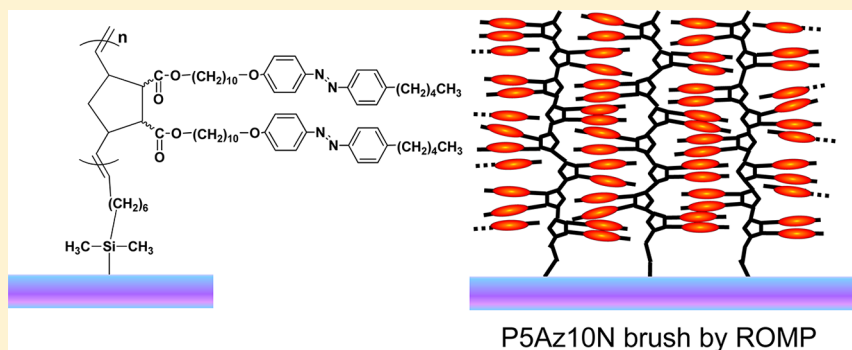


High-Density Liquid-Crystalline Azobenzene Polymer Brush Attained by Surface-Initiated Ring-Opening Metathesis Polymerization

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S Supporting Information



ABSTRACT: High-density polynorbornene azobenzene liquid-crystalline brushes are synthesized on quartz substrates by surface-initiated ring-opening metathesis polymerization (SI-ROMP) using Grubbs third-generation catalyst. The grafting process is controlled over the thickness of the brush from a solid-supported substrate in a stoichiometric manner. A highly ordered liquid-crystal arrangement was formed for such brushes as revealed by spectroscopic measurements and grazing angle X-ray diffraction analysis. Marked features of this method in the structure and photoalignment behavior are unveiled by comparison with brushes made by surface-initiated atom-transfer radical polymerization (SI-ATRP).

■ INTRODUCTION

The creation of functional surfaces and/or stimuli-responsive polymer surfaces controlled by light as an external stimulus has garnered considerable interest from the viewpoint of scientific developments such as the photocontrol of wettability,^{1–3} adsorption,⁴ microfluidics,⁵ biocompatibility,⁶ liquid-crystal alignment,^{7,8} and liquid motions.^{9,10} Solid-supported grafted polymer films, particularly polymer brushes, provide such types of fascinating stimuli-responsive surfaces.

To prepare polymer brushes possessing a sufficient graft density, the surface-initiated (SI) (grafting-from) strategy has been extensively utilized. In this regard, controlled radical polymerization techniques such as atom-transfer radical polymerization (ATRP), reversible addition–fragmentation chain transfer (RAFT), nitroxide-mediated polymerization (NMP), and photoiniferter-mediated polymerization (PIMP) are mostly conducted.¹¹ Among them, SI-ATRP has been proven to be a favorable technique for synthesizing polymer brushes because of its chemical versatility, compatibility with a large assortment of monomers and functional groups, and tolerance to a relatively high degree of impurities.^{12–14}

During the last two decades, the synthesis community has witnessed the power of olefin metathesis reactions. Various olefin metathesis polymerization methods, such as ring-opening metathesis polymerization (ROMP),^{15–18} acyclic diene meta-

thesis (ADMET) polymerization,¹⁹ and cyclopolymerization,^{20,21} have been widely used to synthesize various types of polymers. Among them, ROMP is a robust and efficient synthesis strategy for the living polymerization of cyclic olefins by using metal alkylidene initiators.^{22–27} Numerous reports on olefin metathesis reactions by ROMP are available for synthesizing well-defined block copolymers,^{28,29} patterned polymer surfaces,³⁰ block brush copolymers,³¹ end-function-alized polymers,³² dielectric layers,³³ and various other polymeric materials with complex architectures.^{17,18,25} Thus, SI-ROMP has been widely recognized as a versatile platform for the surface grafting of polymers.^{1,17,30,34–36} However, no attempt has been made to synthesize liquid-crystalline (LC) polymer brush films by SI-ROMP. In this letter, we show that the SI-ROMP technique is of particular value for preparing a high-density LC azobenzene (Az) brush film, providing stoichiometric control over the thickness of the grafting chain length. To manifest the features of the brushes by SI-ROMP, the LC structures and light-responding properties are compared to those of the relevant brushes prepared by the SI-ATRP technique.^{37,38} This work unveils the distinct features and

