Two-Stage Grafting onto Polyethylene Fiber by Radiation-Induced Graft Polymerization and Atom Transfer Radical Polymerization

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ABSTRACT: Two-stage graft polymerization onto polyethylene (PE) fiber was demonstrated. The graft side chain was formed by radiation-induced graft polymerization. A PE fiber was irradiated with an electron beam and immersed in a vinyl monomer solution. The terminal of the formed graft chain was halogenated using N-bromosuccinimide. The halogenated graft chain was then extended by atom transfer radical polymerization to obtain block-copolymer grafted PE fibers. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 3369–3375, 2010

Key words: two-stage graft polymerizarion; radiation induced graft polymerization; atom transfer radical polymerization; functionalization of polymers

INTRODUCTION

Living radical polymerization[1] is an epoch-making reaction that provides polymers with relatively narrow molecular weight distributions, and many studies of this reaction have been reported in recent years. Atom transfer radical polymerization (ATRP)[2–7] is a particularly versatile reaction, because it can be carried out under mild conditions, i.e., at relatively low temperature. Investigations into the introduction of polymer chains onto inorganic materials using ATRP have been reported. For example, initiating groups for ATRP have been introduced onto silicon substrates,[8–10] glass filters,[11] or silica gel particles[12,13] followed by surface-initiated ATRP. Investigations of graft polymer synthesis using living radical polymerization have also been reported.[14–17] The introduction of graft chains onto polyolefin substrates such as polyethylene (PE) or polypropylene (PP) by living radical polymerization has been known to be difficult, because these are chemically inert surfaces when compared to silicon surfaces. ATRP initiators have been introduced onto the surfaces of the polyolefin substrates by ultraviolet irradiation and block copolymer chains grafted onto the substrates.[18–21] However, the structures of the monomers for this method are limited, and it is particularly difficult to graft water-soluble monomers, because the surface of the polyolefin substrate is hydrophobic.

To solve these problems, we have conducted studies aimed at providing a versatile method that can be applied to various monomers while maintaining the form of the polyolefin substrate during ATRP. In this study, a two-stage grafting method onto molded PE was examined. In first grafting step, grafted side chains are formed on a molded PE substrate using radiation-induced graft polymerization (RIGP),[22–25] subsequent introduction of ATRP initiators to the ends of the grafted side chains. In second step, the graft side chains were extended by the ATRP in the presence of copper(I) complexes (Scheme 1). In this study, several monomers were used in the two-stage grafting method, and block copolymer chains were introduced onto a PE substrate as graft chains. Hydrophilic treatment of the PE substrate and attachment of initiating groups were conducted simultaneously by RIGP using a hydrophilic monomer, styrene sulfonate, by grafting onto the resulting PE substrate using ATRP in aqueous solution, which has typically been difficult.

EXPERIMENTAL

Materials

A commercially available PE nonwoven fabric (Tyvek 1059B, DuPont) was used as the substrate for the grafting of methyl methacrylate (MMA). The substrate had a thickness of 160 μm, density of 63 g/m^2 and was made of 100% high-density PE

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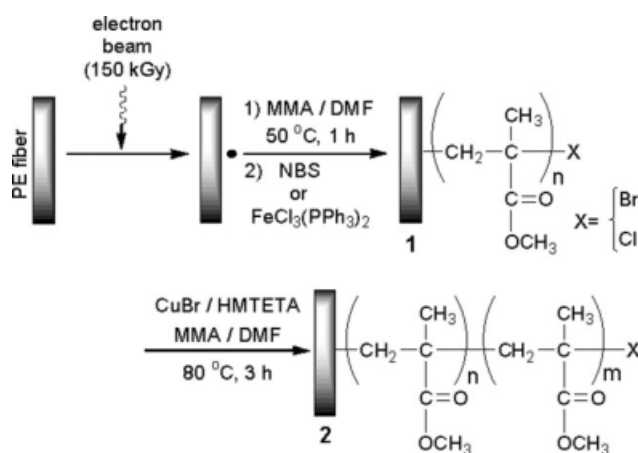
Scheme 1 Two-stage grafting of MMA onto PE fiber by RIGP and ATRP.

