Highly Efficient Solid-State Intra-Track Polymerization of Ethynyl-Substituted Spirobifluorenes Triggered by Swift Heavy Ion Irradiations

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Acetylenes are the first monomer to polymerize by the energy deposited by ionizing radiations. Herein we report an extremely efficient solid state polymerization of ethynyl-substituted 9,9’-spirobi[9H-fluorene]s (SBFs) via a unique nano-fabrication technique referred to as Single Particle Trigged Linear Polymerization (STLiP) initiated by high energy charged particles. The resulted nanowires of polymerized/crosslinked SBFs show a gradual transformation from flexible to rigid rod-like with an increase in the reaction efficiency mediated by the ethynyl substitution. The overall efficiency of initiation/propagation/crosslinking reactions is remarkably high even in comparison with the primary yield of ionization events in the radiation chemical processes, marking up to \( G > 80 \ (100 \text{ eV})^{-1} \), which is suggestive of efficient chain reactions in the propagation steps. The present results demonstrate efficient solid-state polymerization reactions, which are neither topochemical polymerization reactions nor acid/base catalyzed reactions, expand the versatility of STLiP technique to fabricate 1D nanomaterials based on a variety of organic compounds.

Keywords: Nanowire, High-energy particle, Spirobifluorene, Solid-state polymerization, Acetylene

1. Introduction

Ionizing radiation met polymeric materials in the third decade of the 20th century [1–3], although the first report on the radiation induced polymerization reactions appeared in 1874, where electric discharge in acetylene vapor atmosphere gave “condensed materials” on the wall of the discharge tube in spite of both “polymer” and “ionizing radiation” had not been yet discovered and remained unknown [4]. Since the pioneering works on the radiation induced polymerization reactions, a variety of monomeric molecules have been demonstrated both in their gas and condensed phases as effective substances to polymerize via initiating free radical species and subsequent chain propagation reactions [5–7].

Ionizing radiations have been often discussed in terms of Linear Energy Transfer (LET) reflecting...
the rate of released kinetic energy from the incident particles or photons along their trajectory, and the value of LET is given with the unit of eV nm\(^{-1}\) [8]. Typical value of LET for X-rays or \(\gamma\) rays ranges 0.1–0.5 eV nm\(^{-1}\) in condensed phases of organic molecular substances [9]. Considering the G-values or W-values of ionization events, one can presume the dispersive events without inter-correlation even in the condensed phase. This leads to homogeneous distribution of reactive intermediates, and thus advantageous for the subsequent quantitative analysis of radiation induced reactions. In contrast to the low-LET radiations, the LET values of \(\alpha\)-particles or high energy heavy particles reach up to 1000 eV nm\(^{-1}\) [9–11], where the above schema of dispersive reactive intermediates are no longer available, giving critical overlap of ionization events and intercorrelation of reactive intermediates in small confined spatial area, which is often referred as an ion track.

Based on this convergence of released energy along the ionizing radiation trajectory, the subsequent chemical reactions within an ion track have been applied as the track detectors [12], nanopore formation [13], and nanochannel fabrication [14]. The merits of the high energy convergence have been also developed in our unique technique: “STLiP” which affords size- and number density-controlled nanostructures with extremely high aspect ratio via intra-track polymerization reactions (Fig. 1). The key factor in the STLiP technique is to achieve gelation with high enough insolubility against successive wet development process with strong solvent for initial target molecules [15–18], and thus to trigger efficiently the initiation reactions and promote propagation reactions in a charged particle track.

To maximize the efficiency of the initiation as well as of propagation reaction, herein we have developed new molecular systems based on 9,9’-spirobi[9H-fluorene] (SBF) with Br or acetylene substituents; the former is expected to lead high yield of free radicals via the dissociative electron attachment (DEA) reactions, whereas the latter promotes highly efficient propagation reactions in condensed phases.

