Single-Molecule Imaging of Photodegradation Reaction in a Chiral Helical π-Conjugated Polymer Chain

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ABSTRACT: How does the chemical reaction of a single polymer chain progress? This question is not proven, as long as it is studied the data of the ensemble average from the large number of molecules. In this study, we succeeded for the first time in the direct measurement of when, where, and how the chemical reaction of a polymer chain proceeds on a nanometer scale. That is, single-molecule imaging of the photodegradation reaction of a chiral helical π-conjugated polymer following laser irradiation of 405 nm was conducted. Analysis of the chemical kinetics showed that the photodegradation of the single polymer chain proceeded stepwise as a quantum phenomenon. When the motility of the chain-end increased, reactivity of the photodegradation increased. It was also discovered that the photodegradation of the polymer chain proceeded continuously in one direction, like the "domino effect." Our method allowed dynamic imaging of single polymer chains at a solid/liquid interface, and hence can be applied to the study of many types of polymers. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 4103–4107, 2010

KEYWORDS: AFM; chemical kinetics; chiral; conjugated polymers; molecular motion; photodegradation; single-molecule imaging

INTRODUCTION π-Conjugated polymers possess unique photo/electronic properties.[1–3] However, because of the structural diversity of polymers, it is difficult to understand their structure and properties at the molecular levels with ensemble measurements. Observing a single polymer chain clearly explains the correlation between the structure and the properties of the π-conjugated polymer chain. Toward this goal, we began the research and development of single-molecule imaging of a π-conjugated polymer.[4–9] We already reported the single-molecule imaging of the micro-Brownian motion of a supramolecular π-conjugated polymer chain[10] and a chiral helical π-conjugated polymer chain, (−)-poly(MtOCAPA)[11] by high-speed (fast-scan) atomic force microscope (AFM).[12,13] In this study, using high-speed AFM, we succeeded for the first time in real-time imaging of the photodegradation process of a polymer chain in which a π-conjugated main-chain forms a chiral helix on a nanometer scale.

EXPERIMENTAL

We cast tetrahydrofuran (THF, 50 μL × 3) on freshly cleaved mica to remove water and cast n-octylbenzene (5 μL) imme-diately. Then a dilute THF solution (10^{-6} mol/L, 5 μL) of a chiral helical π-conjugated substituted phenylacetylene polymer, (−)-poly(MtOCAPA) (the appearance is a yellow solid. $M_w = 1.05 \times 10^6$, $M_w/M_n = 3.30$ (SEC (size exclusion chromatography), polystyrene standard), cis content > 90% (^{1}H-NMR), $[\alpha]_D^{25} = -499°$ (c 0.0183, CHCl$_3$)), was cast on a mica substrate for single-molecule imaging by a high-speed AFM. A violet laser (wavelength: 405-nm, power: 20 mW, continuous wave (CW), VLSU405H2, Digital Stream Corp., Kanagawa, Japan) was used for photodegradation reaction. The incident 405-nm laser beam was focused on a mica surface through an objective (CFI Plan FluorELWD20xC, Nikon, Tokyo, Japan). Other optical parts including the filters and mirrors (Sigma Koki, Tokyo, Japan) were used in assembling the optical system. The other single-molecule imaging methods were described in our previous report.[11]

