

FOCUS REVIEW

Direct polymer brush grafting to polymer fibers and films by surface-initiated polymerization

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Direct surface modification of polymer fibers and films by surface-initiated polymerization has been investigated. The introduction of initiating sites on polymer materials and their successive polymerization produce surface-tethered polymer chains on the polymer surface. The surface-selective modification controls the surface properties, such as wetting, lubrication and anti-fouling, without sacrificing bulk performance. Among the various procedures for introduction of initiating groups and subsequent polymerization proposed to date, this focused review article highlights our studies on polymer brush grafting to electrospun polymer fibers and polymer films through surface-initiated polymerization. We review studies focusing on grafting polymer chains to five different types of solid polymers: poly(methyl methacrylate)-based copolymers, Br-containing polyolefins, poly(vinylidene fluoride-co-trifluoroethylene), poly(butylene terephthalate), and poly(ether-ether ketone).

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INTRODUCTION

Surface modifications of polymer fibers and molded articles have been studied because of their importance in industry. Polymer products are required to adjust the surface properties, such as their wetting, lubrication, anti-fouling, adhesion, scratch-resistance and tactile impression properties, depending on the application.

Corona discharge and plasma treatments have been applied for enhancing surface wettability and paintability.^{1,2} These oxidation processes produce carbonyl, hydroxy and carboxylate groups on polymer surfaces. The introduced polar groups increase the surface energy and improve the wetting and adhesive properties. Although such treatments are effective and useful for high-speed industrial production, the modified surface properties are not stable because of the migration of the thermally active chains and subsequent segregation of the low free-energy components to the outermost surface. Moreover, additives are commonly used for modifying the surface performance.^{3,4} The compatibility of the additives and polymer matrix should be optimized to allow the additives to segregate to the surface. However, tuning the compatibility often sacrifices the effectiveness of the additives and bulk performance of the polymer matrix.

Polymer chain grafting on polymer articles is a straightforward approach for inducing long-lived surface modification.^{5–7} Typically, polymer chain grafting is performed by attaching polymer chains that are able to bind to substrates, the so-called ‘grafting-to’ approach, or by polymerizing monomers from the substrate surface, the so-called ‘grafting-from’ approach.⁸ The ‘grafting-from’ method is often preferable for producing a thick polymer layer consisting of densely surface-tethered

polymer chains. As the polymer chains propagate from the initiating sites on the substrates, the grafting process is free from the inhibition caused by pre-existing bulky chains. UV light radiation and γ -ray radiation have been applied to direct polymer chain grafting on polymer surfaces by surface-initiated polymerization.^{9,10} Recent progress in controlled radical polymerization, such as atom transfer radical polymerization (ATRP), permits regulating the chain growth to produce markedly high graft-density polymeric brushes with controlled molecular weight.^{11,12} The outstanding anti-fouling^{13–17} and lubrication^{18,19} performances of charged polymer brushes have been reported. As polymerization initiating sites must be activated during the polymerization process, the polymer surface is required to be swollen by the reaction solution, whereas the polymer articles must be insoluble in the solution. Ishihara *et al.*²⁰ have reported the surface modification of ultrahigh molecular weight polyethylene and poly(ether-ether ketone) (PEEK) with poly(2-methacryloyloxyethylphosphorylcholine) (PMPC) brushes by the chain growth from radical species generated by UV light irradiation.^{20–24} The resulting PMPC-modified polymers exhibit a low friction coefficient in water, as well as superior biocompatibility, which are promising properties for artificial joint applications.²⁵ We have reported surface-initiated ATRP (SI-ATRP) from polymeric solids, such as electrospun fibers and films.^{26–33} Various polymers with different physicochemical properties have been introduced on the polymer surfaces to modify the surface properties without sacrificing the bulk performance and morphology of the polymeric solids.

