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A novel shortened electrospun nanofiber modified with a ‘concentrated’ polymer brush

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Abstract
We report the fabrication of shortened electrospun polymer fibers with a well-defined concentrated polymer brush. We first prepared electrospun nanofibers from a random copolymer of styrene and 4-vinylbenzyl 2-bromopropionate, with number-average molecular weight $M_n = 105 200$ and weight-average molecular weight $M_w = 296 700$ ($M_w/M_n = 2.82$). The fibers had a diameter of $593 \pm 74 \text{ nm}$ and contained initiating sites for surface-initiated atom transfer radical polymerization (SI-ATRP). Then, SI-ATRP of hydrophilic styrene sodium sulfonate (SSNa) was carried out in the presence of a free initiator and the hydrophobic fibers. Gel permeation chromatography confirmed that $M_n$ and $M_w/M_n$ values were almost the same for free polymers and graft polymers. $M_n$ agreed well with the theoretical prediction, and $M_w/M_n$ was relatively low ($<1.3$) in all the examined cases, indicating that this polymerization proceeded in a living manner. Using the values of the graft amount measured by Fourier transform infrared spectroscopy, the surface area, and $M_n$, we calculated the graft density $\sigma$ as $0.22 \text{ chains nm}^{-2}$. This value was nearly equal to the density obtained on silicon wafers ($\sigma = 0.24 \text{ chains nm}^{-2}$), which is categorized into the concentrated brush regime. Finally, we mechanically cut the fibers with a concentrated poly(SSNa) brush by a homogenizer. With increasing cutting time, the fiber length became shorter and more homogenous ($11 \pm 17 \mu \text{m after 3 h}$). The shortened fibers exhibited excellent water dispersibility owing to the hydrophilic poly(SSNa) brush layer.

Keywords: electrospinning, nanofiber, surface-initiated atom transfer radical polymerization, concentrated polymer brush, fiber cutting

1. Introduction
Electrospinning has attracted much interest in medical, environmental, catalysis and optoelectronics fields, because it can fabricate fibers of various polymers with diameters ranging from several tens of nanometers to a few micrometers, with high yield and at low cost [1,2]. This technique generally produces nonwoven mats and sponges composed of continuous long fibers, having large surface area and tunable chemical and mechanical properties. Therefore, electrospun fibers have been expected for various applications such as sensors, filters, tissue engineering scaffolds, wound cover
materials, solar cells, etc. However, the fibers produced by the conventional electrospinning technique are limited in shape to mats [1,2] and sponges [3].

Recently, many studies have focused on surface functionalization of electrospun fibers using coaxial spinning [4], phase separation of blend polymers and block copolymers [5–7], and grafting-to/from polymerization [8–12]. However, the functional polymer layers prepared by the first two methods are typically unstable at the interface between the outer and inner layers against solvents, temperature and mechanical stress. Although grafting-to/from polymerization has an advantage of providing a chemically and physically stable interface between two polymer layers, there are only a few reports on grafting polymers onto electrospun fibers [8–12].

To meet the requisite for controlling shape and surface functionality of electrospun fibers, in this work, we aimed to develop a new type of electrospun fiber, possessing a short length, a rod-like shape, and surface functionality. These fibers can find new applications as fibril fillers and substrates for drug delivery system, among others.

Surface-initiated living radical polymerization (SI-LRP) is one of the most promising polymer-grafting techniques because it can produce well-defined polymers on various surfaces with extremely high graft density [13–21]. Such densely grafted polymers can be considered as a concentrated polymer brush having structure and properties quite different from those of semi-dilute brushes prepared by conventional methods [21–27]. For example, in a good solvent, the chains in the concentrated brush are highly stretched, nearly to their full length. Owing to the unique extended structure, the swollen brush layer shows strong modulation, super lubrication and size-exclusion effect. Even in a dry state, the concentrated brush shows different characteristics in a glass transition temperature, miscibility, and so on [21,25–27]. Therefore, by taking advantage of the unique and unprecedented properties of concentrated brushes, the ‘shortened’ fiber with ‘concentrated’ brush would be a novel fiber-based material with advanced surface functionality.

