

Photoregulated Living Supramolecular Polymerization Established by Combining Energy Landscapes of Photoisomerization and Nucleation–Elongation Processes

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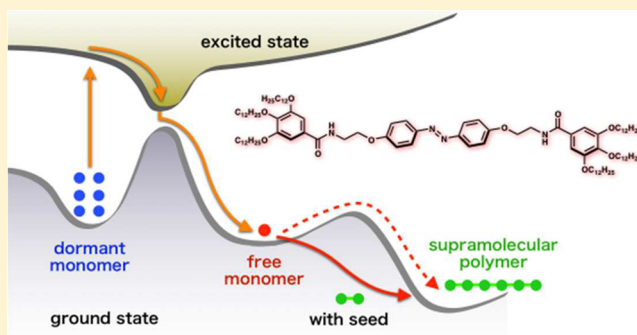
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Supporting Information

ABSTRACT: The significant contribution of conventional living polymerization to polymer science assures that living supramolecular polymerization will also lead to a variety of novel phenomena and applications. However, the monomer scope still remains limited in terms of the self-assembly energy landscape; a kinetic trap that retards spontaneous nucleation has to be coupled with a supramolecular polymerization pathway, which is challenging to achieve by molecular design. Herein, we report a rational approach to addressing this issue. We combined the supramolecular polymerization and photoisomerization processes to build the energy landscape, wherein the monomer can be activated/deactivated by light irradiation. In this way, the supramolecular polymerization and kinetic trap can be independently designed in the energy landscape. When the “dormant” monomer was activated by light in the presence of the seed of the supramolecular polymer, the “activated” free monomer was polymerized at the termini of the seed in a chain-growth manner. As a result, we achieved supramolecular polymers with controlled lengths and a narrow polydispersity. Although photoisomerization has been extensively employed in supramolecular polymer chemistry, most studies have focused on the stimuli responsiveness. In this respect, the present study would provoke supramolecular chemists to revisit stimuli-responsive supramolecular polymer systems as potential candidates for devising living supramolecular polymerization.



INTRODUCTION

Since living polymerization was first invented in 1956 for anionic polymerization,¹ substantial effort has been devoted to establishing a similar synthetic methodology for other polymerization mechanisms.² Nowadays, even polycondensations, which are believed to proceed in a step-growth mechanism, are controllable in a living manner, allowing access to unprecedented polymeric materials.³ However, until very recently,^{4,5} living polymerization had not been realized for a new type of polymer in which monomer units are brought together by noncovalent bonds, i.e., supramolecular polymers.^{6,7}

The uniqueness of supramolecular polymers in comparison to conventional polymers originates in the dynamic nature of the noncovalent bonds; owing to this, recyclability, self-healing ability, and stimuli responsiveness have been achieved.^{6,7} However, this attractive feature in turn makes controlling the supramolecular polymerization difficult. As the supramolecular

polymerization occurs spontaneously and reversibly at equilibrium, the polydispersity index (PDI) of supramolecular polymers is thermodynamically determined to be 2.0.^{6a}

Recently, we and others showed that supramolecular polymerization under kinetic control potentially leads to living supramolecular polymerization.^{4,5} To this end, the nucleation–elongation process of supramolecular polymerization has to be coupled with a competing kinetic trap, wherein the monomer becomes dormant (Figure 1b). The competing pre-equilibrium sequesters the free monomer, thereby preventing spontaneous nucleation (i.e., pathway A). However, the kinetically trapped monomer can bypass the barrier through pathway B with the aid of a seed^{4a,c–e} (or tailored initiator^{4b}), whereupon supramolecular polymerization is initiated.⁸ Because propagation occurs only at the termini of the supramolecular polymers

