

# Surface Modification of Nanoparticles by Grafting of Polymers

Masaaki Takamura

Doctor Program in Advance Materials Science and  
Production Systems Engineering  
Graduate School of Science and Technology  
Niigata University

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## **Chapter 1**

### **GENERAL INTRODUCTION**

## 1.1 Nanoparticles and carbon blacks as industrial materials

Inorganic nanoparticles such as silica and titanium oxide are widely used industrially as fillers and pigments for polymer materials. Inorganic nanoparticles have excellent properties such as heat, chemical and weather resistance, lightweight, and low thermal expansion. For example, the mechanical properties of polymer materials are known to be remarkably improved by the addition of these nanoparticles [1-3].

On the other hand, carbon black is one of carbonaceous materials, such as graphite, carbon fibers, and carbon nanotube. Carbon black has excellent properties, such as heat, chemical and weather resistance, light weight, electro conductivity, and low thermal expansion [3,4]. It is widely used industrially as a conductive and deep black filler of polymer composites. In addition, it is well known that carbon materials have environmental compatibility.

In addition, carbon nanotube (CNT) is new class of carbon fiber with a diameter of nm orders and length of  $\mu\text{m}$  orders, and has various shapes [5,6]. For example, multi-walled CNT (MWCNT) has the structure in which the tube of many layers is laminating. Single-walled CNT (SWCNT) has the structure in which the tube of a layer is laminating. Cup-stacked CNT (CSCNT) is not cylindrical, but is more like stacked truncated conic sections. CNT has excellent properties, such as mechanical, chemical, electrical, and structural properties, with that CNT is of considerable interest for applications to fabricating new engineering materials.

$\text{C}_{60}$  fullerene has a variety of interesting properties, such as the ability to accept and release electrons [7], free-radical trapping [8], physiological activity [9], photoactivity [10], biocompatibility, and relatively high chemical reactivity allowing structural modification [11]. The features of  $\text{C}_{60}$  fullerene have aroused the hope of a successful use in many kinds of fields, such as biological and polymeric material, *etc.* Namely,  $\text{C}_{60}$  fullerene becomes to

be one of available materials both industrially and commercially.

Graphene, a single layer of carbon atoms in a hexagonal lattice, has recently attracted much attention due to its novel electronic and mechanical properties. Graphene is usually prepared by the reduction of its precursor graphene oxide, a typical pseudo-two-dimensional oxygen-containing solid in bulk form, possesses functional groups including hydroxyls, epoxides, and carboxyls [12-16]. Both graphene and graphene oxide papers show very high mechanical properties with good biocompatibility, and they have potential application as biomaterials.

## **1.2 Why surface grafting of polymers onto nanoparticles and nanocarbons is required ?**

However, dispersing nanoparticles, such as silica nanoparticle and carbon black, uniformly into a polymer or organic solvents is very difficult because of aggregation of these particles. In addition, the mechanical properties of composite are considered to be depend on not only the mechanical properties of the polymer matrix, but also on the properties of interfacial regions between surface of nanoparticles and matrix polymer [17].

Recently, the surface modification and the application of surface modified on inorganic particles have become of major interest [1-3]. The surface modification is very important to design the functional materials with high quality.

The chemical and physical modifications of silica nanoparticle and carbon black surface, therefore, have been extensively studied. The chemical modification of surface is permanent, but physical modification is temporary. Tsubokawa and his coworkers have pointed out that the dispersibility of silica nanoparticles and carbon black is extremely improved by surface grafting of polymers, namely, chemical binding of polymers, onto silica nanoparticle and carbon black surfaces [1-3].

In addition, grafting of polymers onto these surface interests us for designing new functional organic-inorganic hybrid materials which have the excellent properties both of nanoparticles as mentioned above and of grafted polymers, such as photosensitivity, curing ability, bioactivity, and pharmacological activity [18-21].

The grafting of polymers onto silica nanoparticle and carbon black by the reaction of functional groups on these surfaces with polymers having functional groups, such as hydroxyl and amino groups. For example, Tsubokawa et al have reported that surface reactive groups, such as isocyanate, acyl chloride, epoxide and acid anhydride, previously introduced onto the carbon black surface, readily react with hydroxyl- and amino-terminated polymers to give the corresponding polymer-grafted carbon black [22]. Lin et al. have reported the grafting of poly(ethylene glycol) onto carbon black surfaces having carboxyl groups by a simple impregnation method [23].

