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Preparation and Surface Characterization of Surface-modified Electrospun Poly(methyl methacrylate) Copolymer Nanofibers

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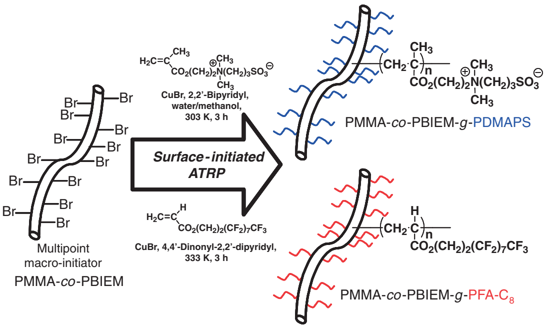
We developed a surface modification of electrospun nonwoven nanofiber mat by surface-initiated atom transfer radical polymerization (ATRP). Nanofibers of poly(methyl methacrylate)-*co*-poly[2-(2-bromoisobutyryloxy)ethyl methacrylate] were prepared by electrospinning to form a nonwoven nanofiber mat containing bromoalkyl groups, which initiated ATRP of 3-[dimethyl(methacryloyloxyethyl)ammonio]propanesulfonate (DMAPS) and 2-(perfluorooctyl)ethyl acrylate (FA-C_8), respectively, without deformation of nanofiber structure. The surface of the obtained electrospun nonwoven nanofiber mat was characterized by XPS, SEM, AFM, and contact angle measurement before and after surface modification.



Scheme 1. Surface-initiated ATRP of PDMAPS and FA-C_8 from the electrospun nonwoven nanofiber mat.

Functional nanofiber is expected to have many applications in various fields including environmental, medical, and nanosciences,[1,2] and preparation methods have been actively researched. Electrospinning is one facile method to prepare fibers from nano to submicro order size. Many types of solvents can be used for electrospinning, and nanofibers can be prepared under normal air pressure at room temperature. Therefore, electrospinning is one of the most attractive nanofiber preparation method.[3,4]

In this study, we propose a novel surface modification of nanofibers combined with electrospinning and surface-initiated atom transfer radical polymerization (ATRP). The authors reported the precise control of surface properties of polymers by direct surface-initiated ATRP from polymer surface with halogen groups.[5,6] We introduced 2-(2-bromoisobutyryloxy)ethyl methacrylate (BIEM) as an initiator comonomer. BIEM has a bromoalkyl group on the side chain, which can initiate ATRP (Scheme 1). The obtained PMMA-*co*-PBIEM possesses sufficient ATRP initiating points to generate densely grafted chains compared with conventional bromo-terminated polymer.[7] Therefore, our method can be expected to improve the grafting density of polymer on the nanofiber surface. We evaluated the detailed physical properties and morphologies of the electrospun nanofibers before and after surface modification and discussed wettability change of the nanofiber mats by surface modification.

PMMA-*co*-PBIEM was synthesized by free radical copolymerization with AIBN. The composition of the copolymer was PMMA/PBIEM = 16/1 (mol) estimated from the ^{1}H NMR spectrum. The number-average molecular weight M_n and PDI were 179000 and 1.99, respectively.

Nanofibers of PMMA-*co*-PBIEM were fabricated on a Si-wafer substrate by electrospinning from 7.5% copolymer solution of DMF and hexafluoro-2-propanol (HFIP) using NANON-01A (MECC Co., Ltd.). Figure 1a shows a SEM image of nanofibers prepared from PMMA-*co*-PBIEM HFIP solution. The diameter of fiber was approximately 850 nm (±190 nm). Surface morphology and diameter of nanofibers are largely dependent on the polymer concentration and the solvent. For instance, electrospinning using chloroform solution of the copolymer also afforded nanofibers. However, porous structure was formed on the nanofiber surface due to the phase separation induced by rapid evaporation of the solvent.[8,9] Smooth surfaces without any nanopores were observed in the nanofibers prepared from HFIP and DMF solutions. The high boiling point of DMF and high viscosity of HFIP solution might suppress phase separation during the solvent evaporation.[10]

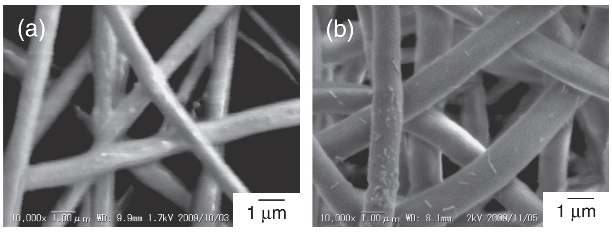


Figure 1. SEM images of electrospun PMMA-*co*-PBIEM nanofibers (a) before modification and (b) after modification by surface-initiated ATRP of FA-C_8.

