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Supramolecular Depolymerization of Nanowires Self-Assembled from Micelles

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ABSTRACT: Supramolecular polymerization has been a fascinating frontier of supramolecular chemistry in fabricating well-defined hierarchical nanostructures. However, the reverse process, that is, supramolecular depolymerization in which superstructures disassemble into subunits, is far less explored. In particular, the mechanism and kinetics of supramolecular depolymerization have not yet been reported. In this work, we discovered a thermal-induced supramolecular depolymerization of nanowires formed by supramolecular step-growth polymerization of preassembled micelles. With increasing temperature, the intermicelle interaction between the micellar subunits is broken, resulting in depolymerization of the nanowires into micellar subunits. Accompanying the supramolecular depolymerization, chain transfer between the subunits occurs. A theoretical model was proposed to reveal the mechanism and kinetics of the supramolecular depolymerization. It was found that the depolymerization behavior obeys the



Article

rules of random depolymerization. The present work could provide useful information for understanding the underlying principles of supramolecular degradation. In addition, the temperature-induced supramolecular depolymerization of hierarchical nanostructures may find potential applications in biomedical fields.

INTRODUCTION

Assembly and disassembly are the ultimate building principles of nature, which have shown fascinating behaviors in biological systems.^{1–4} These two processes play a significant role in maintaining the stable functions of living entities such as the metabolism and self-replication of cellular tissues. One example is the cell cytoskeleton in which globular actin (G-actin) can noncovalently polymerize into microfilaments after combining with adenosine triphosphate (ATP).^{5,6} The ordered filaments could in turn undergo depolymerization to regenerate the G-actin upon hydrolysis of ATP into adenosine diphosphate. This reconfiguration process is crucial for cell division and cytoplasmic circulation.

Scientists have devoted much efforts in mimicking the selfassembly process in nature. One of the most intriguing structures is the one-dimensional (1D) hierarchical nanostructure, which can be formed by the supramolecular polymerization of micellar subunits.^{4,7–19} Recently, the preparation of 1D hierarchical nanostructures has drawn increasing attention because of their dynamic and responsive performances, which make them extremely interesting for promising applications in biomedical fields such as sensing and drug delivery.^{10,20–22} For instance, Müller et al. prepared well-defined hierarchical supracolloidal nanostructures through polymerization of the preassembled ABC triblock terpolymer micelles with tunable patches.^{9,23} Cai et al. reported that the spindle-like micelles formed by poly(γ -benzyl-L-glutamate)-graft-poly(ethylene glycol) (PBLG-g-PEG) graft copolymers are able to polymerize into 1D nanowires.^{14,24} For the spindle-like micelles, the rigid PBLG chains are arranged in a paralleled order along the long axis of the micelles, and the PEG chains extend into the solution stabilizing the micelles. Partial open ends exist in the spindle-like micelles because of the imperfect coverage of the micelle core by the short PEG chains. By varying the solution conditions, the ends of micelle can be activated, which induces the polymerization of the micelles. In a recent work, it was found that at lower temperatures, the solubility of the PBLG in the solvent decreases, and the solvophobic attraction between PBLG increases.²⁴ This variation in the solvophobic attraction activates the micellar ends, and the spindle-like micelles polymerize into nanowires through physical bonding to eliminate the unfavorable ends.

As demonstrated above, the 1D self-assembly process of nanoscale motifs such as micelles has been studied. $^{4,9,14,17,25-30}$ However, the reverse process, that is, supramolecular depolymerization in which superstructures

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Figure 1. (a) Schematic illustration of supramolecular polymerization of the initial subunits and depolymerization of the nanowires. (b) TEM image of the spindle-like subunits self-assembled from PBLG-g-PEG copolymers at 40 °C. (c) TEM image of the nanowires formed through the supramolecular polymerization of subunits at 5 °C. (d) TEM image of the aggregates depolymerized from nanowires at 40 °C. Scale bars: 1 μ m. (e) Variation in R_h during supramolecular polymerization and depolymerization. (f) Time evolution of the R_h distribution of the nanowires in solution at 40 °C. The scattering angle for DLS experiments was 90°. The arrow is included as a guide to the eye. The water content of the micelle solution in (b–f) is 13.0 vol %.