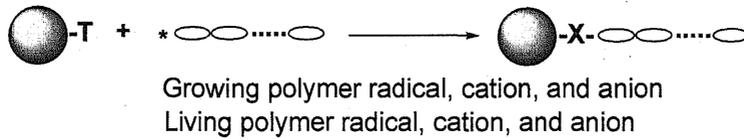
### **1.3 Methodology of surface grafting of polymers onto nanoparticles and nanocarbons**

Several methodologies of the surface grafting of polymers onto nanoparticles have been developed for the preparation of various kind of graft copolymers. These methodologies can be applied to the preparation of polymer-grafted nanoparticles. In general, one of the following principles may be applied to prepare polymer-grafted nanoparticles (Figure 1-1) [1-3].

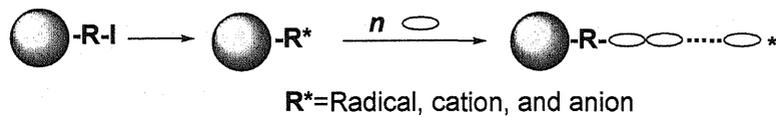
- (1) Grafting onto process: the terminated of growing polymer radical, cation, and anion, formed during the polymerization of various monomers initiated by conventional initiator in the presence of nanoparticles and the deactivation of living polymer radical, cation, and anion with functional groups on nanoparticle surface.

- (2) Grafting from process: the initiation of graft polymerization of various monomers from radical, cationic and anionic initiating groups previously introduced onto nanoparticle surface.
- (3) Polymer reaction process: the reaction of surface functional groups on nanoparticles with polymers having functional groups, such as hydroxyl, carboxyl, and amino groups.
- (4) Stepwise growth process: the polymer chains are grown from surface functional groups on nanoparticles by repeated reaction of low molecular compounds by dendrimer synthesis methodology.

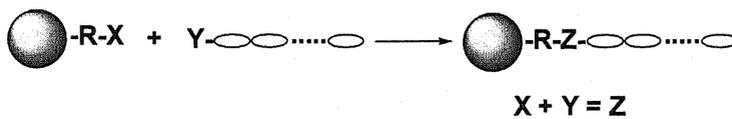
(1) "Grafting onto" process



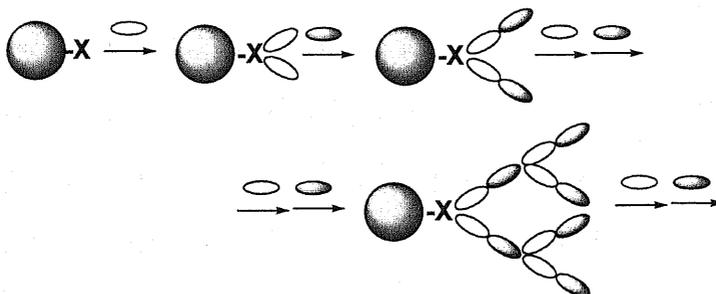
(2) "Grafting from" process



(3) "Polymer reaction" process



(4) "Stepwise growth" process



**Figure 1-1 Methodology of surface grafting of polymers onto silica nanoparticle and carbon black**

Process (1), although polymer-grafted nanoparticles can be obtained, the percentage of grafting onto nanoparticles is less than 10%, because of the preferential formation of ungrafted polymers. On the contrary, by the termination of living polymer, polymers with well-defined molecular weight and narrow molecular weight distribution can be grafted onto nanoparticle surface.

Process (2) is one the most favorable for the preparation of polymer-grafted nanoparticles with a high percentage of grafting. The molecular weight and number of grafted polymer chains can be controlled by use of surface initiated living polymerization.

An important characteristic of process (3) is that not only the molecular weight and the number of grafted chains on nanoparticle surface were easily controlled, but also commercially available polymers having a well defined structure can be grafted. But the number of grafted polymer chains on nanoparticle surface decreases with increasing molecular weight of polymer, because steric hindrance.

In addition, by process (4), although dendron with theoretical structure was not easily grafted, hyperbranched polymers having a large number of terminal functional groups can be grafted onto nanoparticle surface.

