)). In addition, in the UV spectrum, a decrease of the maximum absorbance of the films was observed after CPL irradiation, while it was not observed after LPL irradiation (Figure S24). Some azobenzene moieties reorient parallel to the direction of incident light with the helical structures out-of-plane.\textsuperscript{19,46,47}

Interestingly, the disperse alternating copolymer Azo-Si\textsubscript{22} remains CD silent after CPL irradiation, while all alternating copolymers exhibit a CD signal using the same conditions of irradiation (Figure 4(d)). Therefore, we conclude that the existence of highly organized structures is essential to produce supramolecular photo-induced chirality, and that the discrete design of the oDMS block plays a crucial role in the organization process.

The ordered structures formed by light irradiation display an excellent stability, with the LD and CD spectra showing no change after storage of the thin films for 1 month at room temperature in the dark (Figure S25). Moreover, the structures are erasable by thermal treatment at temperatures above $T_1$ for 30 min and/or photo-isomerization of the azobenzene moieties (Figure 4(c), (f), Figure S18).

Finally, we also demonstrated the possibility of reversibly switching the orientation and chirality of the supramolecular structures by alternating LPL and CPL irradiation, without the addition of plasticizing agents. Thin films of Azo-Si\textsubscript{16} display switching of their LD signal upon irradiation with perpendicular LPL, with or without intermediate erasing step (heating with UV irradiation), indicating a successive reorientation of the cylinders perpendicular to $E$ of light (Figure 6(a-b)). Furthermore, switching between the two enantiomeric supramolecular structures of Azo-Si\textsubscript{8} by alternating irradiation with left and right CPL was observed (Figure 6(c)).

In contrast to the LPL switching, helical inversion required first erasing of the chirality by irradiation with UV light (Figure 6(d)). This can be due to photobleaching as a result of reorientation of the azobenzene chromophores toward the direction of light upon CPL irradiation.\textsuperscript{46,47}
2.3 | In-situ observation of molecular alignment during photo-irradiation in thin films

To elucidate the mechanism of photo-switching and how the morphologies influence the effect of light, we performed in-situ measurements in thin films by tracking the change in depolarization of the transmitted light over heating and cooling during irradiation. These measurements are different from those reported in Figure 6. In these investigations, the temperature of the films was controlled by a hot-stage and the degree of polarization of the transmitted light was measured every 30 min while the film was continuously irradiated with fully polarized light, either LPL or CPL (Figure S26). The thin films are initially aligned by LPL with vertical E direction and the measurements start after rotation of the polarizer at 45°/C14 counterclockwise viewed from the light source. The depolarization of transmitted light, \( \Delta g_{\text{trans}} = g_{\text{trans}} - g_{\text{trans,initial}} \), is reported in Figure 7. This differential describes the change in the degree of polarization of the transmitted LPL or CPL upon changing the temperature of the polymer film. Here \( g_{\text{trans,initial}} \) is the dissymmetry factor of the transmitted light at the start of the temperature ramp. Because the incident light is fully polarized, \( g_{\text{trans,initial}} \) is a large number typically close to 1 and much larger than the dissymmetry factor \( g_{\text{CD}} \) from a conventional CD measurement using unpolarized incoming light. In our experiment, a structural change in the polymer film brought about by the intense, polarized illumination and the change in temperature will lead to a variation of \( \Delta g_{\text{trans}} \) away from zero. An increase in \( \Delta g_{\text{trans}} \) implies less depolarization of transmitted light, while a decrease in \( \Delta g_{\text{trans}} \) means further depolarization of transmitted light. The value of \( g_{\text{trans-LPL}} \) is maximum when \( E \) of transmitted LPL is perpendicular to the direction of the polarizer (45°/C14 counterclockwise from the vertical direction viewed from the light source), indicating that the azobenzenes aligned with the polarizer.