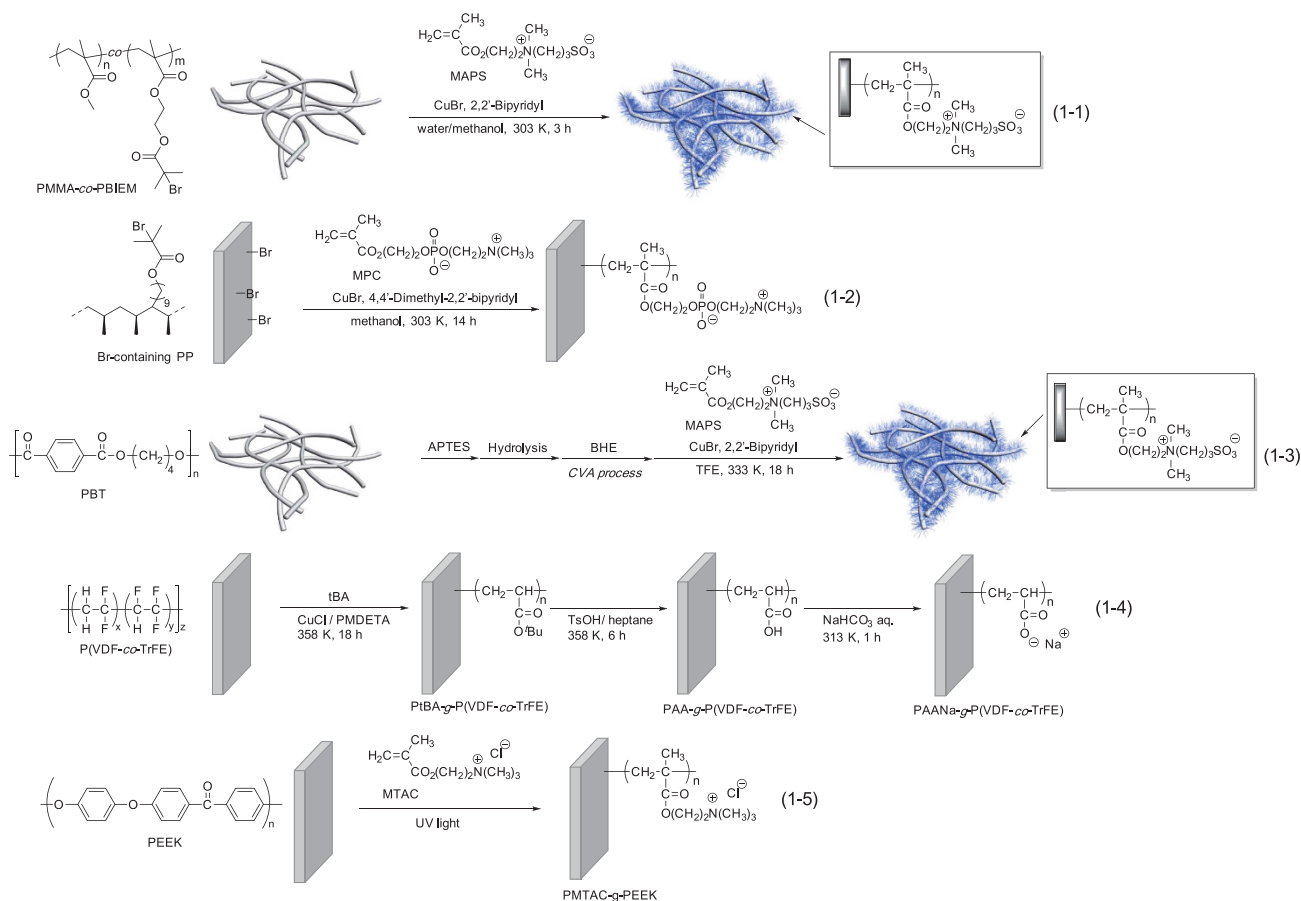
In this focused review article, our studies on the surface-modification of electrospun polymer fibers and polymer films by surface-initiated

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Scheme 1 Surface modification of polymer fibers and films by polymer brush grafting through surface-initiated polymerization from (1-1) PMMA-*co*-PBIEM fibers, (1-2) Br-containing PP films, (1-3) PBT fibers, (1-4) P(VDF-*co*-TrFE) films and (1-5) PEEK sheets. Abbreviations: APTES, aminopropyltriethoxysilane; BHE, (2-bromo-2-methyl)-propionyloxyhexyltriethoxysilane; CuBr, copper(I) bromide; CuCl, copper(I) chloride; CVA, chemical vapor adsorption; PMDETA, *N,N,N',N'',N'''*-pentamethyldiethylenetriamine; TFE, 2,2,2-trifluoroethanol; TsOH, *p*-toluenesulfonic acid.

polymerization are highlighted. We describe polymer brush grafting on five types of polymer substrates: poly(methyl methacrylate) (PMMA)-based copolymers,^{26,27} Br-containing polyolefins,^{28,29} poly(vinylidene fluoride-*co*-trifluoroethylene) (P(VDF-*co*-TrFE)) copolymers,^{30,31} poly(butylene terephthalate) (PBT)³² and PEEK³³ (Scheme 1).

PMMA-BASED COPOLYMERS

The ATRP-initiating sites can be easily introduced by copolymerizing monomers bearing bromoalkyl groups, which is a typical ATRP-initiating group.^{26,27} A copolymer of methyl methacrylate and 2-(2-bromoisobutyryloxy)-ethyl methacrylate (PMMA-*co*-PBIEM) has been synthesized by free radical polymerization with an AIBN initiator. The morphology of the electrospun fibers and the stability of the Taylor cone at the needle tip during the spinning process strongly depend on the physical properties of the solutions, as well as the spinning conditions.³⁴ The solution surface tension, viscosity and volatility must be optimized to fabricate fibers with a controlled diameter and smooth surface. The electrospun fibers of the PMMA-*co*-PBIEM exhibit a porous geometry when tetrahydrofuran, chloroform and dichloromethane are used as solvents, whereas fibers with smooth surfaces can be obtained by using dimethyl formamide and hexafluoro-2-propanol as solvents. The fiber diameter can be adjusted by changing the solution concentration and smooth cylindrically shaped fibers with a diameter of 850 nm (± 190 nm) have been obtained from a 7.5 wt% hexafluoro-2-propanol solution.