### **1.3.1 Grafting from process**

The initiation of the graft polymerization from initiating groups introduced onto nanoparticle surface. This process is the one most favorable for the preparation of polymer-grafted nanoparticle with a high percentage of grafting. It is difficult, however, to control the molecular weight and number of grafted polymer chains.

On the other hand, the grafting of polymers with well defined molecular weight onto particle surfaces with high graft density has been achieved by surface-initiated living radical polymerization. It can be obtained "polymer brushes" on glass plate and polymer surface by

surface-initiated living radical polymerization [24-26].

For example, the grafting of polymers with well defined polymer onto carbon black with high graft density was achieved by atom transfer radical polymerization of butyl acrylate from  $\alpha$ -bromo ester functionalized carbon black surface in the presence of  $\text{CuCl}_2$  [27]. In addition, living radical graft polymerization from nanoparticle surface by 2,2,6,6-tetramethylpiperidiny-1-oxyl/benzoyl peroxide system [28] or reversible addition-fragmentation chain transfer polymerization [29] were reported. Furthermore, grafting of vinyl polymer onto carbon nanotube surface by living radical polymerization were reported [30,31].

### **1.3.2 Grafting onto process**

The termination and chain transfer reaction of growing polymer radical (cation or anion) with functional groups on the surface which can deactivate the growing polymer chain. This process, polymer-grafted nanoparticle with a higher percentage of grafting cannot be obtained because of the preferential formation of ungrafted polymers.

It has been reported that the grafting of functional polymers having amino and hydroxyl groups onto carbon black surface by direct condensation with carboxyl groups on the surface successfully proceeded in the presence of *N,N*-dicyclohexylcarbodiimide as a catalyst [32]. However, *N,N'*-dicyclohexylurea, whose solubility in solvent is very small, was formed during the grafting reaction. Therefore, the isolation of polymer-grafted carbon black from the reaction mixture containing *N,N'*-dicyclohexylurea was hardly conducted.

### **1.4 Polymers used for the surface grafting onto nanoparticles in this work**

Surfaces modification of nanoparticles by grafting polymers in this work. The grafting

of polymers onto nanoparticles using rare-earth triflates as catalyst, and the grafting of biodegradable polymers onto nanoparticles were investigated to improve dispersibility of nanoparticles in organic solvent. In addition, the crosslinking of the liquid rubbers by silica nanoparticles having amino groups and carbon black using rare-earth triflate ( $\text{Sc}(\text{OTf})_3$ ) as catalyst was discussed.

#### **1.4.1 Liquid rubbers**

Liquid rubbers, when molding is processed, a lot of processes are not needed. They are oligomers having terminal amino group, hydroxyl group, carboxyl group, isocyanate group, thiol group, and halogen group, such as polybutadiene rubber (BR), styrene-butadiene rubber (SBR), nitrile rubber (NBR), polyurethane rubber, silicone rubbers, and polysulfide rubbers [33-35].

Liquid rubbers are a kind of rubber. It is well known that liquid rubbers are crosslinked with organic peroxide, metallic oxide, organic amine compound. Liquid rubbers were prepared by the depolymerization of the corresponding crude rubbers, and by the living anionic polymerization. Recently, liquid rubbers widely used industrially such as a paint, a coating agent, an adhesion bond, and a resinic modifier [36,37].

