

博 士 論 文

Surface Modification of Fluorocarbon Polymer by Radical Graft Polymerization

ラジカルグラフト重合によるフッ素樹脂の表面改質

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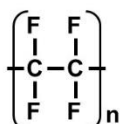
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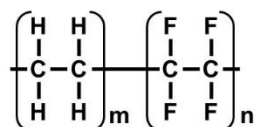
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Chapter I. General Introduction

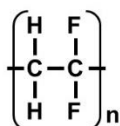
Fluorocarbon polymers represented by poly(1,1,2,2-tetrafluoroethylene) (PTFE) are widely used in our daily lives such as automobile parts, cooking equipment, environmental and aesthetic buildings. The various applications of the fluorocarbon polymers are realized by their specific properties such as heat resistance, chemical resistance, nonflammability and electronic properties ^[1-2]. For instance, the high weather resistant property of fluorocarbon polymers facilitates to protect steel moieties (the main tower, girders, and wires) of the Akashi Kaikyo Bridge, which is the important infrastructure connecting Honshu and Shikoku islands. Furthermore, it is used as a paint for aircrafts flying under severe conditions; it flies at 900 km/h rate accompanying strong shock and at altitudes of 10,000 m where it is exposed to ultraviolet light. Using fluorocarbon polymer can prolong the period between the maintenance of bridges and aircrafts, which brings considerable economic impact for our lives.



Poly(1,1,2,2-tetrafluoroethylene) (PTFE)



Poly(ethene-co-1,1,2,2-tetrafluoroethylene) (ETFE)



Poly-1,1-difluoroethene (PVDF)

Fig. I-1 Fluorocarbon polymers

Several kinds of fluorocarbon polymers have been developed depending on diverse purposes, among which PTFE is the most common and occupies 60% of the global demands for fluorocarbon polymers. Poly(ethene-*co*-1,1,2,2,-tetrafluoroethylene) (ETFE) and poly-1,1-difluoroethene (PVDF) are also widely employed because these polymers have advantageous properties compared to PTFE.

Copolymer ETFE is used as a coating for aircraft wires.^[3] This is because ETFE has excellent resistance properties; creep resistance, cut-through resistance (to sharp edges), and scratch resistance. Since the maximum temperature for continuous use of ETFE (150 °C) is lower than that of PTFE (260 °C), which results in the narrow range of temperature for treatability. On the other hand, ETFE exhibits excellent formability because the melt viscosity is 100 to 1000 Pa·s, which is considerably lower than that of PTFE (10,000 Pa·s at 380 °C). Furthermore, high light transmittance and good spreadability of ETFE is suitable for the use as a film for green houses. Although excellent properties of ETFE facilitate to use as an architectural film for the various purpose, drawbacks such as poor adhesiveness and poor dyeability prevents the further use. Hence, it is highly demanded to modify the ETFE surface, which addresses the above issues ^[4-5].

PVDF occupies 20% of the global demands for fluorocarbon polymers next to PTFE. PVDF is a structural isomer of ETFE, thus, it exhibits good formability (melt viscosity: 100 to 1000 Pa·s, at from 200 to 290 °C) that is similar to ETFE. On the other hand, there is a large difference between PVDF and ETFE in terms of other properties. The melting point of PVDF is from 172 to 175 °C, which is lower than that of other fluororesins (PTFE: 327 °C, ETFE: 270 °C), and the dielectric constant

of PVDF (6.43×10^4 Hz) is much larger than those of PTFE ($<2.1 \times 10^4$ Hz) and ETFE (2.6×10^4 Hz) [3]. The large difference in properties is caused by the unsymmetry of the main chain of PVDF and the dipole moment of the C–F bond. Although PVDF is inferior in chemical resistance, PVDF is soluble in polar solvents such as DMSO and acetone, which facilitates the excellent formability. Furthermore, PVDF is inexpensive, thus, PVDF is applied to a wide range of uses [3], among which use for building exteriors is most important owing to their weatherability. In addition, other uses such as electric wire and filters for ultrapure water production process are also known [6-7].

As so far, fluorocarbon polymers are widely used due to their specific properties. If other functions such as adhesiveness and dyeability are added on the surface, the range of applications of fluorocarbon polymers are considerably expanded. For this purpose, it is effective to use graft polymers; different types of polymers are attached on the surface of fluorocarbon polymers. Three strategies are commonly used for preparation of graft polymers [8-9]; 1) grafting through method (Fig. I-2), 2) grafting to method (Fig. I-3), and 3) grafting from method (Fig. I-4). The “grafting through method” a polymerization method using a macromonomer, in which the main polymer chain is constructed (Fig. I-2). The “grafting to method” is a cross coupling reaction of a main polymer and grafting polymers (Fig. I-3). The third strategy is “grafting from method” which undergoes graft polymerization on the main polymer (Fig. I-4). In order to add different property on the fluorocarbon polymers, “grafting from method” is considered to be suitable.

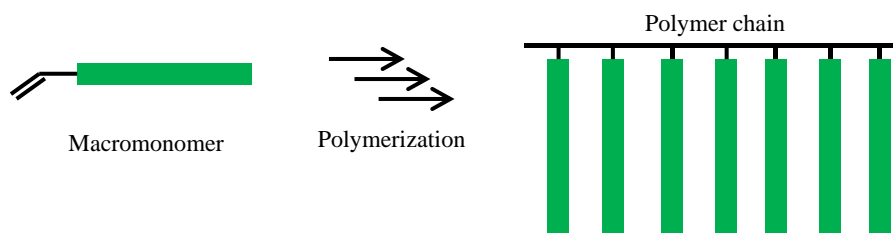


Fig. I-2 Grafting through method

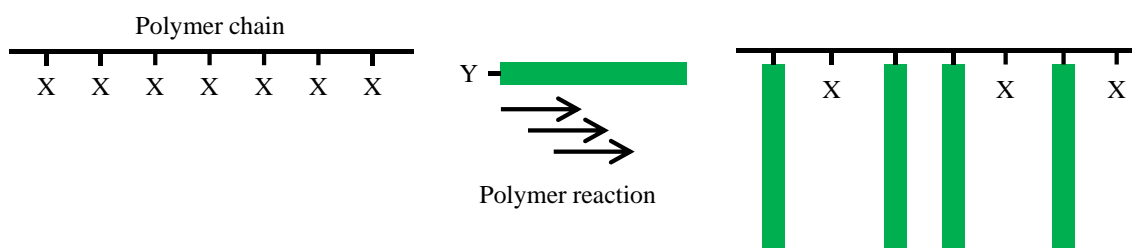


Fig. I-3 Grafting to method

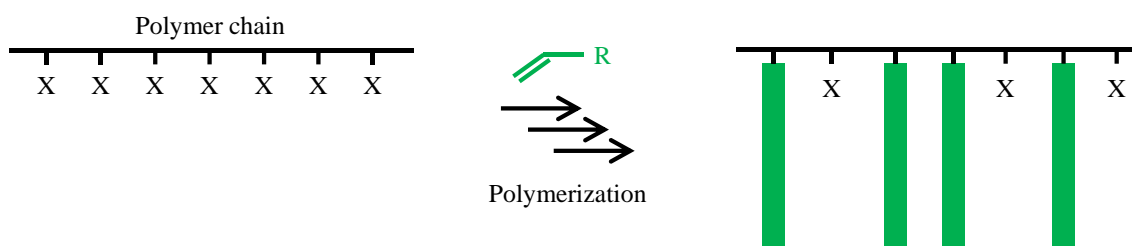


Fig. I-4 Grafting from method (This study)

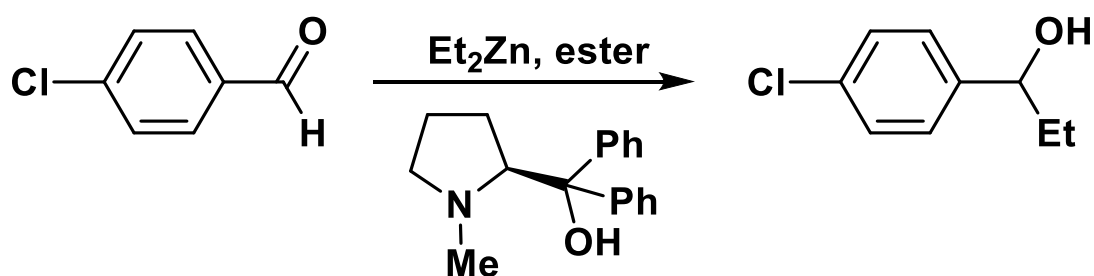
The “grafting from method”, graft polymerization with a monomer possessing a functional group, has attracted much attention to modify the surface property of fluorocarbon polymers. Since graft polymerization commonly proceeds through radical mechanism, it is necessary to generate radicals on the polymer surface. Indeed, several methods are known, among which irradiation of gamma ray or electron beam is mainly employed. The stronger irradiation increases the graft yield; however, deterioration of the fluorocarbon polymers itself also occurs. Furthermore,

the use of high energy beam affords adverse effect influences on human body and environment. Requirement of large facilities and more than two step processes also prevent the practical use. Because of these disadvantages, it is highly demanded to develop a new graft polymerization method for fluorocarbon polymer, which is conducted with simple experimental manipulations under mild conditions without use of high energy beam. The aim of this study is to establish a simple method for the surface modification by radical graft polymerization using a radical initiator to generate radicals on the surface of fluorocarbon polymer.

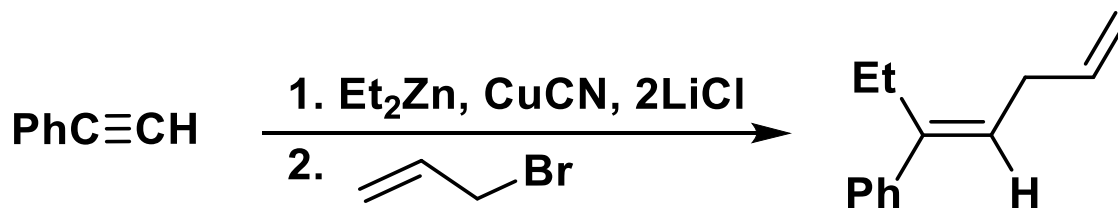
The doctoral dissertation consists of five chapters. Chapter I is a general introduction. Results and discussion are described in subsequent Chapters II–IV. In Chapter II, surface functionalization of ETFE film with poly(methyl methacrylate) via radical polymerization, was proposed. Chapter III is aimed to graft polymerization of methyl methacrylate on the surface of ETFE using benzoyl peroxide as initiator. In Chapter IV, graft polymerization of methyl methacrylate on the surface of PVDF using TBB as initiator. Chapter V is a conclusion. Radical initiators used in this study are shown below.

Diethylzinc (Used in Chapter II)

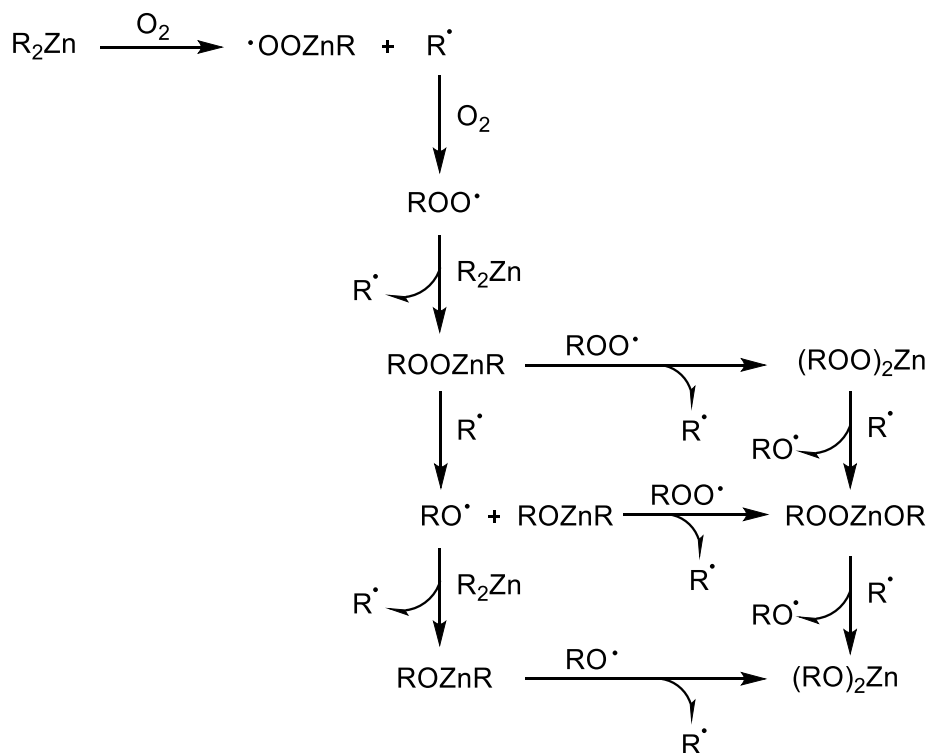
Lewis acids such as alkylaluminum, alkylborane, and alkylzinc serve as and alkylating reagents in organic syntheses. Diethylzinc (DEZ), one of the alkylzinc reagents, is widely used as a nucleophile in addition reactions to alkenes, alkynes, ketones, aldehydes and imines ^[10-14].



Scheme I-1. Addition reaction to a carbonyl compound using diethylzinc ^[15]



Scheme I-2. Addition reaction to a compound having a triple bond using diethylzinc ^[16]



Scheme I-3. Reaction mechanism of dialkyl zinc with oxygen ^[17]

DEZ also generates free radicals upon treatment with molecular oxygen at room temperature, which serves as an initiator for polymerization ^[17]. Indeed, DEZ-initiated radical generation is applied to polymerization of vinyl monomers such as styrene and methyl methacrylate (MMA) and ring-opening polymerization of L-lactide ^[18-21]. However, DEZ shows self-igniting property in the air, and there is currently no way to extinguish the ignited DEZ. Furthermore, there are few reports of using DEZ with polar solvents such as water and methanol because DEZ is hydrolyzed fast in the air. The difficulty to handle DEZ restricts the practical use.

Diethyl(1,10-phenanthroline N1,N10)zinc (Phen-DEZ) (Used in Chapter II)

DEZ is a Lewis acid to form a complex with a Lewis base such as α -iminoketone and diamines [22-25]. A complex (Phen-DEZ) formed by a combination of DEZ and 1,10-phenanthroline (Phen) [24] is one of the complexes derived from DEZ, but it has not been studied enough. I paid my attention to this complex because it is relatively stable to be handled in air and water, which is due to the rigid structure and the strong Zn–N bonds. Indeed, DEZ exhibited high activity as an initiator for emulsion polymerization using aqueous system [27].



Fig. I-2 Diethyl(1,10-phenanthroline N1,N10)zinc (Phen-DEZ)

Dibenzoyl peroxide (BPO) (Used in Chapter III)

Dibenzoyl peroxide (BPO) is one of the practically usable polymerization initiators because it is inexpensive and readily available from a commercial source. Decomposition of BPO generates free radicals as shown in Fig. 3 and serves as a radical initiator for polymerization of methacrylates and styrenes. Moreover, a combination of BPO and Lewis base is used as redox initiator for dental medical devices such as resin cement. Although BPO is relatively stable compared to other initiators such as DEZ in the air, BPO should be handled as an explosive material. Indeed, there was an explosion accident at a chemical plant in May 1990. Hence, the commercially available BPO is moistened with water to decrease the purity to 75% to prevent explosion, and a metal spoon should be avoided when BPO is handled.

