Fabrication of Nanowires Based on Polystyrene Derivatives by Single Particle Nano-Fabrication Technique

Atsushi Asanoa, Yuta Maeyoshia, Katsuyoshi Takanoa, Masaaki Omichia, Masaki Sugimotob, Masahito Yoshikawa, Satoshi Tsukudac, Shun-ichiro Tanakac, Akinori Saekia and Shu Sekia*

aDepartment of Applied Chemistry, Graduate School of Engineering, Osaka University, Osaka 565-0871, Japan
bJapan Atomic Energy Agency, Takasaki Advanced Radiation Research Institute, Gunma 370-1292, Japan
cInstitute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan

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1. Introduction

Radiation promotes various chemical effects not only in inorganic but also in organic materials. The predominant effects of radiation on the primary structural changes in polymeric materials have been analyzed statistically, and controlled in terms of chain scission and cross-linking reaction efficiencies.1-2 We have succeeded in direct formation of 1-dimensional nanostructures based on the cross-linking reactions in the thin films of several kinds of synthetic polymers by irradiation of high energy charged particles; single particle nano-fabrication technique (SPNT).3-7 The MeV-order high energy charged particles release non-homogeneously their kinetic energy to the materials, and induce reactive intermediates (ion radicals, neutral radicals, etc.) distributed cylindrically along the particle trajectories, which is called as charged particle tracks.8,9 Because of effective and high-density formation of neutral radical species, their recombination reactions within an ion track produce highly-efficient cross-linking of polymer backbones, resulting in 1-D nano-structured polymer gels with fairly controlled sizes. Unlikely to the case of focused beam of charged particles used commonly as a probe of nanofabrication, no dispersion of “a” particle secures intrinsically the nm-scaled area of released energy and cross-linking reactions, leading to the potentials of “a” high energy charged particle as a tool to fabricate polymeric materials with ultra-high aspect ratio.10

Polystyrene also gives the well-controlled nano-structures in length and number density by SPNT.3,11 However with an increase in the aspect ratio of nanowires higher than a few hundreds, fragmentation of nanowires is often observed by atomic force microscope (AFM) measurement. Due to a low cross-linking efficiency of polystyrene upon irradiation, nanowires with low mechanical strength are considerably affected by the development conditions; handling, development time, and solvent. In this study, several polystyrene derivatives were polymerized from styrene monomers appended with functional groups to increase cross-linking efficiency. We also demonstrated precise formation of 1D-nanowires via the effective cross-linking reaction of the functional groups with high aspect-ratio reaching up to ~103, as well as orientation control of nanowires based on adamantane modified polystyrene derivatives.

2. Method

All reagents and solvents used in the synthesis were purchased from Wako Pure Chemical Industries or Sigma Aldrich Chemical Co. and of the best commercial quality available and used without further purification unless otherwise noted. Polystyrene (PS) and poly(styrene-co-4-chloromethylstyrene) (PSCIS) were synthesized from styrene and
Table 1. The values of cross-linking efficiency and radius of nanowires based on polystyrene derivatives fabricated by the SPNT.

<table>
<thead>
<tr>
<th>Ion beams</th>
<th>G(x) and ( r / \text{nm} )</th>
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<tbody>
<tr>
<td></td>
<td>PS</td>
</tr>
<tr>
<td>450 MeV ( ^{129}\text{Xe}^{23+} )</td>
<td>—</td>
</tr>
<tr>
<td>490 MeV ( ^{192}\text{Os}^{30+} )</td>
<td>0.60 (4.5)</td>
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Figure 1. Chemical structures of polystyrene derivatives; (a) PS (\( M_n = 17200, \text{PDI} = 1.18 \)), (b) PSClS (\( M_n = 13900, \text{PDI} = 1.82, m = 0.37 \)), (c) PSAS (\( M_n = 14500, \text{PDI} = 1.81, m = 0.35 \)), and (d) PSAdS (\( M_n = 15200, \text{PDI} = 1.35, m = 0.25 \)).

4-chloromethylstyrene by using standard nitroxide-mediated radical polymerization (NMP)\(^{12-14}\) with \( N\)-tert-butyl-\( N\)-(2-methyl-1-phenylpropyl)-\( o\)-(1-phenylethyl)hydroxylamine at 110 °C under an atmosphere of nitrogen, respectively. Poly(styrene-co-4-azidemethylstyrene) (PSAS) was prepared using chloromethyl groups of PSAS in the presence of sodium azide in \( N, N\)-dimethylformamide (DMF) at 50 °C for 48 h\(^{15}\). Poly(styrene-co-4-(adamantanyltriazolyl)styrene) (PSAdS)\(^{16}\) was synthesized from poly(styrene-co-4-ethynylstyrene)\(^{17}\) reacted with 1-adamantane azide in the presence of catalytic amount of Cu(I) in THF for 14 h. All polystyrene derivatives were reprecipitated from 2-propanol and dried under reduced pressure. PS, PSCS and PSAS were dissolved 10 wt% in toluene, and spin-coated on Si substrate. The thickness of the films was confirmed by a Dektak 150 surface profiler. PSAdS was dissolved at 5wt% in toluene, and spin-coated or drop-casted on a Si substrate. The films of the all polystyrene derivatives were irradiated by 450 MeV Xe and 490 MeV Os ion beams from cyclotron accelerator at Japan Atomic Energy Agency, Takasaki Advanced Radiation Research Institute. The number of incident particles was controlled from \( 1 \times 10^7 \) to \( 1 \times 10^8 \text{ cm}^{-2} \) to prevent over lapping of the particle trajectories. The irradiated films were developed directly immersing into THF or toluene for 30 min for 24 h. The sizes and shapes of the nanostructure formed along particle trajectories were observed using a SPI-4000 atomic force microscope (AFM) from Seiko Instruments Inc.