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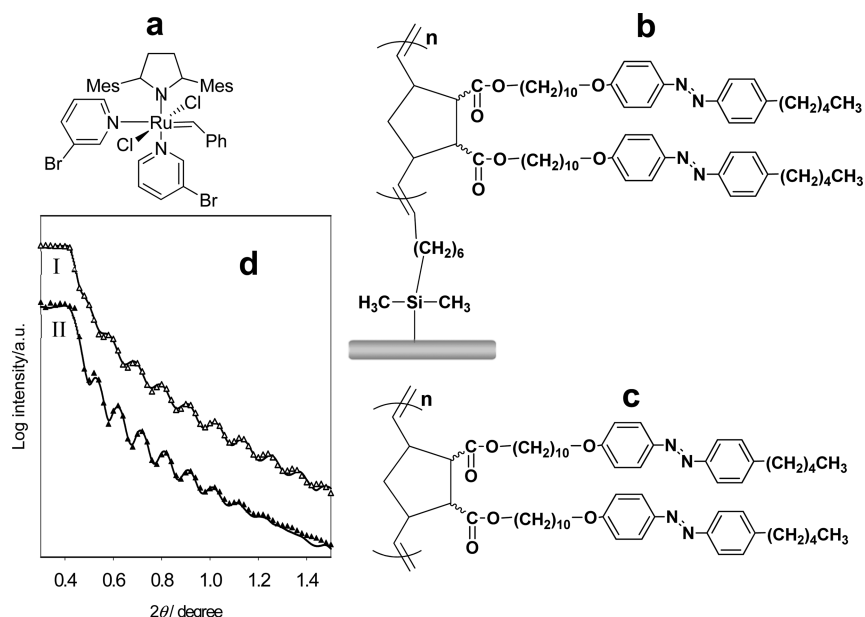


Figure 1. Molecular formula of (a) a third-generation Grubbs catalyst and (b) P5Az10N grafted and (c) spin-cast films. (d) XRR fitting profiles of brush (I) and spin-cast (II) films. Solid lines and symbols are experimental and simulated curves, respectively.

utilities of the ROMP strategy for the fabrication of surface-grafted high-density LC brushes.

RESULTS AND DISCUSSION

The synthesis of azobenzene-containing norbornene monomer (\pm)endo,exo-5,6-di{[10-[4'-(4"-pentyl-phenylazo)-phenoxy]-dedecyloxycarbonyl]bicyclo[2.2.1]hept-2-ene} (5Az10N) and procedures for SI-ROMP are described in the Supporting Information. First, a self-assembled monolayer (SAM) of 7-octenyldimethylchlorosilane (ODS) was prepared on a quartz surface and a ruthenium complex Grubbs catalyst was coordinated on the olefin site on the top. Then the norbornene monomer of 5Az10N dissolved in dichloromethane was added and subjected to ROMP. We explored the potential to use Ru-mediated carbon–carbon ($C=C$) double-bond exchange processes with the help of the Grubbs catalysts. The first-, second-, and third-generation Grubbs catalysts were employed individually to investigate the grafting efficiency.^{39,40} The third-generation catalyst (Figure 1a) was found to be the most efficient catalyst for the present strategy (Figures S2 and S3, Supporting Information). Therefore, we focused our attention on preparing LC brush films (Figure 1b) by the third-generation catalyst. Initial monomer concentrations for grafting brushes were 0.0375, 0.075, 0.15, 0.20, and 0.25 mol dm⁻³ for five different runs. The number-average molecular weight (M_n) of the obtained P5Az10N-free polymers was $(1.5\text{--}6.7) \times 10^4$ with M_w/M_n (polydispersity) ranging from 1.1 to 1.25. The thermophysical properties of the P5Az10N polymer were glass (46 °C), smectic A (95 °C), nematic (115 °C), and isotropic as estimated by differential scanning calorimetry and polarized optical microscopy analyses (Figure S4, Supporting Information). The packing state and molecular orientations were also evaluated in comparison to those of spin-cast films (Figure 1c) of an identical LC polymer.