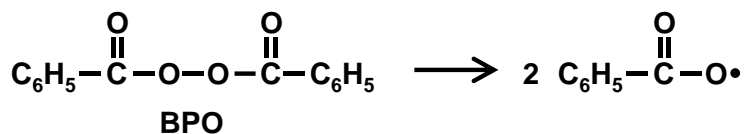
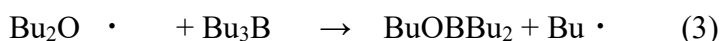
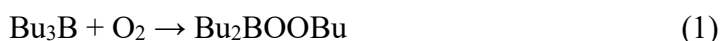


Fig. I-3 Decomposition of BPO

Tributylborane (TBB) (Used in Chapter IV)

While borane forms a dimer using a three-centered-two electron bonds to mitigate the electron-deficiency, tributylborane (TBB) cannot form a dimer due to steric hindrance of the butyl group. Therefore, TBB is relatively active to react with oxygen molecules even at room temperature, which exhibits pyrophoricity. Organoboron compounds (R_3B) including TBB serve as an initiator for radical polymerization at low temperature when molecular oxygen exists. Research on TBB was initiated by Furukawa in 1957, but little chemical progress was made. This is presumably due to the cumbersome handling caused by pyrophoricity; however, TBB has a potential to be an excellent initiator that efficiently generates free radicals even at low temperatures. The initiation step is considered to occur as follows. TBB reacts with oxygen to form a peroxide and the homolysis generates alkoxy radicals. Then the alkoxy radical reacts with another TBB to generate an alkyl radical, which undergoes the radical polymerization ^[28-29].



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Chapter II.

Surface Functionalization of Ethylene–Tetrafluoroethylene Copolymer Film with Poly(methyl methacrylate) via Chemical Radical Polymerization

Introduction

Fluorocarbon resins contain multiple carbon–fluorine bonds and exhibit characteristic properties such as excellent thermal and chemical stability, a low friction coefficient, excellent water repellent and weather resistant properties. Consequently, fluorocarbon resins have been widely applied as coating materials and films. Among them, poly(ethene-*co*-1,1,2,2,-tetrafluoroethylene) (ETFE) is a fluorocarbon resin that offers excellent material facilities that require brightness and comfort. The flexibility and lightness of the film are possible to use for free-form structures and open spaces using light ^[1–3].

Recently, the application of ETFE films to semiconductors and fuel cell membranes has attracted much attention. For example, surface modification by grafting and polymerization of ETFE films provides properties such as gas impermeability and proton conductivity in semiconductor films. Graft polymerization is a commonly used technique for improving the surface properties of a polymer. The use of electron beams and radiation has also been reported as a method for the introduction of functional monomers onto the surface of ETFE films ^[4–10]. For example, Chen and Seko reported graft polymerization of chloromethylstyrene under simultaneous gamma-ray irradiation onto an ETFE film ^[11]. With irradiation doses of 80 and 15 kGy, they reported a graft yield of 75% and 334%, respectively. Hamada *et al.* also reported radiation-induced graft polymerization of an aniline-containing monomer

onto an ETFE film ^[12], and found that the graft yield increased according to the reaction time. However, the use of an electron beam as the radiation source suffer from the considerable radiation released into the surrounding environment and radiation-induced deterioration of the ETFE film.

There is very few reports of graft polymerization of a vinyl monomer to ETFE by chemical reaction methods using common radical initiators such as 2,2'-(diazene-1,2-diyl)bis(2-methylpropanenitrile) (AIBN) or dibenzyl peroxide (BPO) instead of using an electron beam or gamma radiation. To the contrary, diethyl zinc (DEZ) produces free radicals at low temperatures to undergo side reactions under high temperature ^[13–16]. Moreover, radical polymerization of vinyl monomers can be initiated even when it was conducted at room temperature. This system can rapidly initiate polymerization reactions (homopolymerization and graft polymerization) at room temperature without necessity of external stimulation by corona discharge, plasma, or high temperature conditions ^[17,18]. However, DEZ is extremely reactive and spontaneously ignites in air, and it rapidly hydrolyzes in polar solvents such as water and methanol. Thus, the applicability of DEZ is somewhat restricted.

On the other hand, DEZ and N-donor ligand produces a Lewis acid–base complex, which can increase the stability ^[19–21]. In our previous work, the complex prepared from DEZ and 1,10-phenanthroline (Phen-DEZ) was found to be relatively stable which enables to handle safely. We have reported the radical graft polymerization of methyl methacrylate (MMA) onto polyolefin films ^[22] or on cotton surfaces ^[23], using Phen-DEZ as a radical initiator. This method facilitated graft polymerization on polypropylene films either at high (60°C) or at low (0°C) temperature. Since Phen-DEZ is a stable and reactive initiator, it surely initiates polymerization at room

temperature without necessity of special conditions such as heating; however, it has not been clarified whether Phen-DEZ can efficiently initiate graft polymerization of vinyl monomers to ETFE or not. In this chapter, I studied development of Phen-DEZ initiated graft polymerization of MMA on the ETFE surface under mild conditions.

Experimental Section

Materials

The ETFE film (Fluon 100 N NT 100 μm) was supplied by AGC and washed with chloroform and dried under vacuum before use. Methyl methacrylate (MMA), purchased from FUJIFILM Wako Pure Chemical Corporation, was washed with aqueous sodium hydroxide and subsequently distilled water, and dried over magnesium sulfate prior to use. DEZ was purchased from Nippon Aluminum Alkyls, Ltd. 1,10-phenanthroline, toluene, hexane and chloroform were purchased from FUJIFILM Wako Pure Chemical Corporation. Stain SDN was purchased from Osaka Kaseihin. Co., Ltd., respectively.

Measurements

Fourier transform infrared (FT-IR) spectra were obtained using a Jasco FT/IT-480 Plus spectrometer. Raman spectra were measured using an HR800 Horiba Raman spectrometer. Thermogravimetric analysis (Hitachi, STA 7200 RV) was performed in air at 25–550 $^{\circ}\text{C}$ (10 $^{\circ}\text{C}/\text{min}$) at a flow rate of 25 $\text{mL}^{-1} \text{min}^{-1}$. X-Ray diffraction (XRD) patterns were measured under ambient conditions with Cu-K α radiation. Atomic force microscopy (Nanoscope II, Digital Instruments) was conducted to analyze the morphology of the grafted ETFE films. The contact angle ($n=3$) was measured using a portable contact analyzer (PGX). The molecular weight of PMMA homopolymers were measured using Sizeexclusion chromatography (SEC, Jasco PU-2080 Plus pump and RI-2031 Plus Intelligent RI detector). CHCl_3 was used as the eluent. The grafted ETFE film was stained for 5 min at 70 $^{\circ}\text{C}$ by SDN.

Synthesis of 1,10-phenanthroline and diethylzinc complex (Phen-DEZ)

The synthesis of Phen-DEZ was performed according to the method in the previous report^[23]. DEZ (0.7 mL) was slowly dropped into 1,10-phenanthroline (1080 mg) in hexane (15 mL) in a 50 mL two-neck flask under argon gas. The reaction mixture was stirred for 24 h at 23°C. The orange crystalline product was obtained from the reaction mixture, and was collected by filtration and dried overnight in vacuo.

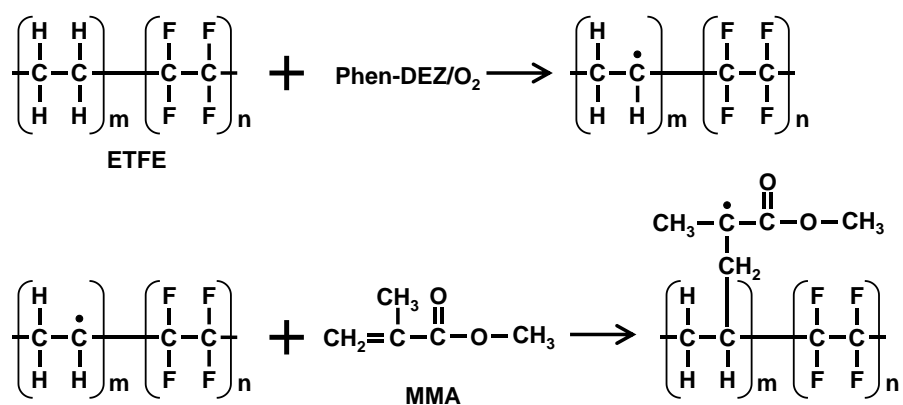
Graft polymerization of MMA onto ETFE

All graft polymerization reactions were carried out under argon atmosphere. Several ETFE films (16 mg, 1.0 × 1.0 cm, 100 μm) were placed in 20 mL round bottomed flask, into which argon was bubbled for 10 min to remove air. Phen-DEZ (120 mg), toluene (2.0 mL), and MMA (4.0 mL) were then added under argon atmosphere, and the flask was sealed. Equimolar amount of oxygen with Phen-DEZ was introduced into the solution under stirring. The solution was stirred for 18 h to allow for polymerization of MMA using Phen-DEZ to furnish grafted PMMA and ungrafted PMMA. Ungrafted PMMA (Homopolymer) and MMA were washed away with CHCl₃ using a Soxhlet extraction equipment for 12 h. The graft yield was calculated from the weight change, as follows:

$$\text{Graft yield (\%)} = \frac{\text{weight of grafted ETFE} - \text{weight of original ETFE}}{\text{weight of original ETFE}}$$

Results and Discussions

The polymerization was carried out under two reaction conditions; in a toluene solution and in a bulk polymerization system. The graft polymerization reaction successfully proceeded except for the reaction in toluene solution at 23°C. This reaction was initiated with radical formation induced by the reaction of DEZ and oxygen molecules. The Phen-DEZ complex was very stable in the absence of oxygen and did not pyrolyze below 50°C. In addition, graft reaction occurred neither in the absence of oxygen nor in the presence of more than 2 equivalents of oxygen. Therefore, these graft polymerizations are considered to occur through radical formation by the reaction of DEZ with equimolar oxygen. The formed radicals attack the methylene group of ETFE to form an active site on a carbon atom, and then MMA was grafted on the surface of ETFE. The plausible reaction scheme is shown in Scheme II-1.



Scheme II-1 The possible mechanism of graft polymerization process of MMA onto ETFE.

It is difficult to extract a F atom from CF₂-CF₂-unit to form (CF•) radical. Hence, the extraction of H atom from CH₂-CH₂-unit was proposed, which forms (CH•) radical.

The reaction conditions such as solvent, polymerization time, and temperature were optimized, and the results are summarized in Table II-1. The Phen-DEZ complex was thus demonstrated to undergo the graft polymerization of MMA on the surface of ETFE films under mild conditions with a simple procedure.

Table II-1 Graft polymerization of MMA onto ETFE films using the Phen-DEZ initiator.

Entry	Solvent	Time (h)	Temp. (°C)	Grafting Yield (%)	Homopolymer			
					Yield (%)	<i>M_n</i>	<i>M_w</i>	PDI
1	Toluene	18	23	–	47	140,000	430,000	3.1
2	Toluene	18	50	3	31	120,000	510,000	4.1
3	Bulk	18	23	3	65	150,000	660,000	4.3
4	Bulk	1	50	1	12	66,000	130,000	2.0
5	Bulk	3	50	2	46	86,000	430,000	5.0
6	Bulk	6	50	5	47	93,000	400,000	4.3
7	Bulk	18	50	8	57	96,000	320,000	3.3

When Phen-DEZ was added to a solution of MMA in the presence of ETFE film at 23 °C, polymerization proceeded; however, no graft polymerization occurred (Table II-1, entry 1). This low reactivity was because toluene serves as the chain transfer agent. Even though radical was generated, radical transfer to the solvent occurs to afford stable benzyl radical, which suppresses the regeneration of radical on the ETFE surface to prevent the graft polymerization. Elevating the reaction temperature to 50 °C was effective to undergo the graft polymerization with 3% of graft yield (entry 2). To avoid the undesired radical transfer, bulk polymerization without using toluene was studied. Graft polymerization of MMA onto ETFE films proceeded with 3% of graft yield at 23 °C (entry 3). The graft polymerization proceeded faster at 50 °C, and the graft yield increased the up to 8% when reaction was conducted for 18 h (entries 4–7). The different graft yields between in solution and in the bulk showed that the monomer concentration was a critical factor. The molecular weight (M_w) of PMMA was 320,000 that was determined by SEC when the reaction was conducted using bulk system at 50°C (entry 7). This value was considerably lower than that ($M_w = 660,000$) in the reaction conducted at 23°C (entry 3). This is because the larger number of radicals are formed at higher temperature, hence the polymer length was accordingly shortened.

A significant change was observed in the visual appearances of the ETFE films after polymerization. When graft polymerization was conducted, the ETFE films became cloudy as shown Fig. II-1, by which it was confirmed that surface modification of the films was successfully achieved.

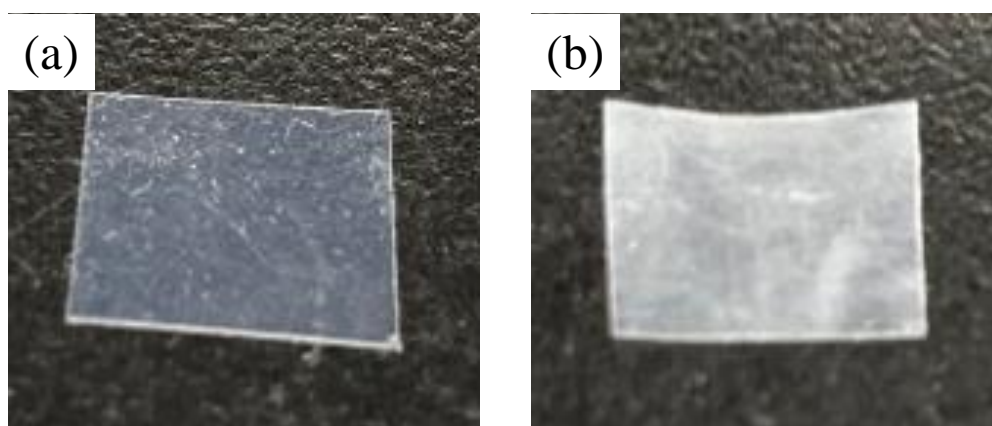


Fig. II-1 Visual appearance of: (a) ETFE film, and (b) ETFE-*g*-PMMA film.

FT-IR spectra of an ETFE film and polymethyl-methacrylate-grafted-poly(ethene-*co*-1,1,2,2,-tetrafluoroethylene) (ETFE-*g*-PMMA) were shown in Fig. II-2. Characteristic absorption peaks of ETFE were observed at 1481 and 1448 cm^{-1} [24,25] and attributed to bending vibrations of the $-\text{CH}_2-$ groups. Stretching vibrations of the $-\text{CH}_2-$ groups were also observed at 735 and 780 cm^{-1} . On the other hand, an absorption assigned to an ester carbonyl stretching vibration was observed at 1737 cm^{-1} , which indicates the successful graft polymerization of MMA onto the ETFE film. In addition, a weak characteristic absorption band was observed at 758 cm^{-1} , corresponding to CH_2 rocking modes; however, the absorptions at 1395 cm^{-1} (OCH_3 deformation), 1447 cm^{-1} (CH_3 asymmetric stretching), and 1481 cm^{-1} (CH_2

scissoring) were overlapped with the absorption bands of ETFE. These spectral changes revealed that graft polymerization of MMA was successfully achieved onto ETFE films using the Phen-DEZ initiator.