#### **1.4.2 Biodegradable polymers**

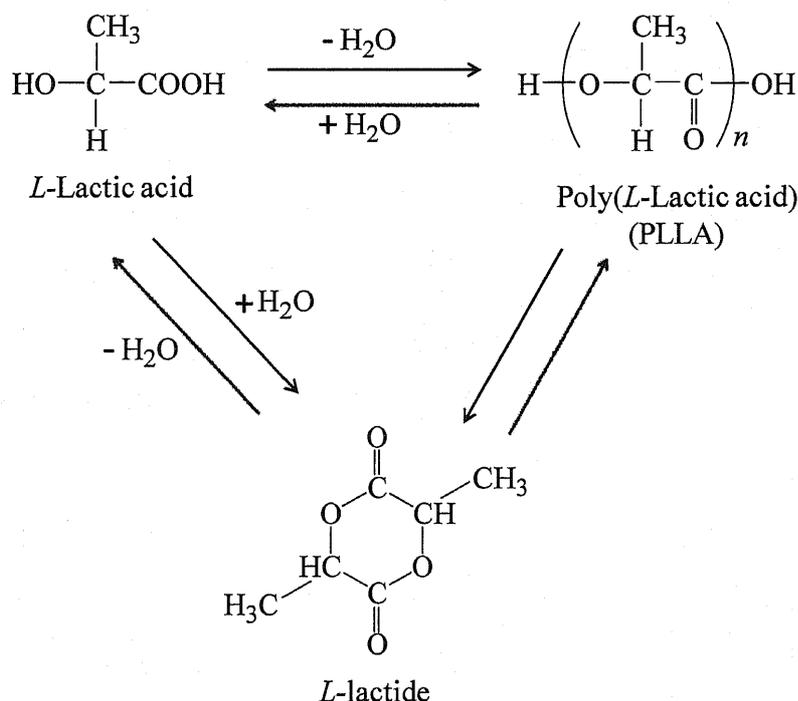
Recently, environmental problems attract attention. This problem is what should be paid attention for the field of the chemistry. Therefore, a lot of environment-friendly is researched in the field of the chemistry today [38-40].

For example, biodegradable polymers have noticed as environmentally friendly

materials. Poly(*L*-lactic acid) [poly(*L*-lactide), PLLA], a well-known bioabsorbable and biodegradable material, is an attractive raw material produced from renewable resources such as corn [41], potato, and garbage. Because of the advantage of having a carbon neutral, the use of PLLA in industrial fields has been rapidly increasing in the form of molded parts for personal computers [42,43], mobile phones [44], and automobiles [45].

It is also anticipated to have many other future applications where environmentally compatible materials are required, such as in mulching film and nursery boxes. However, PLLA needs a large amount of energy to be produced from the renewable resources and has poor biodegradability in certain environments [46]. Thus, other strategies for the effective use of PLLA are required.

PLLA is generally prepared by the ring-opening polymerization of *L,L*-lactide as a cyclic monomer [47-49], and during its thermal degradation *L,L*-lactide is recovered as a result of the depolymerization of PLLA (Scheme 1-1) [50].



**Scheme 1-1 Synthetic reaction and decomposition reaction of PLLA**

In addition, the grafting of PLLA onto nanomaterial surfaces has been reported [51-61]. For example, Feng et al. have reported the grafting of PLLA onto the surface of magnetic multi-walled carbon nanotubes (m-MWCNTs) by in-situ ring-opening polymerization of lactide [58]. It has been reported by Luo et al. that the surface of TiO<sub>2</sub> was successfully grafted with PLLA layer by in situ melt polycondensation of *L*-lactic acid (LLA) [59]. Moreover, Kim et al. have reported the incorporation of a small amount of PLLA-grafted MWCNTs improved the thermal and electrical properties of PLLA composites [60]. Yan et al. have pointed out that PLLA oligomer was directly grafted onto the surface silanol groups of silica nanoparticles by condensation of LLA without any catalyst [61].

### **1.5 A novel catalyst used in this work**

The grafting of polymers onto silica nanoparticle and carbon black by the reaction of functional groups on these surfaces with polymers having functional groups, such as hydroxyl and amino groups. For example, we have reported that surface reactive groups, such as isocyanate, acyl chloride, epoxide and acid anhydride, previously introduced onto carbon black surface, readily react with hydroxyl- and amino-terminated polymers to give the corresponding polymer-grafted carbon black [22]. Lin et al. have reported the grafting of poly(ethylene glycol) onto carbon black surfaces having carboxyl groups by a simple impregnation method [62].