SI-ATRP using three types of monomers, hydroxyethyl methacrylate (HEMA), 3-(*N*-2-methacryloyloxyethyl-*N,N*-dimethyl) ammonatopropanesulfonate (MAPS) and 2-perfluorooctylethyl acrylate (FAC₈), has been conducted in the presence of non-woven electrospun PMMA-*co*-PBIEM fiber mats (Scheme 1-1). In that experiment, the polymerization was carried out with a methanol/water mixed solvent to prevent dissolution of the PMMA-*co*-PBIEM. The X-ray photoelectron spectroscopy (XPS) spectra of the PMMA-*co*-PBIEM fiber mats modified with poly(hydroxyethyl methacrylate (PHEMA), poly[3-(*N*-2-methacryloyloxyethyl-*N,N*-dimethyl) ammonatopropanesulfonate] (PMAPS) and poly(2-perfluorooctylethyl acrylate) (PFAC₈) showed characteristic peaks of the grafted polymers, and the atomic composition corresponded to the theoretical values, thus indicating that the PMMA-*co*-PBIEM fiber surfaces were covered with the polymer brush layers. The fiber diameter expanded to 1.2 μ m, thus indicating that the thickness of the grafted layer was ~ 100 –300 nm. The PMMA/water interface became swollen and produced a diffuse solid/liquid interface, even though water is a non-solvent for PMMA.³⁵ When the water/methanol mixed solvent was used, the solvents and monomers penetrated into the fibers to a moderate depth, thus causing polymerization in the swollen region.

The PMMA-*co*-PBIEM fiber mats exhibited a static contact angle of 127°, whereas that of the PMMA-*co*-PBIEM spin-coated films was 76° (Figure 1a). The difference between the static contact angles indicated that the electrospun fiber mats produced heterogeneous composite

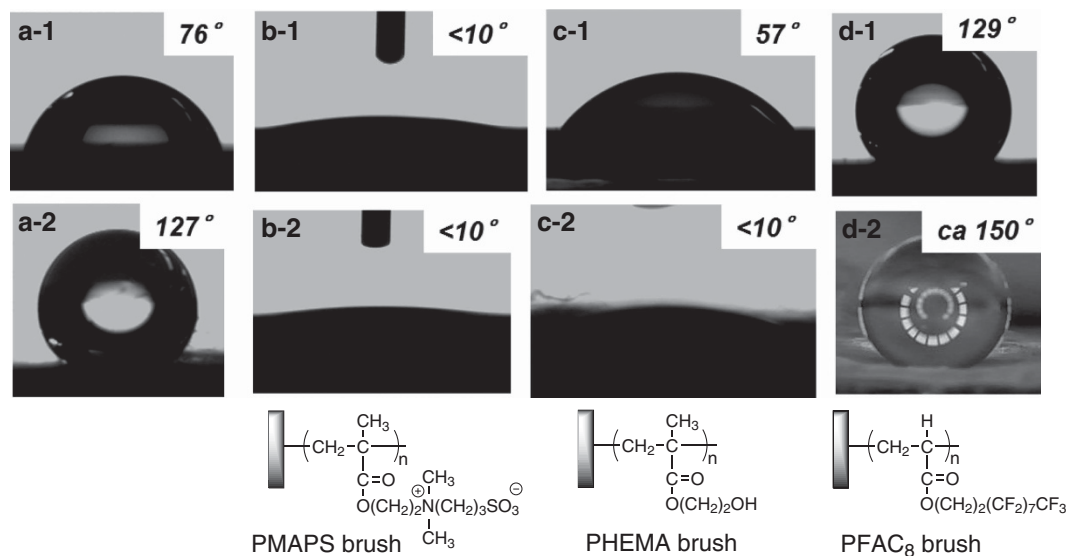


Figure 1 Side view of the water droplets on spin-coated films (upper images, 1) and non-woven electrospun fiber mats (bottom images, 2) of (a) the PMMA-co-PBIEM and the (b) PMAPS-grafted, (c) PHEMA-grafted and (d) PFAC₈-grafted PMMA-co-PBIEM. Reproduced from Yano *et al.*²⁶ with permission from Nature Publishing Group.