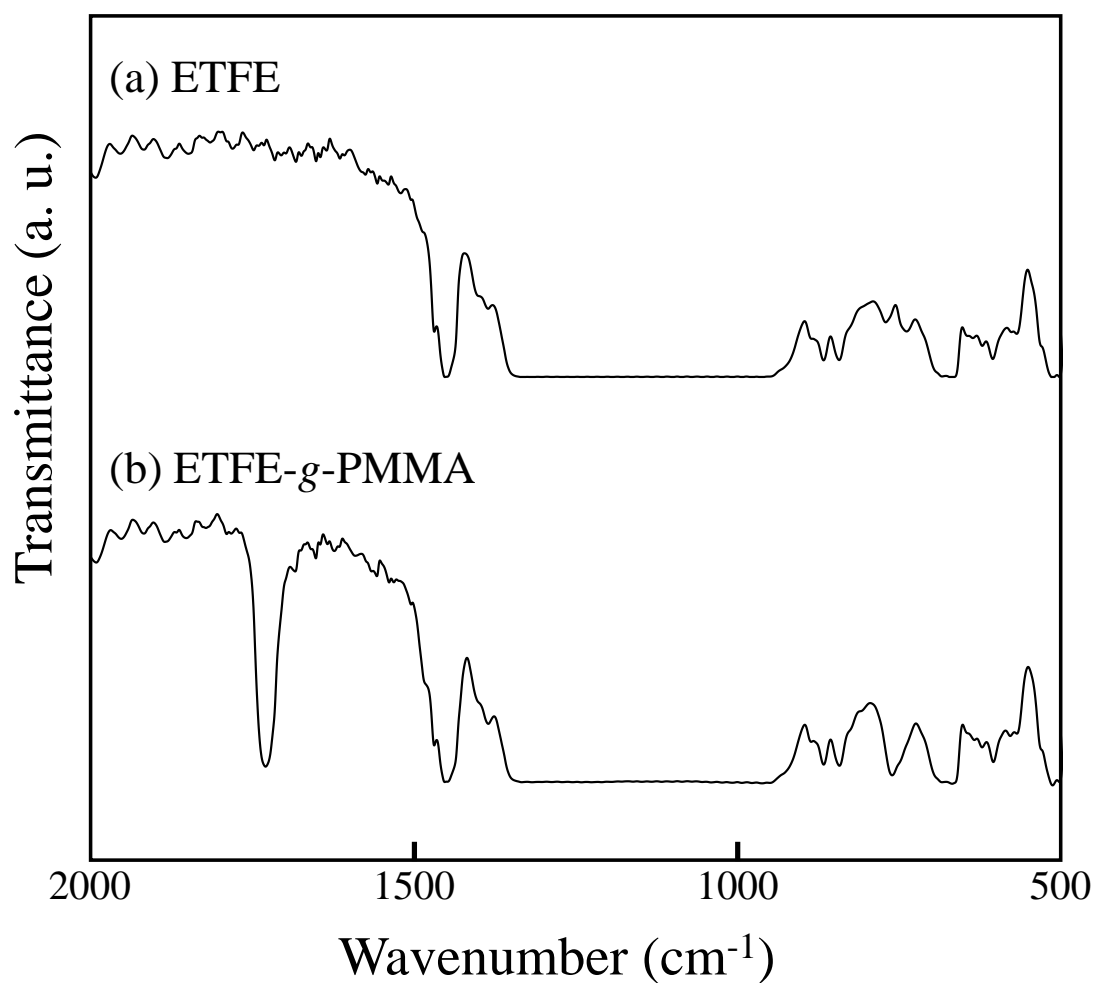


Fig. II-2 FT-IR spectra of an ETFE film (a) and ETFE-g-PMMA (b, Table II-1, entry 7).

Raman spectra of an ETFE film and grafted ETFE were also measured (Fig. II-3). The ETFE film exhibited two intense bands at approximately 833 and 2965 cm^{-1} which are corresponding to CF_2 and CH_2 groups, respectively. While common absorptions were observed between ETFE and ETFE-*g*-PMMA films, absorptions assigned to C=O stretching and O-C=O deformation vibrations in PMMA were observed at 1730 and 660 cm^{-1} , respectively [26,27]. This result obviously reveals PMMA grafting occurred on the film.

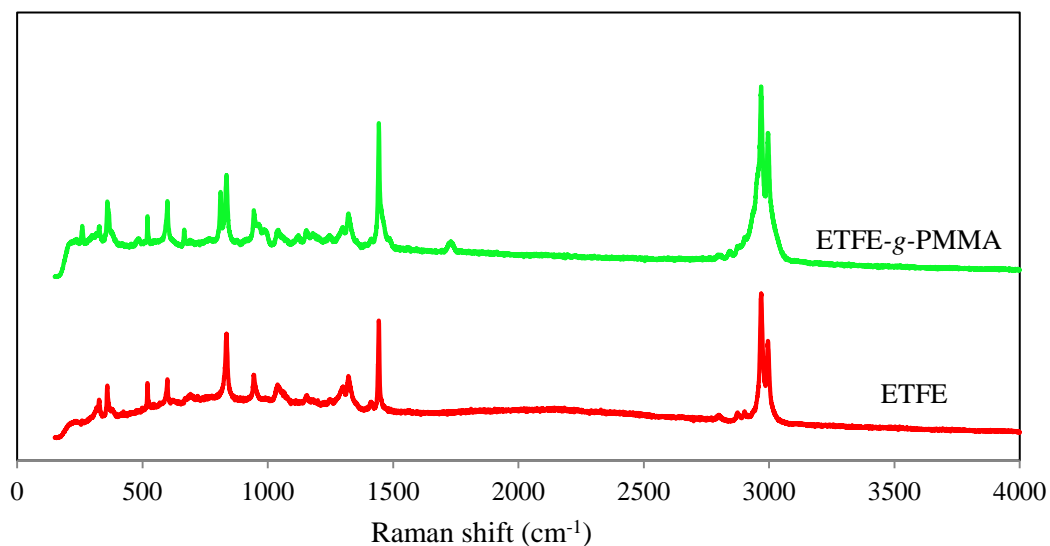


Fig. II-3 Raman spectra of an ETFE and ETFE-*g*-PMMA.

To obtain insights for a mechanism of the present radical polymerization caused by Phen-DEZ, ETFE film was treated with Phen-DEZ in the absence of MMA, and the the surface state was compared with that of raw ETFE film. However, notable difference between them were not observed by IR and Raman spectra because ETFE

is a highly stable resin. Then, TGA measurements were performed in the air to know the effect of grafting on the thermal stability of ETFE; TGA of ETFE film, ETFE-*g*-PMMA and homo PMMA (Fig. II-4). The thermal decomposition of ETFE-*g*-PMMA was observed through two stages. In the first stage, from 2% to 12% of weight was lost during the elevating temperature from 290 to 350 °C. In the second stage, 12% to 99% of weight change was observed when the temperature was raised from 350 to 470 °C. The first weight loss step was corresponding to the disruption of the grafted PMMA polymer, while the second degradation step was presumably due to thermal disruption of ETFE itself. The thermal stability of the ETFE film significantly changed upon grafting with PMMA. Thus, the TGA curves is one of the proofs for grafting of MMA on the ETFE film.

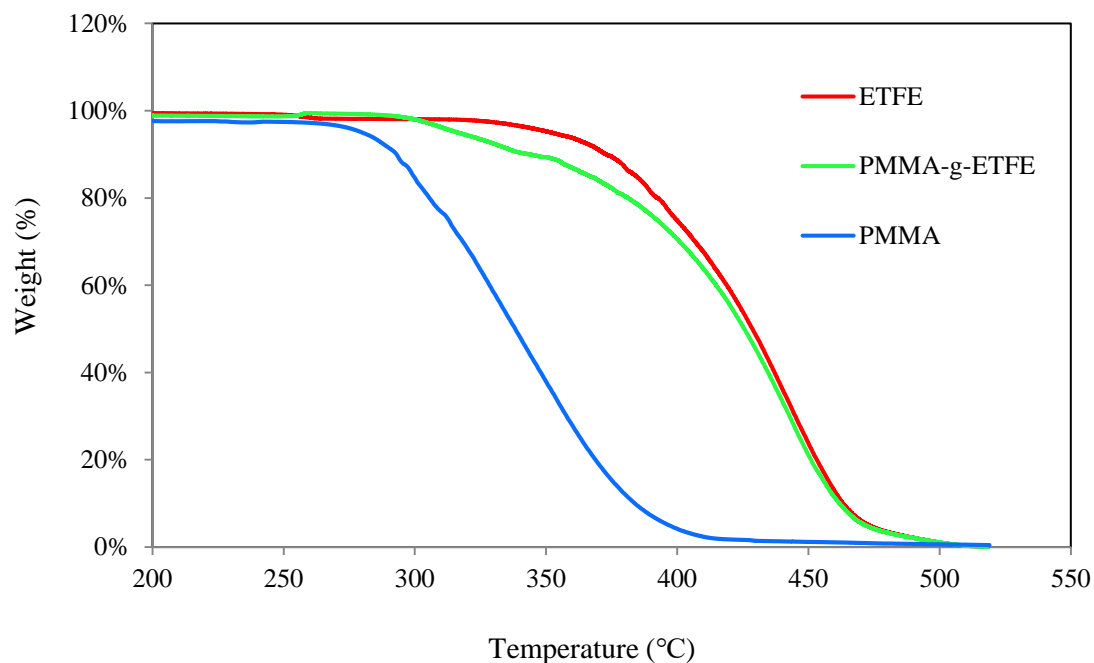


Fig. II-4 TGA curves for ETFE, PMMA homopolymer, and ETFE-*g*-PMMA.

Fig. II-5 shows XRD spectra of the original ETFE film and ETFE-*g*-PMMA. The semi-crystalline ETFE structure exhibited characteristic peaks at 18–20° and 40°. In addition, the diffraction pattern of ETFE-*g*-PMMA resembles that of the original ETFE film, but the peak intensities were different. The decreasing of intensity for ETFE-*g*-PMMA film was caused by generation of branched chains, which were intertwined with one other. These results showed that MMA was grafted on the surface of ETFE film without affecting its inherent crystal structure.

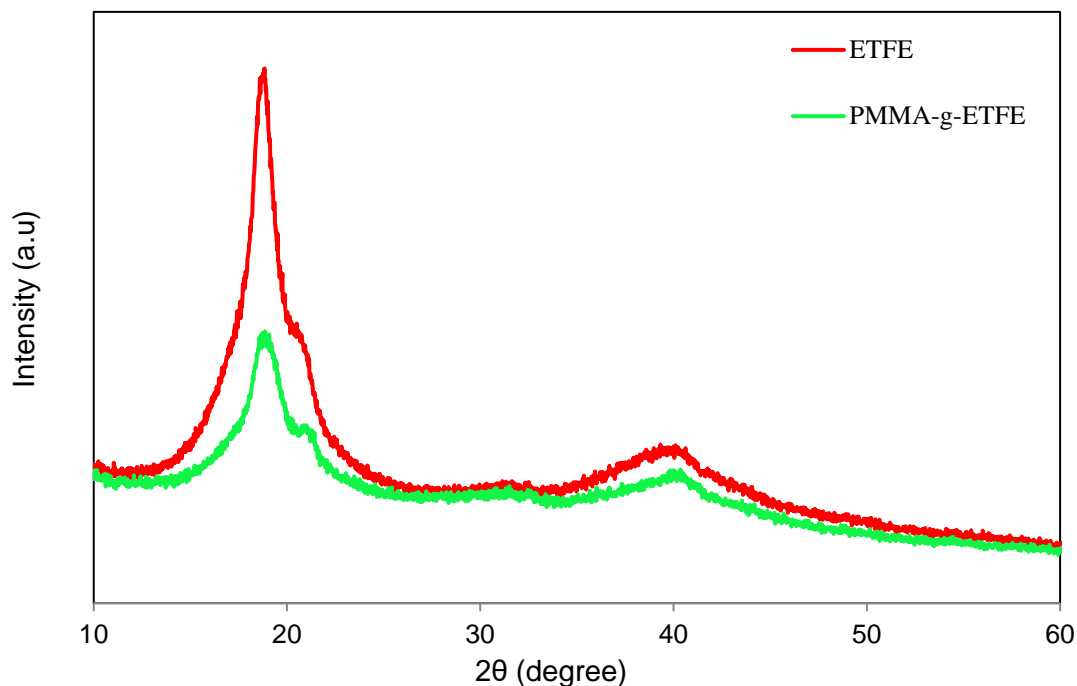


Fig. II-5 XRD patterns of ETFE and ETFE-*g*-PMMA.

Fig. II-6 shows surface morphologies of the original and grafted ETFE films. The roughness of the original ETFE film was 20.1 nm. The original ETFE film exhibited a relatively flat and even surface structure. On the other hand, ETFE-*g*-PMMA did not exhibit the same surface structure as the ETFE film, but the roughness value increased to 39.1 nm, and several spiked projections were observed on the surface of the grafted ETFE film. The transparency of the film decreased upon grafting treatment of ETFE film, which indicates that surface of the ETFE film was grafted by PMMA.

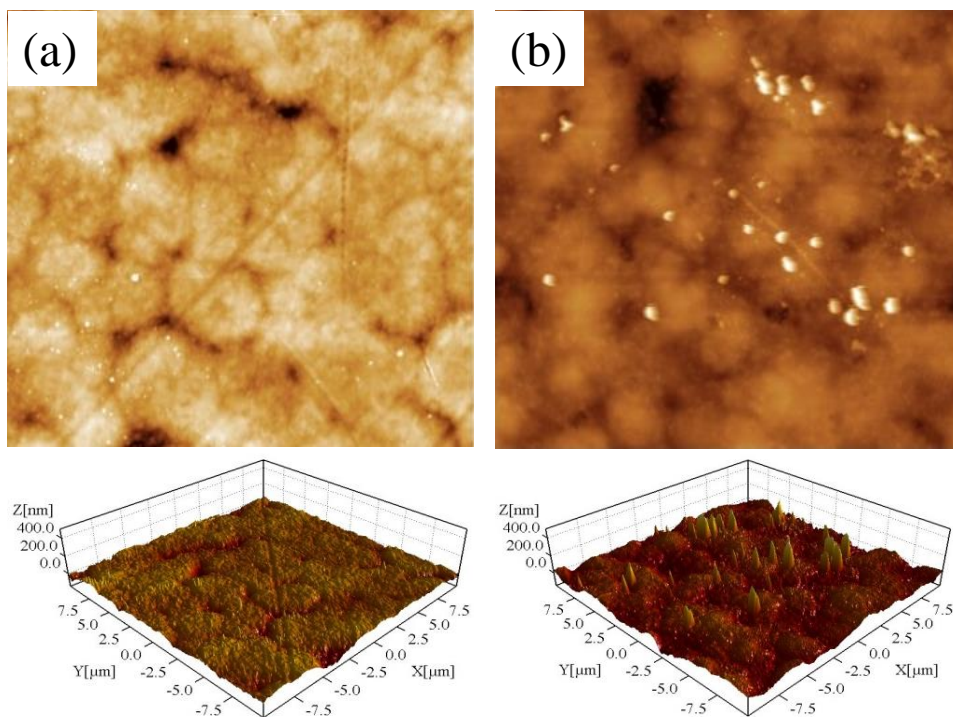


Fig. II-6 AFM topologies of: (a) ETFE and (b) ETFE-*g*-PMMA.

The water contact angle was measured (Fig. II-7). While the contact angle (94.2°) of ungrafted ETFE changed to 73.9° upon grafting with PMMA on the ETFE surface. This change indicates the hydrophobic surface of the ETFE film obtained hydrophilic property by introducing polar functional groups such as an ester function. This is also a proof of the PMMA grafting of the ETFE film.

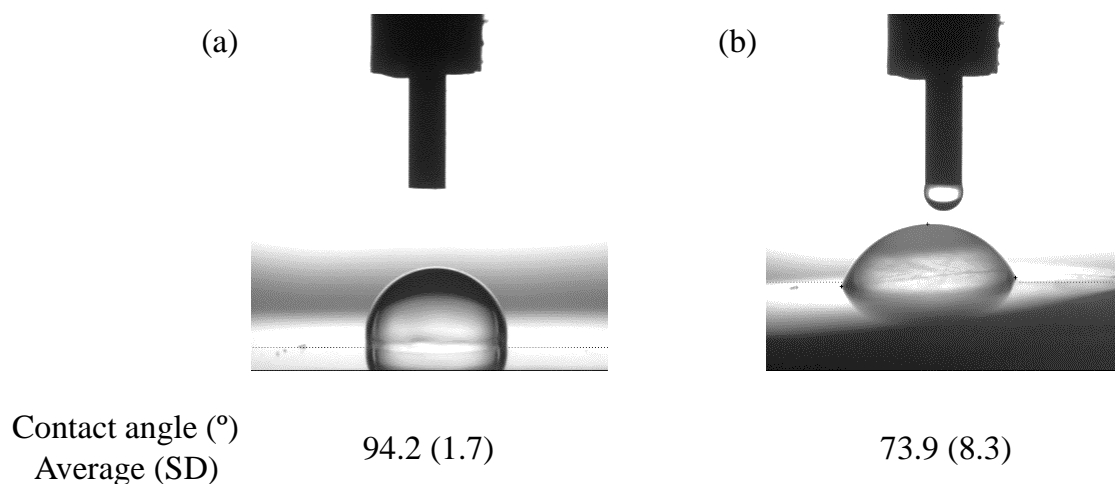


Fig. II-7 Contact angles on: (a) ETFE and (b) ETFE-*g*-PMMA.