A few recent studies reported the surface modification of electrospun nanofibers by surface-initiated atom transfer radical polymerization (SI-ATRP), one of LRPs [8–12]. Unfortunately, they could not characterize molecular weight and polydispersity of the graft polymers, i.e. the graft density, which is required to determine the physical structure of the brush layer.

In this report, by optimizing experimental conditions, we fabricated concentrated brushes of a hydrophilic polystyrene sodium sulfonate (PSSNa) on electrospun fibers of a polystyrene-based hydrophobic copolymer by SI-ATRP. We then shortened the fibers by mechanical cutting with a homogenizer. We also characterized molecular weight and polydispersity of grafted polymers to confirm the graft density. Our homogenizing system can produce a large amount of shortened fibers, and their length can be controlled by varying the batch scale and cutting time.

2. Experimental details

2.1. Materials

Styrene (ST, 99%, Wako Pure Chemical, Japan) was purified by distillation under vacuum; 4-vinylbenzyl alcohol (VBA) was kindly donated by Seimi Chemical. Methanol (MeOH, 99.9%, Wako), 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (VR110, 99.9%, Wako), Cu(I)Br (99.99%, Wako), Cu(II)Br (99.99%, Wako), SSNa (99.9%, Wako), 2,2′-bipyridine (bpy, 99.9%, Nacalai Tesque, Japan) and potassium hydroxide (KOH, 85%, Wako) were used as received. 4-vinylbenzyl 2-bromopropionate (VPB) was synthesized from VBA according to the literature [28]; poly(ethylene glycol) (PEG, n = 7) based macroinitiator (PEGBr), a free initiator for ATRP, was prepared as in [29]; and 3-(2-bromo-2-isobutoxy)propyltriethoxysilane (BPE), a fixed initiator for ATRP, was synthesized as in [30].

2.2. Preparation of random copolymers of ST and VBP

A solution of ST (13.86 g, 133 mmol), VBP (2.04 g, 7.6 mmol) and VR110 (2.3 mg, 0.009 mmol) was prepared in a Schlenk tube with a three-way stopcock, degassed with five freeze-evacuate-thaw cycles, and backfilled with nitrogen. The polymerization tube was heated to 110°C for 9 h. After the polymerization, poly(ST-r-VBP) was precipitated with MeOH. The molecular weight and polydispersity of poly(ST-r-VBP) were determined by gel permeation chromatography (GPC) in N,N-dimethylformamide (DMF) with 10 mM LiCl. The composition of poly(ST-r-VBP) was determined by nuclear magnetic resonance (1H-NMR) measurements in deuterated chloroform (CDCl3).

2.3. Electrospinning nanofibers of copolymers

The high voltage for the electrospinning process was provided by an HSP-30k-2 supply (Nippon Stabilizer Industry Co. Ltd, Osaka, Japan), and the spinning rate was controlled using a syringe pump. A 30 wt% solution of poly(ST-r-VBP) in DMF was electrospun to fabricate nanofibers at an applied potential of 20 kV using a needle inner of about 0.45 mm diameter and a solution feeding rate of 1 ml h⁻¹. The obtained fiber mats were observed with a scanning electron microscope (SEM). The average diameter was calculated from more than 60 fibers, imaged in 3 different areas on a nonwoven mat (1 × 1 cm²). The surface area of the nonwoven mat, S_BET, was determined by Brunauer–Emmett–Teller (BET) analysis of two different samples.