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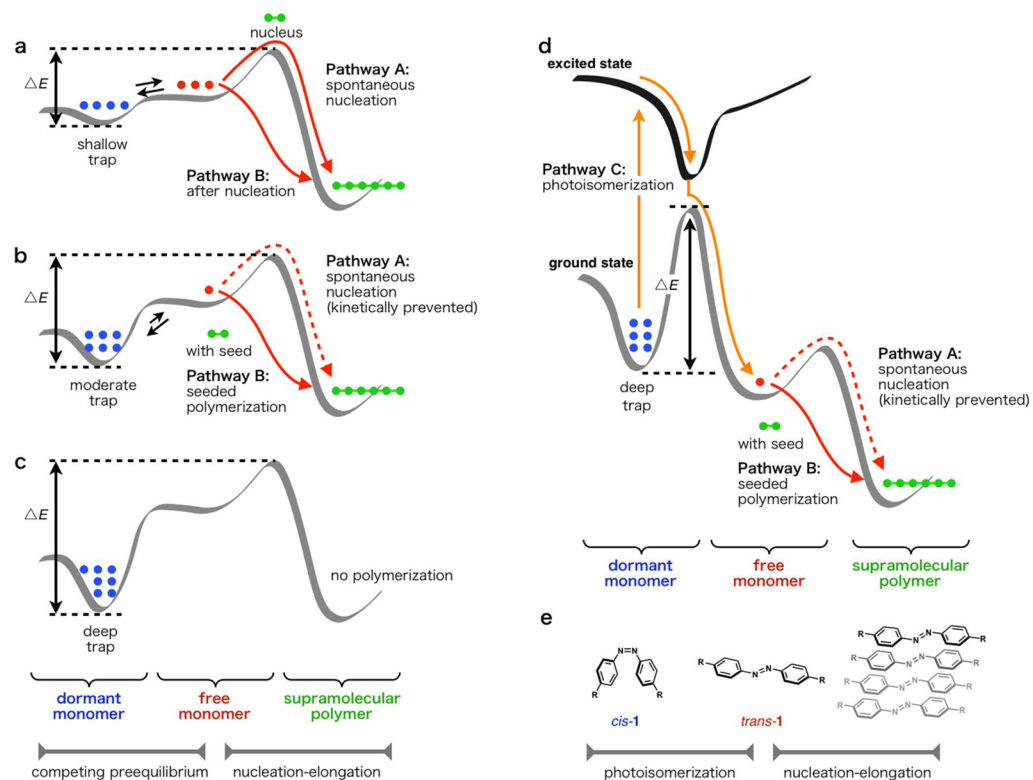


Figure 1. Energy landscapes of supramolecular polymerization coupled with a competing kinetic trap. The kinetic trap is (a) too shallow to prevent spontaneous nucleation–elongation, (b) ideal for realizing living supramolecular polymerization, or (c) too deep to initiate supramolecular polymerization. In (b), pathway A is kinetically prevented, but supramolecular polymerization can be initiated through pathway B with the addition of a “seed.” (d) Photoisomerization process used to create the kinetic trap. Even though the trap is very deep, the energy barrier (ΔE) can be circumvented through photoisomerization pathway C, supplying free monomer for subsequent seeded polymerization pathway B. (e) Photoisomerization and supramolecular polymerization of **1**, shown corresponding to the above energy landscape (d). Note that the energy landscape of the nucleation–elongation process is dependent on monomer concentration; for example, at very high concentration, the nucleation process may become downhill.¹¹ However, uphill nucleation is the requirement for achieving living supramolecular polymerization (i.e., propagation in a chain growth manner).^{4,5} Thus, the energy landscapes shown here are depicted on the supposition that the concentration of the monomer is optimized.

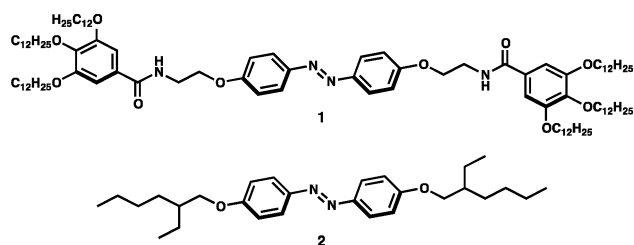
in the nucleation–elongation mechanism, the length of the obtained supramolecular polymer is determined by the feed ratio of the monomer to the seed (or initiator), a property analogous to living polymerization.