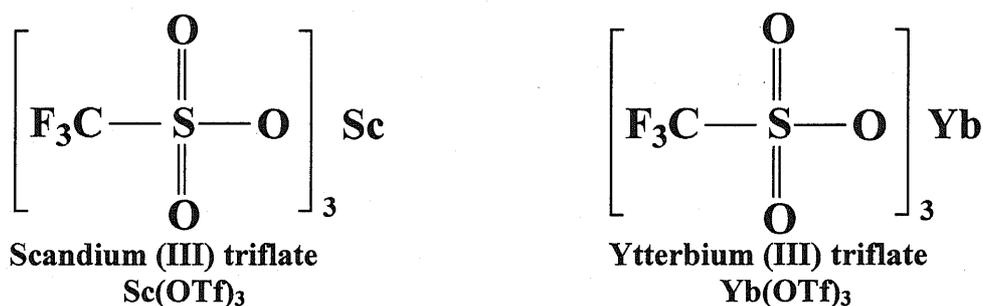
The grafting of polymers onto colloidal silica surface by the reaction of silanol groups on the surface with polymers having terminal alkoxyethyl groups have been reported by Yoshinaga et al [63].

In addition, the grafting of polymers onto the surface was achieved by the direct condensation reaction of surface carboxyl groups on carbon black with hydroxyl groups of poly(ethylene glycol) in the presence of a catalyst, such as *N, N'*-dicyclohexylcarbodiimide

as mentioned above [32].

Recently, in the catalyst, rare-earth triflates are very interested for the following reasons (Scheme 1-2):

- (1) they are insensitive to protic compounds, and it is well-known that rare-earth triflates catalyze some reactions even in water because of the high exchange constant with water and low hydrolysis constant,
- (2) one advantage of the catalyst is that the catalyst can be quantitatively recovered after the reactions are completed and reused, which are suitable for the molecular design in "Green Polymer Chemistry".



**Scheme 1-2 Structure of rare-earth triflates**

Therefore, it was reported that scandium (III) triflate ( $\text{Sc}(\text{OTf})_3$ ) catalyzed the reaction of alcohols with carboxylic anhydride and activated esters at low temperature [64-66]. It was also found that  $\text{Sc}(\text{OTf})_3$  catalyzed direct esterification of aliphatic alcohol with carboxylic acid at room temperature [67].

## 1.6 Objectives of this work

In this thesis, the surface modification nanoparticles, such as silica and carbon black, by the surface grafting of several polymers such as poly(ethylene glycol) and PLLA, onto the

nanoparticles by using an environment-friendly catalyst was investigated.

As mentioned above, it has been reported that the grafting of functional polymers having amino and hydroxyl groups onto carbon black surface by direct condensation with carboxyl groups on the surface successfully proceeded in the presence of *N,N*-dicyclohexylcarbodiimide as a catalyst [27]. However, *N,N'*-dicyclohexylurea, whose solubility in solvent is very small, was formed during the grafting reaction. Therefore, the isolation of polymer-grafted carbon black from the reaction mixture containing *N,N'*-dicyclohexylurea was hardly conducted.

On the contrary, it is expected that by use of rare-earth triflates as catalysts for the grafting reaction, polymer-grafted carbon black nanoparticle can be easily separated from the reaction mixture, because by-product is water and rare-earth triflate are readily soluble in various solvents. Therefore, the grafting of poly(ethylene glycol) with carbon black using rare-earth triflates as catalyst by grafting onto process was investigated in **Chapter 2**.

Based on the results of Chapter 2, the grafting and crosslinking reaction of carboxyl-terminated liquid rubbers with silica nanoparticle and carbon black using  $\text{Sc}(\text{OTf})_3$  as catalyst was investigated in **Chapter 3**.

Namely in this Chapter, the grafting reactions of carboxyl-terminated liquid rubbers, mainly polybutadiene and nitrile rubber, with amino groups on silica nanoparticles and phenolic hydroxyl groups on carbon black, were investigated using  $\text{Sc}(\text{OTf})_3$  as catalyst by grafting onto process. In addition, the crosslinking of the liquid rubbers by silica nanoparticles having amino groups and carbon black using  $\text{Sc}(\text{OTf})_3$  as catalyst was investigated.

In **Chapter 4**, in order to improve the dispersibility of carbon black and silica in organic solvents, the grafting of PLLA onto carbon black surface by polycondensation of LLA in the presence of carbon black using  $\text{Sc}(\text{OTf})_3$  as catalyst by grafting from and/or grafting onto process was investigated. In addition, the grafting of PLLA onto carbon black

surface by the reaction with PLLA using  $\text{Sc}(\text{OTf})_3$  as catalyst by grafting onto process was also investigated.