2.4. Graft polymerization

A MeOH/water solution (10 ml, 1/3, v/v) of Cu(II)Br₂ (2.56 mg, 0.018 mmol), Cu(II)Br (1.71 mg, 0.0077 mmol), bpy (8.0 mg, 0.051 mmol), PEGBr (12.7 mg, 0.026 mmol) and SSNa (1.05 g, 5.1 mmol) were prepared under nitrogen atmosphere and added to a Schlenk tube with poly(ST-r-VBP) electrospun fibers (20 mg). Prior to the polymerization, the fibers were dried for 2 days under vacuum. The
polymerization solution was heated at 30 °C for prescribed time (figure 2). After the polymerization, \( M_n \) and \( M_w/M_n \) for the free polymers were determined by standard PSSNa-calibrated GPC. The conversion was estimated from the known peak area and the initial feeding ratio. The PSSNa-grafted fibers were washed with water 15 times, and we verified that further washing did not change the graft amount. SEM observations confirmed that the morphology of the fibers little changed after the SI-ATRP.

The grafted PSSNa was cleaved from the fibers as follows: the PSSNa-grafted fibers (15 mg) were refluxed with a KOH aqueous solution (1 mol l\(^{-1}\)) for 0.5 h, followed: the PSSNa-grafted fibers (15 mg) were refluxed with a KOH aqueous solution (1 mol l\(^{-1}\), 10 ml, MeOH/water = 1/2) at 60 °C for 6 h. After neutralization, the cleaved PSSNa was collected by dialysis and then subjected to GPC.

The graft amount of PSSNa on the fiber, \( A \) (gm\(^{-2}\)), was estimated by Fourier transform infrared spectroscopy (FTIR). The graft density \( \sigma \) was calculated as

\[
\sigma = (N_A/A)/M_n 10^{-18},
\]

where \( N_A \) is the Avogadro number.

The surface occupancy was estimated as

\[
\sigma^* = a^2 \sigma,
\]

where \( a^2 \) is the cross-sectional area per monomer unit.

We also carried out SI-ATRP of SSNa from silicon wafers as follows: a BPE-immobilized silicon wafer (BPE \( \approx 2.7 \times 10^{-7} \) mmol) was immersed in a nitrogen-purged MeOH/water solution (10 ml, 1/3, v/v) of Cu(I)Br (2.56 mg, 0.018 mmol), Cu(II)Br\(_2\) (1.71 mg, 0.0077 mmol), bpy (8.0 mg, 0.051 mmol), PEGBr (12.7 mg, 0.026 mmol) and SSNa (1.05 g, 5.1 mmol). The solution was heated to 30 °C for 1.5, 2, 3, and 4 h. After the polymerization, the solution was diluted with water/acetonitrile to a known concentration and analyzed by GPC. All the substrates were washed with MeOH to remove physisorbed free polymers and impurities. The graft thickness was measured with an ellipsometer. The graft density \( \sigma \) on a silicon wafer was calculated as

\[
\sigma = L \rho N_A/M_n,
\]

where \( L \) is the thickness of the graft layer and \( \rho \) is the bulk density of PSSNa. The averaged \( \sigma \) was 0.24 chains nm\(^{-2}\) (\( \sigma^* = 0.32 \)).

2.5. Cutting nanofibers with a homogenizer

The electrospun fibers with or without PSSNa brushes were cut with a homogenizer (IKA, ULTRA-TURRAX T25) in water and a phase-separated liquid system of water and hexane, respectively [31].

As we described before [31], our cutting technique using a homogenizer provides advantages of short time operation, easy operation, high recovery (\( \sim 80\% \)), controlled supply and length from a few to tens \( \mu \)m, as compared with the previously reported techniques.

2.6. Measurements

The GPC analysis for poly(ST-\( r \)-VBP) was carried out on a TOSOH HLC-8220 at a flow rate of 0.8 ml min\(^{-1}\) using DMF with 10 mM LiCl as eluent (40 °C). The column system was calibrated with Shodex PST standards. The GPC analysis for PSSNa was carried out on a Shodex GPC-101 at a flow rate of 0.8 ml min\(^{-1}\) using water/acetonitrile (6/4) with 10 mM LiCl as eluent (40 °C). The column system was calibrated using PSSNa standards.