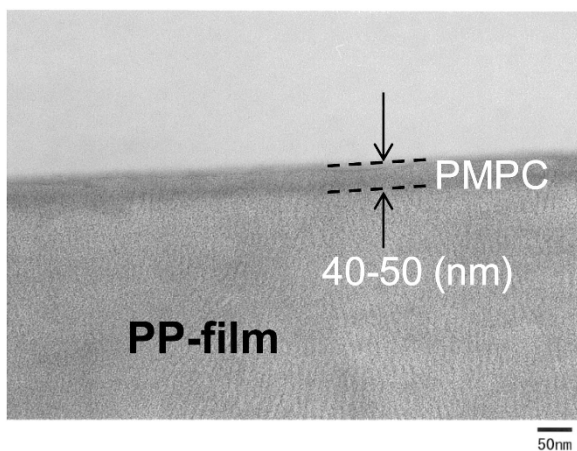


Figure 2 Transmission electron microscopy (TEM) image of the cross-section of the PMPC-g-PP film. The sample was stained with RuO₄. Reproduced from Kobayashi *et al.*²⁹ with permission from The Royal Society of Chemistry.

surfaces that consist of solid regions and regions of air trapped in the undulated topographic surface. The wetting state is the so-called Cassie–Baxter state.³⁶

The polymer brush grafting drastically changed the wettability of the electrospun fiber mats (Figure 1b–d). Both the static contact angles of the PMMA-co-PBIEM spin-coated films and electrospun non-woven fiber mats increased after the PFAC₈ brush grafting. The PFAC₈ brush-modified fiber mats repelled water droplets and the water droplets on the fiber mat easily rolled off. In contrast, the PMAPS and PHEMA brushes drastically decreased the water droplet contact angles. In the case of PHEMA brush grafting, the water droplets exhibited static contact angles of 57° and <10° on the PHEMA brush-grafted spin-coated film and electrospun fiber mat, respectively. The water droplets spread on the surface because of the affinity of water for the hydrophilic PHEMA. The water spreading phenomenon is assisted by surface roughness.³⁷ The PMAPS brush grafting dramatically

promoted water wetting, thus resulting in static contact angles <10°, even for the spin-coating film.

POLYOLEFINS

Polyolefins are the most widely used commercial polymers for the production of molding materials.³⁸ Their mechanical strength, toughness and chemical stability can be tuned by changing their tacticity and branching structure. However, the surface properties are difficult to modify because of the surface rearrangement of thermally active amorphous polyolefin chains. Therefore, effective surface modification approaches have been explored by using both chemical and physical treatments.^{39,40} Singh and colleagues⁴¹ have introduced alkyl bromide onto a polypropylene (PP) film surface through γ -ray irradiation in the presence of bromine vapor. Alkyl bromide-initiated ATRP of *N*-isopropylacrylamide on a polyolefin film has been found to produce thermosensitive hydrophilic polymeric brushes. Unique polyolefins consisting of α -olefins and ω -hydroxy- α -olefins have been developed by Mitsui Chemicals (Tokyo, Japan) through use of their excellent metallocene polymerization catalysts.⁴² The molecular weight and comonomer ratios are precisely controlled and the polyolefins are converted into polyolefin macroinitiators for ATRP by converting the hydroxy groups into alkyl halide.²⁸ Through use of the Br-containing isotactic PP macroinitiator (PP-MI) or Br-containing polyethylene macroinitiator, direct grafting of PMPC chains has been performed through SI-ATRP (Scheme 1-2).²⁹

The XPS spectrum of the PP-MI exhibits a peak attributed to the bromine atoms in the 2-bromo-isobutyl groups, whereas the PMPC-grafted PP (PMPC-g-PP) film shows peaks assigned to N_{1s}, P_{2s} and P_{2p}, indicating the presence of PMPC chains. The PMPC brush layer has also been identified from transmission electron microscopy observations of a RuO₄-stained microtomed cross-section of the PMPC-g-PP film (Figure 2). The PMPC outermost layer is clearly present and the thickness has been estimated to be 40–50 nm. A well-stained amorphous PP phase has been observed below the PMPC layer, thus suggesting that the ATRP initiates from the amorphous top layer. The 2-bromo-isobutyl groups would be locally present in the amorphous phase, because they are excluded from the PP lamellar

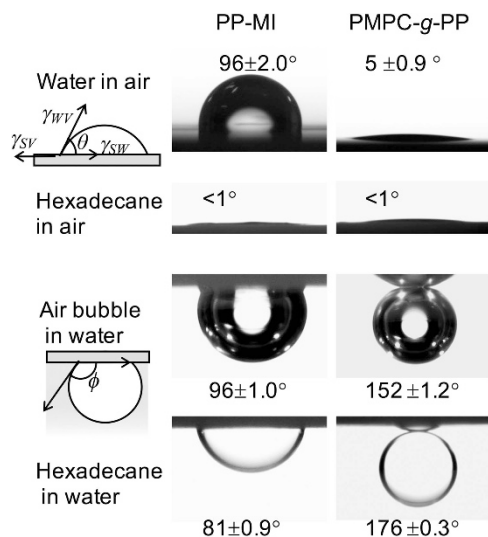


Figure 3 Side view of liquid droplets and air bubbles on an isotactic PP macroinitiator film (PP-MI, left images) and a PMPC-grafted PP film (PMPC-g-PP, right images) at 298 K. Reproduced from Kobayashi *et al.*²⁹ with permission from The Royal Society of Chemistry.

crystals. The crystalline ordered PP phase is hardly swollen in the methanol reaction solvent; thus, the film geometry is maintained during the polymerization process. The surface of the polyolefin film has a lower crystallinity than the bulk and the amorphous region includes 2-bromo-isobutyl groups; hence, the surface layer is swollen with a reaction solution to enable SI-ATRP.