(HDPE) fiber with an average pore diameter of 7 μm and a fiber diameter of 0.5–10 μm. Another commercially available PE nonwoven fabric (OEX-EF4, Kurashiki Textile Manufacturing) was used as a substrate for grafting of the hydrophilic monomer. This substrate had a density of 65 g/m², thickness of 300–350 μm, and air permeability of 110–130 cm³/cm² s, and was made of 100% HDPE fiber with an average diameter of ∼ 15 μm.

Chemicals

Triphenylphosphine (PPh₃; Wako Pure Chemical Industries) was recrystallized from EtOH. N-Bromosuccinimide (NBS; Wako) was recrystallized from a water-MeOH mixture. Lithium styrene sulfonate (LiSS; Tosoh Corp.) was recrystallized from EtOH. N,N-Dimethylformamide (DMF; Wako), acrylic acid (AAc; Wako), N-vinylpyrrolidone (NVP; Wako), and N,N-(dimethylamino)ethyl methacrylate (DMAEMA; Wako) were bubbled with nitrogen before use. MMA (Wako) was purified through a column containing alumina (Alumina B Super I, MP Biomedicals, LLC) before use. Sodium styrene sulfonate (NaSS; Tosoh), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA; Sigma-Aldrich Corp.), iron(III) chloride hexahydrate (Wako), copper(I) bromide (Wako), copper(II) bromide (Wako), and 2,2'-bipyridyl (bpy; Wako) were used as received without any further purification.

Preparation of iron(III) complex DMF solution[21]

A DMF solution of 0.01M trichlorobis(triphenylphosphine)iron(III) complex (100 mL) was prepared by dissolving iron(III) chloride hexahydrate (270.3 mg, 1 mmol) and PPh₃ (786.9 mg, 3 mmol) with DMF in a 100 mL measuring flask.

Electron beam irradiation and RIGP onto PE nonwoven fabric (common method)

A sheet of PE nonwoven fabric was placed in a zippered PE bag, which was sealed after nitrogen substitution, and irradiated with an electron beam (150 kGy dose) using a curtain type accelerator (EC300/30/180L, Iwasaki Electric) at ambient temperature under a nitrogen atmosphere. The accelerator was operated with an acceleration voltage of 0.3 MV and a beam current of 1.0 mA. Immediately after irradiation, the bag containing the sample was placed in a glove box under a nitrogen atmosphere to prevent generated radicals from being lost. In the glove box, the PE nonwoven fabric sheet was removed from the bag, impregnated with monomer solution, and placed in a glass tube, which was then sealed with a screw cap. The glass tube was then removed from the glove box. The graft polymerization reaction was carried out by allowing the glass tube to stand in a constant temperature bath at a predetermined temperature for a predetermined time.

Measurement of grafting ratio

Grafting ratio (%) is expressed as $100 \times (W_g - W_0)/W_0$, where W_g is the weight of the sample after graft polymerization, and W_0 is the weight of the PE nonwoven fabric sheet before graft polymerization.

RIGP of MMA onto PE nonwoven fabric and introduction of initiator

A sheet of electron beam-irradiated PE nonwoven fabric (612.3 mg, 8.0 × 12.0 cm²) was immersed in purified MMA in a glove box (total weight after immersion: 1102 mg). After immersion, the sample was placed in a glass tube and sealed. The glass tube was then removed from the glove box and the graft polymerization reaction was carried out by allowing it to stand in a constant temperature bath at 50°C for 1 h. The glass tube was returned to the glove box and uncapped to add a solution of NBS (178 mg, 1.0 mmol, 100 mL) in DMF that had been bubbled with nitrogen for 15 min. The solution was then stirred at room temperature for 1 h. An MMA-grafted nonwoven fabric **1a** (979.7 mg) with a grafting ratio of 60.0% was obtained by washing with acetone, further washing with THF using a Soxhlet extractor for 16 h, and then drying with a hot air dryer at 60°C for 3 h.