\(^1\)H-NMR spectra were recorded with a Bruker DMX500 (500 MHz) spectrometer in CDCl\(_3\). Fibers were imaged with a JEOL JSM-5610 SEM at an acceleration voltage of 20 kV. Prior to imaging, a thin Pt layer was evaporated onto the fiber materials to render them electrically conductive.

X-ray photoelectron spectroscopy (XPS) measurements were preformed with a PHI Quantera (SXM ULVAC-PHI) system equipped with a monochromatic Al K\(_x\) x-ray source operated at 20 kV. The photoelectron takeoff angle was 45° and the results were averaged over at least two samples. FTIR measurements were performed with a Shimadzu FTIR-8400s system.

3. Results and discussion

3.1. Electrospinning of poly(ST-\( r \)-VBP)

We synthesized a random copolymer of ST and VBP, poly(ST-\( r \)-VBP), having initiating sites for SI-ATRP, by conventional radical polymerization (Scheme 1). \( M_n = 105\,200 \) and \( M_w/M_n = 2.82 \) for the copolymer were measured by GPC. The composition of PBVP to PST in poly(ST-\( r \)-VBP), \( f_{\text{VBP}} \), was determined by \(^1\)H-NMR as 6%, almost equal to the monomer feeding ratio. Then, we electrospun a DMF solution of this copolymer, yielding nanofibers with a diameter of 593 ± 74 nm. Figure 1(a) showed a SEM image of the electrospun fibers collected on an Al foil (nonwoven mat). XPS measurement confirmed that the amount of bromine, an initiating site for SI-ATRP, on the fibers (the nonwoven mat) was 0.48 atom%. As a reference, we examined with XPS an equivalent film spin-cast from 30 wt% poly(ST-\( r \)-VBP) solution in DMF onto a glass slide (0.23 atom%). Although the amounts of bromine were different on the fibers and the cast film, the former value had a significant uncertainty because of the porous structure of the fiber mat. While XPS measurement could not determine the number of initiating groups on the fibers, it showed that bromine, an initiating group, exists on or near the fiber surface. We considered that the value \( f_{\text{VBP}} = 6\% \) was sufficient for the formation of a concentrated polymer brush because a concentrated polymer brush was fabricated on the fibers of this copolymer as well as on the silicon wafers as detailed below.

The surface area of the nonwoven mat was measured as \( S_{\text{BET}} = 8.76\, \text{m}^2\, \text{g}^{-1} \). This value is almost equal to the value calculated from the fiber diameter (6.41 m\(^2\) g\(^{-1}\)).
Scheme 1. Schematics of (a) random copolymerization of ST and VBP (poly(ST-r-vBP)) and (b) SI-ATRP of SSNa with electrospun fibers of poly(ST-r-VBP).

Figure 1. SEM images of the electrospun fibers: (a) before ATRP (diameter = 593 ± 74 nm) and (b) after 3 h of ATRP (597 ± 54 nm).

3.2. SI-ATRP of SSNa from the electrospun fibers

We carried out SI-ATRP of SSNa with the fiber mat (fiber diameter 593 ± 74 nm) in the presence of PEGBr as a free initiator, Cu(I)Br, Cu(II)Br₂ and bpy at 30°C, in aqueous MeOH (25 vol%). As we reported previously [32], graft polymerization from polymeric substrates requires a proper choice of solvent to prevent the substrates from swelling. When a substrate is swollen in a solvent at ambient or elevated temperature, polymer chains grow from its deep inside to form a thick boundary layer. In such case, the apparent graft density may seem to be sufficiently high, i.e. in the concentrated brush regime, however, such polymer layer will never form a ‘concentrated’ brush structure. Thus we carefully chose a mixed solution of MeOH/water, which is non-solvent for PST and PVBP, and carried out the polymerization at a mild temperature of 30°C to prevent swelling.