Figure 1d shows the X-ray reflectivity (XRR) profiles of the P5Az10N brush and spin-cast films by fringes I and II, respectively. Using a method reported previously,⁴¹ we determined the thicknesses of the brush and spin-cast films

to be 78 and 80 nm, respectively. These values were consistent with the results of AFM imaging (Figure S6, Supporting Information).

When this type of polymer brush was synthesized by SI-ATRP, the polymerization of an azobenzene-containing methacrylate monomer (5Az10MA, Supporting Information)^{37,38} yielded only 30-nm-thick brush films at most, and efforts to increase the chain length by this method either by increasing the monomer ratio or by a reinitiation process (Figure S1, Supporting Information) failed. In addition, grafting polymerization did not take place if there was any air (oxygen) in the reaction system and the reaction was carried out at elevated temperatures in an airtight vessel.

In the case of cyclic olefins, the catalytic activity of Ru is significantly increased by strongly ligating NHCs (N-heterocyclic carbenes) with weakly coordinating pyridines developed in the third-generation Grubbs catalyst.^{39,40} The living nature of the Ru catalyst is persistent for the subsequent ROMP process. Moreover, the reaction could be carried out at room temperature and also showed some resistance against ambient air (Figure S5, Supporting Information). The brush lengths obtained at concentrations of 0.0375, 0.075, 0.15, 0.20, and 0.25 mol dm⁻³ were 10, 22, 44, 59, and 78 nm respectively, showing a linear progression (Figure S3, Supporting Information), which is an indication of stoichiometric grafting control over the brush thickness.

Figure 2 shows UV–visible absorption spectra of (a) the grafted P5Az10N brush and (b) spin-cast film on quartz substrates taken with the normal incidence for as-prepared states (solid lines) and after annealing at 90 °C for 10 min (dashed lines). The LC Az blocks of P5Az10N homopolymer brushes showed peaks at around 240 nm ($\phi\text{--}\phi^*$) and 340 nm ($\pi\text{--}\pi^*$). The spectrum for the P5Az10N brush exhibited partial H aggregation ($\pi\text{--}\pi^*$ band at 335 nm), and after having been annealed at 90 °C, the $A_{\phi\text{--}\phi^*}/A_{\pi\text{--}\pi^*}$ ratio did not change significantly (0.56 to 0.59), indicating the constancy of the planar orientation of Az mesogens. However, the spin-cast film showed strong H aggregation ($\pi\text{--}\pi^*$ band at 325 nm), and

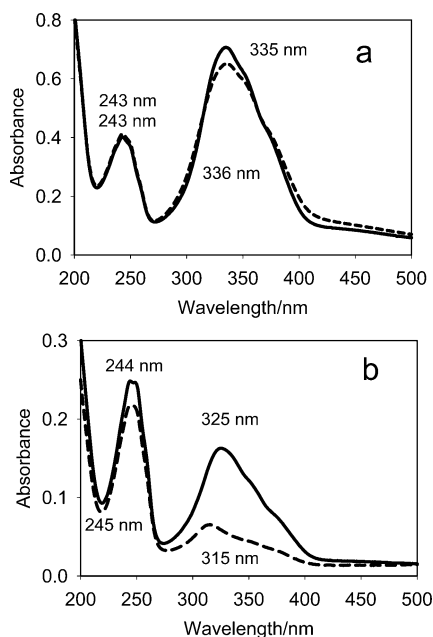


Figure 2. UV-vis absorption spectra of (a) 78 nm grafted and (b) 80 nm spin-cast films of P5Az10N on quartz plates. λ_{max} values are shown. Solid and dashed lines indicate spectra before and after annealing at 90 °C, respectively.

after being annealed at 90 °C for 10 min, a large spectral change was observed for the π - π^* absorption band and the $A_{\phi-\phi^*}/A_{\pi-\pi^*}$ ratio increased from 1.52 to 3.7. This is ascribed to an orientation change to a more perpendicular state to the substrate (i.e., the homeotropic alignment of Az groups featuring a smectic layer parallel to the substrate was adopted). The structural features are nearly the same as those obtained by SI-ATRP, but the spectral changes between the surface-grafted and spin-cast films become more pronounced.