To confirm the surface of the ETFE film was modified by graft polymerization, the ETFE-*g*-PMMA film was stained with SDN (Fig. II-8). The top view (Fig. II-8-a) and side view (Fig. II-8-b) show only surface of ETFE film was stained but not inside of the film. This result reveals that only surface was modified because free radical generates on the surface of ETFE and subsequent graft polymerization by MMA occurs from the surface.

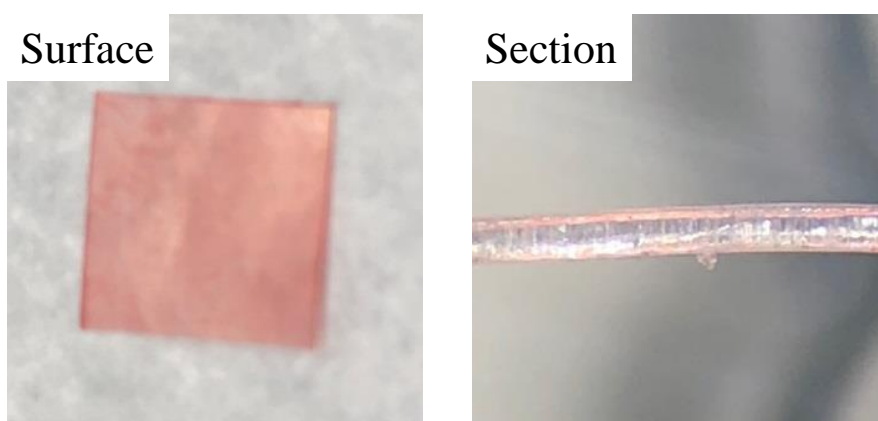


Fig. II-8 Staining of ETFE-*g*-PMMA (left: surface, right: section)

Conclusion

A simple modification method of the ETFE surface was presented, which proceeds through radical polymerization of MMA initiated by an alkyl zinc complex (Phen-DEZ) under mild conditions. In this polymerization, radicals generated on the inert surface of the ETFE film by a combination of Phen-DEZ and oxygen molecule. The subsequent radical polymerization of MMA was initiated from the surface of the ETFE film, which results in the modified surface. Grafting of MMA on the ETFE surface was confirmed by FT-IR, Raman, UV-vis spectroscopies, XRD spectra and thermogravimetric analysis. In addition, changes of the surface morphology were confirmed by AFM measurement. Introduction of polar functional groups afforded modified surface. The hydrophobic property of the ETFE surface attained hydrophilic property by PMMA. Indeed, only surface of the ETFE-*g*-PMMA film was stained while the inside of the film was remained intact.

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Chapter III.

Graft Polymerization of Methyl Methacrylate on the Surface of Poly(ethylene-*co*-tetrafluoroethylene) Using Benzoyl Peroxide as an Initiator

Introduction

Fluorocarbon polymers possess several advantageous properties such as high heat resistance, low friction coefficient, high hydrophobicity, and weather resistance. These properties facilitate the use for various applications such as coating materials [1]. Among these polymers, poly(1,1,2,2-tetrafluoroethylene) (PTFE) consists of only fluorocarbon segments, and shows excellent chemical, electrical, and high-energy radiation resistance,^[2] by which highly resistant to radical reactions is revealed.

Poly(ethene-*co*-1,1,2,2-tetrafluoroethylene) (ETFE) is a fluorocarbon polymers composed of an ethylene unit and a tetrafluoroethylene unit. ETFE has excellent characteristics such as higher mechanical strength, greater flexibility, and lighter weight compared to PTFE. In addition, it is superior to PTFE in terms of weather resistance, transparency, and moldability [2,3]. Because of these advantages, ETFE is widely used as a coating film for buildings in regions with harsh weather conditions [3,4]. Furthermore, ETFE films the high thermal stability of fluorocarbon resins has attracted much attention because it facilitates their use as semiconductors and fuel cell membranes. However, ETFE films have inherent shortcomings such as high gas permeability and low proton conductivity, which should be addressed [5-7]. For this purpose, graft polymerization is useful add different properties from that of the scaffold polymer on the surface of the film [5,8-22].

Electron beams and radiation are commonly used for introducing functionalized polymer chains on the surface of ETFE films. Chen and Seko succeeded the graft polymerization of (chloromethyl)styrene on an ETFE film using gamma radiation, in which the graft yield could be controlled from 75% to 334% by altering the irradiation dose from 15 kGy to 80 kGy ^[12]. They also investigated the effect of a reversible addition-fragmentation chain transfer (RAFT) agent on graft polymerization ^[7]. Moreover, UV-induced photografting and electron beam-induced crosslinking techniques were also reported for preparing ETFE-based fuel cell membranes ^[21]. Hamada *et al.* achieved radiation-induced graft polymerization of aniline-containing monomers on the surface of an ETFE film, in which the graft yield was increased when reaction time was prolonged ^[20]. Atom-transfer radical polymerization was shown to be effective for the radiation grafting of 2-bromotetrafluoroethyl trifluorovinyl ether ^[22]. Although these are powerful and useful methods for graft polymerization on ETFE film surfaces, they suffer from several shortcomings such as the necessity of expensive high-energy facilities and harsh reaction conditions as well as hazard for the health of the operators and environments. In addition, the deterioration of ETFE films is a major problem when irradiated. Hence, an alternative facile method is in high demand.

As mentioned in the last chapter, graft polymerization is a useful technique for investing additional property such as dyeability, printability, and adhesiveness on the ETFE surface ^[23]. I focused on radical polymerization using an initiator such as 2,2'-(diazene-1,2-diyl)bis(2-methylpropanenitrile) or dibenzoyl peroxide (BPO), which are common reagents for undergoing radical polymerization, but it has not been used for graft polymerization to ETFE. Contrast to the above-mentioned

methods, this method is conducted with simple manipulations without necessity of any special facilities or reagents, which facilitates the practical use. However, graft polymerization of ETFE using radical initiator has not been studied well because fluorocarbon segments show strong resistance to radical reactions as well as excellent chemical, electrical, and high-energy radiation resistance. On the other hand, graft polymerization of polyethylene is known. Thus, I considered the ethylene units in ETFE can react with radicals to undergo the graft polymerization.

In the last chapter, modification of the surface of ETFE was demonstrated, in which a combination of diethyl(1,10-phenanthroline N1,N10)zinc (Phen-DEZ) and oxygen molecule serves as a radical initiator to undergo the graft polymerization ^[19]. Fourier transform infrared (FT-IR) spectroscopy and thermal analysis revealed that PMMA grafting occurred on the ETFE films. Furthermore, the water contact angle on the surface of ETFE changed significantly due to the introduced PMMA, which indicating the property of the ETFE surface was modified. However, DEZ is extremely reactive and spontaneously ignites in air, and it cannot be used in polar solvents such as water and methanol because of rapid hydrolysis. Although Phen-DEZ is relatively stable and can be handled safely, much stabler and easily procurable initiator instead of Phen-DEZ is required for practical use. Moreover, insights of the graft polymerization can be obtained if the reaction is conducted under mild conditions ^[24].

In this chapter, I investigated the graft polymerization of methyl methacrylate (MMA) on the surface of an ETFE film using BPO, widely used radical initiator in industrial processes, under mild conditions.

Experimental

Materials

The ETFE film (100 μm thickness), provided by AGC Inc., was washed using chloroform and dried under reduced pressure before use. BPO (75% in water) and MMA with purity >99% were purchased from Nacalai Tesque. MMA was washed with aqueous sodium hydroxide and water, and subsequently distilled and dried over magnesium sulfate prior to use. Toluene with purity >99.5% and a disperse dye with an anionic surfactant (product name: SDN) were purchased from FUJIFILM Wako Pure Chemical Corporation and Osaka Kaseihin. Co., Ltd., respectively.

Measurements

The total transmittance and the haze of films were measured by haze meter (NIPPON DENSHOKU INDUSTRIES CO., LTD, NDH4000). Attenuated total reflection Fourier transform infrared (ATR FT-IR) spectra were obtained using an FT/IR-6600 (JASCO Corporation) at a resolution of 4 cm^{-1} with a diamond crystal at an incident angle of 45° . Thermogravimetric analysis (Hitachi, STA 7200 RV) was performed in air with the temperature range of $50\text{--}600\text{ }^\circ\text{C}$ ($10\text{ }^\circ\text{C}/\text{min}$) at a flow rate of $25\text{ mL}/\text{min}$. The morphology of the grafted ETFE films was analyzed using atomic force microscopy (Nanoscope II, Digital Instruments). Scanning electron microscopy (SEM) images were obtained using a field emission (FE)-SEM (Hitachi SU-8020) microscope. The cross-sections of the films were observed through a digital microscope (VHX-6000, KEYENCE CORPORATION). The contact angle between the water (droplet size: 0.04 mL) and the film was measured using a portable contact angle analyzer (PG-X, MATSUBO Corporation). The contact angle was measured

after 5 min of dripping.

Modification of ETFE films by graft polymerization of MMA with BPO

ETFE films (4 pieces, size: 1 cm × 1 cm, thickness: approximately 100 μm) and BPO (97 mg, 0.4 mmol) were placed in a 20 mL round bottomed flask, into which argon was introduced for 10 min to remove air. Then, toluene (6 mL) and MMA (4 mL, 37.6 mmol) were added and the flask was sealed. The flask was heated at 75 °C for 24 h on an oil bath. The ETFE films were taken out from the flask and washed with chloroform using a Soxhlet extractor for 12 h to remove the ungrafted poly(methyl methacrylate) (PMMA) and unreacted MMA. The film was stained for 5 min at 70 °C by disperse dye when a detailed observation was necessary. When the reaction conditions (time of reaction, reaction temperature, and concentration of BPO) were changed, the reaction was conducted in the same manner.

The polymerization yield was calculated from the weight change, as follows ^[25]:

$$\text{Polymerization yield (\%)} = \frac{\text{weight of homo PMMA}}{\text{weight of MMA before polymerization}} \quad \text{Eq. III-1}$$

The graft yield was calculated from the weight changes, as follows ^[26]:

$$\text{Graft yield (\%)} = \frac{\text{weight of grafted ETFE} - \text{weight of original ETFE}}{\text{weight of original ETFE}} \quad \text{Eq. III-2}$$

Results and Discussions

BPO-initiated polymerization of MMA on an ETFE film was conducted in toluene solution at 75 °C for 24 h. The polymerization yields increased according to the prolonged reaction time (Fig. III-1). This result indicated that most of the MMA was converted to homo PMMA after 24 h, and the viscosity of the reaction mixture considerably increased.

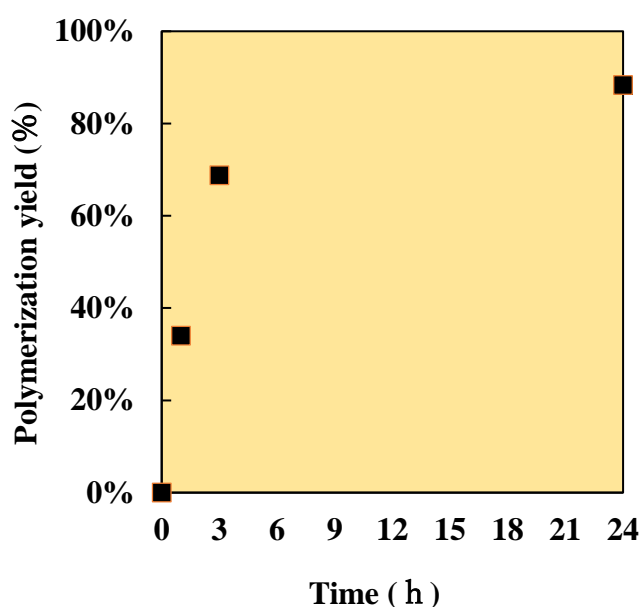


Fig. III-1 Polymerization yield-time plots for solution polymerization of MMA in toluene with ETFE film at 75 °C

Digital microscope observations revealed that the visual appearance of the ETFE films changed after polymerization (Fig. III-2). Untreated ETFE film was transparent (total transmittance 93%, haze 6%), and it remains upon heating at 75 °C without BPO. On the other hand, the ETFE film became cloudy when treated in the

presence of BPO (total transmittance 87%, haze 93%). The change in visual appearance was shown in Fig. 2, which was one of the proofs for the graft polymerization ^[23]. On the basis of these results, it was confirmed that modification of the film surface was achieved by PMMA graft polymerization.

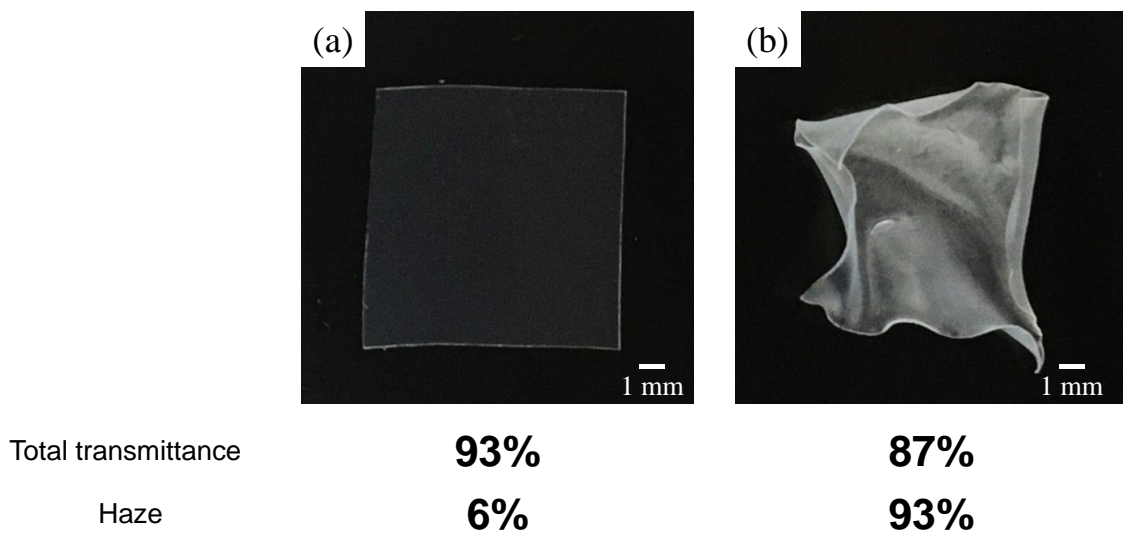


Fig. III-2 Visual appearance of ETFE films before (a) and after (b) polymerization by MMA at 75 °C for 24 h

Fig. III-3 shows the graft yield of the ETFE films with different reaction times. The graft yield increased to 38% within 3 h, however, further increasing was not observed anymore (39%) even when the reaction time was prolonged to 24 h. This result is different from the result shown in Fig. III-1. Similar behavior was also reported for radiation-induced graft polymerization on an ETFE film ^[5]. Since polymerization yield was 68% after 3 h, graft polymerization and homopolymerization of MMA competitively proceeded at earlier stage. After the surface

was grafted by PMMA, MMA was only consumed by the latter polymerization.