We added a free initiator to the polymerization system not only to automatically control the polymerization but also to produce free polymer. Free polymer is known as a good index for $M_n$ and $M_w/M_n$ of graft polymer. Figure 2 shows the first-order kinetic plot of monomer concentration for the polymerization with the fibers. The plot is almost linear, indicating that the radical concentration was constant during the polymerization. Figure 3 shows $M_n$ and $M_w/M_n$ for free polymers against conversion. As discussed above, XPS measurements could not determine the number of initiating groups on the fiber. However, as shown in figure 2, the polymerization rate was almost the same with fibers or silicon wafers, indicating that the number of initiating groups on the fibers was negligibly small compared with that of the free initiator and did not affect the polymerization behavior.
Figure 2. Plot of ln([M]/[M]) versus time of SSNa (10 wt%) polymerization in water/MeOH (1/3 v/v) at 30 ºC with poly(ST-r-VBP) fibers (□) and silicon wafers (●). [SSNa]₀/[PEGBr]₀/[Cu(I)Br]₀/[Cu(II)Br₂]₀/[bpy]₀ = 200/1/0.7/0.3/2.

Figure 3. Dependences of $M_n$ and $M_w/M_n$ of free polymers (□) and graft polymers (■) on the monomer conversion for the polymerization of SSNa (10 wt%) in water/MeOH (1/3 v/v) at 30 ºC with the poly(ST-r-VBP) fibers: [SSNa]₀/[PEGBr]₀/[Cu(I)Br]₀/[Cu(II)Br₂]₀/[bpy]₀ = 200/1/0.7/0.3/2. The solid line represents the calculated values.

Figure 4. GPC charts for free (broken curve) and cleaved solid polymers after 3 h of polymerization at 30 ºC.

Figure 5. Grafted amount of PSSNa versus molecular weight of free polymer.

Thus, we calculated theoretical $M_n$ (solid line in figure 3) with conversion and the initial molar ratio of SSNa to the free initiator, PEGBr. The measured $M_n$ well agreed with the calculation and the $M_w/M_n$ was relatively low (<1.3), indicating that this polymerization system proceeded in a living fashion. After the graft polymerization, in order to remove physisorbed free polymers, the fibers were washed thoroughly with water. FTIR measurement confirmed that the amount of the grafted PSSNa was almost unchanged by further washing. Then, we cleaved the graft polymers from the fiber surfaces by KOH treatment. Figure 4 shows GPC charts of graft and free polymers after 3 h of polymerization. The curve of the graft polymer almost coincides with that of the free polymer, suggesting that the cleavage of the graft polymer was successful. As shown in figure 3, $M_n$ and $M_w/M_n$ for the grafted polymers (open squares) were nearly the same as those for the free polymers (filled squares). Therefore, we used $M_n$ and $M_w/M_n$ of free polymers to calculate the graft density of graft polymers as discussed below.

After SI-ATRP, the graft amount of PSSNa was estimated from FTIR measurements. The graft amount of PSSNa on the fibers was calculated from the integrated ratio of the SO₃⁻ peak of PSSNa (875–1400 cm⁻¹) to the carbonyl group peak of the copolymer (1740 cm⁻¹) and the known surface area $S_{BET}$. As a reference, we carried out SI-ATRP of SSNa with electrospun PST fibers ($M_n = 104,800$, $M_w/M_n = 2.3$, diameter $= 700 ± 190$ nm), which did not have initiating sites for ATRP. No PSSNa peak was observed in FTIR spectra of PST fibers after the polymerization (not shown). This result confirmed that the PSSNa FTIR peaks of the poly(ST-r-VBP) fibers originated from chemically grafted rather than physisorbed
Figure 6. SEM images of the fibers after cutting for (a) 1 h and (b) 3 h.

polymer. Figure 1(b) shows an SEM image of the fibers after 3 h of polymerization. If polymers were ideally grafted on the fiber surface, then the graft amount (0.005 g m\(^{-2}\)) would be equivalent to about 5 nm dry thickness according to the measurement on silicon wafers. Since the graft thickness is much smaller than the diameter of the pristine fiber (593 ± 74 nm), after polymerization, the diameter would not change within the uncertainty of our measurement. The diameter was almost unchanged after SI-ATRP, suggesting that the substrate fibers were hardly swollen during the polymerization process.