RESULTS AND DISCUSSION

Figure 1(A) shows the chemical structure of the chiral helical π-conjugated polymer, (−)-poly(MtOCAPA), used in this study. A higher-order structure where two chains of the
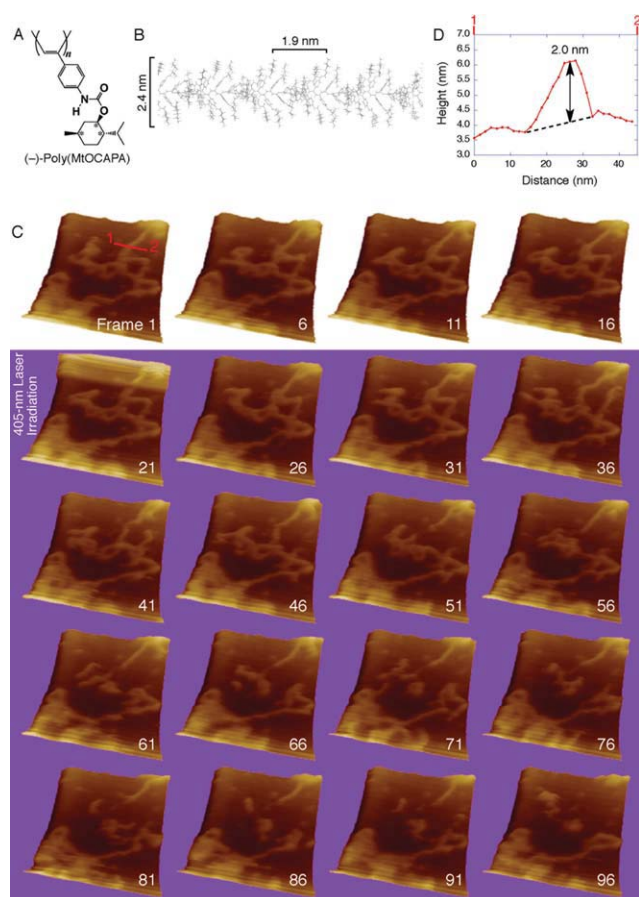
FIGURE 1 (A) Chemical structure of (−)-poly(MtOCAPA). (B) Molecular model of a polymer chain of (−)-poly(MtOCAPA) optimized by the expanded MM3 force field. (C) Single-molecule imaging of a photodegradation reaction of a chiral helical π-conjugated polymer, (−)-poly(MtOCAPA). A violet laser of 405-nm wavelength was irradiated from the 21st frame. The violet background shows a region during laser irradiation. High-speed (fast-scan) AFM images on mica substrate under n-octylbenzene at room temperature. XY: 150 nm × 150 nm, Z: 10 nm. Rate: 80.8 ms per frame (12.4 frames s^{-1}). Laser power: 0.2 mW.[20] (D) A cross section of the line from 1 to 2 indicated in the AFM image of the 1st frame.

helical polymer intertwine with one another to form a double helix was confirmed by scanning tunneling microscopy (STM).[5] Furthermore, structural diversity was confirmed in this polymer chain by AFM imaging and particularly, it was discovered that a coarse dense helical (compressional) structure existed in the single polymer chain.[6] The optimized molecular model of the polymer chain of (−)-poly(MtOCAPA) is shown in Figure 1(B).[14] According to this model, the width of a single polymer chain is 2.4 nm, and the pitch between pendant groups is 1.9 nm.

High-speed AFM images of single chains on mica under n-octylbenzene at room temperature are shown in Figure 1(C). Figure 1(D) is a cross section of the line from 1 to 2 indicated in the AFM image of frame 1 in Figure 1(C). This

height is 2.0 nm, which is almost equal to the size of the single chain [2.4 nm, Fig. 1(B)], confirming that this structure is indeed a single molecule. The structural diversity and flexible molecular motion of the polymer chain were confirmed. This molecular motion is the micro-Brownian motion of the polymer chain partially adsorbed to the substrate surface at the solid/liquid interface.[11] On the other hand, although a portion of the single polymer chain is highly immobile, this is likely due to the strong adsorption of the site onto the substrate surface (Supporting Information Movie S1).

Frames 1 to 20 of the AFM images were recorded prior to the 405-nm violet laser irradiation. The micro-Brownian motion of the polymer chains was observed without a chain cleavage. This shows that the effects of contact of the chain with the AFM probe are negligible. Irradiation by a 405-nm laser is shown starting from frame 21. The noise in the upper part of frame 21 is caused by the delay of the instrumental feedback at the start of laser irradiation. Bond scission by a photodegradation reaction began during laser irradiation. The progression of the reaction was recorded with time as shown in Figure 1(C) (Supporting Information Movie S1). In addition, this reaction has been also confirmed in other area.