Although several examples have been reported,⁴ living supramolecular polymerization is still in its infancy. To devise living supramolecular polymerization, we must carefully consider the pathway complexity of the system based on the energy landscape.^{4,5,9} As shown in Figure 1b, the kinetic trap should be deep enough to retard the spontaneous nucleation; otherwise, we end up with the uncontrollable system illustrated in Figure 1a. In practice, a few hours of lag time is required to perform the subsequent seeded polymerization. However, if the trap is set to be too deep (namely, the energy barrier of ΔE is too large), then supramolecular polymerization would never happen (Figure 1c). In general, the trade-off for a more stable kinetic trap is less of a driving force for the elongation of the supramolecular polymer. The interplay between the kinetic trap and supramolecular polymerization should be in such a delicate balance that it is difficult to rationally establish the appropriate energy landscape. In fact, our recent study revealed that a subtle modification of the monomer structure significantly influences the kinetic behavior of supramolecular polymerization.¹⁰ Furthermore, we should bear in mind that concentration and temperature affect the energy landscape.¹¹ Thus, the method-

ology of living supramolecular polymerization has yet to be developed.

Reflecting on the above issue, it occurred to us that the energy landscape does not necessarily have to be “monolithic” like Figure 1a–c but that we can employ another independent energy landscape (i.e., the excited state). In this study, we adopt a photoisomerization process to create the kinetic trap such that one of the isomers can be a dormant monomer. As shown in Figure 1d, even though the energy barrier (ΔE) is too high to be overcome at a given temperature, it can be circumvented via the excited state (pathway C), thereby supplying free monomers for seeded polymerization. Thus, by combining two independent energy landscapes, we anticipate that we no longer need to address the delicate energy balance. In addition, the photoisomerization rate is governed by the intensity and wavelength of the incident light, which allows for kinetic control of monomer activation. To verify this concept, we exploited the photochromism of the azobenzene chromophore and designed compound **1** bearing hydrogen-bonding sites (Chart 1 and Figure 1e). Although there have been many supramolecular systems using azobenzene derivatives,^{12–15} in what follows, we demonstrate the first photoregulated living supramolecular polymerization founded on the hypothesis described above.

Chart 1



RESULTS AND DISCUSSION

Nucleation–Elongation Energy Landscape. Figure 2a shows temperature-dependent absorption spectra of *trans-1* in a

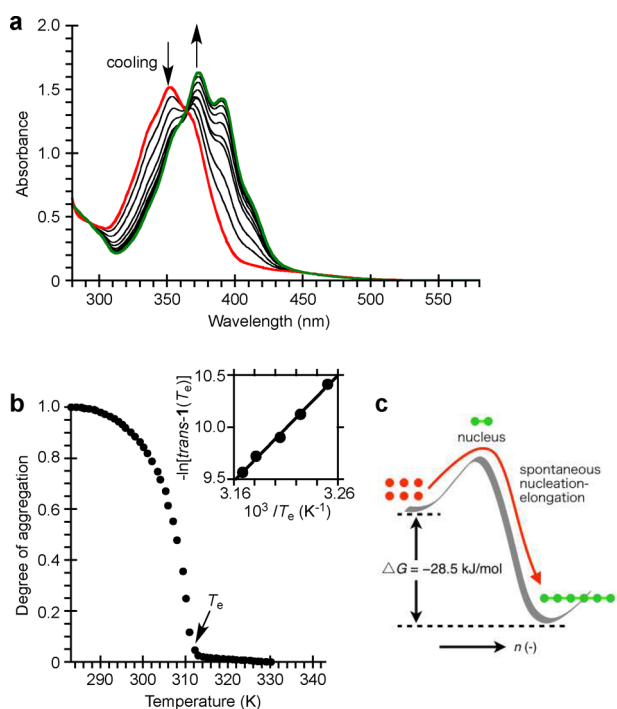


Figure 2. Temperature-dependent (a) UV–vis spectra (red to green upon cooling, -0.1 K/min) and (b) degree of aggregation of *trans-1* in an MCH/toluene mixture (9:1): $[1] = 50$ μM . The inset shows a van't Hoff plot. (c) Energy landscape of the nucleation–elongation process of *trans-1* at 298 K.