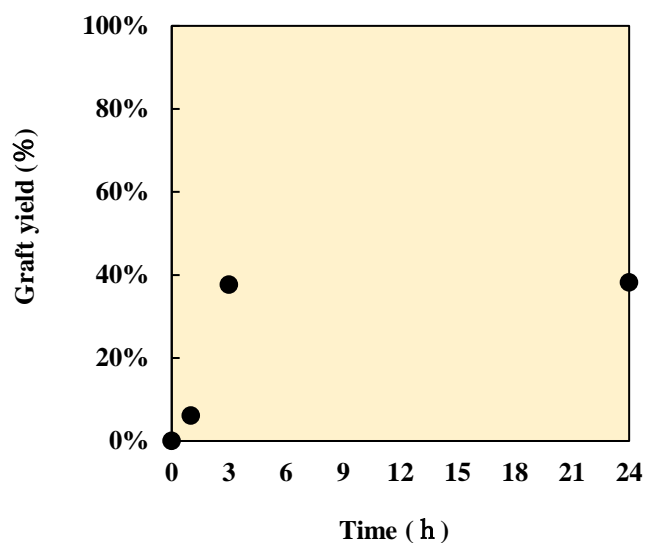


Fig. III-3 Graft yield versus time plots for ETFE films treated with MMA and BPO in toluene at 75 °C, wherein the amount of BPO is 1 mol% of MMA

TGA results for pure ETFE, ETFE-*g*-PMMA, and homo PMMA were shown in Fig. III-4. The thermal decomposition of ETFE-*g*-PMMA occurred via two stages. In the first stage, weight change from 1% to 27% was observed as the temperature was increased from 250 to 350 °C. In the second stage, weight change from 27% to 99% was observed in the range from 350 to 470 °C. On the other hand, the thermal decomposition of pure ETFE and homo PMMA occurred in one stage, which occurred at about 250 °C and 350 °C, respectively. Considering the graft yield (38%) and decomposition temperature (250 °C), the first weight loss is assigned to the disruption of the grafted PMMA polymer, and the second step is assigned to that of ETFE. The thermal stability of the ETFE film was significantly altered upon grafting

with PMMA. This tendency in the TGA curves for grafted ETFE has been also observed in several studies [9,14,23]. Thus, the TGA curves indicated successful grafting of MMA on the ETFE film.

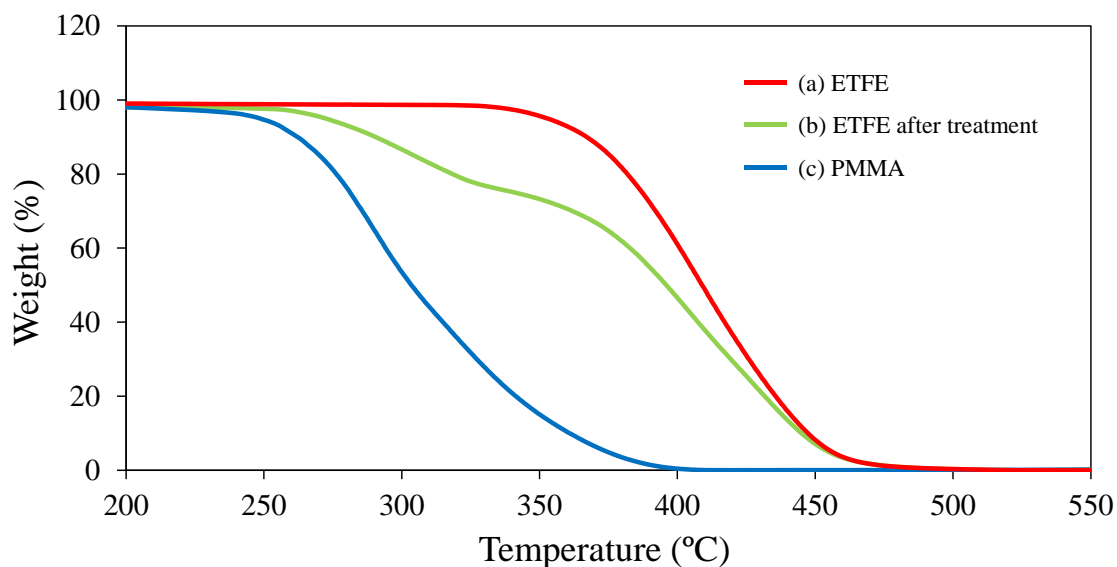


Fig. III-4 TGA curves of ETFE films (a) before and (b) after (graft yield 38%) treatment by MMA with BPO in toluene at 75 °C for 24 h, and (c) PMMA

Attenuated total reflection Fourier transform infrared (ATR FT-IR) spectroscopy was performed to analyze the surface of grafted film (Fig. III-5). Fig. III-5a shows the spectrum of the ETFE film before polymerization, and this pattern is almost identical to that reported by Radice *et al.* [27] The spectrum of ETFE displayed a broad characteristic band in the range of 1000–1500 cm^{-1} representing large dynamical coupling between the strong CF_2 stretchings and CH_2 deformations [27,28]. The spectrum of the modified film (Fig. 5b) showed absorptions around 1730 cm^{-1}

in addition to those attributed to the original ETFE film. In the PMMA spectrum (Fig. III-5c), the characteristic absorption peak were observed at around 1730 cm^{-1} (the stretching carbonyl group C=O), and the bands at around 1435 cm^{-1} and 1146 cm^{-1} assigned to the C-H shear vibration of CH_3 and vibration of the ester group C-O, respectively ^[29]. Comparing the spectrum of the PMMA homopolymer (Fig. III-5c), the absorptions around 1730 cm^{-1} in Fig. III-5b could be assigned to the carbonyl functionalities of PMMA. These results revealed that graft polymerization of MMA proceeded on the surface of the ETFE film. Hence, this modified ETFE film is termed “ETFE-g-PMMA film” hereafter.

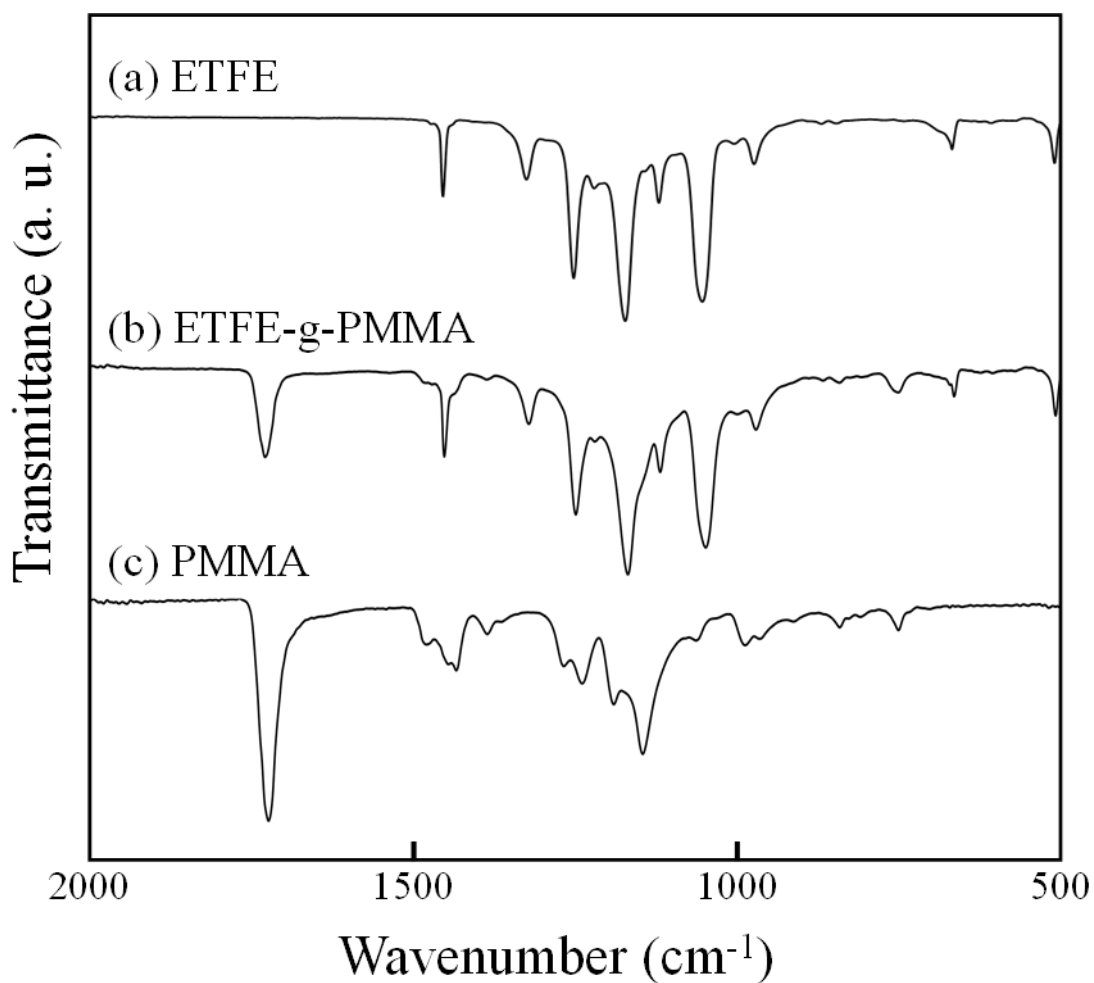


Fig. III-5 FT-IR spectra of surface of ETFE films (a) before and (b) after (graft yield 38%) treatment by MMA with BPO in toluene at 75 °C for 24 h, and (c) PMMA

Fig. III-6 shows the SEM images of the ETFE film and ETFE-g-PMMA. While the surface of ETFE was smooth, that of ETFE-g-PMMA was uneven. This result suggested that the graft polymerization also affected the texture of the film surface.

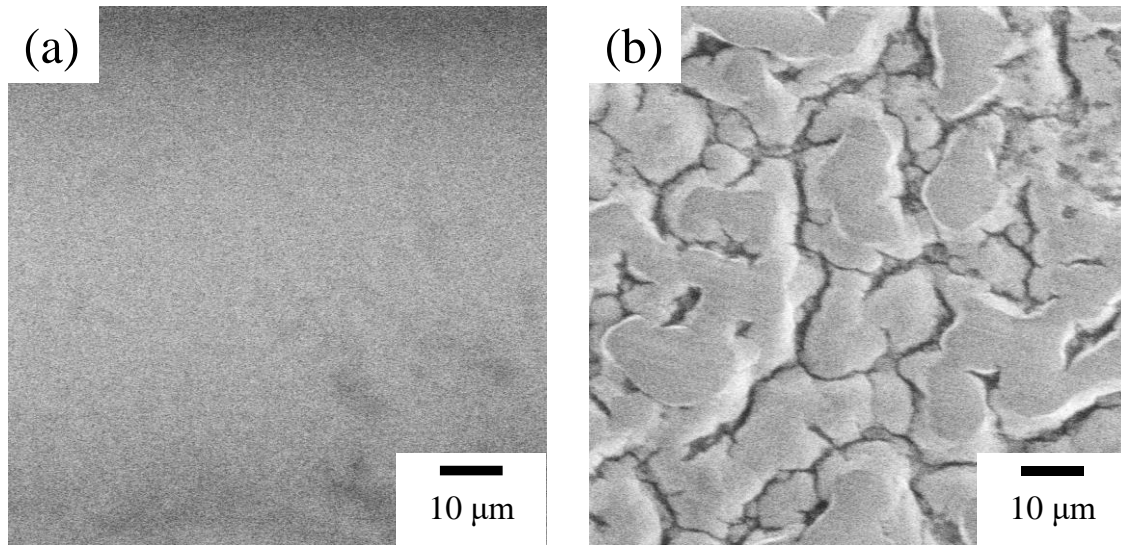


Fig. III-6. SEM images of ETFE films (a) and ETFE-*g*-PMMA (b, graft yield 38%)

Fig. III-7 shows the surface morphologies of the original and grafted ETFE films. The roughness of the original ETFE film was 10.6 nm. The surface of ETFE-*g*-PMMA was observed with the roughness increasing to 50.2 nm. These results indicated that the graft PMMA polymer was heterogeneously distributed on the surface of the ETFE film. An increase in the surface roughness was also observed in the last chapter, where Phen-DEZ was used ^[23]. Moreover, the transparency of the grafted ETFE film was lower than that of the ETFE film due to the MMA groups grafted on the film surface. Thus, the grafting of MMA on the ETFE film was successfully achieved.

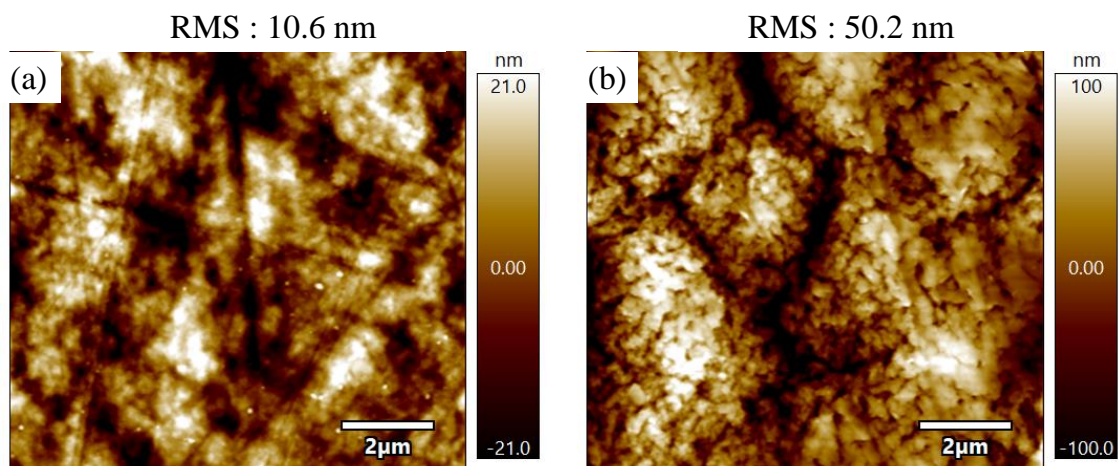
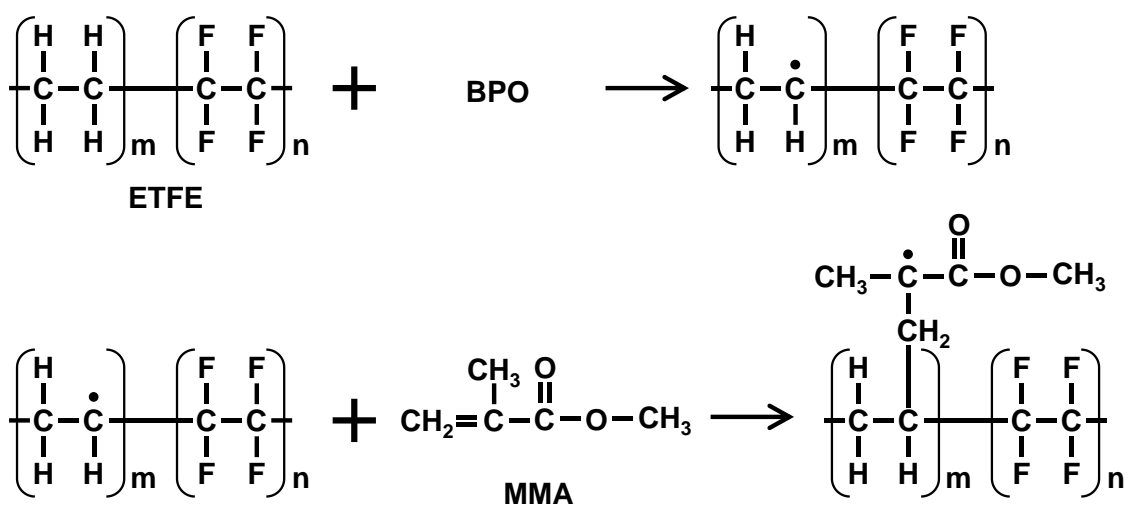


Fig. III-7 AFM topologies of ETFE films (a)
and ETFE-g-PMMA (b, graft yield 38%)



Scheme III-1. Mechanism underlying the graft polymerization of MMA to ETFE

A plausible mechanism for the graft polymerization of MMA to ETFE using BPO is shown in Scheme III-1. Homolysis of BPO occurs upon heating to generate free radicals, which serve as an initiator. Since the bond energy of a C–H bond is smaller

than that of C-F bond possessing partial ionic character [30], the radical abstract hydrogen from the C-H bond in the ETFE, which leading to the formation of free radicals on the film surface. Subsequent graft polymerization then occurs on the film.