The graft polymerization reaction was also carried out on a sheet of electron beam-irradiated PE nonwoven fabric (614.8 mg, 8.0 × 12.0 cm²) using the same procedure. After returning the glass tube to the glove box, a solution of 0.01M trichlorobis(triphenylphosphine)iron(III) complex (100 mL) in DMF, which was bubbled with nitrogen for 15 min,

was added and stirred at room temperature for 1 h. An MMA-grafted nonwoven fabric **1b** (987.4 mg) with a grafting ratio of 60.6% was obtained by washing and drying the sample in the same manner as previously described.

The graft polymerization reaction was also carried out on a sheet of electron beam-irradiated PE nonwoven fabric (634.6 mg, 8.0×12.0 cm^2) using the same procedure. After the graft polymerization, the sample without introduction of halogen atoms at the ends of the graft chains was exposed to air by uncapping the glass tube. An MMA-grafted nonwoven fabric **1c** (1002.7 mg) with a grafting ratio of 58.0% was obtained by washing and drying the sample in the same manner as previously described.

ATRP of MMA onto MMA-grafted nonwoven fabric

Copper(I) bromide (57.4 mg, 0.4 mmol) was placed in a glass tube in a glove box under nitrogen atmosphere and a mixture of HMTETA (184.3 mg, 0.8 mmol), DMF (20 mL), and purified MMA (20 mL), which was bubbled with nitrogen for 15 min, was added and stirred thoroughly to dissolve the copper(I) bromide. Nonwoven fabric **1a** (163.2 mg, 2.0×8.0 cm^2) was then placed in the sealed glass tube and removed from the glove box for the graft polymerization reaction by standing in an oil bath at 80°C for 3 h. After termination of the reaction, MMA-grafted nonwoven fabric **2a** (292.3 mg) with a grafting ratio of 79.1% was obtained by washing the substrate with THF in a Soxhlet extractor for 16 h and drying in an oven at 60°C for 3 h. MMA-grafted nonwoven fabric **2c** (218.1 mg) with a grafting ratio of 30.7% was obtained by reacting MMA onto nonwoven fabric **1c** (166.9 mg, 2.0×8.0 cm^2) using the same procedure.

Graft polymerization of hydrophilic monomer onto PE nonwoven fabric and introduction of initiator

In a glove box, a sheet of electron beam-irradiated PE nonwoven fabric (5.0×5.0 cm^2, 161 mg) was immersed in an aqueous solution of NVP ($w/w = 1/1$) that had been bubbled with nitrogen for 30 min (total weight after immersion: 764 mg). The sheet was placed in a sealed glass tube and removed from

the glove box for the graft polymerization reaction by standing in a constant temperature bath at 60°C for 2 h. The glass tube was returned to the glove box and uncapped to add a DMF solution of NBS (0.1 mol/L, 20 mL), which had been bubbled with nitrogen for 20 min. The solution was stirred at room temperature in the glove box for 1 h. After termination of the reaction, NVP-grafted nonwoven fabric **6** (355.0 mg) with a grafting ratio of 120.5% was obtained by rinsing the substrate with purified water at room temperature, washing in stirred purified water (200 mL) at 50°C for 3 h, and then drying in an oven at 60°C for 3 h.