Figure 5 shows the graft amount of PSSNa on the fibers against \(M_n\) for free polymers. The graft amount increased linearly with increasing \(M_n\), indicating a uniform growth of graft polymer from the surface. From the slope of the line in figure 5, graft density \(\sigma\) of PSSNa brush was estimated to be about 0.22 chains nm\(^{-2}\) (surface occupancy \(\sigma^* = 0.28\)), almost the same as for silicon wafers (\(\sigma = 0.24\) and \(\sigma^* = 0.32\)). According to the scaling theory, the crossover density between semi-dilute and concentrated brushes is around 0.1 in \(\sigma^* (= \sigma^*)\) [21, 33, 34]. Therefore, the PSSNa brush on the fibers (\(\sigma^* > \sigma^*\)) can be categorized as concentrated brush.

3.3. Shortened nanofibers

After 3 h of SI-ATRP, we mechanically cut the continuous long fibers (nonwoven mat) in water using a homogenizer [31]. The fiber length became shorter and more uniform with increasing cutting time. Figure 6 shows SEM images of the shortened fibers after 1 h and 3 h of cutting. The average lengths after 3 h of cutting was 11 ± 17 \(\mu\)m. The cutting process barely changed the diameters or the surface morphology of the electrospun fibers with the PSSNa brush. Jo et al. shortened electrospun fibers by ball milling, but the length could not be controlled [35]. Kriha et al. prepared aligned electrospun fibers with a rotating drum collector and cut the aligned fiber mat in liquid nitrogen with a razor blade [36]. Such cutting allows for length control (about 50–100 \(\mu\)m) but is inefficient. In contrast, our cutting method using a homogenizer is quick and efficient; it is applicable to all fiber mats, not only aligned but also non-aligned ones.

Figure 7. Aqueous solutions of fibers (0.23 wt%) after 3 h cutting. Left: shortened poly(ST-r-VBP) fibers without PSSNa brush, right: shortened fibers with concentrated PSSNa brush.

We examined the dispersion behavior of the shortened fibers (after 3 h of cutting) in water before and after SI-ATRP (figure 7). First, we tried to cut the fibers without a PSSNa brush in water, but this was difficult as the hydrophobic fibers floated on the water surface and escaped the blade of the homogenizer. Then, we applied a mixture of two poor solvents of different density, namely, water and hexane. The two solvents were separated in the mixture, and the fibers concentrated at the water–hexane interface that facilitated their cutting. After 3 h of cutting, we changed the two-phase solvent to water. As detailed in our previous report [31], such systems of two or more liquids facilitate the cutting of electrospun fibers of various polymers. As can be seen in figure 7, while the shortened hydrophobic poly(ST-r-VBP) fibers aggregated at the water–hexane interface, the shortened fibers with the concentrated PSSNa brush were homogeneously dispersed in water owing to the hydrophilic PSSNa brush layer.

Since LRP can precisely design chain architectures, along with the unique properties of concentrated brushes, targeted functionalities can be freely introduced into the brush layer or on its outermost surface. A shortened fiber with a concentrated brush can find numerous applications such as substrates...
for drug delivery, fibril fillers and materials for collecting pollutants in a small space with fluid. Although non-cut fibers with concentrated brushes would also acquire the surface functionalities, their application should be limited owing to the presence of continuous long fibers.

4. Conclusions

We have demonstrated the fabrication of shortened electrospun fibers with a well-defined ‘concentrated’ PSSNa brush. The hydrophilic nature of the brush resulted in a good dispersibility in water. Owing to the three factors, namely (1) the rod-like shape of the shortened fibers, (2) the unique properties of concentrated brushes and (3) the ability of LRP to produce chain architectures, these fibers would find numerous applications, e.g. fibril fillers, biosensors and substrates for drug delivery system, which are difficult to realize with the conventional electrospun fibers.

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