The PMPC-g-PP films show superior hydrophilicity. Water droplets spread on the surface, whereas oil droplets and air bubbles are repelled from the films in aqueous solutions (Figure 3). The PMPC-g-PP films have been found to maintain their surface hydrophilicity after 3 years of storage under ambient conditions. Moreover, the PMPC-g-PP films have shown almost no change in their wetting performance after thermal annealing at 373 K for 1 h. The T_g for isotactic PP is in the range of 267–272 K, which is far below the annealing temperature. The PMPC brush thickness is much thicker than the interlamellar thickness; hence, the thermally active amorphous PP chains remain inside, owing to the networking by the thermally stable PP crystals.

The PMPC-g-PP films show a significant decrease in the friction coefficient to 0.1–0.2 under a humid atmosphere or in water. The friction coefficient depends on the sliding velocity, viscosity of the lubricant and normal pressure, and is associated with well-known classic tribology theory ‘Stribeck curve’.⁴³ At a low sliding velocity, the sliding probe and surface have strong interactions and produce a large friction coefficient, so-called boundary lubrication. The friction coefficient is drastically decreased with increasing sliding velocity as a result of the generation of the hydrodynamic lubrication layer, so-called mixed or hydrodynamic lubrication. The steep friction coefficient reduction in the PMPC-g-PP films indicates that the hydrodynamic lubrication state is induced by the hydrated PMPC brush layer. Hydrodynamic lubrication layer formation assisted by polyelectrolyte brushes has been directly demonstrated by using double-spacer-layer ultrathin-film interferometry.¹⁹ In addition, the PMPC-g-PP films show anti-fouling behavior against fibroblast cells.

POLY(BUTYLENE TEREPHTHALATE)

Polyesters, such as poly(ethylene terephthalate) (PET) and PBT, are semicrystalline engineering thermoplastics that are widely applied in

the production of fibers and molding materials. PBT exhibits rapid crystallization rate, high thermal stability, good mechanical performance and good moldability.⁴⁴

Fadeev and McCarthy⁴⁵ have reported the surface modification of PET films by using 3-aminopropyltriethoxysilane (APTES). In those experiments, the APTES was introduced to the PET surface via aminolysis of the primary amine head groups with negligible degradation of the bulk PET after soaking the PET films into the solution. Subsequent hydrolysis of the ethoxysilane groups produced silanol groups on the PET surface. Genzer and colleagues⁴⁶ have reported polymer brush grafting through SI-ATRP on electrospun PET fibers by using the surface modification procedure reported by Fadeev and McCarthy⁴⁵. They have demonstrated the antibacterial and protein-resistance properties of the PET fiber mats modified with the polymer brushes.

We have proposed the surface modification of electrospun PBT fibers by multistep surface modification consisting of aminolysis by APTES, hydrolysis, the condensation of (2-bromo-2-methyl)-propionylhexyltriethoxysilane (BHE) and SI-ATRP (Scheme 1-3).³² In that work, we prepared electrospun PBT fibers from a 8.0 wt% hexafluoro-2-propanol solution of PBT (Figure 4a). The APTES was introduced by soaking the as-spun PBT fiber mat in an APTES toluene solution through aminolysis. Hydrolysis was induced by the hydrochloric acid, which yielded Si-OH groups on the fiber surface, and BHE was attached to the Si-OH groups using a chemical vapor adsorption (CVA) process instead of a solution process. The chemical vapor adsorption process has advantages for homogeneous modification across fiber mat surfaces, whereas solution processes often suffer from limited wetting inside the fiber networks. As the melting temperature of PBT is $T_m = 472$ K, high-temperature vapor processing at 433 K can be applied for the modification without causing deformation of the microfiber morphology. The BHE-modified PBT fibers exhibit a morphology almost identical to that of the as-spun PBT fibers (Figure 4b).