A sheet of electron beam-irradiated PE nonwoven fabric (5.0×5.0 cm^2, 163.0 mg) was immersed in a DMF solution of DMAEMA ($w/w = 1/1$), which was bubbled with nitrogen for 30 min (total weight after immersion: 817 mg). The graft polymerization reaction was carried out with this sheet in a constant temperature bath at 60°C for 2 h. A DMF solution of NBS ($0.1M$, 20 mL) was added to the mixture and stirred at room temperature in the glove box for 1 h. After termination of the reaction, a DMAEMA-grafted nonwoven fabric **7** (249.4 mg) with a grafting ratio of 53.0% was obtained by washing and drying the substrate in purified water, as for **6**.

ATRP of styrene sulfonate onto hydrophilic PE nonwoven fabric in aqueous solution

In a glove box, LiSS (3.8 g, 20 mmol), bpy (125.0 mg, 0.8 mmol), and MeOH (10 mL) were dissolved in purified water (30 mL) in a 100 mL recovery flask. After nitrogen bubbling for 30 min, the solution was stirred with the addition of copper(I) bromide (57.4 mg, 0.4 mmol). NVP-grafted nonwoven fabric **6** (2.5×2.5 cm^2, 101.1 mg) was then placed in the solution. The flask was sealed with a two-way stopcock using high-vacuum grease and removed from the glove box. After evacuating the flask by vacuum pump for 1 min, the reaction was left to proceed in an oil bath at 50°C for 3 h. The reaction was terminated by exposure to air, and the obtained nonwoven fabric **8b** was treated with hydrochloric acid ($1.0M$, 50 mL) to yield nonwoven fabric **9b** after repeated washing with aliquots of purified water (50 mL), until the pH of the supernatant reached 5 or more.

TABLE I
Radiation-Induced Graft Polymerization of MMA onto PE Fiber

Entry	Sample wt (mg)	Increased wt (mg)	Grafting ratio (wt %)	Additive	X	Product
1	612.3	367.4	60.0	NBS	Br	**1a**
2	614.8	372.6	60.6	FeCl$_3$(pph$_3$)$_2$	Cl	**1b**
3	634.6	368.1	58.0	None	OOH	**1c**

Entry	Substrate	Substrate wt (mg)	CuBr/HMTETA (mmol)	Increased wt (mg)	Grafting ratio (wt %)	Product
1	**1a**	163.2	0.4 / 0.8	129.1	79.1	**2a**
2	**1b**	165.4	0.4 / 0.8	80.4	48.6	**2b**
3	**1c**	166.9	0.4 / 0.8	51.2	30.7	**2c**
4	**1a**	162.5	None	<1.0	<0.1	–
5	**1b**	163.4	None	<1.0	<0.1	–
6	**1c**	164.7	None	<1.0	<0.1	–

Nonwoven fabric **9b** was immersed and stirred in an aqueous solution (50 mL) of NaCl (1.0 g) for 6 h. The NaCl solution was then analyzed by neutralization titration with 0.02N NaOH. The analysis revealed that the salt-splitting capacity of **9b** was 0.0615 mmol. Based on this value and the molecular weight of LiSS (190.15), it was determined that the weight of LiSS grafted onto **8b** was 17.3 mg, and thus the grafting ratio of **8b** was 17.1%.

Characterization methods

Scanning electronic microscopy (SEM) measurements of the samples were carried out using a Jeol JSM-5800-LV operated at an acceleration voltage of 15 kV. Energy-dispersive X-ray (EDX) analysis spectra of the samples were obtained using an Oxford Instruments LINK ISIS scanning electron microscope.

RESULTS AND DISCUSSION

RIGP of MMA to PE nonwoven fabric and introduction of initiator (first grafting)