Upon LPL irradiation in the heating process, \textit{Azo-Si}_{16} and \textit{Azo-Si}_{24} showed large changes in polarization \( \Delta g_{\text{trans-LPL}} \) around the order–disorder transition temperature \( T_{1} \), indicating that switching occurs in a narrow temperature range around the phase transition. At this temperature, the phase transforms from a cylindrical morphology with well-ordered, liquid crystalline azobenzene domains to an amorphous segregated state.
FIGURE 7  Changes in g-value of transmitted light upon cooling under continuous irradiation (LPL irradiation in a-1, b-1, c-1 and CPL irradiation in a-2, b-2, c-2) and DSC traces of Azo-Si₈ polymers. (a-1,b-1,c-1) before the measurement, all the films were aligned by LPL irradiation with 405 nm LED (8 mW/cm²) in the cooling from (a-1) 210°C or (b-1,c-1) 180°C to 100°C for 20 min to begin with a linearly aligned state. After the alignment, the intensity of incident LPL was reduced to ~0.8 mW/cm², temperature change was started, the E direction of incident LPL was switched 45° counterclockwise from the direction for initial linear alignment and the measurement was started. (a-2,b-2,c-2) before the measurement, all the films were thermally annealed at (a-2) 210°C or (b-2,c-2) 180°C for 30 min and cooled to 100°C for 10 min to begin with a non-aligned state. After the annealing, temperature change and R-CPL irradiation were started, and the measurement was started. The experiments were carried out by continuous irradiation with 405 nm LED (~0.8 mW/cm²) and a temperature ramp of 5 K min⁻¹ was used. The various curves in a-1, b-1, c-1, a-2, b-2, c-2 represent different monitoring wavelengths between 400–414 nm, and blue lines and red curves represent the data of 400 nm and 414 nm, respectively. The thickness of films were (a-1) ~150 nm, (b-1) ~100 nm, (c-1) ~100 nm, (a-2) ~760 nm, (b-2) ~810 nm, and (c-2) ~930 nm. (a-3,b-3,c-3) DSC traces (second heating and cooling run). A temperature ramp of 10 K min⁻¹ was used. Exothermic heat flows have a positive value [Color figure can be viewed at wileyonlinelibrary.com]
The large polarization observed indicates that the azobenzene moieties have enough mobility at $T_1$ to reorient orthogonal to $E$ of the incident LPL (Figure 7(a-1,7), (b-1,7), (b-1,7)). The smallest changes of $\Delta g_{\text{trans-LPL}}$ are observed in the Azo-Si$_{16}$ film, suggesting that the reorientation of the azobenzene moieties in the lamellar morphology is limited due to the $\pi$-stacking that was observed in the SAXS profile (Figure 3). Intriguingly, the jumps of $\Delta g_{\text{trans-LPL}}$ between heating (at $T_1$) and cooling (at $T_2$) have different intensities (Figure 7(a-1,7), (b-1,7), (c-1,7)). Azo-Si$_8$ and Azo-Si$_{34}$ showed comparable depolarization between $T_1$ and $T_2$ with large jumps, suggesting reorientation of the azobenzene moieties to accommodate the formation of the ordered structures and competition between the crystallization of the azobenzenes and the siloxane phase segregation (Figure 7(a-1,7), (c-1,7)). In contrast, Azo-Si$_{16}$ only showed a slight change of depolarization around $T_2$ (Figure 7(b-1,7)), which could indicate that the symmetry of the hexagonal cylindrical morphology of Azo-Si$_{16}$ leads to smaller reorientation of the chromophores during the formation of the segregated structures. In the hexagonal symmetric structure, the chromophores can rotate without structural changes, and hence a better linear alignment of the structures is obtained upon light irradiation. Moreover, this result explains the large LD signal of Azo-Si$_{16}$ compared with Azo-Si$_8$ and Azo-Si$_{34}$ (Figure 4).