Percec et al.[15] have already proposed a reaction mechanism for the photodegradation of cis-poly(phenylacetylene). On the basis of the reaction mechanism and our experimental results, we propose that the polymer chain of (−)-poly(MtO-CAPA) reacted in the following five steps as shown in Scheme 1. In the first step, photoexcitation, a π electron in the π-conjugated polymer chain absorbed a photon at a wavelength of 405-nm [$\varepsilon_{405} = 1.82 \times 10^3$ M/cm (monomer-units conversion), Figure 2] and converted it to an excited singlet state. In the second step, the singlet state underwent an intersystem crossing to an excited triplet state. In the third step, photosensitization,[16,17] the triplet energy in the polymer chain transfered to a π* electron in the ground-state triplet oxygen molecules, $O_2(^3\Sigma_g^-)$, dissolved in the n-octyl-benzene, and the excited-state singlet oxygen molecules, $O_2(^1\Delta_g)$, were generated. In the fourth step, an $O_2(^1\Delta_g)$ molecule reacted with an alkene (C=C) in the polymer chain by [2 + 2] cycloaddition. In the fifth step, the resulting 1,2-dioxetane rearranged to an aldehyde and a ketone followed by chain cleavage.[18]

This reaction mechanism was also supported by the results of the spectral measurements (Supporting Information Fig. S1). The reaction rate increased with increasing laser power. Moreover, a photodegradation reaction continued while the π electrons excited by a 405-nm laser irradiation existed (Fig. 2). At the completion of the reaction, π-conjugated chains fragmented to the oligomers [$M_w = 2.90 \times 10^3$, $M_w/M_n = 1.34$, content >93% (SEC)].[19]

To solve the single-molecule chemical kinetics of photodegradation of the π-conjugated polymer on a nanometer scale, isolated single polymer chains were studied as shown in Figure 3(A) (Supporting Information Movie S2). We
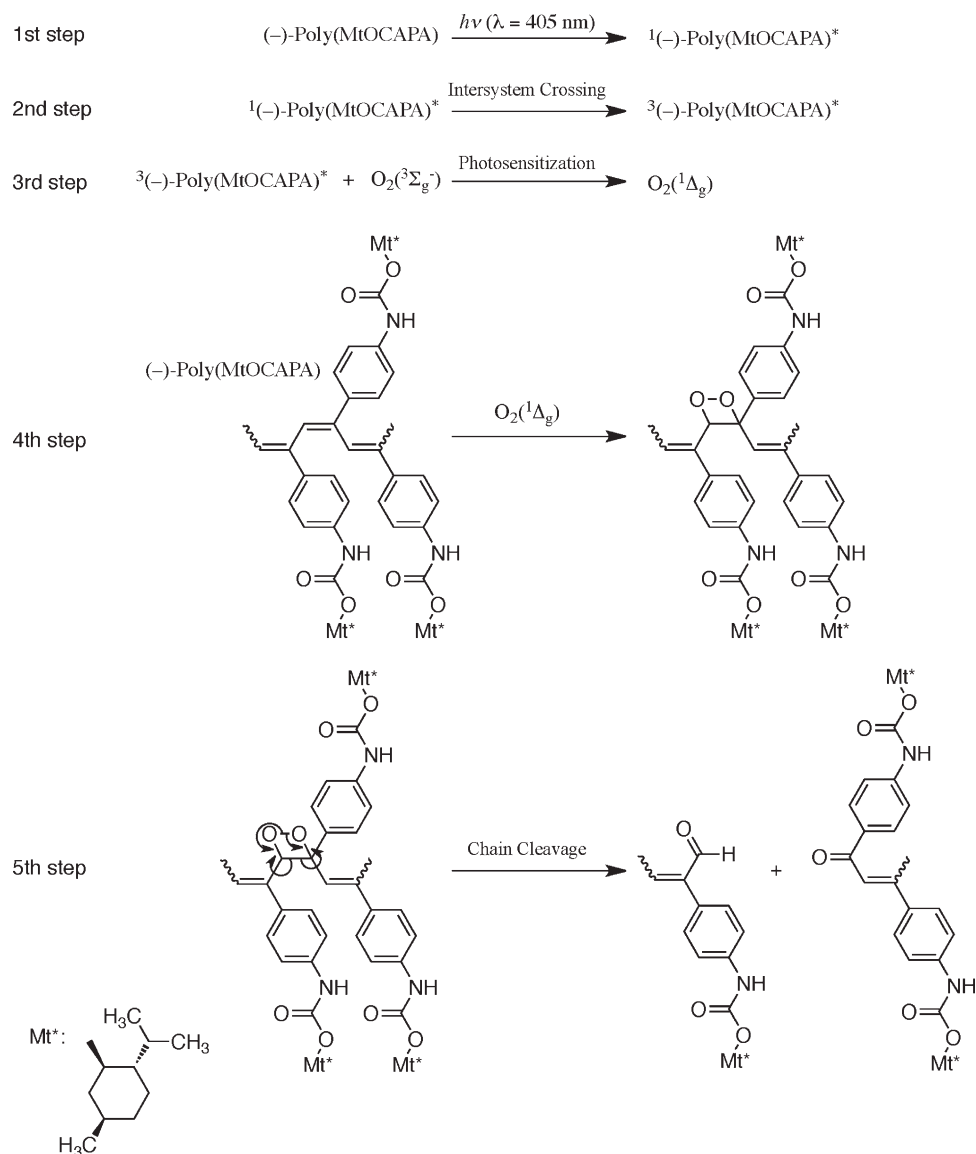
SCHEME 1 Illustration of the proposed reaction mechanism of a photodegradation in a molecular chain of (−)-poly(MtOCAPA).