Table I shows that the grafting ratio was almost the same, regardless of the reaction termination method for RIGP. However, it was considered that the difference in the reaction termination method leads to a difference in the terminal structure of the graft side chains. When NBS was used as a radical trapping agent (entry 1), the terminal of each growing graft side chain may be trapped by the bromine atom of NBS, resulting in bromine occupying the terminal X
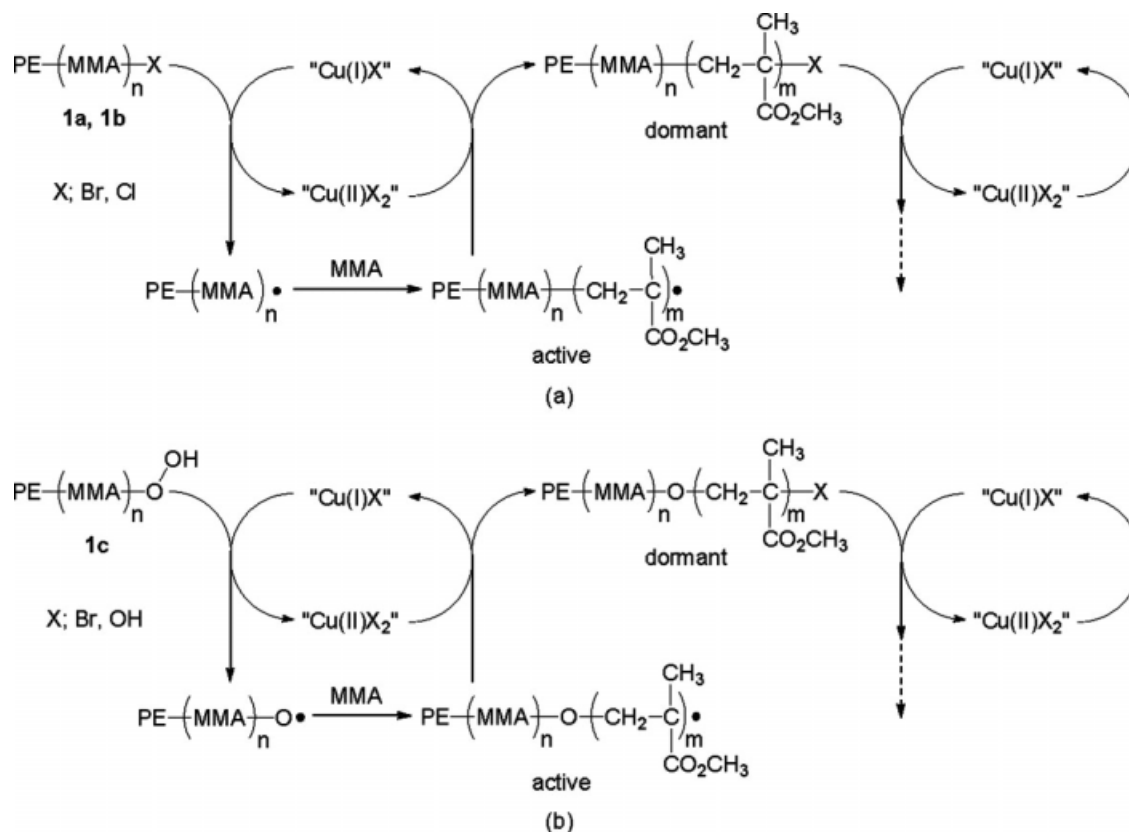
**Scheme 2** Role of Cu catalyst in the ATRP of MMA.
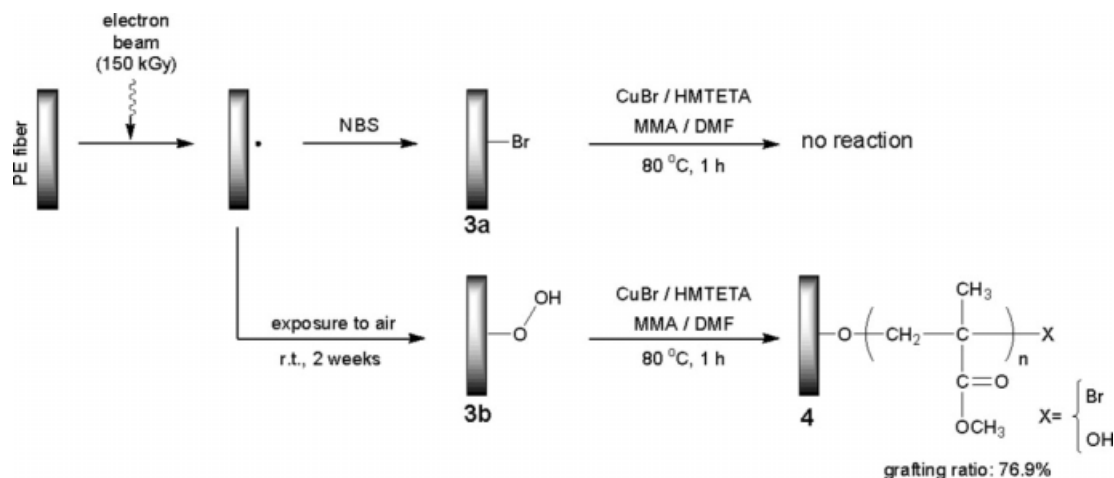
Scheme 3 ATRP of MMA onto irradiated PE fiber.