transform into supramolecular monomers, is far less explored. The complexity and instantaneous change of the supramolecular structures make it difficult to monitor the structural variation, especially the kinetics of supramolecular depolymerization. However, revealing the depolymerization mechanism of the 1D nanostructures is of fundamental significance and could contribute to the understanding of the fascinating biological phenomena in nature and the preparation of hierarchical structures with desired functions.^{31–33}

In this work, we studied the depolymerization of 1D nanowires in solution. The nanowires were synthesized via low-temperature-induced supramolecular polymerization of the preassembled subunits of PBLG-g-PEG graft copolymers. With increasing temperature, the hydrophobic attraction of PBLG is decreased, and the activity of molecular motion is increased. Consequently, the physical interaction between the connected micelle subunits is disrupted, and the nanowires are depolymerized into nanowire fragments and micellar subunits. The polymer chain transfer occurs during supramolecular depolymerization, which highlights the characteristics of such a supramolecular depolymerization when compared with the traditional degradation behavior of covalently bonded polymers. In addition, we propose a theoretical model to reveal the mechanism of supramolecular depolymerization. Kinetic studies suggest that the thermal depolymerization of the nanowires obeys the rules of random depolymerization.

EXPERIMENTAL SECTION

Synthesis of Polymers. A PBLG homopolymer was synthesized through ring opening polymerization of γ -benzyl-L-glutamate-N-

carboxyanhydride initiated by triethylamine in an anhydrous 1,4dioxane solvent.^{34–36} The polymerization was performed for 3 days at 15 °C. PBLG-g-PEG graft copolymers were prepared through the ester exchange reactions between PBLG and mPEG-OH.³⁷ The reaction was performed at 55 °C in 1,2-dichloroethane for approximately 1 h. At the completion of the two reactions, the reaction mixtures were precipitated into a large volume of anhydrous methanol. The products were purified twice by repeated precipitation from a chloroform solution to a large volume of anhydrous methanol and dried under vacuum. Detailed information on the PBLG homopolymer and PBLG-g-PEG graft copolymer is presented in Section S1 of the Supporting Information.

Preparation of Subunits and Nanowires. To prepare the polymer assemblies, the PBLG-g-PEG graft copolymers were first dissolved in the tetrahydrofuran (THF) and N,N'-dimethylformamide (DMF) mixture solvent (THF/DMF, 1/1, v/v) at a concentration of 0.4 g/L. Then, 1.5 mL of deionized H₂O, a selective solvent for PEG blocks, was added to 10 mL of the PBLG-g-PEG solution with vigorous stirring to obtain subunits at 40 °C. After stabilizing for at least 10 h, the subunit solution was subjected to 5 °C for 100 days. Nanowires were formed via supramolecular step-growth polymerization of the subunits.

Supramolecular Depolymerization of Nanowires. In order to investigate the degradation of the nanowire in solution, the nanowire solution was heated and annealed separately at 40, 35, 33, 30, and 20 °C. To observe the temporal variation of the micelle morphologies at each temperature, we pipetted 0.5 mL of the sample solution into a large amount of H_2O (ca. 15 mL) to freeze the morphologies at various time intervals. The sample solution was dialyzed against deionized H_2O for 3 days to ensure that all the organic solvents were removed. Details are presented in Section S1.4 of the Supporting Information.

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Figure 2. (a–d) TEM images of the aggregates depolymerized from nanowires after annealing for 190 h at various temperatures. The insets are high-magnification images, and the arrows indicate the nodes of the nanowires. The water content of the micelle solution in (a–d) is 13.0 vol %. Scale bars: 1 μ m. (e) Number fraction (f_x) of the nanowires with degree of polymerization X at various temperatures. (f) Variation in the D of the nanowires as a function of temperature. The depolymerization time was 190 h in (e,f).