mixed solvent of methylcyclohexane (MCH) and toluene (9:1). The red-shifted absorption maximum and pronounced vibronic structures at lower temperatures with regard to the monomeric *trans-1* suggest the formation of a well-defined J-aggregate. The degree of aggregation (α_{agg}) as a function of temperature showed a nonsigmoidal transition as characterized by a critical elongation temperature, T_e (Figures 2b and S1). This result indicates that the supramolecular polymerization of *trans-1* occurs in the cooperative nucleation–elongation mechanism. The natural logarithm of the reciprocal concentration of *trans-1* at T_e (i.e., $-\ln[\text{trans-1}(T_e)]$) as a function of reciprocal T_e showed a linear relationship (van't Hoff plot, Figure 2b, inset).^{6d} Thus, we estimated the standard enthalpy (ΔH°) and entropy (ΔS°) for the elongation process to be -84.8 kJ/mol and -189.1 J/(mol K), respectively. Accordingly, a Gibbs free energy (ΔG°) of -28.5 kJ/mol at 298 K was obtained (Figure 2c). These values are comparable to those of supramolecular polymers formed through concerted hydrogen-bonding and

π – π interactions.⁶ Atomic force microscopy (AFM) visualized one-dimensional supramolecular polymers of several micrometers in length (Figure 3a), as commonly observed for those

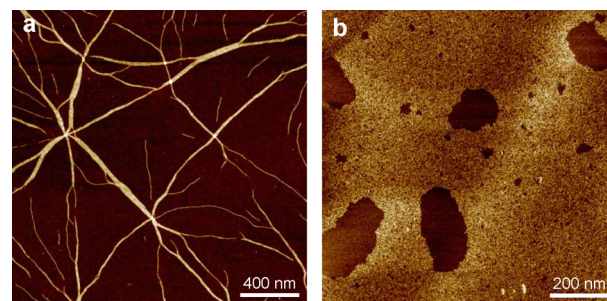


Figure 3. AFM images of (a) the supramolecular polymer of *trans-1* formed spontaneously from a hot solution and (b) the amorphous film obtained from a solution of *cis-1* (PSS_{UV}): $[1] = 50$ μM , MCH/toluene mixture (9:1), spin-coated on graphite substrates.

formed by the nucleation–elongation mechanism. In contrast, *cis-1*, which was prepared by cooling a hot solution of *trans-1* under continuous UV irradiation (351 nm), was unable to form such supramolecular polymers most likely as a result of the bent conformation (AFM image, see Figure 3b: its absorption spectrum is shown in Figure S2).^{13,16} These results indicate that *trans-1* is an active monomer whereas *cis-1* serves as a dormant monomer as expected.

Photoisomerization Energy Landscape. To investigate the photoisomerization pathway in detail, we used reference compound **2** that lacks the hydrogen-bonding sites and is thus incapable of supramolecular polymerization (Chart 1). Pure *trans-2* shows a characteristic π – π^* absorption band at 354 nm and a weak n – π^* band at around 430 nm (Figure 4a). Upon UV irradiation (351 nm), the π – π^* band was attenuated, whereas another prominent n – π^* band at 450 nm appeared, characteristic of the photoisomerization from the *trans* to *cis* form. In the photostationary state under UV light (PSS_{UV}), the ratio of *trans-2* to *cis-2* was 3:97 (Figure S3),¹⁶ demonstrating the high conversion efficiency. The reversion from *cis-2* to *trans-2* was induced by visible light irradiation (520 nm, at which *cis-2* can be selectively excited), which was also efficient, yielding a *cis-2* to *trans-2* ratio of 7:93 at PSS_{vis}. Importantly, the photoreversion rate is controlled by varying the bandwidth of the light source (Figure S4), which allows for kinetic control over monomer activation.

The thermal stability of *cis-2* was assessed by probing the fading of the *cis-2* absorption band at different temperatures as a function of time (Figure 4b). An Arrhenius plot for the thermal reversion process of *cis-2* estimated the activation energy and the half-life at 298 K to be 84.5 kJ/mol and 436 min, respectively. As a result, we established the photoisomerization energy landscape as shown in Figure 4c.