Upon CPL irradiation during the heating process, Azo-Si$_8$ showed relatively larger polarization changes at $T_1$ compared with Azo-Si$_{16}$ and Azo-Si$_{34}$. Moreover, the change started below $T_1$ (at $130^\circ$C with CPL instead of $160^\circ$C with LPL), indicating that the lamellae of Azo-Si$_8$ require less energy to reorient with CPL irradiation than with LPL irradiation (Figure 7(A-1,7), (a-2,7)). This can be rationalized by the lamellar morphology of Azo-Si$_8$, with the oDMS layer offering better mobility to allow chiral twisting between the lamellae. Besides, Azo-Si$_{16}$ showed almost no changes in polarization during the heating process, while Azo-Si$_{34}$ showed moderate changes, suggesting that the helical arrangement of the azobenzenes in the phase-segregated cylinders is more difficult to reach, especially in the symmetric structure of Azo-Si$_{16}$. In the cooling process from the isotropic phase, all Azo-Si$_n$ alternating copolymers showed depolarization, suggesting that these helical photo-organized structures are easily disturbed by ordering of the azobenzenes domains. It is noteworthy that Azo-Si$_8$ showed a phase transition at higher temperatures than $T_1$ in the cooling process under polarized light irradiation (about $20^\circ$C, Figure 7(a)). This shift can be attributed to the preorganization of azobenzenes in the isotropic phase induced by light.

To complete the analysis and rationalize the CD spectra obtained with CPL irradiation (Figure 4), we also performed in-situ kinetic measurements under the conditions of the photo-induced chirality experiments (in part 2.2). The measurements were performed with the same protocol (see SI), that is, the films are irradiated at a temperature just below $T_1$, cooled to $100^\circ$C at a rate of $5\text{ K min}^{-1}$ and removed from the hotplate at $100^\circ$C for measurements (Figure S27). When the samples are heated just below $T_1$ (phase [i] in Figure S27), all three polymers Azo-Si$_n$ show some change of polarization, indicative of a change in orientation of the azobenzenes by light. While cooling to $100^\circ$C (phase [ii] in Figure S27), Azo-Si$_{16}$ and Azo-Si$_{34}$ showed a significant increase in depolarization that is stable over time, suggesting that any photo-induced helical organization induced at high temperature is easily disturbed by ordering of the azobenzene domains induced by lowering of $T$. In contrast, Azo-Si$_8$ showed an increase in polarization while cooling to $100^\circ$C, indicating formation of helical structures due to twisting of subdomains. Over long-time irradiation (phase [iii] in Figure S27), the polarization decreases presumably due to destabilization of the helical arrangement by the $\pi$-stacking of the azobenzenes. Overall, these results provide an indication as to why Azo-Si$_8$ displays a larger induced CD signal than Azo-Si$_{16}$ and Azo-Si$_{34}$ (Figure 4). The lamellar structure of Azo-Si$_8$ films seems to better facilitate imprinting of helical organization in comparison to the cylindrical structures.

3 | CONCLUSION

We have explored the assembly of azobenzene-oDMS alternating copolymers into photo-switchable materials with well-ordered nano-morphologies. By varying the length of the discrete siloxane blocks, the phase morphology varies from lamellar to hexagonal and rectangular cylinders with sub-10 nm features sizes. These alternating copolymers composed of discrete blocks exhibit liquid crystalline properties similar to low molecular weight liquid crystal molecules. Upon photoisomerization of the azobenzenes with LPL or CPL around the phase transition, the materials imprint the polarization of light into their nanoscale organization. Stable cholesteric-like molecular arrangements could be obtained without the use of chiral dopant or plasticizers, and easily erased by heat. By using a disperse oDMS block in the copolymer, no photo-induced chiroptical property was observed, showing that the formation of highly ordered structures generated by the discrete siloxane moieties plays a crucial role in the supramolecular helical organization. By tracking the depolarization of the transmitted light during
irradiation, we directly observed the imprinting of molecular alignment and chirality in-situ in the thin films. Factors such as symmetry of the morphology and molecular interaction within the structures were found to be critical to explain the mechanism of photo-switching. These results unravel the structure–property relationship between mechanisms of photo-switching and morphologies of the copolymer assembly. With this study, we demonstrate that alternating copolymers containing oDMSs of discrete length have great potential to produce unique dynamic photo-switching materials.

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

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REFERENCES


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