In **Chapter 5**, the grafting of PLLA onto silica surface by ring-opening polymerization of *L*-lactide in the presence of silica having amino groups using an amidine catalyst by grafting from process was investigated. The dispersibility of PLLA-grafted silica was also discussed.

Conclusions are presented in **Chapter 6**.

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## **Chapter 2**

**Grafting reaction of poly(ethylene glycol) with carbon black using  
rare-earth triflates as catalyst**

## SUMMARY

In the presence of scandium (III) triflate ( $\text{Sc}(\text{OTf})_3$ ) and ytterbium (III) triflate ( $\text{Yb}(\text{OTf})_3$ ) as catalysts, the grafting of poly(ethylene glycol) (PEG), with carboxyl groups on carbon black (CB) surfaces was investigated. In the absence of the catalyst, the grafting of the PEG onto CB hardly proceeded. On the contrary, hydroxyl groups of the PEG readily reacted with carboxyl groups on CB in the presence of  $\text{Sc}(\text{OTf})_3$  or  $\text{Yb}(\text{OTf})_3$  to give PEG-grafted CB even at room temperature. The percentage of PEG grafting onto CB in the presence of  $\text{Sc}(\text{OTf})_3$  and  $\text{Yb}(\text{OTf})_3$  increased with increasing reaction time and reached 42.1 % and 26.3 %, respectively. The effects of reaction conditions on the grafting reaction onto CB were discussed. After the grafting reaction,  $\text{Sc}(\text{OTf})_3$  was easily recovered and the recovered  $\text{Sc}(\text{OTf})_3$  could be reused for the grafting of the PEG onto CB. PEG-grafted CB gave dispersions in methanol. The result suggests that the aggregation of CB particles was considerably destroyed and prevented by surface grafting of PEG onto surface.

## 2.1 INTRODUCTION

Surface functional groups on silica nanoparticles, silicagels, and carbon black (CB) undergo conventional organic reactions, such as esterification and amidation [1–5]. In addition, surface functional groups can be used as grafting sites for various polymers [6–9]. For example, Tsubokawa and his coworkers have reported the grafting of various polymers onto these surfaces by the radical [10,11], anionic [12], and cationic polymerization [13] initiated by azo and peroxyester, potassium carboxylate, and acylium perchlorate groups, respectively, previously introduced onto these surfaces. Recently, the preparation of polymer brushes was successfully achieved by the surface initiated living radical and living anionic polymerization [14,15].

On the other hand, the grafting of polymers onto silica nanoparticles and CB by the reaction of functional groups on these surfaces with polymers having functional groups, such as hydroxyl and amino groups can be achieved. For example, Tsubokawa et al have reported that surface reactive groups, such as isocyanate, acyl chloride, epoxide and acid anhydride, previously introduced onto the CB surface, readily react with hydroxyl- and amino-terminated polymers to give the corresponding polymer grafted CB [16].

Lin et al. have reported the grafting of poly(ethylene glycol) (PEG) onto CB surfaces having carboxyl groups by a simple impregnation method [17]. The grafting of polymers onto colloidal silica surfaces by the reaction of silanol groups on the surface with polymers having terminal alkoxysilyl groups have been reported by Yoshinaga [18].

In addition, the grafting of polymers onto the surface was achieved by the direct condensation reaction of surface carboxyl groups on CB with hydroxyl groups of PEG in the presence of a catalyst, such as *N,N*-dicyclohexylcarbodiimide (DCC) [19]. However, *N,N*-dicyclohexylurea (DCU), whose solubility in solvent is very small, was formed during the grafting reaction. Therefore, the isolation of polymer-grafted CB from the reaction

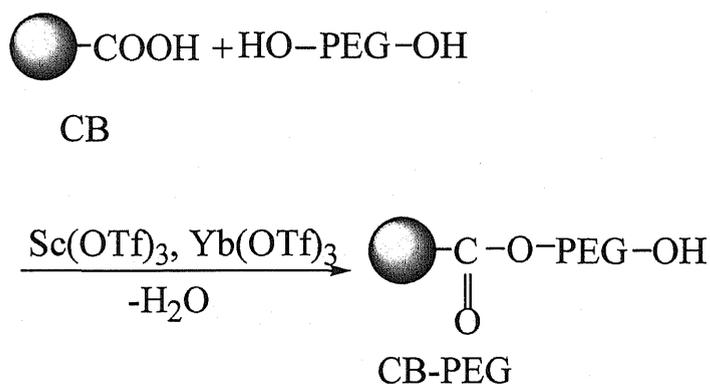
mixture containing DCU was hardly conducted.