Thermal Initiation and Photoinitiation of Supramolecular Polymerization. Combining the two energy landscapes shown in Figures 2c and 4c constructs the energy landscape that potentially realizes photoregulated living supramolecular polymerization (Figure 1d). To investigate the kinetically trapped state, time-dependent absorption spectral changes of *cis-1* (PSS_{UV}) were measured at 298 K in the dark (Figure 5).

In the early stage (~ 4 h, red regime), the thermal reversion of *cis-1* to monomeric *trans-1* occurred with an accompanying

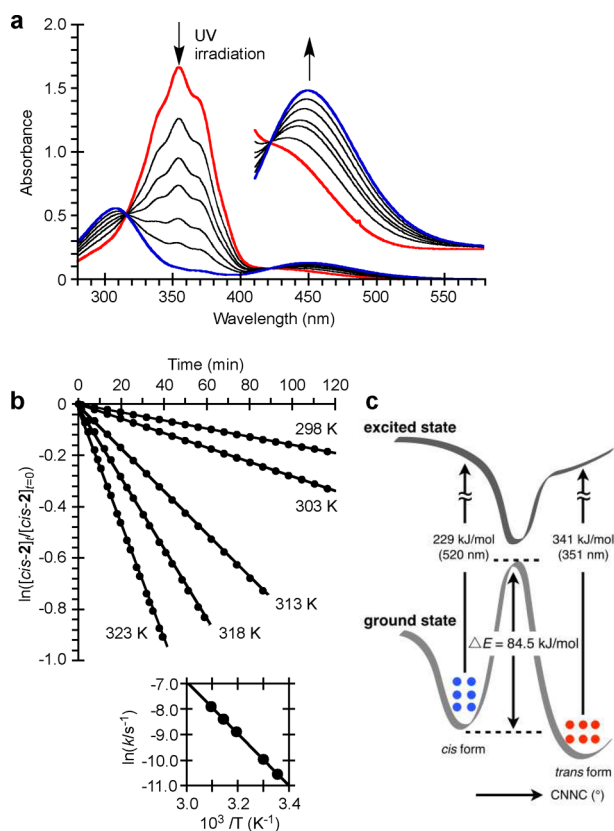


Figure 4. (a) Absorption spectral change of *trans*-2 (red line) to *cis*-2 (PSS_{UV}) induced by UV irradiation (351 nm) in an MCH/toluene mixture (9:1): $[2] = 50 \mu M$. (b) Thermal fading of *cis*-2 at different temperatures. The inset shows an Arrhenius plot. (c) Energy landscape of the photoisomerization process of **2**.

isobestic point at 312 nm (Figure 5b). Consequently, monomeric *trans*-1 was gradually accumulated to reach the critical concentration for nucleation ($\sim 10 \mu M$, Figure S5), which eventually underwent J-aggregate formation, as implied by the red shift of the absorption maximum (4–7.5 h, light-green regime). In this stage, there is an interplay among *cis*-1, monomeric *trans*-1, and aggregated *trans*-1, and thus, a deviation from the isobestic point was observed. Finally, monomeric *trans*-1 became virtually negligible, suggesting that the degree of aggregation has reached unity and that the system consisted of *cis*-1 and a supramolecular polymer of *trans*-1. In the last stage (7.5–16.5 h, green regime), the thermal reversion and elongation processes are strongly coupled as evidenced by the new isobestic point at 325 nm. Figure 5c shows plots of the changes in the absorbance at 353 and 390 nm, which are characteristic of monomeric and aggregated forms of *trans*-1, respectively. The three regimes are clearly distinguished by distinct slopes; therefore, the ratio of these values ($\Delta A_{390}/\Delta A_{353}$) was found to be a good indicator of the lag time for the nucleation process (Figure 5d). Specifically, a lag time of 4 h was available at a $50 \mu M$ concentration and 298 K.