Characterization of Micellar Aggregates. The morphologies of the assemblies were characterized by transmission electron microscopy (TEM, JEM-1400, JEOL, 100 kV) and scanning electron microscopy (SEM, S4800, Hitachi, 15 kV). The hydrodynamic radius and the average aggregation number of polymers in one subunit were measured by dynamic and static light scattering (DLS and SLS, ALV/CGS-5022, laser wavelength of 632.8 nm), respectively. Detailed experimental information is available in Section S2 of the Supporting Information.

RESULTS AND DISCUSSION

Supramolecular Depolymerization of the Nanowires. Figure 1a schematically shows the processes of supramolecular polymerization of subunits into nanowires and depolymerization of the nanowires under temperature stimuli. In a typical experiment, the initial micellar subunits were prepared by adding 1.5 mL of selective solvent (water) into 10 mL of PBLG-g-PEG solution at 40 °C (0.4 g/L, DMF/THF, 1/1, v/ v). The water content of the subunit solution was 13.0 vol %. Figure 1b shows a TEM image of the initial subunits with average length and diameter of approximately 500 and 100 nm, respectively. The subunits were stable in the solution at 40 $^{\circ}$ C, and the morphology did not change with time (Figure S3). To induce the supramolecular polymerization, the micellar solution was cooled to 5 °C, and 1D nanowires with nodes were formed (Figure 1c). According to our previous report,²⁴ structural defects exist at the ends of the spindle-like subunits because of the imperfect coverage of the micelle core. At a lower temperature, the solubility of the PBLG block in the solvent decreases, and the solvophobic interaction between PBLG blocks increases. As a result, the micellar ends become active, and the spindles polymerize into nanowires through physical bonding in solution. Contrary to the polymerization process, when the temperature was increased and the nanowire solution (formed at 5 °C) was annealed at a higher temperature (typically 40 °C), as shown in Figure 1d, supramolecular depolymerization of the nanowires occurred and subunits were obtained. Interestingly, the subunits depolymerized from the nanowires remained reactive and could polymerize into nanowires again after the temperature was decreased (Figure S4). These results demonstrate that

such supramolecular polymerization and depolymerization processes are reversible. We also examined the effect of the molecular weight of PBLG on the depolymerization of nanowires, where the nanowires were formed by graft copolymers in which the molecular weight of PBLG was 70,000, 120,000, and 170,000. The nanowires in all three cases can depolymerize into subunits at 40 °C. The molecular weight of copolymers negligibly affects the supramolecular depolymerization of nanowires under the present conditions.

The supramolecular polymerization and depolymerization processes were also monitored by DLS. As shown in Figure 1e, DLS measurements reveal that, in the polymerization process, the apparent hydrodynamic radius $(R_{\rm h})$ gradually increases with time from 152 to 334 nm because of the polymerization of subunits into nanowires at 5 °C. In contrast, in the depolymerization process, the value of $R_{\rm h}$ decreases rapidly from 334 to 182 nm at 40 °C. Meanwhile, the distribution of $R_{\rm b}$ becomes narrower with time during the depolymerization of nanowires into subunits (Figure 1f). This is because that the nanowires formed by subunits are polydisperse in the degree of polymerization. The change in R_h demonstrates that the nanowires rapidly degrade into subunits at 40 $^{\circ}$ C. $R_{\rm h}$ shows no obvious changes after 48 h, indicating that the depolymerization of nanowires has reached equilibrium. The DLS results agree well with the morphological observations (Figure 1c,d).