2. Experimental
2.1. Materials

SBF derivatives 1–4 were purchased from Tokyo Chemical Industry Co. and used as-received. Compounds 5–7 were synthesized according to the literature [19]. The molecular structures of the compounds employed are shown in Fig. 2. \(^1\)H NMR spectra were recorded in CDCl\(_3\) on a JEOL model AL-400 spectrometer operating at 400 MHz, where chemical shifts were determined with respect to tetramethylsilane (TMS) as an internal reference.

Fig. 2. Chemical structures of the spirobifluorene derivatives 1–7 in this study.

Fig. 3. AFM topographic images and the radius distributions of the nanowires from spin-coated film of (a) 1, (b) 2, (c) 3, (d) 4. Nanowires were fabricated by irradiation with 450 MeV \(^{129}\)Xe\(^{23+}\) particles at the fluence of 1.0 \(\times\) \(10^{10}\) cm\(^{-2}\).
2.2. Method

Si substrates were cut into 1.5 × 1.5 cm² square pieces, sonicated in 2-propanol, dried, and treated with UV-O₃ irradiation prior to the use. All compounds were dissolved in CHCl₃ and spin-coated onto the Si substrate to yield thin films. The thickness of the films was evaluated by a Veeco Instruments Inc. model Dektak 150 surface profiler. 450 MeV ¹²⁹Xe²⁺⁺ particles were generated from a cyclotron accelerator at Takasaki Advanced Radiation Research Institute. The prepared thin films were exposed to the above ion beam in a vacuum chamber (~ 1 × 10⁻⁴ Pa). The two-dimensional areal number density of incident particles was controlled at 10⁹–10¹¹ particles cm⁻². No sublimation under vacuum was confirmed based on the film thickness. Then, the irradiated films were further cut into small pieces and developed by immersing them into toluene for ~1 min at room temperature. The morphology of the isolated nanowires was characterized by using a Bruker Co. model Multimode 8 atomic force microscopy (AFM). The loss of kinetic energy of ions due to penetration through the SBF films was estimated using the SRIM 2010 calculation code. Transition states of presumed neutral radical species in the propagation steps of polymerization reaction of 5–7 were calculated by Gaussian09 code.

3. Results and discussion

We previously reported that SBF frameworks were likely to be reacted upon irradiation of high LET charged particles and formed into clear and uniform nanowires by the STLiP process [16]. Halogenation of aromatic rings of SBF enhances the overall polymerization reactions mediated by free radicals remarkably due to DEA. In this study, irradiation of 450 MeV ¹²⁹Xe²⁺⁺ particles also give nanowires with high enough durability against the wet-development processes by strong solvents such as CHCl₃ and tetrahydrofuran. The nano-fabrication of ethynyl-substituted derivatives was also conducted by an identical protocol. Considering that nano-gelation within an ion track by polymerization/crosslinking reactions causes the steep change in solubility of the molecular substances. Hence, we could estimate the total volume of the nano-gels, and the overall yield of the reactions by direct tracing of the nanowire radius by AFM. The energy density released by a swift heavy ion can be regarded to be attenuated along with an inverse square law of r: the radial distance from the center of an ion track [22]. This allows us to calculate the energy density theoretical at the nanowire surface: the boundary of irradiated and non-irradiated part. Cross-sectional shapes of the resulted nanowires are presumed to suffer considerable deformation via strong interaction.

Fig. 4. AFM topographic images and the radius distributions of the nanowires from spin-coated film of (a) 1, (b) 5, (c) 6, (d) 7. Nanowires were fabricated by irradiation with 450 MeV ¹²⁹Xe²⁺⁺ particles at the fluence of 1.0 × 10⁹ cm⁻².