To confirm whether the graft polymerization proceeded solely on the surface of the ETFE film or not, the ETFE-g-PMMA films were stained. As shown in Fig. III-8, the untreated ETFE film was not dyed. In contrast, a thin layer of stained PMMA was observed on the surface of ETFE-g-PMMA, but not in its bulk. These results suggest that graft polymerization occurred only on the surface of the ETFE film. Moreover, as shown Fig. III-8, the non-uniform dyed ETFE-g-PMMA film indicates that the surface is considered to be non-uniform; some areas of the surface were thought to be significantly graft-polymerized but the other parts were not. The additional graft polymerization might occur from the PMMA chain grafted on the film.

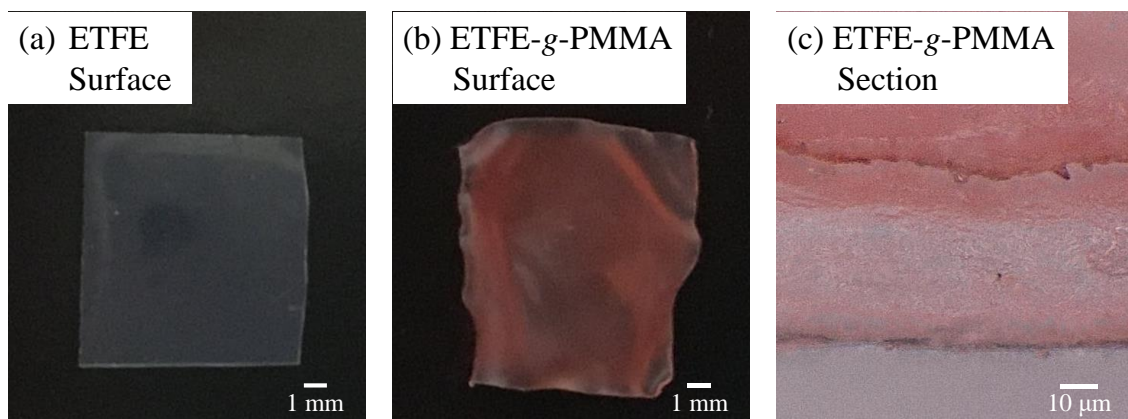


Fig. III-8 Visual appearance of ETFE (a) and ETFE-g-PMMA (b, graft yield 38%) films and cross-section of ETFE-g-PMMA (c, graft yield 38%) films after staining with PMMA

Furthermore, the modified surface was evaluated by measuring the contact angle between water and the surface of the film (Fig. III-9). The contact angle between water and the pristine ETFE film was 94.2° , by which ETFE surface was confirmed to be hydrophobic. To the contrary, the contact angle of ETFE-g-PMMA decreased to 80.9° , which reveals the surface became hydrophilic because of the polar ester groups of PMMA on the film surface. This result is similar to that obtained in the last chapter [23].

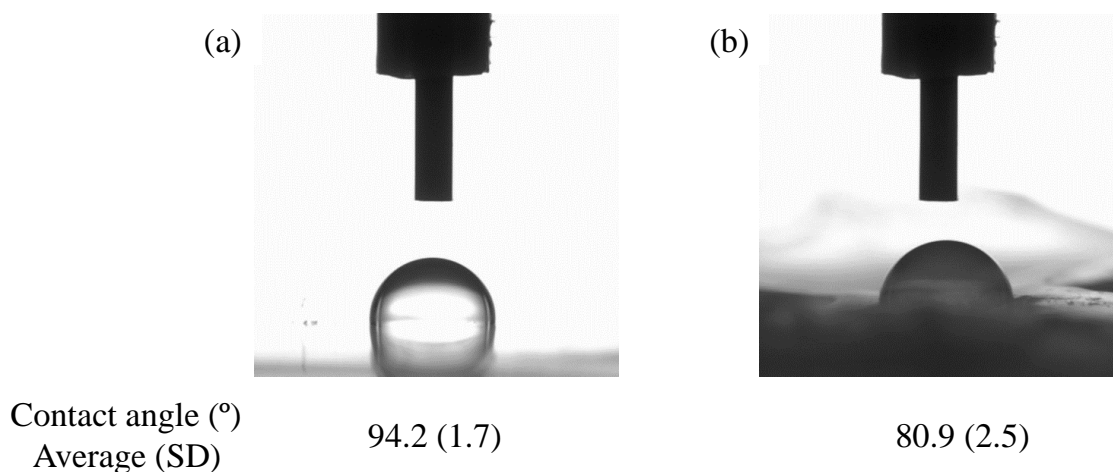


Fig. III-9 Contact angles between water and the ETFE film (a) before and (b) after (graft yield 38%) polymerization by MMA using BPO at 75°C for 24 h

The polymerization yield was influenced by the reaction temperature (Fig. III-10). When the reaction was conducted at 75°C , polymerization yield of MMA was 89%. While similar polymerization yield was observed at 100°C , the graft yield slightly decreased. This is presumably because larger amounts of BPO decompose at higher temperature, by which radical species are formed not only on the ETFE film but also

in the solution. Hence, homo-polymerization of MMA proceeded, and graft polymerization is consequently suppressed. Indeed, the 10 h half-life temperature of BPO is known to be around 75 °C. Similar phenomena were reported when grafting styrene to random ethylene-propylene diene monomer^[31], MMA to polyethersulfone^[32], and acrylic acid to polyamide fibers^[33]. Therefore, it is crucial to control the radical concentration for the efficient graft polymerization by the control of the reaction temperature.

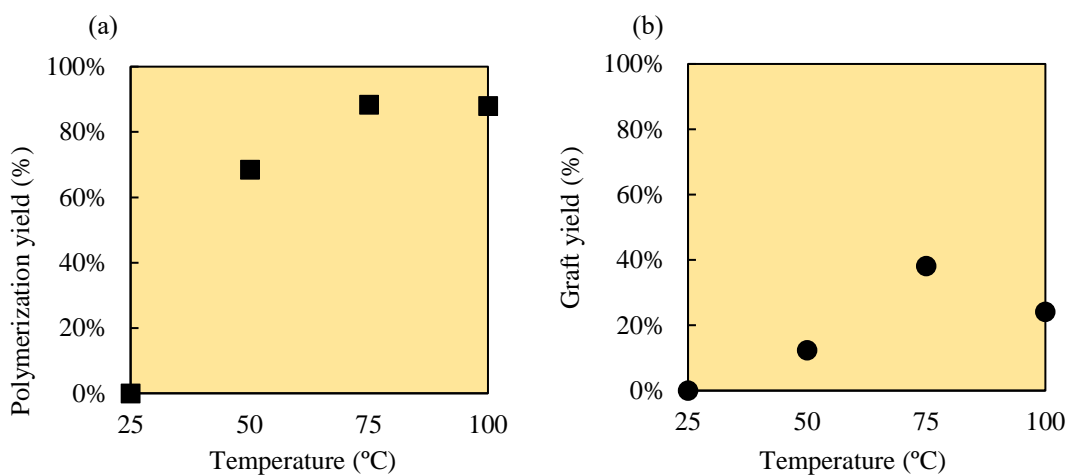


Fig. III-10 Polymerization yield versus temperature plot for the solution polymerization of MMA in toluene with ETFE film after 24 h, in which the amount of BPO is 1 mol% of MMA (a); graft yield versus temperature plot for ETFE-g-PMMA films (b)

The concentration of BPO also affected the graft yield (Fig. III-11). When BPO was used at higher concentrations than 0.1 mol%, the polymerization yield remained nearly constant (87% to 89%). The highest graft yield was obtained at 0.1 mol%, but

the yield decreased as the concentration was further increased. This is because higher concentrations increase the formation of radical species in the reaction mixture, which undergo competitive side-reactions such as polymerization of MMA in the solution. Similar observations were also reported in the grafting of monomers on the surface of other materials [31,33]. Therefore, the concentration of BPO strongly influenced the graft yield of ETFE-*g*-PMMA.

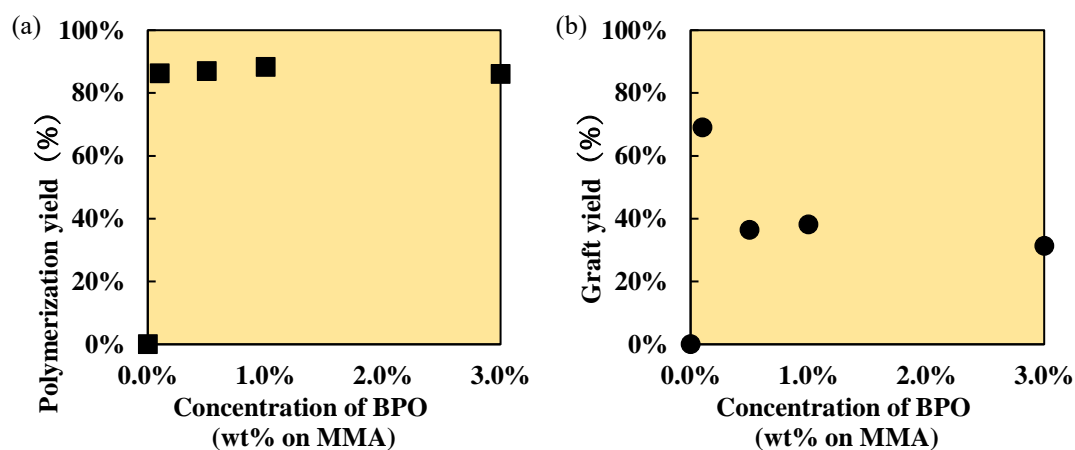


Fig. III-11 (a) Plots of polymerization yield of BPO versus its concentration for solution polymerization of MMA in toluene with ETFE film at 75 °C after 24 h and (b) graft yield versus temperature plots for ETFE-*g*-PMMA films

Conclusion

ETFE films were superficially modified by graft polymerization of MMA using BPO as an initiator. The graft yield of ETFE-*g*-PMMA depended on the temperature and the concentration of BPO, and the maximum graft yield (69%) was achieved. The surface roughness of ETFE film increased from 10.6 nm to 50.2 nm by the graft polymerization, and the visual appearance obviously changed. FT-IR spectroscopy and cross-sectional micrographs revealed that only the surface of the ETFE film was modified by MMA. Furthermore, the water contact angle on ETFE-*g*-PMMA (80.9°) was lower than pure ETFE film (94.2°), by which increasing of the hydrophilicity of the ETFE film was confirmed.

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Chapter IV.

Graft Polymerization of Methyl Methacrylate on the Surface of Poly(vinylidene fluoride) Using Tributylborane as an Initiator

Introduction

Fluorocarbon resins exhibit advantageous properties, such as high thermal stability, chemical stability, water repellency, and weatherability, that are suitable properties for coating materials or films in various application uses ^[1]. Among fluorocarbon resins, poly-1,1-difluoroethene (PVDF) is a popular membrane material owing to its unique properties, such as mechanical strength, thermal stability, and ease of fabrication, which facilitate a wide range of industrial applications. If different properties are added to the PVDF surface, novel applications will be realized, which is currently highly demanded ^[2,3].

Several attempts have been made to modify PVDF surfaces ^[4-17]. Näsman *et al.* succeeded graft polymerization using an electron beam to introduce carboxylic acid, trimethylammonium, and *N*-isopropyl amide functionalities on the PVDF membrane. As a result, the surface acquired cation exchange, anion exchange, and temperature-sensitive properties, respectively ^[4]. Huang *et al.* reported a useful method for obtaining highly hydrophilic PVDF membranes: the plasma-induced graft polymerization of methacrylic acid (MAA) on a PVDF surface by tethering superhydrophilic silica nanoparticles on the PVDF film grafted with PMAA (PVDF-*g*-PMMA) ^[5]. Ozone was also an effective agent for graft polymerization, which was initiated by the peroxide formed on the PVDF framework ^[6-10]. Controlled/living radical polymerizations, such as atom transfer radical polymerization (ATRP) and

reversible addition-fragmentation chain transfer (RAFT), were also employed for this purpose. Antifouling properties could be incorporated to the PVDF membranes when hydroxyethyl methacrylate (HEMA) ^[11], 2-(*N,N*-dimethylamino)ethyl methacrylate, 2-oligo(ethylene glycol) monomethyl ether methacrylate ^[12], zwitterionic sulfobetaine methacrylate ^[13], and poly(ethylene glycol) methyl ether methacrylate ^[14] were used as the functional monomers. On the other hand, radical polymerization using an initiator, such as 2,2'-(diazene-1,2-diyl)bis(2-methylpropanenitrile) (AIBN) or benzoyl peroxide (BPO), is the simplest method to modify the PVDF surface because only single-step experimental manipulation is required. Furthermore, pretreatment, special facilities and reagents are not necessary. Li *et al.* reported the AIBN-initiated graft polymerization of a zwitterionic monomer which imparted the PVDF membrane with antifouling abilities; however, this method suffered from low graft yield (0.7 mg/cm² max), which was presumably due to the low activity of AIBN in the hydrogen abstraction step ^[17].

In our previous report, we demonstrated a tributylborane (TBB)-initiated one-step graft polymerization of 3-(4-ethenylphenyl)thiophene on a polypropylene powder and film, in which TBB exhibited superior hydrogen abstraction activity to generate free radicals for graft polymerization ^[18]. Inspired by this result, I studied graft polymerization on PVDF films using TBB as an initiator in this chapter.

Experimental

Materials

PVDF films (100 μm thickness) were provided by AGC Inc. and washed with chloroform and dried under reduced pressure before use. MMA with purity >99%, and deoxidized toluene were purchased from FUJIFILM Wako Pure Chemical Corporation. MMA was washed with aqueous sodium hydroxide and water, and then distilled and dried over magnesium sulfate. TBB was supplied by Nippon Aluminum Alkyls Ltd. while disperse dye with anionic surfactant (product name: SDN) was purchased from Osaka Kaseihin Co., Ltd.

Measurement

The total transmittance and the haze of films were measured by haze meter (NIPPON DENSHOKU INDUSTRIES CO., LTD, NDH4000). Attenuated total reflection Fourier transform infrared (ATR FT-IR) spectra were measured using an FT/IR-6600 (JASCO Corporation) at a resolution of 4 cm^{-1} using a diamond crystal at an incident angle of 45° . Thermogravimetric analysis (Hitachi, STA 7200 RV) was performed in air at range of $25\text{--}600\text{ }^\circ\text{C}$ ($10\text{ }^\circ\text{C}/\text{min}$) at a flow rate of $25\text{ mL}/\text{min}$. Scanning electron microscopy (SEM) images were obtained using a field emission (FE)-SEM (Hitachi SU-8020) microscope. Cross-sections of the films were observed using a digital microscope (VHX-6000, KEYENCE CORPORATION). Contact angles between water (droplet size: 0.04 mL) and the film were measured using a portable contact angle analyzer (PG-X, MATSUBO Corporation). The contact angle was measured after 5 minutes dripping.