ATRP of MAPS has been performed in the presence of a BHE-modified electrospun PBT fiber mat by using 2,2,2-trifluoroethanol (TFE) as a solvent. In those experiments, the fiber morphology was maintained and the fiber diameter was unchanged (Figure 4c). The PMAPS brush grafting was indicated by the drastic change in the hydrophilicity and XPS spectroscopic analysis. As crystalline polyesters composed of terephthalate units exhibit a high melting temperature, the electrospun PBT fibers exhibited a superior heat resistance to amorphous vinyl polymers and aliphatic polyesters. The differential scanning calorimetry thermogram of the PMAPS-grafted PBT fibers exhibited an endothermic peak that was assigned to the melting of PBT crystals. The crystalline structure in the PMAPS-grafted PBT fibers was also confirmed by X-ray diffraction measurements. The thermal stability of the surface wetting properties was demonstrated by tracking the water droplet contact angle after annealing at various temperatures. The PMAPS-grafted PBT fiber mats maintained the hydrophilic nature up to an annealing temperature of 453 K. However, the contact angle of the water droplets increased to 128° after thermal annealing at 473 K. As the fiber morphology was preserved even after annealing at 473 K (Figure 4d), the surface composition change induced by the surface migration of hydrophobic unmodified polymer chains triggered the transition of surface wetting.

POLY(VINYLDENE FLUORIDE-CO-TRIFLUOROETHYLENE)

Fluorinated polymers are outstanding polymer materials with a variety of special physical properties that are mainly attributed to the low polarizability and the strong electronegativity of their fluorine atoms.⁴⁷

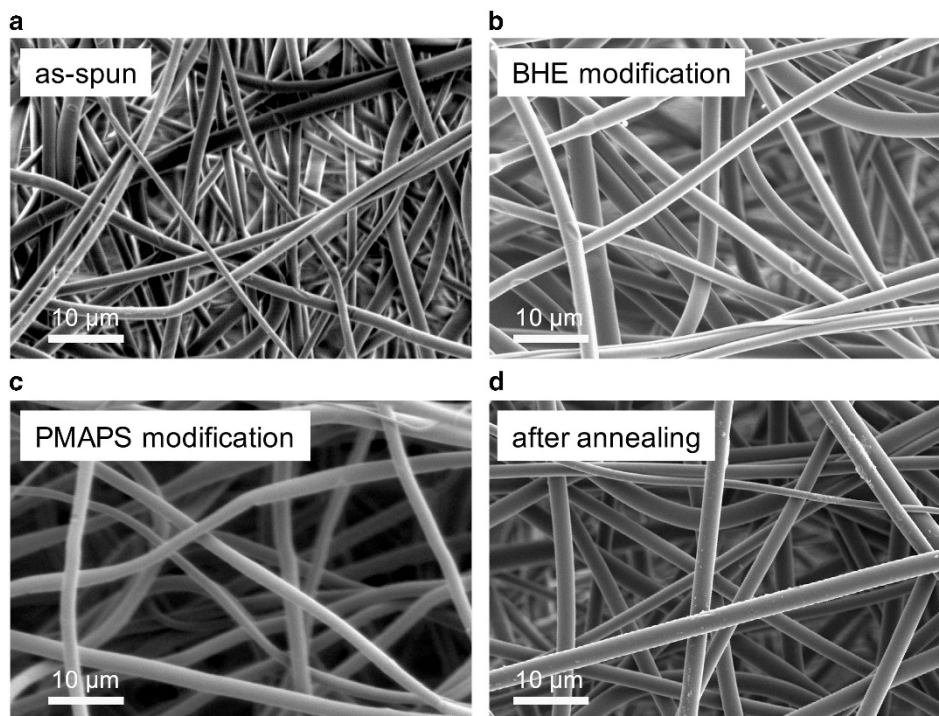


Figure 4 Scanning electron microscopy (SEM) images of the (a) as-spun fibers, (b) (2-bromo-2-methyl)-propionyloxyhexyltriethoxysilane (BHE)-modified, PBT fibers, (c) PMAPS-grafted PBT (PMAPS-*g*-PBT) fibers and (d) PMAPS-*g*-PBT fibers after thermal annealing at 473 K for 2 h. Reproduced from Higaki *et al.*³² with permission from John Wiley and Sons.

In addition, polyvinylidene fluoride and vinylidene fluoride (VDF) copolymers are well known as piezoelectric polymers.^{48,49} Because of their intrinsic low surface tension, fluorinated polymers often show poor adhesiveness. Therefore, surface modification is required to adjust their wetting performance for integration with other materials without compromising the bulk performances.