Fig. 5. Energy distribution in the penumbra region for compound (a) 1, (b) 4, (c) 7 calculated from Eq. (2). Densities of compound 1 and 4 are presumed from the articles [20,21].
with substrate surfaces during the development processes with the strong solvents. Thus, the volume of nano-gels was assessed by taking an ellipsoidal model for the cross-sectional shape; The $r$ was defined as $r = (w r_h) ^{1/2}$, where $w$, $r$, and $r_h$ are the half-width and half-height of the cross-section of the nanowires, respectively. The values of $r$, as well as their distribution, are averaged over more than 30 isolated nanowires for respective compounds (Figs. 3 and 4). The values of $r$ showed a good correlation with the intramolecular composition of bromine atom or ethynyl groups. It should be noted that the rather remarkable increase of $r$ was observed with ethynylation than bromination of the target molecules. Ethynyl groups are expected to play a significant role in efficient polymerization/propagation reactions [23,24], and this is the case giving the dramatic increase in $r$.

To discuss quantitatively on the efficiency of polymerization reactions, we adopted the following theoretical model for the radial energy density in an ion track depicted by two distinctive area: core and penumbra area. The radial energy density distribution in the two distinctive area: $\rho_c(r)$ and $\rho_p(r)$ are given by Eqs. (1) and (2). [22]

$$\rho_c = \frac{\text{LET}}{2} \left[ \pi r_c^2 \right]^{-1} + \frac{\text{LET}}{2} \left[ 2\pi r_c^2 \ln \left( \frac{e^{1/2} r_c^2}{r_c} \right) \right]^{-1}, r \leq r_c \quad (1)$$

and

$$\rho_p(r) = \frac{\text{LET}}{2} \left[ 2\pi r^2 \ln \left( \frac{e^{1/2} r_c^2}{r_c} \right) \right]^{-1}, r_c < r \leq r_p \quad (2)$$

where $r$ and $e$ are the calculated radius of the nanowire and an exponential factor, $r_c$ and $r_p$ are the radii of the core and penumbra areas given by the theoretical equation for the interaction of charged particles with matters. As can be seen from the energy distributions in Fig. 5, the spatial deposited energy distributions are coalesced with each other for non-substituted or substituted SBF, and the observed values of $r$ in the range of penumbra in all cases. This is strongly suggestive of $r$ defined clearly by the contribution of reactive intermediates from respective compounds to the efficiency of initiation/polymerization(propagation) reactions.

The overall efficiency of reactions contributing to the gelation of the present system can be discussed in terms of $G(x)$ that is defined as the number of overall reactions per absorbed 100 eV. Derived values of $r$ reflect precisely the total volume of nanogels, thus $G(x)$ is in good correlation with $r$ as given by Eq. (3) [25],

$$G(x) = \frac{400 \pi \rho N_A r^2}{\text{LET} \cdot M} \ln \left( \frac{e^{1/2} r_c}{r_c} \right) \quad (3)$$

where $\rho$ is the density of the material, $N_A$ is Avogadro’s number, and $M$ is the molecular weight, respectively. The derived values of $G(x)$ for all compounds are summarized in Table 1.

Radiation-induced polymerization reactions including initiation and propagation reactions usually proceed through free-radical reactions, where a series of investigations have revealed the high-efficient polymerization from organic molecules (e.g. acetylene, propylene, butylene, methyl methacrylate, and styrene) since the early 20th century [26–29]. Especially, it has been reported that aromatic compounds show much less reactivity to radiation than the alkanes and alkenes because excitation of a $\pi$-electron appears as delocalized energy distribution due to transitions to lower energy level through the entire $\pi$-system. While, dissociative electron attachment has been known a candidate to raise the radical generation efficiency from aromatic compounds. The $G$ value for primary yield of neutral radicals via DEA has been determined as 3.5–22.3 (100 eV)$^{-1}$ for chloride and bromide hydrocarbons [30], which is much higher than that of free ion yield of aromatic molecules such as benzene ($G = 0.052$ (100 eV)$^{-1}$) [31,32]. These values are almost the upper limit of the efficiency of radiation induced free radical formation reactions. The observed values of $G(x)$ in Br-substituted SBF are even higher than those of DEA, and $G(x) > \sim 10$ (100 eV)$^{-1}$ is often interpreted as the evidence of chain reaction in their propagation/polymerization reactions (Scheme 1). Furthermore, the increase of the reaction efficiency by multi-substitution with Br atoms also suggests that products can contribute again as electron acceptors acting as platforms for the subsequent polymerization/propagation by further DEA.