Modification of PVDF films by graft polymerization of MMA with TBB

Four pieces of PVDF film (1 cm × 1 cm, approximately 100 μm thickness) were placed in a 20 mL round-bottomed flask. The flask was equipped with a balloon filled with the necessary amount of air to initiate the reaction. Deoxidized toluene (5.6 mL), MMA (4 mL, 37.6 mmol), and TBB (1.0 M; 0.4 mL, 0.4 mmol) were added under an argon atmosphere. After opening the stopcock between the flask and the balloon, the mixture was heated at 50 °C for 24 h. The PVDF films were washed with chloroform using a Soxhlet apparatus for 12 h to remove the ungrafted PMMA and unreacted MMA to afford the surface-modified PVDF films. The reaction was conducted using the same procedure when the molar ratios and reaction conditions were changed.

The polymerization yield was calculated from the weight change, as follows ^[19]:

$$\text{Polymerization yield (\%)} = \frac{\text{weight of homo PMMA in toluene after polymerization}}{\text{weight of MMA before polymerization}} \quad \text{Eq. IV-1}$$

The graft yield was calculated from the weight changes, as follows ^[20]:

$$\text{Graft yield (\%)} = \frac{\text{weight of grafted PVDF} - \text{weight of original PVDF}}{\text{weight of original PVDF}} \quad \text{Eq. IV-2}$$

Results and Discussion

The TBB-initiated polymerization of MMA on a PVDF film was conducted in toluene at 50 °C for 24 h. The polymerization yield was estimated from the weight of the ungrafted PMMA homopolymer (Fig. IV-1). Although the viscosity of the system increased as the polymerization of MMA proceeded, more than 30% of the MMA was consumed. After polymerization, the visual appearance of the PVDF films became slightly cloudy, indicating that the surfaces of the PVDF films were successfully modified (Fig. IV-2).

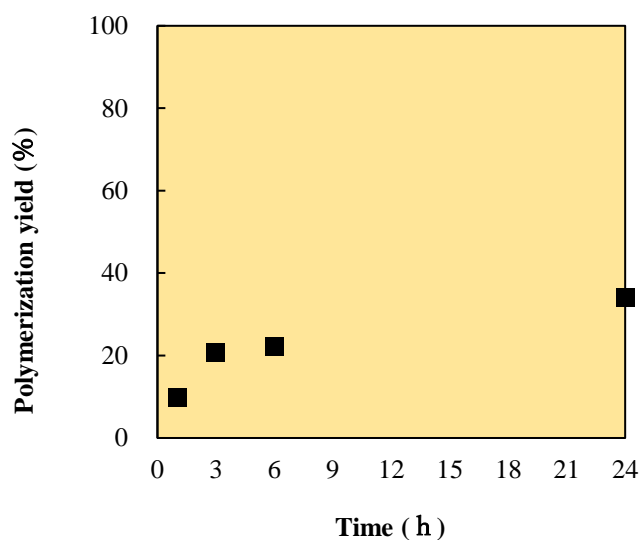


Fig. IV-1 Polymerization yield-time plots for solution polymerization of MMA in toluene with PVDF films and TBB at 50 °C.

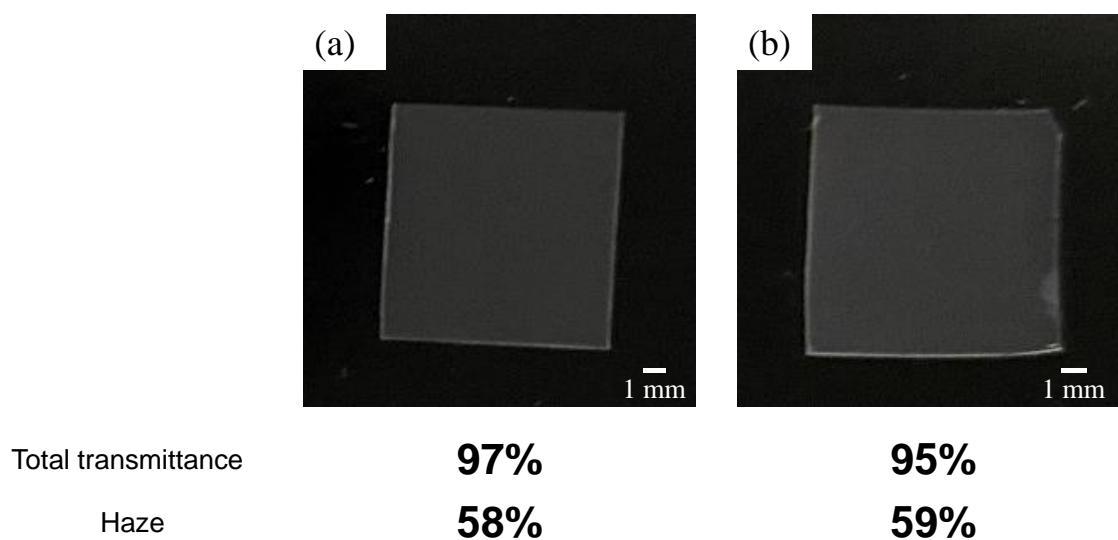


Fig. IV-2 Visual appearance of PVDF film (a) before and (b) after polymerization with MMA at 50 °C for 24 h.

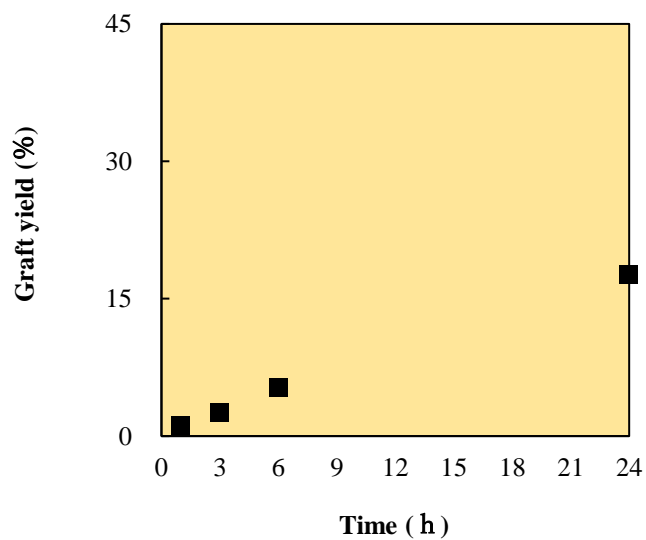


Fig. IV-3 Graft yield versus time plots for PVDF films treated with MMA and TBB (1 mol% of MMA) in toluene at 50 °C.

As shown in Fig. IV-3, the graft yield increased as the reaction time was prolonged. The graft yield increased up to around 18% after heating for 24 h, which suggested that the graft polymerization proceeded on PVDF films.

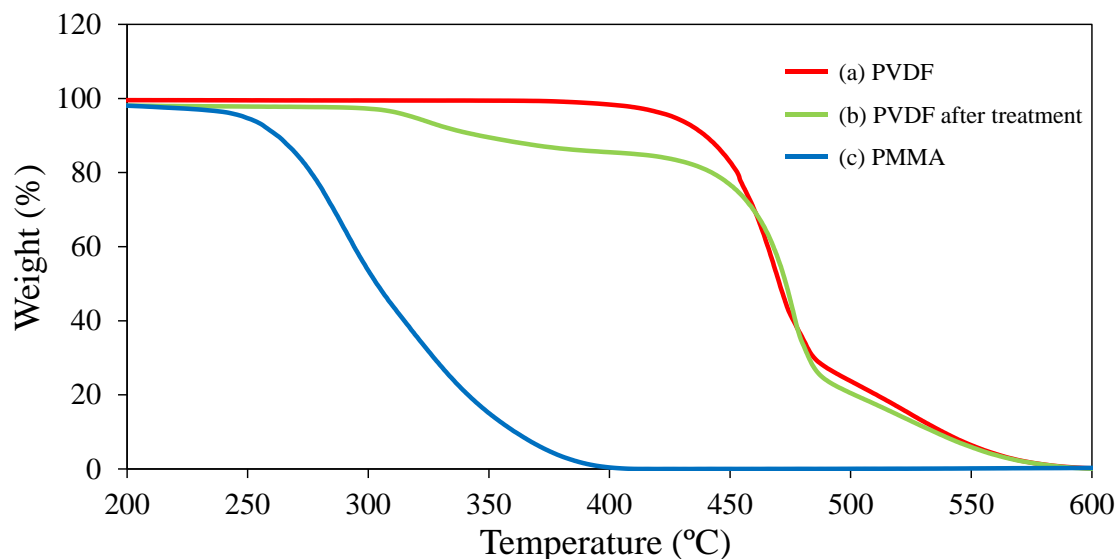


Fig. IV-4 TGA curves of PVDF films (a) before and (b) after (graft yield 18%) treatment by MMA with TBB in toluene at 50 °C for 24 h, and (c) PMMA

TGA were measured for pure PVDF, PVDF-g-PMMA and homo PMMA (Fig. IV-4). The thermal decomposition of PVDF-g-PMMA was observed through two stages. In the first stage, a weight change from 1% to 15% was observed at a range of temperature from 250 to 400 °C. In the second stage, weight change from 15% to 99% was observed at a range temperature from 400 to 600 °C. Considering the graft yield (18%) and decomposition temperature (250 °C), the first weight loss step should be assigned to the disruption of the grafted PMMA polymer. Then, the second

degradation step was caused by thermal disruption of PVDF itself. The thermal stability of the PVDF film was significantly altered upon grafting with PMMA. These TGA curves behavior of grafted PVDF were observed in several papers [7,8,10]. Thus, the TGA curves indicated successful grafting of MMA on the PVDF film. Attenuated total reflection Fourier transform infrared spectroscopy (ATR FT-IR) was performed on the surface-modified PVDF film (Fig. 5). Fig. IV-5a is spectrum of PVDF film before polymerization, which is the almost same pattern in several reports [7,13,16]. A new absorption band was observed at 1720–1700 cm^{-1} (Fig. IV-5b) and assigned as the carbonyl functionalities of PMMA, which shows similar pattern to that of PMMA homopolymer (Fig. IV-5c) [21]. This result revealed that the graft polymerization of MMA on the surface of the PVDF film proceeded successfully to furnish a PVDF-*g*-PMMA film.

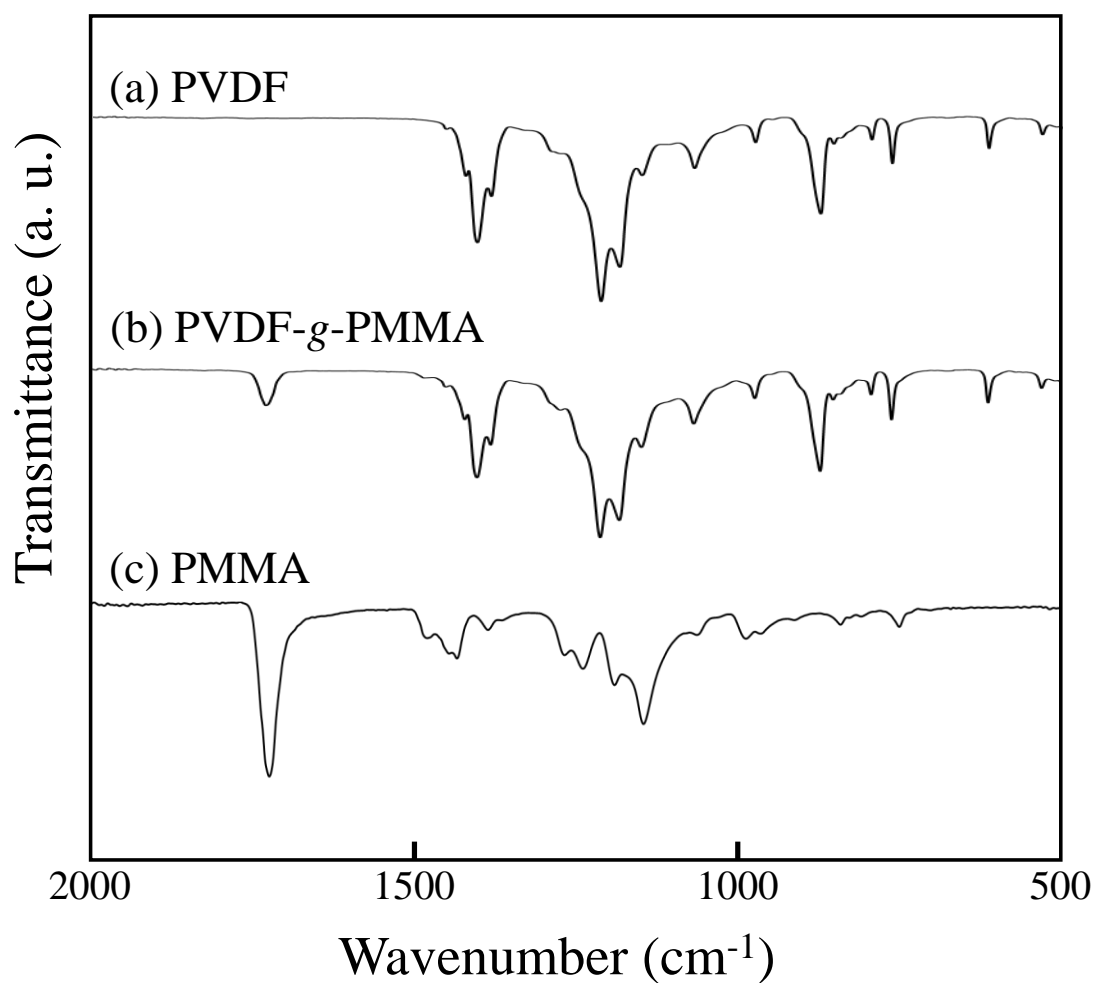


Fig. IV-5 FT-IR spectra of the surfaces of PVDF films (a) before and (b) after (graft yield 18%) treatment with MMA and TBB in toluene at 50 °C for 24 h, and (c) after treatment with PMMA.

Fig. IV-6 shows SEM photographs of PVDF film and PVDF-g-PMMA. The surface of PVDF was smooth, while the surface of PVDF-g-PMMA was uneven. It was suggested that the graft polymerization also affected the shape of the film surface. Moreover, the transparency of the grafted PVDF film was lower than that of the

original PVDF film due to the presence of PMMA on the film surface. Thus, successful grafting of MMA on the PVDF film was confirmed.