The abovementioned results reveal that an increase in temperature can result in the depolymerization of the nanowires. To probe the mechanism of supramolecular depolymerization, we further examined the effect of temperature on the depolymerization of nanowires by annealing the nanowire solution (synthesized at 5 °C) at various temperatures such as 40, 35, 30, and 20 °C. Figure 2a–d shows TEM images of the aggregates after depolymerization for 190 h at various temperatures (it is noted that no obvious morphology change was observed for all the samples with increasing depolymerization time). As shown in the figures, the nanowires depolymerized into nanowire fragments and micellar subunits when temperature is relatively lower. With increasing temperature, the nanowire depolymerization becomes obvious, and at 40 °C, they are completely depolymerized into individual



Figure 3. (a–e) TEM images of the aggregates depolymerized from nanowires at 40 °C at various degradation times *t*. The water content of the micelle solution is 13.0 vol %. Scale bars: 1 μ m. (f) Variation in the average volume (V) of the subunits as a function of the depolymerization time at various temperatures. (g) Hydrodynamic radius (R_h) of the subunits before polymerization at 40 °C and the subunits depolymerized from nanowires at 40 °C in solution. (h) Schematic illustration of supramolecular depolymerization of nanowires.

subunits. Moreover, some of the nodes on the nanowire disappear (indicated by the arrows in the insets of Figure 2) and the distributions of the length and diameter of the subunits (including the individual subunits and the subunits in the fragments) become broader at a higher depolymerization temperature. These results indicate that the polymer chain transfer may occur between the neighboring subunits of nanowires during depolymerization. Note that the size of the preassembled subunits was nearly unchanged over time at 40 $^{\circ}$ C, which suggests that the individual subunits in solution are stable, and the polymer chain transfer only occurs between the neighboring subunits on the nanowires in depolymerization (for details, see Section S5 of the Supporting Information). The chain transfer phenomenon is further verified by SLS measurements in the following sections.

The number fraction, f_X , of the depolymerized nanowires with degree of polymerization X (the number of the subunit in one nanowire) was then examined (details of the statistics are provided in Section S3 of the Supporting Information). Figure 2e shows the statistical data of f_X as a function of X after depolymerization for 190 h at various temperatures. As the temperature increases, the number fraction of subunits (X = 1)increases gradually, accompanied by a decrease in the number fraction of nanowires $(X \ge 2)$. These results suggest that the nanowires cannot completely degrade into subunits at temperatures lower than 40 °C (Figure 2a-c). To further evaluate the influence of temperature, we examined the variation in the polydispersity index D of the nanowires (characterizing the distribution of the degree of polymerization of the nanowires, for details, see Section S3 of the Supporting Information) with temperature. The results are shown in Figure 2f. With increasing the temperature from 5 to 40 °C, the value of *Đ* decreases from 1.56 to 1.01 at the fixed depolymerization time of 190 h.

Supramolecular Depolymerization Kinetics of the Nanowires. The kinetics of the supramolecular depolymerization of the nanowires was then studied. Figure 3a-e shows the typical morphology transition of the nanowires with time t at 40 °C. As shown in the figure, the nanowires randomly degrade into nanowire fragments and some individual subunits at the early stage. The length of the nanowire fragments decreases with time, and subunits are finally observed because of the further degradation of the nanowire fragments. In addition, during the nanowire degradation process, the average length and diameter of the micellar subunits change with time, indicating that the chain transfer between the neighboring micelles could occur. After 48 h, the morphologies of the subunits depolymerized from the nanowires show no obvious changes with time (Figure S5). To gain deep insights into the depolymerization process, we examined the time-dependent volume of the subunits (it should be noted that the subunits in the statistics include both the individual subunits and the subunits in the fragments) at various temperatures. The subunits were simplified as ellipsoids. The semimajor and semiminor axes of an ellipsoid are denoted as a and b, respectively. Therefore, the volume, $V = 4\pi ab^2/3$, of the subunit can be obtained by statistics (more than 400 subunits were analyzed). The results are presented in Figure 3f. The average volume of the subunits increases with depolymerization time at temperatures of 20, 30, 33, 35, and 40 °C. Additionally, subunits with larger volumes were obtained at higher temperatures, which suggests that the chain transfer phenomenon between micellar subunits becomes more obvious. This phenomenon can be because of the decrease in the hydrophobic interaction of graft copolymers and increase in the activity of molecular motion at higher temperatures.