The LC state and orientation of the mesogenic Az groups in the films were explored in more detail by grazing incidence X-ray diffraction (GI-XRD) measurements. Figure 3 shows 2D XRD profiles of (a) the 78 nm brush and (b) the 80 nm spin-cast polymer films recorded on an imaging plate. For the brush structure, a clear in-plane diffraction peak was observed at $2\theta = 2.46^\circ$, which corresponds to a smectic layer spacing of 3.6 nm formed perpendicular to the substrate plane with LC mesogens being aligned parallel to it.^{37,38} This result is in agreement with the data obtained by UV spectroscopy. The spacing corresponds to a long-range ordering of approximately the length of the fully extended Az side chains, suggesting the formation of a structure consisting of interdigitated Az side chains. In contrast, only an out-of-plane diffraction peak at $2\theta = 2.47^\circ$ ($d = 3.6$ nm) was observed for the spin-cast film, which is deduced from the smectic LC phase (Figure 3b). The intensity profile in the out-of-plane direction exhibited clear diffractions up to at least third order, indicating the formation of a highly ordered layer structure. Thus, virtually identical smectic structures are formed in both the grafted and spin-cast polymer films but with contrasting orientations. Also, these layer spacings are similar to those obtained for grafted films by SI-ATRP.^{37,38} It is worth mentioning that the in-plane diffraction peaks for the 78 nm P5Az10N brush (X-ray intensity and peak top signal in the inset of 3a in the P5Az10N brush) were very strong compared to those for the P5Az10MA brush prepared by SI-ATRP (cf. Figure 2 in ref 37 and Figure 7b in ref 38).

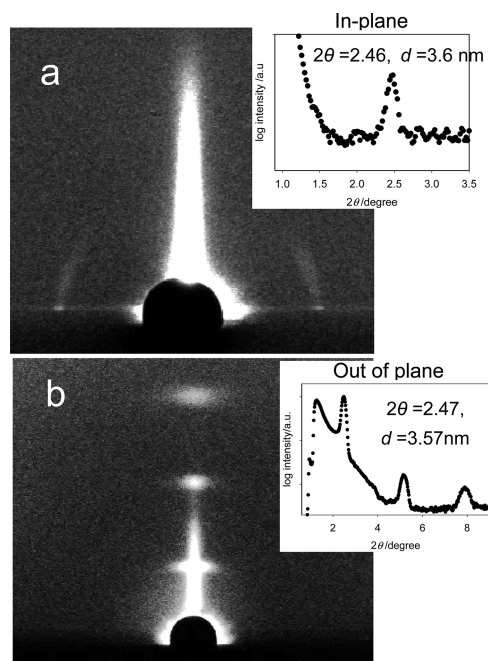


Figure 3. Two-dimensional GI-XRD imaging plate patterns of (a) a grafted brush of 78 nm and (b) a spin-cast film of 80 nm for P5Az10N polymer films recorded on an imaging plate at room temperature. One-dimensional profiles in the in-plane (inset of a, for the brush state) and out-of-plane (inset of b, for spin-cast films) directions extracted from the 2D XRD patterns are shown.

This information suggests that a more regular LC array with the intrinsic packing state of LC mesogens was obtained in the P5Az10N brush.

The photoalignment behavior was next examined. In the case of a P5Az10MA brush prepared by ATRP, no in-plane dichroism was recognized in the prepared state, indicating that the mesogens of the P5Az10N brush formed a polydomain structure before photoorientation.^{37,38,41} For the 44 and 78 nm P5Az10N brushes prepared by SI-ROMP, upon irradiation with 700–1000 mJ cm⁻² linearly polarized light (LPL) at 436 nm and 70 °C, the order parameter (S) calculated by $(A_{\perp} - A_{\parallel}) / (A_{\perp} + 2A_{\parallel})$ ^{37,38} reached values of 0.46 and 0.60 (Figure 4a), respectively, indicating a high anisotropic level achieved by irradiation. Higher doses of LPL irradiation were necessary for the saturation of the anisotropic level for thicker brushes. For ATRP brushes, the highest anisotropy at the optimum temperature (80 °C) was obtained using 500 mJ cm⁻² LPL irradiation. Therefore, the SI-ROMP brush needs a slightly higher dose of light (700–1000 mJ cm⁻²) to reach the saturation level of anisotropy. This fact indicates that the rotational motion of the Az mesogens is restricted to larger extents, probably due to more compact packing via the favorable intrinsic self-assembly of the mesogens. Because the thermal properties of P5Az10N and P5Az10MA were almost the same (glass-transition temperatures of P5Az10N and P5Az10MA are 46 and 51 °C, respectively, and isotropization temperatures are 115 and 108 °C, respectively), the effect of the backbone rigidity seems to have minor significance.