succeeded in the direct measurement of when, where, and how the chemical reaction proceeded. The observed string shape matter was a single molecule, confirmed by the height
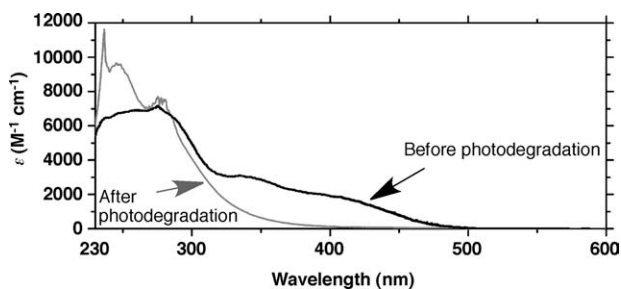

FIGURE 2 UV–visible spectra of (−)-poly(MtOCAPA) in THF at room temperature before and after photodegradation. A violet laser (405 nm, CW) irradiated the THF solution for 90 min.

of 2.1 ± 0.2 nm. In addition, the length of the polymer chain in the observation window was about 200 nm, nearly equal to the average chain length ($\sim$210 nm) that was calculated from the molecular modeling and the average molecular weight as determined by SEC. During irradiation with a 405-nm laser, starting at an observation time of 2.1 s, a globule with a 3-nm height on the left side of the frame decreased in size, consistent with the occurrence of a photodegradation reaction. First, the polymer chain-forming globule was fragmented by a bond scission owing to photodegradation. Then, this fragment desorbed from the substrate surface and diffused to a solvent by collision with solvent molecules. The arrows and numbers in the top part of Figure 3(A) show the starting positions and the order where bond scission was confirmed by the subsequent photodegradation, respectively. These reaction sites have a high motility or bending structure, especially in the reaction site
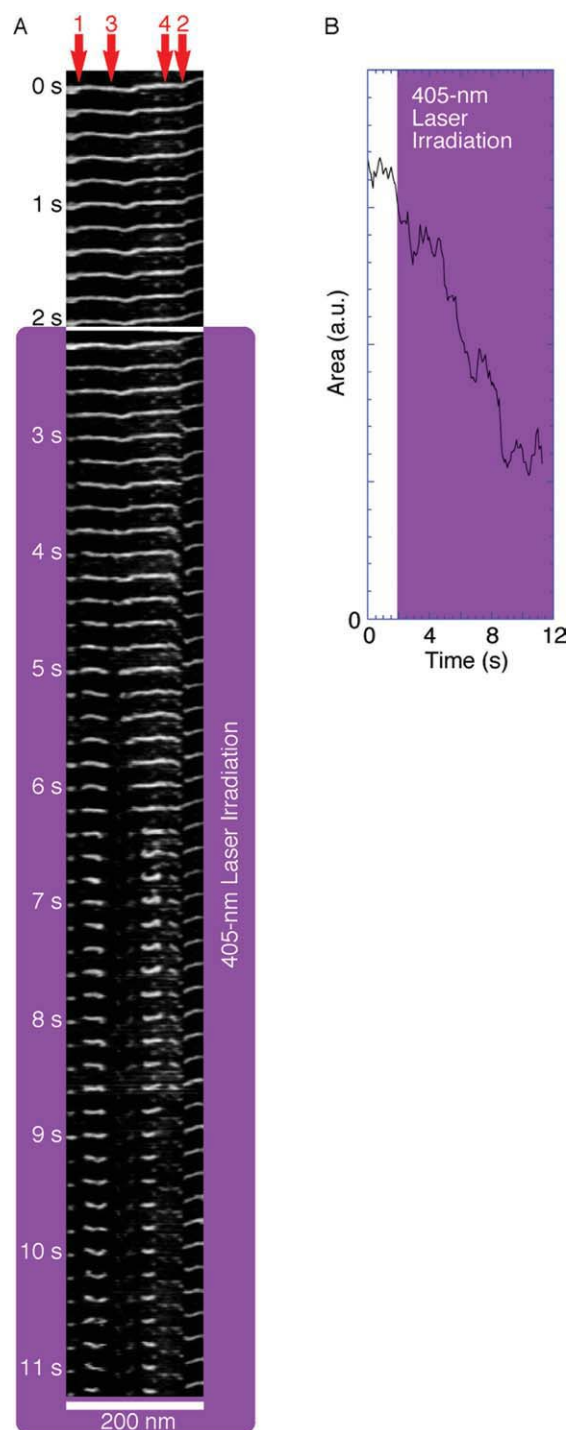