The same time-dependent absorption spectral measurements were performed under visible light irradiation in order to investigate the photoinitiated supramolecular polymerization (i.e., pathway C followed by pathway A in Figure 1d). Except for the kinetics, the spectral changes were similar to those observed for the thermal reversion process (Figure S6). In addition, the morphology of the supramolecular polymer obtained in this way was identical to those shown in Figure

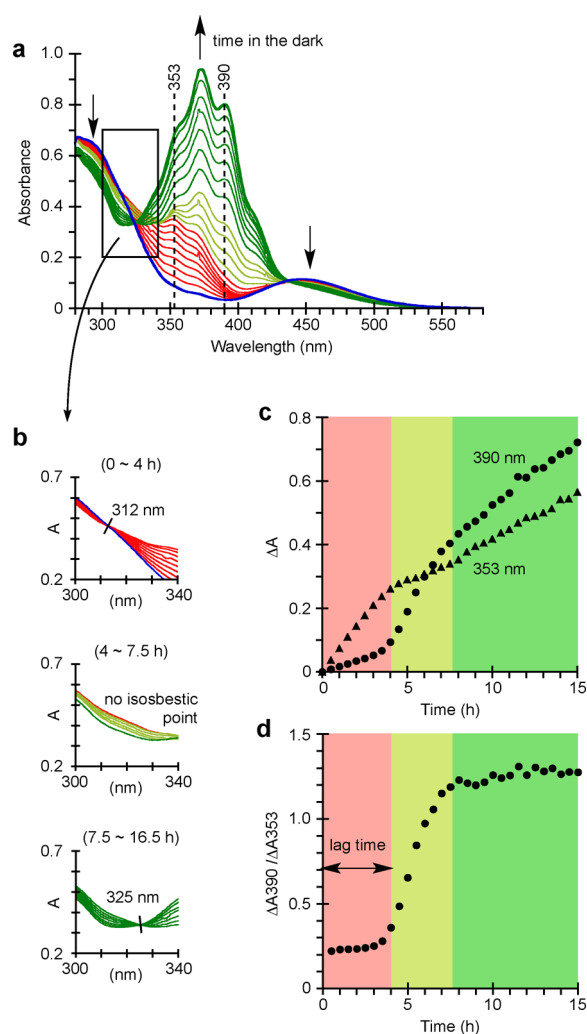


Figure 5. (a) Time-dependent absorption spectral changes of *cis*-1 (PSS_{UV}) at 298 K in the dark: $[1] = 50 \mu M$, MCH/toluene mixture (9:1). (b) enlarged spectral changes showing isobestic points. Plots of (c) ΔA at 353 (▲) and 390 nm (●) and (d) the ratio between these ΔA values.

3a (Figure S7). These results indicate that photoinitiated supramolecular polymerization also proceeds through the nucleation–elongation mechanism. Not surprisingly, the resultant supramolecular polymers are several micrometers and polydisperse in length because the nucleation step is still uncontrolled.

Photoregulated Living Supramolecular Polymerization. To achieve photoregulated living supramolecular polymerization (i.e., pathway C followed by B in Figure 1d), a seed of a supramolecular polymer is needed. We prepared a short supramolecular polymer by applying sonication to the solution of the supramolecular polymer of *trans*-1 at 5 °C for 3 h. The absorption spectrum of the seed was identical to that of the supramolecular polymer, suggesting that the J-aggregation mode was preserved intact (Figure S8). The number-average length (L_n) and weight-average length (L_w) of the seed were 70 and 114 nm, respectively (PDI = 1.6, Figure 6a). It should be noted that the seed is persistent against the visible light irradiation used for the following photoregulated living supramolecular polymerization as it merely absorbs this light ($\epsilon_{520 \text{ nm}} < 10^2 \text{ L mol}^{-1} \text{ cm}^{-1}$).