Figure 4. (a) Variation in the number-average degree of polymerization, X_n , as a function of time at various temperatures. The black solid lines are the fitting curves, according to the proposed theoretical model. (b) Dependence of ln K on 1000/T. K and T are the rate constant of supramolecular depolymerization and experimental temperature, respectively.

Figure 3g shows the $R_{\rm h}$ distributions of the initial subunits at 40 °C, and the subunits depolymerized from nanowires at 40 °C in solution. As compared with the initial subunits, the peak maximum of R_h of the subunits degraded from nanowires is larger, and the R_h distribution is broader. This result further reveals that transfer of polymer chains occurs during depolymerization. Moreover, the number of micellar aggregates in the solution could be estimated through SLS measurements. $^{38-40}$ In the present work, we examined the aggregate concentration of subunits before supramolecular polymerization and after supramolecular depolymerization (see Section S8 of the Supporting Information). Before supramolecular polymerization, the concentration of the initial subunits at 40 °C is 1.77×10^{-10} mol/L. After supramolecular depolymerization at 40 °C for 48 h, the concentration of the subunits becomes 4.57×10^{-11} mol/L (for details, see Table S1). The decrease in the subunit concentration is attributed to the chain transfer during the depolymerization of the nanowires. In the extreme case, all the chains in one subunit are transferred to another one (e.g., fusion of two micelles). As a result, the concentration of the subunits decreases. According to the aforementioned investigation and discussion, the depolymerization mechanism of the nanowires in solution is shown in Figure 3h. At higher temperatures, the hydrophobic attraction between PBLG is decreased, and the activity of molecular motion is increased, the intermicelle interaction between the connected subunits is broken by thermal motion. As a result, the nanowires depolymerize into subunits and nanowire fragments. The polymer chain transfer simultaneously occurs during the depolymerization of nanowires, which gives rise to the variation in the subunit volume.

Moreover, the variation in the number-average degree of polymerization X_n (i.e., $\sum n_X X / \sum n_X$, where n_X is the number of nanowires, including X subunits) with time t was examined. Figure 4a shows that X_n decreases with time at each temperature, and depolymerization becomes faster with increasing temperature. The R_h variations of the nanowires with time t at various temperatures were also examined (as shown in Figure S7). It was shown that the value of R_h decreases with t, and the decrease in R_h becomes obvious at higher depolymerization temperatures. This result is well consistent with the variations in X_n , as shown in Figure 4a.

To deeply understand the supramolecular depolymerization process, we proposed a theoretical model to describe the depolymerization of the nanowires. In depolymerization, the nanowires randomly degrade into several parts, resembling the classical random depolymerization of a polymer. The nanowires and the subunits can be considered to be polymer chains and monomers, respectively. Noted that the subunits with polydisperse sizes are obtained because of the chain transfer. Therefore, the variation in the aggregation number in the subunits is considered in our model. Because of the material conservation of the micelle system, the total number of polymer chains in the solution, N_{totaly} can be expressed as

$$N_{\text{total}} = N_{\text{sub}} \cdot n_{\text{sub}} = X_n \cdot N \cdot n_{\text{sub}} \tag{1}$$

where N_{sub} , n_{sub} , X_n , and N are number of subunits in the solution, number-average aggregation number of polymer chains per subunit, number-average degree of polymerization of the nanowire (i.e., the number-average number of subunits per nanowire), and total number of nanowires in the solution, respectively. The variations in N and n_{sub} are related to the depolymerization of nanowires and the chain transfer process, respectively (see Section S4 of the Supporting Information). As random depolymerization of nanowires and chain transfer are both considered in this model, the kinetics equation for this depolymerization process can be given by