of the graft side chains in **1a**. When $FeCl_3(PPh_3)_2$ was used as a radical trapping agent (entry 2),[21] chlorine atoms of iron(III) complexes may be supplied to the terminals of growing chains, resulting in chlorine occupying the terminal X of the graft side chains with the accompanying formation of $FeCl_2(PPh_3)_2$. When the reaction is terminated by exposure to air (entry 3), free radicals at the terminals of growing chains may react with molecular oxygen, resulting in peroxide mainly occupying the terminal X of growing chains.

ATRP of MMA onto MMA-grafted nonwoven fabric 1 (second grafting)

The ATRP of MMA onto nonwoven fabric **1** was carried out using copper(I) complexes,[5] and the result was compared with that of the reaction conducted without the addition of copper(I) complexes (Table II). While little polymerization occurred in the absence of copper(I) complexes (entries 4–6), the graft polymerization was achieved in the presence of copper(I) complexes in all cases (entries 1–3). In the cases of **1a** and **1b** processed in the presence of copper(I) complexes, the halogen atom at each terminal was withdrawn by the copper(I) complexes, producing divalent complexes and generating free radicals at the terminals. Through the reaction of MMA with free radicals, the generated radicals were trapped by halogen supplied from the copper(II) complexes. Thus, the reversible generation of radicals at the terminals may promote the ATRP process [Scheme 2(a)]. In the case of **1c**, hydroxy radicals were withdrawn from the peroxide at the terminals by
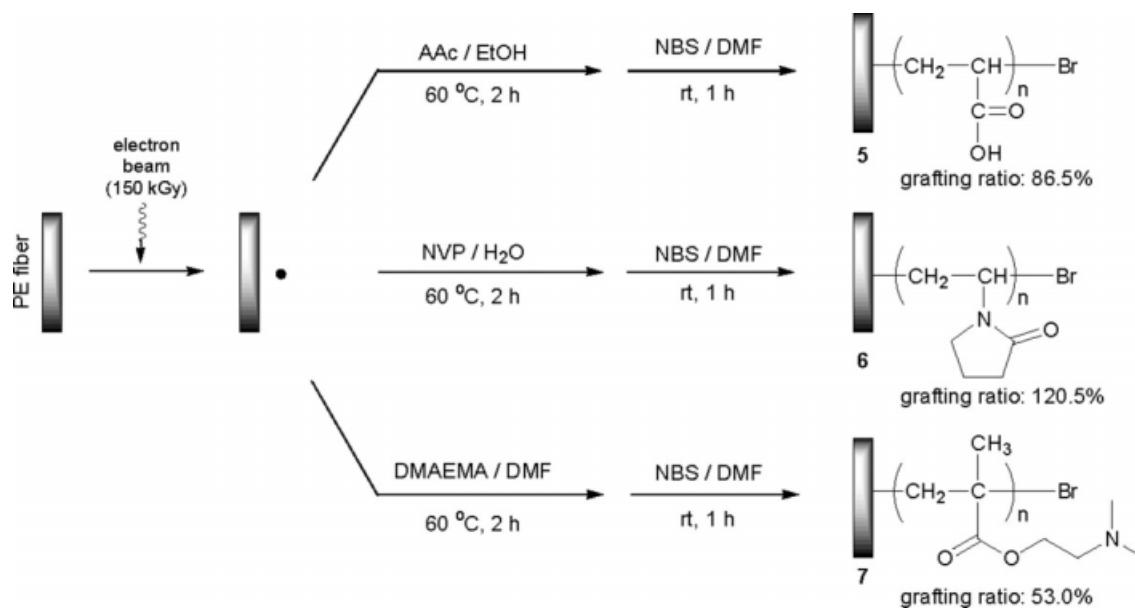
Scheme 4 Radiation-induced graft polymerization of hydrophilic monomer onto PE fiber.
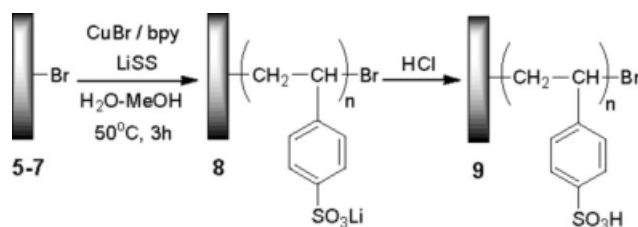
Scheme 5 ATRP of LiSS onto hydrophilic nonwoven fabric in aqueous solution.