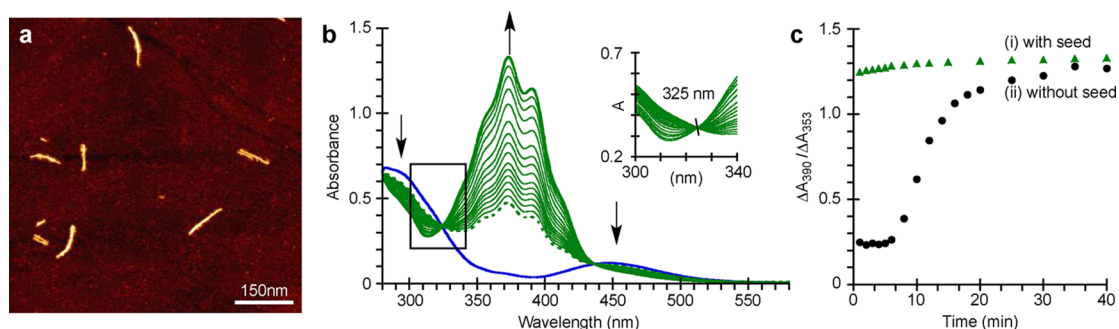


Figure 6. (a) Typical AFM image of the seed of *trans-1* obtained through sonication. (b) Absorption spectral changes observed during the photoregulated living supramolecular polymerization. To a solution of *cis-1* (PSS_{UV}, blue line), a seed of *trans-1* was added (dotted green line), and then irradiation by visible light was conducted. The 50 μM solutions (MCH/toluene mixture, 9:1) of *cis-1* and seed were mixed in a 3:1 volume ratio (i.e., [*cis-1*] = 37.5 μM and [seed] = 12.5 μM in the initial mixture). The concentration of the seed was set above the critical nucleation concentration (Figure S5) so that it would not dissociate into the monomer. (c) Plots of $\Delta A_{390}/\Delta A_{353}$ as a function of the time under visible light irradiation (520 nm, bandwidth 5 nm) in the (i) presence and (ii) absence of the seed: note that the lag time was eliminated in the presence of the seed.

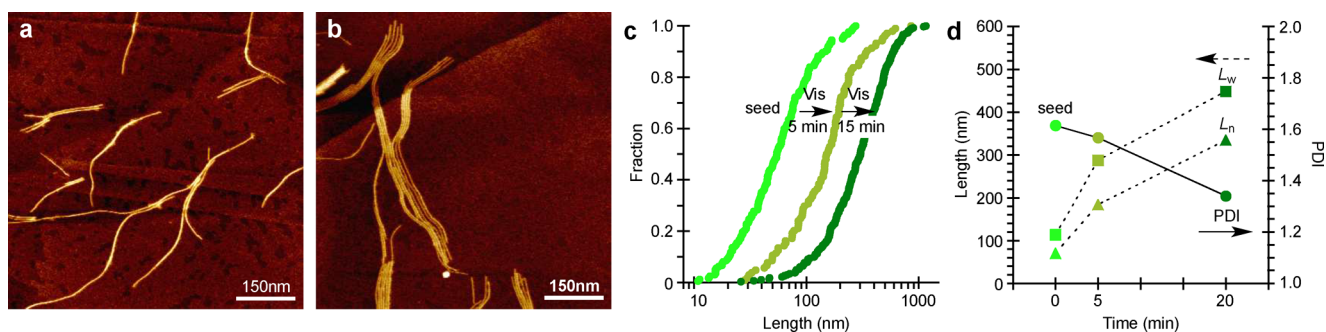


Figure 7. Typical AFM images of supramolecular polymers obtained through photoregulated living supramolecular polymerization conducted for (a) 5 and (b) 20 min. (c) Cumulative histogram of the length distributions of the seed (161 objects) and supramolecular polymers (103 and 261 objects for 5 and 20 min samples, respectively). (d) Plots of the number-averaged length (L_n), weight-averaged length (L_w), and PDI (L_w/L_n) of the seed and supramolecular polymers.

Having the seed in hand, we undertook photoregulated living supramolecular polymerization. First, we measured time-dependent absorption spectral change of a mixture of the seed and *cis-1* in the dark (Figure S9). The J-aggregate propagated with a small rate constant of $2.56 \times 10^{-5} \text{ s}^{-1}$. This value is consistent with the thermal reversion rate of *cis* to *trans* at the given temperature ($2.65 \times 10^{-5} \text{ s}^{-1}$ at 298 K, see Figure 4b), suggesting that the thermal reversion process is the rate-determining step of the polymerization in the absence of light. This result indicates that the seed itself is inert to *cis-1* to *trans-1* reversion (for example, by a template effect) and the isomerization and supramolecular polymerization processes are practically separated in the ground state.