These efficient free radical formation reactions, in contrast, cannot be expected in ethynyl-substituted SBFs. Nevertheless, the surprisingly

| Table 1. Summary of density $\rho$, calculated linear energy transfer (LET), observed nanowire radii $r$, and estimated crosslinking reaction efficiencies $G(x)$ for each compound. |
| Compounds | $\rho$ (g mol$^{-1}$) | LET (eV nm$^{-1}$) | $r$ (nm) | $G(x)$ (100 eV)$^{-1}$ |
|-----------|----------------|-----------------|---------|-----------------|
|           | 1 | 2 | 3 | 4 |
| $\rho$ | 1.25 | 1.48 | 1.63 | 1.84 |
| LET | 11800 | 12000 | 12300 | 12400 |
| $r$ | 4.2 ± 0.3 | 4.4 ± 0.4 | 4.7 ± 0.3 | 5.2 ± 0.3 |
| $G(x)$ | 29 | 37 | 44 | 59 |

- **Compounds**: 5, 6, 7

| Compounds | $\rho$ (g mol$^{-1}$) | LET (eV nm$^{-1}$) | $r$ (nm) | $G(x)$ (100 eV)$^{-1}$ |
|-----------|----------------|-----------------|---------|-----------------|
|           | 1 | 2 | 3 | 4 |
| $\rho$ | 1.29 | 1.29 | 1.31 |
| LET | 11700 | 11700 | 11800 |
| $r$ | 5.2 ± 0.4 | 5.7 ± 0.3 | 7.1 ± 0.5 |
| $G(x)$ | 47 | 57 | 87 |
high $G(x)$ over $\sim 80$ (100 eV)$^{-1}$ beyond those in Br-substituted SBFs was recorded in 7. Going back to the pioneering works on radiation-induced polymerization of gas and/or liquid acetylenes extensively investigated since 1960s, the polymerization yield of acetylene into cuprene had been reported $G > 70$ (100 eV)$^{-1}$ upon irradiation to a variety of radiation sources including $\gamma$-rays, $\beta$-rays and swift heavy ions [7,33,34]. The major two reaction mechanisms were proposed to illustrate the chain reaction in the polymerization: 1) initiating from excited state of an acetylene molecule formed by (geminate or bulk) charge recombination followed by capturing neutral acetylene molecules, and 2) terminal hydrogen dissociation from the excited state of acetylene leading to free radicals for subsequent chain reactions. Considering the restricted molecular motions in the solid phase, the former mechanism rarely occur in the STLiP process. Therefore, the formation of polymeric nanowire can be well explained by free-radical chain reactions proceed via the highly reactive vinyl radicals.

4. Conclusion

Organic nanowires with desired number density and length were fabricated through the charged particle-initiated solid-state polymerization reactions of SBF and its brominated and ethynyl-substituted derivatives. The evaluation of the radius of the isolated nanowires and following estimation of $G$ values indicated that the polymerization efficiency was increased upon bromination of SBF, which likely originates from the enhanced radical generation yields via DEA reactions. The estimated $G$ values for ethynyl-substituted SBFs are further increased, reaching up to those of gas-phase polymerization of acetylenes in the case of tetra-ethynyl SBF. The observed remarkably high reactivity is possibly due to the generation of highly-reactive vinyl radicals as a result of the reaction between an initially-generated radical and carbon-carbon triple bond, which eventually results in the efficient propagation reactions in the solid state.

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