The reorientation behavior of the molecular orientations by a subsequent exposure to LPL with the orthogonal polarization direction was examined at 70 °C. Figure 4b shows the change in S upon irradiation with orthogonal 436 nm LPL. Here, the negative sign of S indicates that the molecular orientation in the

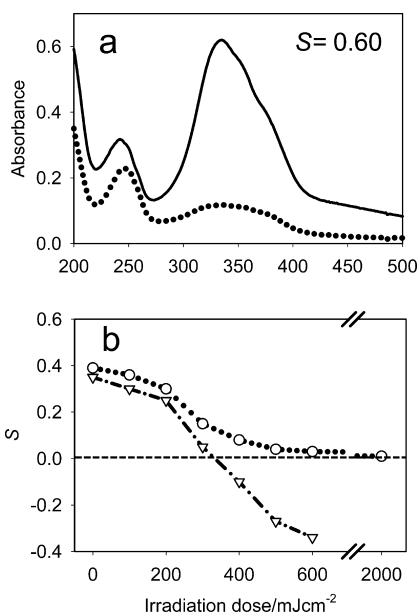


Figure 4. (a) Dichroic nature of P5Az10N brush upon 436 nm LPL irradiation at 70 °C with 1 J cm⁻² for the 78 nm P5Az10N brush and (b) comparative changes in *S* (order parameter) between P5Az10N (circles) by SI-ROMP and P5Az10MA (triangles) by SI-ATRP brushes during exposure to the 436 nm LPL set orthogonal to the initial alignment at 70 °C (b). The P5Az10MA curve has been taken from Figure 9b in ref 41.

orthogonal direction from the initial is enhanced compared to that of the unirradiated film. For the film prepared by SI-ATRP, the reorientation to the orthogonal direction fully occurred after 600 mJ cm⁻². At this energy dose, *S* was fully inverted to negative values (triangles). In contrast, only a depression in *S* was observed by the orthogonal LPL irradiation period for the SI-ROMP film. *S* for the SI-ROMP film did not shift to the negative region even after 2000 mJ cm⁻² (circles). Thus, irradiation with orthogonal LPL did not lead to the reorientation, but rather the effect was restricted to a level of orientation randomization. This result can be related to the orientation order of Az mesogens evaluated by GI-XRD. A more ordered smectic layer is formed for the SI-ROMP film than for the SI-ATRP film, and this situation suggests that the Az mesogens are more firmly packed for the SI-ROMP film. The smooth reorientation can be hindered by the well-packed Az mesogenic groups. This in turn implies that the reorientation requires a certain level of initial structural disorder that should provide some freedom for the rotational motions.

CONCLUSIONS

This work demonstrates the utility of SI-ROMP for the synthesis of high-density surface-grafted LC azobenzene polymer brush films. The features and advantages to adopting SI-ROMP as opposed to SI-ATRP can be summarized as follows. (i) Because of the robust nature of ROMP, longer grafted chains are readily available and stoichiometric grafting control can be accomplished. (ii) SI-ROMP can proceed in air, unlike SI-ATRP. (iii) A more highly ordered smectic layer structure with more strongly packed Az units is formed. (iv) The Az mesogenic groups are firmly packed to a level that hinders the photoinduced in-plane reorientation of Az. Thus, SI-ROMP widens opportunities to explore suitable techniques for the synthesis of desired materials in lieu of using SI-ATRP.

Utilizing the stable living nature of this method makes the extension of this strategy to LC SI-block copolymers readily available. Work in this direction is now in progress.

ASSOCIATED CONTENT

Supporting Information

Synthesis and experimental procedures, DSC, POM, AFM, and X-ray (bulk) data. 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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