3. Results

After development procedure in toluene for 30 min, the surfaces of Si substrate were observed by AFM measurement under dry conditions. Figure 2 (a) and (b) show the AFM micrograph of the nanowires based on PSAdS and PS, respectively. Under this development condition, fragmentation of the nanowires based on PS was confirmed, giving random distribution of the nanowire length. PSAdS and other polystyrene derivatives gave the nanowires with perfectly uniform length and number density. The cross-sectional profiles of the nanowire are also greatly changed between PS and PSAdS as shown in figure 2(c). The cross-linking efficiency can be estimated by the semi-empirical modeling of nanowire sizes.\(^{18}\) The radius of the nanowire was obtained by cross-sectional measurements, and the values are summarized in table 1 as well.

Figure 2. AFM micrographs of nanowires based on (a) PSAdS and (b) PS. Images (a) and (b) were observed in the films at 510 nm and 280 nm thickness after irradiation of 490 MeV \( ^{192}\text{Os}^{30+} \) particles at \( 1.0 \times 10^9 \text{ ions cm}^{-2} \), respectively. (c) Cross-sectional profiles of nanowires. The profile were measured at the position indicated by lines in the corresponding AFM images.
as the values of efficiency for polystyrene and polystyrene derivatives, respectively. Radiation induced cross-linking efficiency has been often characterized in terms of G-value \((G(x))\); number of crosslinks produced per absorbed energy of 100 eV by the polymer material. The values of PSCS: \(G(x)\) as > 4.6 (100 eV)\(^{-1}\), PSAS: \(G(x)\) as > 2.1 (100 eV)\(^{-1}\), and PSAdS: \(G(x)\) as > (100 eV)\(^{-1}\) are higher than the value of PS: \(G(x)\) as > 0.6 (100 eV)\(^{-1}\). PSAdS indicates the highest cross-linking efficiency.

This result means the cross-linking efficiency of polystyrene is drastically changed by introducing functional groups into the styrene monomers. In particular, adamantane moieties play an important role to promote cross-linking reactions. High stability of adamantane radicals were observed upon irradiation of neat adamantane with clear EPR signals at 230 K, and the signals were postulated even at 300 ~ 400K though the signal had shown no longer hyperfine structures.\(^{19}\) Especially, 1-adamantyl radical showed extremely higher stability than that of 2-adamantyl ones, leading to the polymerized products under the irradiation conditions. This is the case giving extremely higher efficiency is observed for cross-linking reactions in PSAdS, reflected as the dramatic increase in the thickness of the nanowires.

The nanowires with ultra-high aspect ratio were demonstrated for the drop-casted film of PSAdS (~ 38 μm thick) as shown in figure 3(a). A long nanowire is observed clearly on the substrate. The length of the nanowire is almost identical to the initial film thickness without fragmentation. This result indicates that the nanowires based on PSAdS have high mechanical strength by densely induced crosslinks in the nanowires via interconnection of adamantane moieties. This was also evident from the fact that fragmentation of the nanowires was not observed under the hard development conditions; with good solvents for PSAdS (THF, chloroform, and toluene) and extremely long time (~ 24h) immersing into the solvents.

With an increase in the number density of the nanowires on the substrate, the long nanowires are bundled as shown in figure 3(b). Figure 3(c) shows the cross-sectional profile of the aggregated structure. Aggregated number of nanowires in the cross-sectional profile is countable, given as configured 6 nanowires. The height of aggregated structure is almost constant, and identical to the height of single nanowire as shown in figure 2(c). This result clearly demonstrates the self-organization of 1D nanowires forming into 2D sheet-like structures with the help of surface interaction of the nanowires. It is also plausible that the interaction between the nanowires and the surface is even higher than the inter-nanowire interaction, leading to the 2-D sheet-like structures without pilling up of the nanowires on the substrate.

It should be noted that the bottom-side terminal of the nanowire is tightly connected to the substrate. Based on the high mechanical strength and the presence of tightly connected ends on the surfaces, the orientation control of the nanowires was examined by developing the nanowires in solvent flow along one direction. The lines of the nanowire apsides are oriented...
clearly along the directions of solvent flows as shown in figure 4 (a) and (b). Simple dipping processes of the substrate into solvents give highly oriented surface structures of nanowires with ultra-high aspect ratio.

In conclusion, the introduction of functional groups and molecule into the polystyrene backbones can control the cross-linking efficiency of polystyrene derivatives upon exposure to MeV-order charged particles. Adamantane modified polystyrene: PSAdS showed dramatic increase in the cross-linking efficiency via radiation induced interconnection of adamantane moieties, providing high density crosslinks inside the nanowires, hence the higher mechanical strength than that of polystyrene based nanowires. The tough nanowires with ultra-high aspect ratio of ~750 were successfully produced in the present study, and in-plane orientation of the nanowires was also fairly controlled by the simple dipping process of the nanowires with connected ends on the substrate.

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References