FIGURE 3 (A) High-speed (fast-scan) AFM images for the single-molecule chemical kinetics of photodegradation of the π-conjugated polymer, ($-$)-poly(MtOCAPA), on mica substrate under n-octylbenzene at room temperature, irradiated by violet laser of 405-nm wavelength after 2.1 s. The violet background shows a region during laser irradiation. Rate 100.1 ms per frame (9.99 frames s^{-1}) display in the two-frame interval, XY: 200 nm $\times$ 38 nm, Z: 2.5 nm. Laser power: 0.4 mW. (B) The change in the area of the single-molecule image during all observation times. The purple background shows a region during laser irradiation.[20]

as shown by arrow 3 in which a polymer chain is cut off. It was found that a photodegradation reaction proceeded continuously at the chain-end, and that the chain became shorter from left to right from 5.0 to 6.0 s. The photodegradation rate of the chain-length during this period was found to be $k_{length} = 16.7$ nm/s. That is, $k_{repeating-unit} = 84.3$ U/s when the photodegradation rate in the repeating-unit of the polymer was calculated based on k_{length} and the molecular model [Fig. 1(B)]. The change in the area of the single-molecule image during all observation times is shown in Figure 3(B). As shown in the graph, the photodegradation proceeded immediately following the laser irradiation. In particular, it is important to note that the photodegradation reaction proceeded stepwise, and that the chemical reaction was a quantum phenomenon. These phenomena were observed mainly in other areas (Supporting Information Movie S3).