copper(I) complexes, producing oxy radicals. The ATRP reaction may proceed as shown in Scheme 2(b) through the reaction of MMA with oxy radicals. The difference in grafting ratio between entries 1 to 3 may reflect the number of active terminals in each material that can be processed by ATRP. It is understood that in the absence of copper(I) complexes (entries 4–6), carbon–halogen or carbon–oxygen bonds are not cleaved, and no free radical was generated at the terminals, which inhibits progress of the ATRP process.

ATRP of MMA onto PE nonwoven fabric without RIGP

In place of nonwoven fabric **1**, ATRP of MMA onto irradiated PE nonwoven fabric was studied in the presence of copper(I) complexes. Irradiated PE nonwoven fabric was treated with NBS, and then no polymerization occurred onto the nonwoven fabric **3a**, even when copper(I) complexes were used. This result suggests that the carbon–bromine homolytic bond dissociation energy of **3a** is too large compared with that of **1a**. In contrast, irradiated PE nonwoven fabric was exposed to air at room temperature for 2 weeks, and then MMA was graft-polymerized onto the nonwoven fabric **3b** in the presence of copper(I) complexes. This result indicates that hydroxy radicals are withdrawn from the peroxidized fabric **3b** by copper(I) complexes, which promotes the ATRP process (Scheme 3).

Graft polymerization of hydrophilic monomer onto PE nonwoven fabric and introduction of initiator (first grafting)

It is expected that if the application of two-stage grafting allows the introduction of an ATRP initiator (halogen atoms) to PE as well as the addition of hydrophilicity in the first grafting, the subsequent ATRP process can be carried out in aqueous solution under mild conditions. To verify this possibility, AAc, NVP, and DMAEMA were used as the first grafting monomers for the polymerization reaction, followed by the addition of NBS. All of the resultant nonwoven fabrics (**5–7**) were highly hydrophilic and spontaneously absorbed water (Scheme 4).