Direct 'grafting-from' surface modification procedures for fluorinated polymer membranes have been reported.⁶ Because of the chemical stability of fluorinated polymers, pretreatments are usually required for the 'grafting-from' procedure. On the other hand, direct 'grafting-from' surface modification of fluoropolymers without any pretreatment by means of C–X bond activation has been proposed.^{50–53} Because C–F bonds are too stable (*ca.* 486 kJ mol^{−1}) to initiate polymerization, VDF-based fluoropolymers have been used to initiate ATRP.⁴⁷

The direct SI-ATRP of vinyl monomers using commercially available P(VDF-*co*-TrFE) films has been investigated, and a detailed spectroscopic analysis for ATRP with a P(VDF-*co*-TrFE) macroinitiator has been conducted by ¹⁹F and ¹H nuclear magnetic resonance to elucidate the polymerization mechanism (Scheme 1-4).³¹ In those experiments, P(VDF-*co*-TrFE) film (thickness: 80 μm) containing 75 mol% VDF units was pressed between polished Si wafers under vacuum at 363 K under 40 MPa for 10 min. The ATRP of *tert*-butyl acrylate was performed in the presence of the P(VDF-*co*-TrFE) film and free initiator of ethyl 2-chloropropionate. The *tert*-butyl groups in the poly(*tert*-butyl acrylate) (PtBA) chains were hydrolyzed by soaking the PtBA-grafted P(VDF-*co*-TrFE) film into an aqueous solution of *p*-toluenesulfonic acid monohydrate at 358 K for 6 h, thus yielding a poly(acrylic acid)-modified P(VDF-*co*-TrFE) film. The poly(acrylic acid)-modified P(VDF-*co*-TrFE) film was introduced into a NaHCO₃ aqueous solution and heated at 313 K for 60 min to produce a poly(acrylic acid sodium salt)-modified P(VDF-*co*-TrFE) film.

We have explored direct polymer chain grafting to the P(VDF-*co*-TrFE) films by nuclear magnetic resonance measurements. The P(VDF-*co*-TrFE) film was dissolved in dimethyl formamide and ATRP of *tert*-butyl acrylate was carried out in the absence of free initiator to produce PtBA-grafted P(VDF-*co*-TrFE) comb-shaped polymers to highlight the chemical structures of the grafting points. ¹H and ¹⁹F nuclear magnetic resonance analyses of the resulting polymers revealed that the grafted chains were covalently bound to the TrFE units in the fluoropolymer backbone, moreover suggesting that homolytic cleavage of the C–F bonds in the –CF₂– of TrFE units occurred in the presence of a Cu catalyst. We assumed that halogen exchange from the fluorine to the chloride would occur during ATRP and the C–Cl groups exhibited reversible activation through oxidation/reduction cycles with CuCl/ligand complex catalysts. This unique reactivity of the TrFE units triggered C–F bond cleavage, which was followed by free radical generation; thus, the introduction of TrFE units enables surface modification of polyvinylidene fluoride-based fluorine polymers through direct 'grafting-from' ATRP.

The attenuated total reflection IR spectroscopy spectrum of the PtBA-grafted P(VDF-*co*-TrFE) film showed a characteristic absorption band for PtBA at 1723 cm^{−1} that was assigned to the ester carbonyl groups. After the hydrolysis reaction, the carbonyl stretching absorption band caused broadening and the absorptions assigned to the C–H bonds decreased because of the elimination of the *tert*-butyl groups. The neutralization produced a new peak at 1575 cm^{−1} that was assigned to carboxylic acid with its counter cation. The chemical conversion of the grafted PtBA chains was also indicated by XPS measurements.

The wettability of the P(VDF-*co*-TrFE) films changed after PtBA grafting, hydrolysis of the *tert*-butyl groups and neutralization. The hydrolysis of the *tert*-butyl groups decreased the water droplet contact angle, but the contact angle remained at 60° because of the

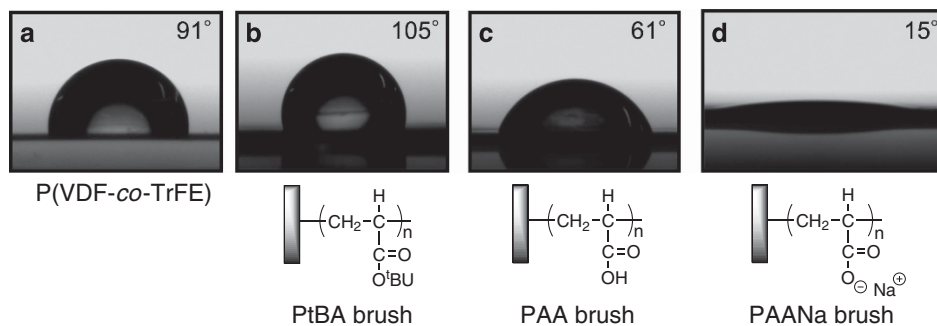


Figure 5 Sideview of water droplets on (a) the P(VDF-*co*-TrFE), (b) PtBA-grafted P(VDF-*co*-TrFE) (PtBA-*g*-P(VDF-*co*-TrFE)), (c) poly(acrylic acid)-modified P(VDF-*co*-TrFE) (PAA-*g*-P(VDF-*co*-TrFE)) and (d) poly(acrylic acid sodium salt)-modified P(VDF-*co*-TrFE) (PAANa-*g*-P(VDF-*co*-TrFE)). The static water contact angles are shown in the corner of the images. Reproduced from Kobayashi *et al.*³¹ with permission from The Royal Society of Chemistry.

protonation. The neutralization drastically decreased the water droplet contact angle because of the electrostatic interactions (Figure 5). These results clearly indicate the occurrence of PtBA brush grafting to the P(VDF-*co*-TrFE) films.