The excitation frequency of a single polymer chain under the experimental conditions was calculated as $\chi = 4.49 \times 10^4$ photons/s/molecule (Table 1). Thus, although the photoexcitation sites of π electrons in the polymer chain could not be specified, the photoexcitation of π electrons was carried out an average 44,900 times per second in the initial state during laser irradiation. However, as mentioned earlier, the rate of photodegradation at the site indicated by arrow 3 in the observed region was $k_{repeating-unit} = 84.3$ U/s if the degradation proceeded in succession at the chain-end for every repeating-unit of polymer (that is the calculated maximum value). The reaction quantum yield was $\varphi = 0.188\%$, which was less than the value calculated from the equation of $\varphi = k/\chi \times 100$. φ is the value at the initial state of the reaction because χ decreases as the degradation proceeds. This low φ is possibly caused by the low probability of forming the triplet exciton in the polymer chain at the second step of the above-mentioned reaction mechanism (Scheme 1). That is, the low generation efficiency of the lowest excited singlet of oxygen molecule, $O_2(^1\Delta_g)$, by the triplet energy transfer from π-conjugated polymer chain results in a low value for k. In other words, the high stability of this π-conjugated polymer chain is precisely evaluated by a single-molecule measurement. Finally, when a reaction started in this region [arrow 3 in Fig. 3(A)], the photodegradation of the polymer chain proceeded continuously in one direction, like the "domino effect." This continuity of the reaction results from an increase in the reactivity due to an increase of the motility at the cut off chain-end of the π-conjugated polymer. This phenomenon has repeatability that was observed in other areas (Supporting Information Movie S4). However, the cause of the directionality of this reaction is unknown and research is ongoing on whether this phenomenon is due to the structural anisotropy of a chiral helical π-conjugated polymer chain.

In this study, we succeeded for the first time in the direct measurement of when, where, and how a photodegradation reaction of a π-conjugated polymer chain on a nanometer scale proceeds. Furthermore, the single-molecule chemical kinetics was also reported. We anticipate that this will

TABLE 1 Parameters for Calculation of the Excitation Frequency in a Single Chain of (−)-Poly(MtOCAPA)

	Symbol, Equation	Value	Unit
Laser power (at objective)	P_{ex}	4.00×10^{-4}	W (J/s)
Energy of single photon (405 nm)	$E = hc/\lambda_{405}$	4.90×10^{-19}	J
Photon number per 1 s	$N_{ex} = P_{ex}/E$	8.16×10^{14}	photons/s
Irradiation area (114 μm × 144 μm ellipse)	Area	13,456 $= 1.35 \times 10^{-4}$	μm^2 cm^2
Intensity of excitation laser	$I_s = N_{ex}/\text{Area}$	6.04×10^{18}	photons/s/cm^2
Molar absorptivity of polymer at 405 nm, based on repeating units	ε_{405}	1.82×10^3	/M/cm
Average polymerization degree	DP$_n$	1.06×10^3	
Molar absorptivity of polymer at 405 nm, average per a single chain	$\varepsilon_{405}' = \varepsilon_{405} \times \text{DP}_n$	1.93×10^6	/M/cm
Absorption cross section	$\sigma = \ln 10 \times \varepsilon'$	4.44×10^6 $= 7.43 \times 10^{-15}$	/M/cm cm^2/molecule
Excitation frequency	$\chi = \sigma \times I_s$	4.49×10^4	photons/s/molecule

advance the research methods for single-molecule dynamic imaging in real-time.

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18 Another reaction mechanism was also considered; it was the reaction that a radical was generated by photoexcitation, and the main chain was cleaved. However, in consideration of an experimental result and the condition of single-molecule imaging, we proposed the reaction mechanism of Scheme 1.

19 On the other hand, this photodegradation reaction causes a quenching in the fluorescence observed. (Ref. 7)

20 Supporting Information (movies S1–S4 and figure S1) is also available electronically on the journal web site.