### ATRP of styrene sulfonate onto hydrophilic PE nonwoven Fabric (second grafting)

The ATRP of LiSS onto nonwoven fabrics **5–7** in the presence of copper(I) bromide-2,2′-bipyridyl complexes[5] was carried out at 50°C in a water-MeOH mixture. For the nonwoven fabric **8** obtained by this process, it was considered that an accurate measurement of the grafting ratio based on the weight would be difficult, due to its extremely high hygroscopicity. Therefore, the grafting ratio was calculated by measuring the salt-splitting capacity by titration after treatment of the nonwoven fabric **8** with hydrochloric acid to obtain a H-form sulfonic acid **9** (Scheme 5). All the resultant nonwoven fabrics (**9a**, **9b**, and **9c**) had salt-splitting capacity; the calculated results revealed that the grafting ratio of LiSS onto nonwoven fabrics **5–7** was 17.0, 17.1, and 18.6%, respectively (Table III). In addition, the presence of the sulfonic acid group was also confirmed by EDX analysis for sulfur [Fig. 1(b)]. Nonwoven fabric **7** was also used to carry out the ATRP in NaSS under the same conditions. The result revealed that NaSS was polymerized at a grafting ratio of 9.3%. Thus, it has been demonstrated that for hydrophobic substrates such as PE nonwoven fabric, the ATRP process can be performed in an aqueous solution of

TABLE III
ATRP of LiSS onto Hydrophilic Nonwoven Fabric in Aqueous Solution

Entry	Substrate	Substrate wt (mg)	Salt-splitting capacity of 9 (mmol)	Wt of grafting LiSS on 8 (mg)[a]	Grafting ratio of 8 (%)[b]	Product
1	5	68.4	0.0615	11.7	17.0	**8a, 9a**
2	6	101.1	0.091	17.3	17.1	**8a, 9b**
3	7	60.3	0.059	11.2	18.6	**8c, 9c**

[a] Calculated from salt-splitting capacity of 9 and molecular weight of LiSS (=190.15).
[b] Calculated from substrate weight (5–7) and weight of grafted LiSS of 8.
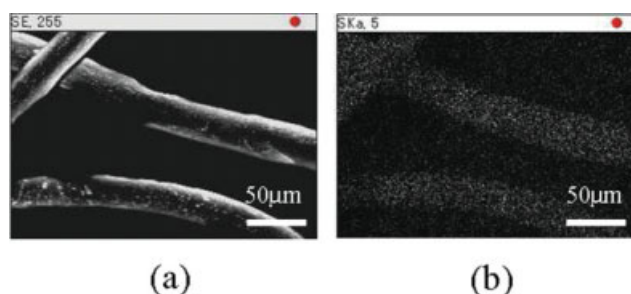
Figure 1 (a) Surface SEM image and (b) EDX mapping image of **9b**. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

water soluble monomers, e.g., LiSS, given that the first grafting allows the simultaneous introduction of an ATRP initiator and hydrophilicity.

For comparison, nonwoven fabrics **5–7** were used to conduct the reaction in the absence of copper(I) complexes. The samples obtained were treated with hydrochloric acid, and their salt-splitting capacity was measured. The results revealed that all of the samples had no salt-splitting capacity and LiSS was not polymerized. In addition, nonwoven fabric **1a** (prepared through the graft polymerization of MMA and the addition of NBS) was used to carry out ATRP of LiSS with copper(I) complexes under the same conditions. The polymerization reaction did not proceed, which may suggest that copper(I) complexes or monomers dissolved in the aqueous solution could not approach the graft chain terminals on **1a**, due to its hydrophobicity.

CONCLUSIONS

By using two-stage grafting method, styrene sulfonate was grafted onto molded PE substrate while maintaining the form of the substrate during ATRP. Materials contain sulfonic acid group is extremely versatile, because it can be applied to ion exchange filter for metal removal, battery separator, or polyelectrolyte for fuel cell. However, these materials are produced through sulfonation process in almost all cases. Accordingly, sulfonation causes coloring and degradation of the base material. Therefore, graft po-

lymerization of styrene sulfonate onto molded substrate is favorable process, because it does not include sulfonation process, and it is expected that two-stage grafting method will be applied to the syntheses of various functional materials.

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