$$\ln \frac{X_n}{X_0} = -\left(K_{\rm d}t + K_{\rm c} \int_0^t n_{\rm sub} \, {\rm d}t\right) \tag{2}$$

where K_d and K_c are the apparent rate constants for the random depolymerization and the chain transfer, respectively. Note that only the chain transfer between two neighboring subunits is considered in this model. By integrating eq 2, an expression for the X_n of the nanowires as a function of time t, $X_n(t)$, is obtained

$$X_n = X_0 e^{-Kt}$$
(3)

Here, $K = K_d + K_c \cdot \overline{n}_{sub}$ is the total rate constant of depolymerization, \overline{n}_{sub} is the average value of n_{sub} in the depolymerization process, and X_0 is the initial number-average degree of polymerization for nanowires. For details of the derivation of the equations, see Section S4 of the Supporting Information. We used the proposed model to fit the data, as shown in Figure 4a. It was found that the experimental data can be generally fitted with eq 3 (the lines in Figure 4a). The X_n exponentially decreases with time, yielding a depolymerization rate constant *K* at each temperature. We then plot ln *K* versus 1000/T, as shown in Figure 4b. With increasing 1000/T, ln *K* decreases. The Arrhenius rate equation was used to fit the experimental data

$$\ln K(T) = \ln A(T) - \frac{E(T)}{RT}$$
(4)

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Figure 5. (a–d) SEM images of the aggregates depolymerized from the nanowires in solution with various water contents at 40 °C for 190 h: (a) 18.4, (b) 23.8, (c) 28.5, and (d) 32.6 vol %. Scale bars: 1 μ m. (e) Number fraction (f_X) of the nanowires as a function of the degree of polymerization (X) at various water contents after depolymerization for 190 h. (f) Variation in the D of the nanowires as a function of the water content after depolymerization for 190 h. (g) Variation in the number-average degree of polymerization, X_n , with time for various water contents at 40 °C. The black solid lines are the fitting curves, according to the proposed theoretical model. (h) Dependence of ln K on the water content.

where *R* is the gas constant, and *A* is a process-dependent constant.⁴¹ It was found that the data can be well fitted. Setting the slope of the plot equal to -E/RT, we can calculate the activation energy *E*, which is 231 kJ/mol. This value of *E* is comparable to the activation energy of thermal degradation for the classical polymer system (ca.70–300 kJ/mol).⁴² In the present work, the activation barrier for the supramolecular depolymerization of 1D nanowires is attributed to the hydrophobic interaction between the PBLG blocks and the chain transfer between the subunits of the nanowires.

Effects of intermicelle Interactions on the Supramolecular Depolymerization of Nanowires. As seen from the above studies, supramolecular depolymerization occurs because thermal motion breaks the physical interactions between the PBLG blocks at the micelle ends. Variation in the physical interaction can be envisaged to possibly result in different depolymerization behaviors. Here, the physical interaction caused by the hydrophobicity of PBLG blocks can be manipulated by changing the content of water added. The higher the water content, the stronger is the physical interaction. Therefore, we examined the effect of the water content on the depolymerization of nanowires in solution. First, a nanowire solution was obtained via the supramolecular polymerization of preassembled subunits at 5 °C. Then, nanowire solutions with various water contents were prepared by diluting the nanowire solution using the mixture solvents of THF/DMF/H₂O (THF/DMF, 1/1, v/v). The final polymer concentration was fixed at 0.19 g/L for all the samples. Figure 5a-d shows SEM images of the aggregates depolymerized

from nanowires for 190 h at 40 °C, where the water contents are 18.4, 23.8, 28.5, and 32.6 vol %, respectively. It was found that the depolymerization of nanowires becomes difficult at higher water contents. When the water content reaches 32.6 vol %, the nanowires barely change with time (Figures 5d and S8). Figure 5e shows the variation in f_X with X at various water contents after depolymerization for 190 h. As shown in the figure, the f_X of subunits after depolymerization decreases with increasing water contents. In addition, we examined the variation in the D of nanowires during depolymerization. As shown in Figure 5f, D increases with the water content.