However, on visible light irradiation of the mixture of the seed and *cis-1*, we observed much faster absorption spectral changes. This process accompanies a clear isosbestic point at 325 nm (Figure 6b) that coincides with the third stage in Figure 5, indicative of the consumption of *cis-1* and the propagation of the supramolecular polymer of *trans-1*. Importantly, the lag time was eliminated in the presence of the seed (Figure 6c), thus indicating that the photoreversion and elongation processes are coupled in the presence of the seed.

Figure 7a,b shows the supramolecular polymers obtained after 5 and 20 min of photoregulated living supramolecular polymerization (see also Figures S10 and S11). The length of the supramolecular polymer was dependent on the duration of

visible light irradiation, and PDIs remained as low as 1.3 (Figure 7c,d).¹⁷ These results are in clear contrast to those obtained in the absence of the seed (Figure S7), indicating that *trans-1* supplied via pathway C is polymerized at the termini of the seed in the chain-growth manner. To the best of our knowledge, this is the first demonstration of photoregulated living supramolecular polymerization.

It is noteworthy that the intensity and wavelength of the visible light used for monomer activation were determinants of whether the photoregulated living supramolecular polymerization was successful. Under the conditions in which *cis-1* to *trans-1* isomerization occurs rapidly (520 nm, bandwidth = 20 nm), the spontaneous nucleation of *trans-1* (pathway A) cannot be controlled even in the presence of the seed; as a result, supramolecular polymers with a broad length distribution are obtained (Figure S12). These results illustrate the importance of kinetic control of monomer activation, which is precisely achieved in the present system by optimizing the photoisomerization conditions.

CONCLUSIONS

We succeeded in establishing photoregulated living supramolecular polymerization for the first time. So far, the monomer scope of living supramolecular polymerization has remained limited because it is difficult to establish an energy landscape that allows for kinetic control over spontaneous nucleation. In the present system, the kinetic trap (i.e.,

photoisomerization) and supramolecular polymerization processes can be independently designed in the ground state; however, they are coupled through the excited state. This strategy achieved living supramolecular polymerization without managing the delicate interplay of pathway complexity.

To date, photochromic molecules have been extensively used in supramolecular polymer chemistry; however, most studies have focused on their unique stimuli responsiveness.^{12–15} Of these, Meijer et al.¹⁴ have reported a photoregulation of supramolecular polymerization: a system, conceptually related to the present study, in which the degree of polymerization was controlled by a photochromic auxiliary. In this context, the present study discovered a new potential of photochromic molecules in supramolecular polymer chemistry. It is worthwhile to revisit stimuli-responsive supramolecular polymer systems as potential candidates for devising living supramolecular polymerization.¹⁸ In addition, in this way, activation of the monomer can be achieved spatially and temporally by light,^{19,20} which we believe will further advance living supramolecular polymerization and its applications.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b08145.

Syntheses of **1** and **2** and their ¹H and ¹³C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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(16) See the Supporting Information.

(17) By making the seeds shorter, we believe that the PDI of the supramolecular polymer becomes closer to 1.^{8b} An investigation of the effect of sonication on seed formation is in progress.

(18) One of the reviewers pointed out the similarity between the present system and enzyme-assisted self-assembly reported by Ulijn and co-workers. We agree that such self-assembly systems coupled

with chemical reaction are also potential candidates because monomer activation is governed by the reaction “rate”. Williams, R. J.; Smith, A. M.; Collins, R.; Hodson, N.; Das, A. K.; Ulijn, R. V. *Nat. Nanotechnol.* **2009**, *4*, 19.

(19) Photocontrolled polymerization has attracted increasing amounts of attention in polymer chemistry.²⁰ In this context, our study will further advance controlled supramolecular polymerization and its applications.

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