POLY(ETHER-ETHER KETONE)

PEEK is an engineering plastic that is rapidly gaining attention because of its attractive thermal and mechanical properties, outstanding chemical resistance and high specific strength.⁵⁴ These advantages have promoted the industrial usage of PEEK as a molding material that can replace metal parts in many applications. However, its hydrophobicity and high surface friction are drawbacks that may lead to premature failure and shortened service life in harsh environments. Various surface modification approaches have been examined to improve the surface performance of PEEK. Ishihara and colleagues^{22,24} have reported the surface modification of PEEK sheets and carbon fiber-reinforced PEEK sheets by using surface-initiated free radical polymerization activated by UV light irradiation. In those studies, PMPC chains were introduced on the surface to achieve antiprotein adsorption, as well as excellent lubrication performance and wear resistance.

Polymer brushes of a polycation, poly[(2-methacryloyloxy)ethyl] trimethylammonium chloride (PMTAC) and a polyanion, poly(3-sulfopropyl methacrylate potassium salt) (PSPMK), have been grafted onto Victrex PEEK sheets via a previously established UV light irradiation-induced self-initiated free radical polymerization procedure (Scheme 1-5).²² In those experiments, PEEK sheets were cleaned by sonication in ethanol and subsequently dried under vacuum overnight. The monomer solution was purged with argon and the PEEK sheet was soaked in the monomer aqueous solution. Then, the samples were exposed to UV light at room temperature at an overall light intensity of 4.5 mW cm⁻².

The occurrence of polymer brush grafting was confirmed by attenuated total reflection IR spectroscopy and XPS measurements. The characteristic IR absorptions and XPS signals for the grafted polymer chains were observed, thus indicating that the UV light induced activation of the benzophenone moieties through the pinacolization reaction and this was followed by the propagation of polymer brushes at the surface.⁵⁵ The chemical composition calculated from the intensity of the XPS signals approached the theoretical values of the grafted polymer chains with increasing UV light exposure time, thus indicating that the thickness of the polymer brushes on the PEEK substrate increased along with the UV light exposure time, because the number of grafted polymer chains increased along with the successive activation of PEEK.

Polymer chain grafting has also been demonstrated by atomic force microscopy topography imaging. The surface geometry of the PMTAC-grafted PEEK sheet was smooth in the dry state, because the grafted chains collapsed under dry conditions, whereas the PMTAC-grafted PEEK sheet/water interface showed large geometric undulations. The surface roughness in water ($R_{q, \text{water}}$) increased with increasing UV light exposure time, thus indicating the successive grafting of positively charged polyelectrolyte chains by the continuous activation of the PEEK backbone. The large $R_{q, \text{water}}$ value was attributed to several factors, including the UV light penetration depth, large polydispersity index and heterogeneous grafting location of the polymer brushes. The UV light was absorbed by the aromatic rings in PEEK; therefore, the UV light traveling depth was shallow. However, to some extent, the light generated active free radicals at locations slightly beneath the PEEK outermost surface. The broad molecular weight distribution of the polyelectrolyte chains propagated by the free radical process and the inhomogeneous locations of the grafting points caused large-scale density fluctuations at the swollen polymer brush interfaces that resulted in the large $R_{q, \text{water}}$ values.

The friction coefficients under water drastically decreased after grafting of polyelectrolyte brushes. Both cationic and anionic polyelectrolyte brushes afforded similar water-supported hydrodynamic lubrication effects that were enhanced with increasing UV light exposure time. The extremely viscous interfacial layer of the densely grafted and well-hydrated polyelectrolyte brushes induced a hydrodynamic lubrication state with a fluid lubrication layer.^{19,56,57} The viscosity of the swollen polymer brush layer was associated with the graft density and molecular weight. As the graft density increased along with UV light exposure, stable hydrodynamic lubrication was achieved after long-term UV light exposure. The non-uniform interface of the swollen polymer brushes was assumed to have a minor role in determining the friction coefficients, because the swollen polymer brushes were compressed by the sliding probe. Water may have been retained at the gap of the rough geometry and would be preferable for water-assisted lubrication.

CONCLUSIONS

Here we highlighted our studies on direct polymer surface modification through polymer brush grafting using SI-ATRP and SI-free radical polymerization. Surface-initiated polymerization produces thick, stable polymer brush layer on polymer fibers and films. The polymer surfaces are homogeneously covered with polymer brushes without severe defects and the surface properties can be changed without sacrificing bulk performance and the morphology of the polymer surface. We hope that these techniques will aid in the

development of practically applicable efficient processes for achieving long-term stability and mechanical durability in surface coatings.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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