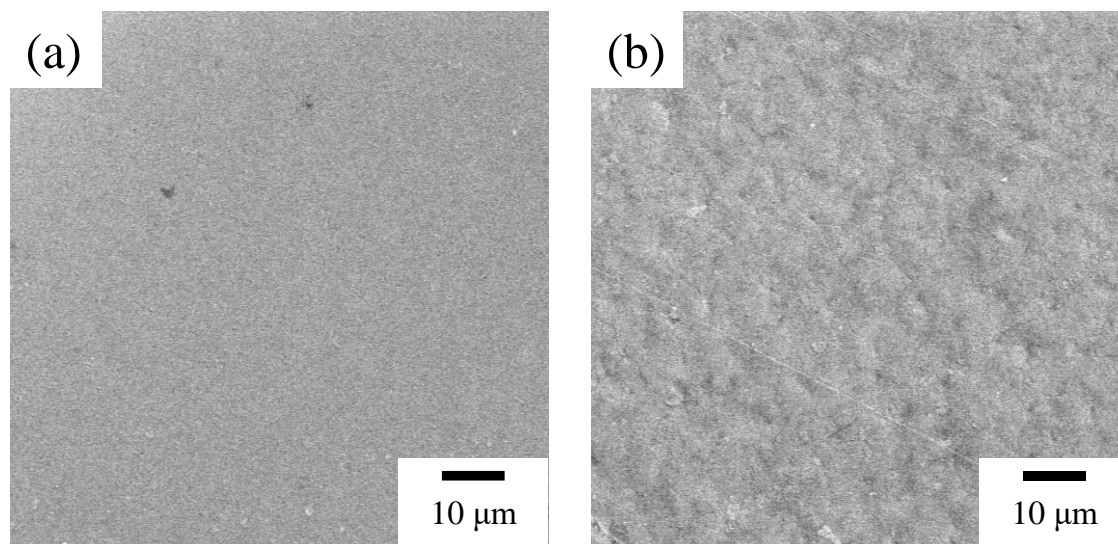
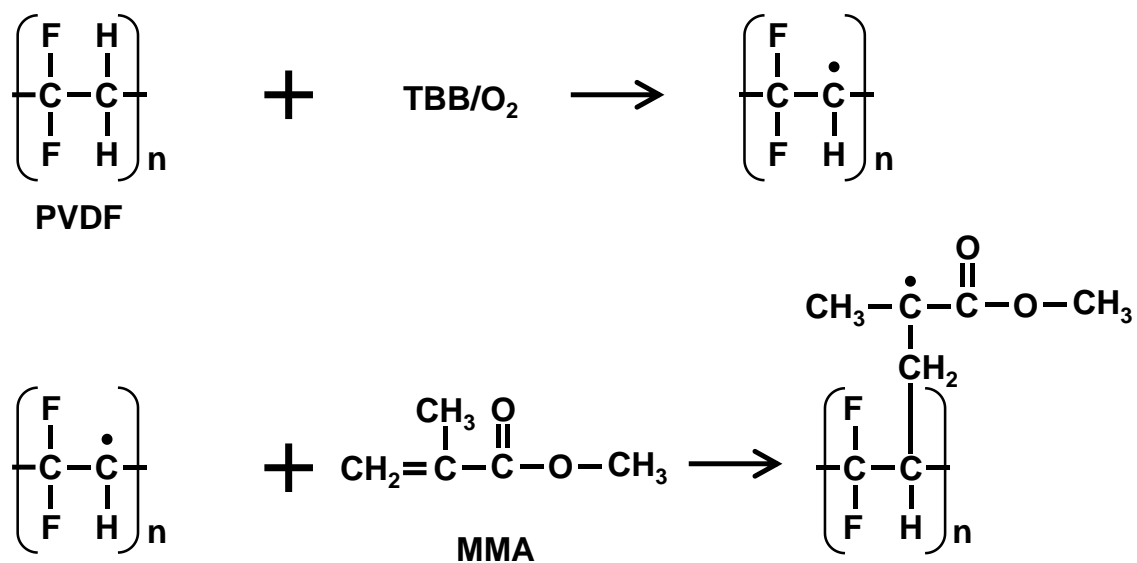


Fig. IV-6 SEM images of PVDF films (a) and PVDF-g-PMMA (b, graft yield 18%)

The reaction mechanism of this graft polymerization is illustrated in Scheme IV-1. In the initiation step, TBB reacts with molecular oxygen to form a butyl radical and peroxy radical^[22]. The butyl radical is highly reactive to abstract a hydrogen atom from the PVDF, and radical species generate on the surface. The subsequent reaction with MMA results in the graft polymerization on the film surface.

The bond energy of a C-H bond is smaller than that of a C-F bond due to the partial ionic character^[23]. Therefore, the propagation reaction of MMA on the PVDF film is presumably initiated by homolysis of the C-H bond at the PVDF surface (Scheme IV-1).



Scheme IV-1 Mechanism of graft polymerization of MMA to PVDF.

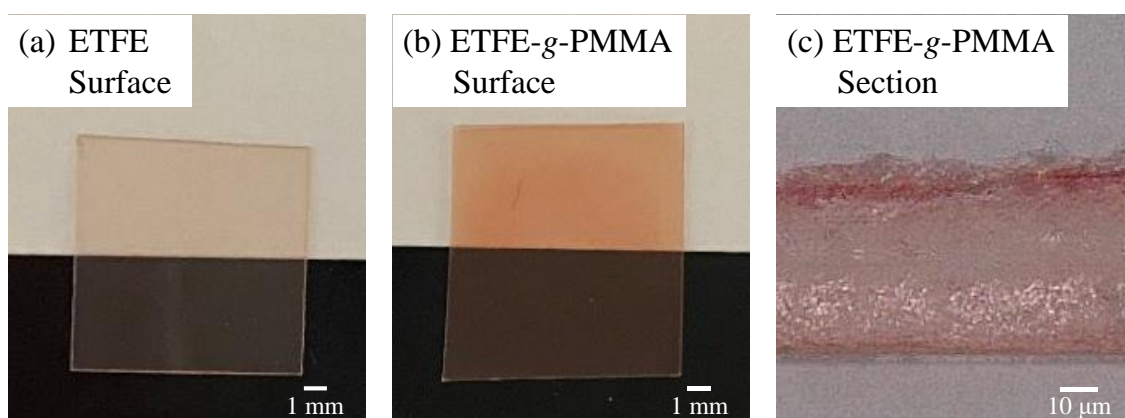


Fig. IV-7 Visual appearances of PVDF (a) and PVDF-*g*-PMMA (b) films, and cross-section of PVDF-*g*-PMMA (c, grafted yield 18%) film after staining with PMMA.

To confirm whether graft polymerization proceeded solely on the surface of the PVDF film or not, the PVDF-*g*-PMMA film was stained with SDN (Fig. IV-7). While

the untreated PVDF film appeared slightly dyed, the surface of the PVDF-g-PMMA film was stained deeply with SDN, but its bulk interior did not show the deep coloration. These results suggest that the formation of polar PMMA accessories changed the properties of the PVDF film surface.

The grafting with PMMA is considered to bring about new property on the PVDF surface. It was evaluated by measuring the contact angle between a water droplet and the surface of the film (Fig. IV-8). The contact angle between the water and the pristine PVDF film was 84.4° , which was almost same value in several report [2]. The PVDF film was hydrophobic because of the non-polar ($\text{CH}_2\text{-CF}_2$) units of the polymer framework. In contrast, the contact angle of the grafted PVDF film with PMMA decreased to 71.3° , indicating increased hydrophilicity which is caused by the polar ester functionalities. These results revealed that different properties could be introduced on the PVDF film surface using the TBB-initiated graft polymerization of MMA.

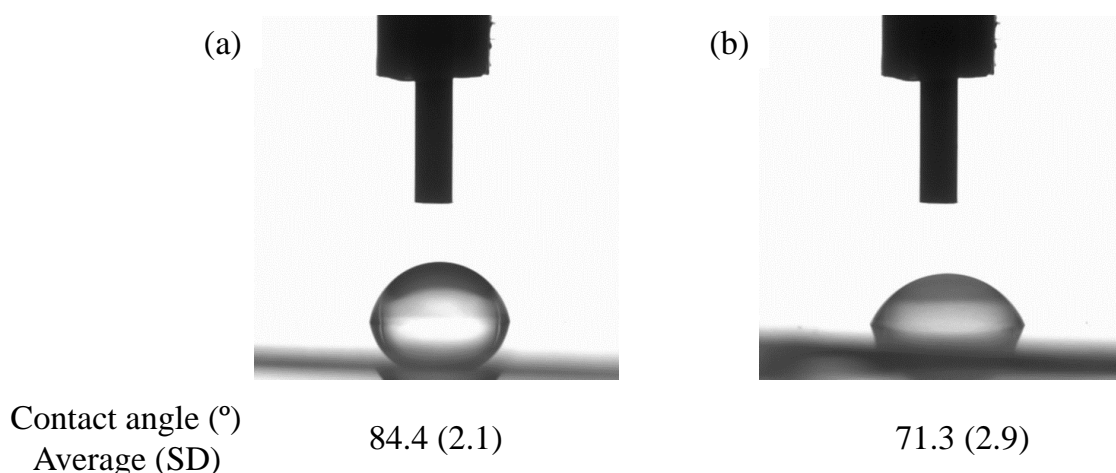


Fig. IV-8 Contact angles between water and the PVDF film (a) before and (b) after polymerization with MMA and TBB at 50°C for 24 h.

Since it was confirmed that graft polymerization on the PVDF surface was possible, additional experiments were performed to increase the reaction efficiency. The conversion was influenced by the reaction temperature as shown in Fig. IV-7. Although the conversion of MMA reached up to 77% when the reaction was conducted at 100 °C, the maximum graft yield (41%, 3.85 mg/cm²) was achieved when the reaction was conducted at 75 °C. At higher temperature, the larger amounts of free radicals were generated, which facilitates the solution polymerization in toluene competitively. Hence, the efficiency of the graft polymerization on the PVDF film was consequently suppressed. Similar phenomena were reported when grafting styrene to random ethylene-propylene diene monomer [24], MMA to polyethersulfone [25], and acrylic acid to polyamide fibers [26]. Therefore, the reaction temperature was determined as a crucial parameter to control the radical concentration. The maximum graft yield (3.85 mg/cm²) was higher than that (approximately 0.7 mg/cm²) achieved when AIBN was employed as an initiator.

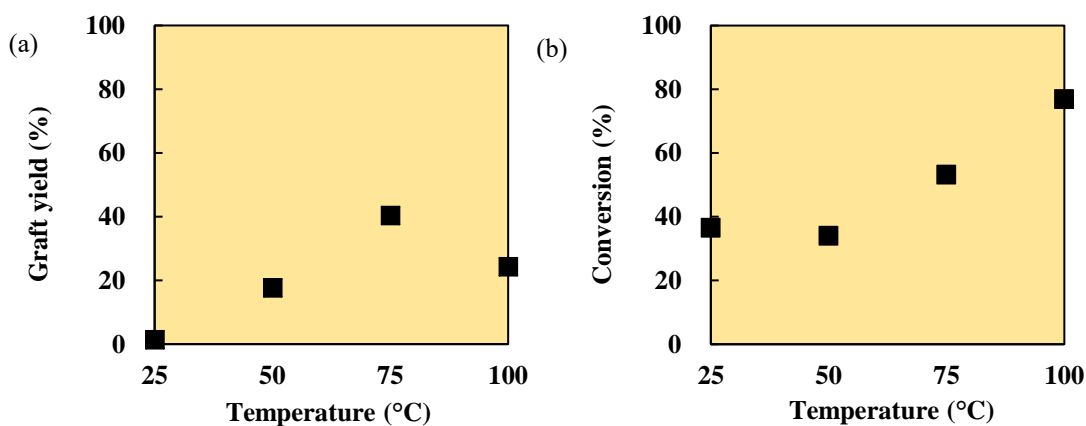


Fig. IV-9 (a) Graft yield versus temperature plots for PVDF-*g*-PMMA films and (b) conversion versus temperature plots for the solution polymerization of MMA in toluene with the PVDF film for 24 h, in the presence of TBB (1 mol% of MMA).

The concentration of TBB also affected the graft yield (Fig. IV-8). While the conversion percentages were not so different (29–36%), the graft yield was found to depend on the concentration of TBB. When 0.5 mol% of TBB was used, the highest graft yield was obtained (36%); however, the yield decreased as the concentration increased, which is presumably due to competitive side reactions such as the polymerization of MMA in the solution. Thus, the concentration of TBB as well as the reaction temperature are an important factor in the graft polymerization of PVDF-*g*-PMMA.

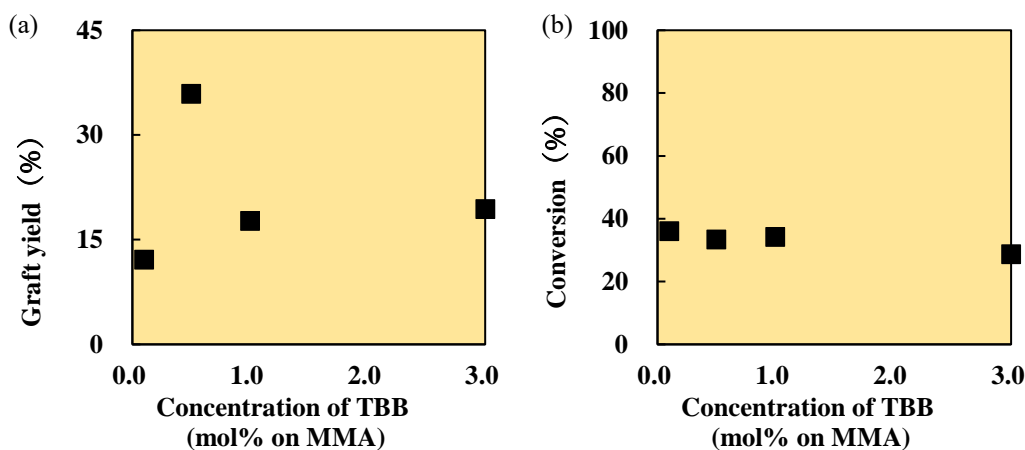


Fig. IV-10 (a) Graft yield versus concentration of TBB plots for PVDF-*g*-PMMA films, and (b) conversion versus concentration of TBB plots for the solution polymerization of MMA in toluene with the PVDF film at 50 °C for 24 h.

Conclusions

Modification of PVDF films was successfully achieved through the graft polymerization of MMA using TBB as an initiator. The graft yield of PVDF-*g*-PMMA depends on the temperature and concentration of TBB. The maximum graft yield was 41% (3.85 mg/cm²), and the reaction efficiency was higher than that of reaction using AIBN as the initiator. FT-IR measurements and cross-section observations revealed that only the surface of the PVDF film was modified by MMA. Furthermore, the change in the water contact angle after modification revealed that the hydrophilicity of the PVDF film was increased by graft polymerization.

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Chapter V. Conclusion

In the present study, modification of fluorocarbon polymers by radical graft polymerization was demonstrated. The results were summarized as follows.

In **Chapter II.**, ETFE surface was successfully modified by simple graft polymerization using Phen-DEZ. Stain experiments showed that graft polymerization occurred only at the ETFE surface and not in the interior of the film. Graft polymerization was found to proceed more rapidly as the monomer concentration was increased. Moreover, introduction of PMMA groups on the surface improved hydrophilicity of ETFE.

In **Chapter III.**, ETFE surface was also modified by simple graft polymerization using BPO that is widely used in plastic industry and dental medical devices. The surface roughness of ETFE film increased from 10.6 nm to 50.2 nm by the graft polymerization, and the visual appearance changed. FT-IR spectroscopy and cross-sectional micrographs revealed that only surface of the ETFE film was modified by MMA. Furthermore, the water contact angle on ETFE-*g*-PMMA (80.9°) was lower than that on pure ETFE film (94.2°). This result revealed that the hydrophilicity of the ETFE film increased by graft polymerization.

In **Chapter IV.**, highly grafted yield of PVDF-*g*-PMMA films were achieved by graft polymerization using TBB. The graft yield of PVDF-*g*-PMMA depends on the temperature and concentration of TBB. The maximum graft yield obtained was 41% (3.85 mg/cm²), and the reaction proceeded more efficiently than reactions when AIBN was used as an initiator.

Results and insights obtained here furnish useful information to researchers investigating fluorocarbon polymers. Modification of the surface provides different property, which facilitates a new application of fluorocarbon polymers in our usual life.

A List of Publications

- 1) Surface Functionalization of Ethylene–Tetrafluoroethylene Copolymer Film with Poly(Methyl Methacrylate) via Chemical Radical Polymerization
Yusuke Mizuta, Hiromu Okada, Chao Zhao, Ryuichi Sugimoto, Nagatoshi Nishiwaki, Kazuya Kobiro
Polymer **2021**, 226, 123826 (6 pages). (Q1)

- 2) Graft polymerization of Methyl Methacrylate on the Surface of Poly(Ethylene–*co*-Tetrafluoroethylene) Using Benzoyl Peroxide as Initiator
Yusuke Mizuta, Hiromu Okada, Chao Zhao, Ryuichi Sugimoto, Nagatoshi Nishiwaki, Kazuya Kobiro
Journal of Applied Polymer Science **2022**, 139, e52415 (8 pages). (Q1)

- 3) Graft Polymerization of Methyl Methacrylate on the Surface of Poly(vinylidene fluoride) Using Tributylborane as an Initiator
Yusuke Mizuta, Ryuichi Sugimoto, Kazuya Kobiro, Nagatoshi Nishiwaki
Polymer Bulletin Under Review. (Q2)