We further examined the variation in X_n with depolymerization time t at different water contents. As shown in Figure 5g, X_n decreases with t. However, X_n is almost constant at the water content of 32.6 vol %, which is consistent with the SEM observations. In addition, the variation in X_n can be fitted with the proposed theoretical model, and the rate constant K at each water content can be obtained. It was found that the Kdecreases with the increasinge water content (Figure 5h). Because of the stronger physical interaction between the connected micelles, the nanowires become more stable, resisting depolymerization into subunits at higher water contents. Additionally, the size of the subunits does not obviously change at higher water contents during depolymerization, where the average volume of the subunits is similar to that of the initial subunits. This result demonstrates that the chain transfer is hindered by the enhanced intermicelle interaction at higher water contents (Figure S9). These abovementioned results confirm that the addition of water to the nanowire solution could increase the intermicelle interaction, which resists supramolecular depolymerization.

In this work, we found a temperature-induced supramolecular depolymerization of 1D hierarchical nanostructures. To the best of our knowledge, this is the first example regarding the quantitative analysis of supramolecular depolymerization of 1D structures self-assembled from micelles, which can deepen the understanding of the principles of supramolecular depolymerization. Thermal supramolecular depolymerization generally follows the rules of random depolymerization. This is because that the structure of the preassembled subunits is not exactly the same owing to the polydispersity of graft copolymers and the different aggregation number of polymers. Structural differences usually exist at the ends of the polymeric micelles, which give rise to different reactivities of the subunits. These differences in reactivity result in variations in the physical strength of the connection joints. Therefore, as the temperature is increased, the weak physical interaction between the connected subunits breaks first, and the nanowire is randomly depolymerized into fragments and subunits. In addition, in the depolymerization process, chain transfer between the neighboring micellar subunits occurs, which is a characteristic of such a kind of supramolecular depolymerization. The chain transfer benefits from the chain mobility of the liquid crystal-like structures in the micelle cores. It has been reported that in such a micelle structure, the PBLG rod blocks take a parallel packing along the long axis of micelles (nematic-like liquid crystal cores). The feature of the liquid crystal is the fluidity that provides the chain mobility for the transfers.²⁴ The present findings may also help deepen our understandings of supramolecular depolymerization in nature. For example, microfilament structures are ubiquitous in cells, and the self-assembly and disassembly between the filaments and G-actin are reversible, which play an important role in metabolism and cell division. The reversible supramolecular polymerization and depolymerization of the 1D superstructures observed in the present work may provide a model for the studies of some natural phenomena.

CONCLUSIONS

In conclusion, we discovered a supramolecular depolymerization of 1D nanowires synthesized by supramolecular polymerization. With increasing temperature, the intermicellar interaction (the hydrophobic interaction) between the connected subunits is broken, which induces random depolymerization of the nanowires into nanowire fragments and subunits. The polymer chain transfer between the micelles accompanies the depolymerization, which highlights the characteristics of such a supramolecular depolymerization. A theoretical model was proposed to describe the process of supramolecular depolymerization. Kinetic studies revealed that the thermal depolymerization rate constant increases with temperatures. In addition, with increasing the water content added to the nanowire solution, the intermicelle interaction becomes stronger, and the depolymerization of the nanowires into subunits becomes difficult. The results obtained from this work could provide useful information for understanding the underlying principles of the supramolecular degradation in nature and help us design and prepare complicated functional nanostructures.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.0c00146.

Synthesis and characterization of copolymers; aggregate preparation; definitions and measurements of parameter; TEM and SEM images; and DLS and SLS results (PDF)

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Notes

The authors declare no competing financial interest.

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