Surface modification of the electrospun nonwoven nanofiber mat was conducted by surface-initiated copper-catalyzed ATRP of hydrophilic DMAPS in methanol/water (14/86, v/v) solution at 30 °C for 3 h and hydrophobic FA-C_8 in a bulk state at 60 °C for 3 h (Scheme 1).[11] Surface-initiated ATRP from flat spin-coated film of PMMA-*co*-PBIEM was also carried out as a control. XPS spectrum of electrospun nonwoven nanofiber mat of PMMA-*co*-PBIEM showed characteristic Br_{3d}, C_{1s}, and O_{1s} peaks corresponding to the theoretical atomic composition of the copolymer. After the surface-initiated ATRP process, the

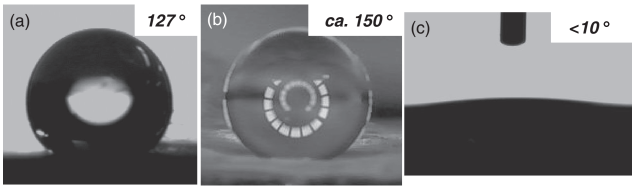


Figure 2. Static water contact angles on electrospun nonwoven nanofiber mats of (a) PMMA-*co*-PBIEM, (b) PMMA-*co*-PBIEM-*g*-PFA-C_8, and (c) PMMA-*co*-PBIEM-*g*-PDMAPS.

intensity of Br_{3d} peak decreased, while the S_{2s}, S_{2p}, and N_{1s} peaks attributed to the grafted PDMAPS appeared on the nanofiber surface. F_{1s} peak was detected in the XPS spectrum of the nanofiber mat modified by surface-initiated ATRP of FA-C_8. The atomic ratios evaluated from the narrow scan XPS analysis corresponded to theoretical atomic ratios of PDMAPS and PFA-C_8, respectively, indicating that the surface of PMMA-*co*-PBIEM nanofibers was almost completely covered with grafted chains of PDMAPS and PFA-C_8.[11]

The important point of applying surface-initiated ATRP for surface modification of electrospun nanofibers is to maintain morphological stability of nanofibers during the polymerization. As shown in Figure 1b, nanofiber shape was retained even after the ATRP of FA-C_8 from the nanofiber surface. The diameter of the modified nanofiber seems to be the same as the original nanofiber. The roughness of the nanofiber surface was apparently reduced by the grafting polymer. Because the reaction solvents for ATRP, such as methanol/water and FA-C_8 monomer, were poor solvents for PMMA-*co*-PBIEM, surface-initiated polymerization successfully proceeded without any appreciable changes in electrospun nanofiber shape and morphology.

Wettability of electrospun nonwoven nanofiber mats was evaluated by static contact-angle measurement using water before and after the surface modification (Figure 2). A contact angle of 76° for PMMA-*co*-PBIEM flat spin-coated film and that of 127° for PMMA-*co*-PBIEM nanofiber mat surface were obtained. This difference was caused by surface roughness of the nanofiber mat. A rough surface forms many air pockets between a water droplet and the nanofiber mat to result in the enhancement of hydrophobicity of the surface, as explained by the Cassie–Baxter model.[12] After the grafting of PFA-C_8, the contact angles of the spin-coated film and the nanofiber mat against water dramatically increased to 129° and to ca. 150°, respectively, due to excellent hydrophobicity of perfluoroalkyl chains and the effect of Cassie–Baxter wetting on the nanofiber mat. On the other hand, significantly lower contact angles, less than 10°, were observed on both PDMAPS-grafted surfaces of the spin-coated film and the nanofiber mat, due to the hydrophilicity of polyelectrolyte grafted chains and Wenzel wetting on hydrophilic nanofiber mat.[13] This suggests that physical properties of the nanofiber surface could be controlled by surface-initiated ATRP.

Did the polymerization really initiate from and take place only on the surface of the nanofiber? To answer this question, cross-sections of the electrospun nanofibers were analyzed by AFM. The surface-modified nanofibers were embedded in epoxy resin (LCR D-800, TOAGOSEI) and sliced by ultramicrotome in order to obtain a cross-section for AFM observation.

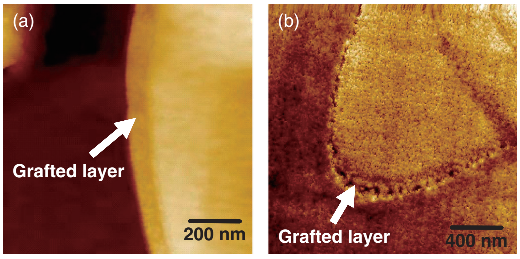


Figure 3. The cross-section images of (a) PMMA-*co*-PBIEM-*g*-PDMAPS nanofibers and (b) PMMA-*co*-PBIEM-*g*-PFA-C_8 nanofibers observed by AFM.

Figure 3a shows the AFM image of a cross-section face of a nanofiber modified with PDMAPS graft. The bright side and dark side are epoxy resin and PMMA-*co*-PBIEM nanofiber, respectively. The grafted layer was observed at the interface between the nanofiber and embedded resin, indicating that the grafted polymers are mostly formed at the outer surface of the nanofibers. Thickness of the grafted polymer layer on nanofiber was estimated to be ca. 70 nm. A similar trend was observed in PFA-C_8 grafted layer on the nanofiber surface (Figure 3b). The thicknesses of grafted layers were larger than those of the modified spin-coated films. This meant that the monomer or solvent penetrated to fiber inside slightly, and polymerization would occur from the area, where the monomers penetrated, of the fiber surface.

In conclusion, we have successfully prepared hydrophilic and hydrophobic nanofiber surfaces by combining electrospinning with surface-initiated ATRP. This technique would be feasible to prepare many types of nanofiber mats which have different surface properties and would expand the applications of electrospun nanofibers.

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