An important characteristic of the grafting by use of polymer reactions is that not only are the molecular weight and the number of grafted chains on the surface easily controlled, but also commercially available polymers having a well-defined structure can be grafted onto the surface [6–9].

On the other hand, it was reported that rare-earth triflates catalyzed the reaction of alcohols with carboxylic anhydride and activated esters at low temperature [20–22]. It was also found that  $\text{Sc}(\text{OTf})_3$  catalyzed direct esterification of aliphatic alcohols with carboxylic acid at room temperature [23].

It is expected that polymer-grafted CB can be easily separated from the reaction mixture, because by-product is water and rare-earth triflates are readily soluble in various solvents.

Therefore, in this Chapter, the grafting reactions of PEG with carboxyl groups on CB by grafting onto process (Scheme 2-1) was investigated by use of rare-earth triflates as catalyst.



**Scheme 2-1 Grafting of PEG onto CB surface using rare-earth triflates as catalyst**

## 2.2 EXPERIMENTAL

### 2.2.1 Materials and reagents

The carbon black (CB) used was channel black FW200 obtained from Degussa AG. The properties of the CB are shown in Table 2-1. The CB was dried *in vacuo* for 48 h before use.

Scandium (III) triflate ( $\text{Sc}(\text{OTf})_3$ ) and ytterbium (III) triflate ( $\text{Yb}(\text{OTf})_3$ ) obtained from Aldrich Chemical Co. Inc. was used without further purification. Poly(ethylene glycol) (PEG) obtained from Aldrich Chemical Co. Inc. was used without further purification.

**Table 2-1 Properties of carbon black**

Sample	Specific surface area ( $\text{m}^2/\text{g}$ )	Particle size (nm)	-OH (mmol/g)	-COOH (mmol/g)
FW200	460	13	0.10	0.61

### 2.2.2 Grafting of poly(ethylene glycol) onto carbon black surface using rare-earth triflates as catalyst

Into a polymerization tube, 0.30 g of CB, 0.15 mmol of PEG, 2.0 mmol of  $\text{Sc}(\text{OTf})_3$  ( $\text{Yb}(\text{OTf})_3$ ) and 15.0 mL of toluene were charged. The mixture was stirred with a magnetic stirrer under nitrogen gas. In order to isolate the resulting CB from the reaction mixture, after the reaction, the product was dispersed in methanol and the dispersion was centrifuged at  $1.5 \times 10^4$  rpm. The methanol precipitated was dispersed in methanol again and the dispersion was centrifuged. These procedures were repeated until no more PEG could be detected in the supernatant solution. The treated CB was dried *in vacuo* at room temperature. The PEG-grafted CB was abbreviated as CB-PEG.

### **2.2.3 Determination of grafting**

The percentage of PEG grafting onto the CB was determined by the following equation:

$$\text{Grafting (\%)} = (A / B) \times 100$$

where A is the weight of PEG grafted (g) and B is the weight of the CB charged (g). The weight of PEG grafted onto the CB surface was determined by the weight loss when PEG-grafted CB was heated at 500 °C by the use of a thermogravimetric analyzer (TGA) (Shimadzu TGA-50).

### **2.2.4 Characterization of poly(ethylene glycol)-grafted carbon black**

Infrared spectra were recorded on a FT-IR spectrophotometer (Shimadzu Manufacturing Co., Ltd. FTIR-8400S).

### **2.2.5 Dispersibility of CB-PEG in solvent**

CB-PEG (1.0 mg) was dispersed in 5.0 mL of methanol under ultrasonic wave irradiation for 10 min and allowed to stand at room temperature.

## 2.3 RESULTS AND DISCUSSION

### 2.3.1 Grafting reaction of poly(ethylene glycol) onto carbon black surface using rare-earth triflates as catalyst

It has been reported that the grafting of functional polymers having amino and hydroxyl groups onto CB surface by direct condensation with carboxyl groups on the surface successfully proceeded in the presence of *N,N*-dicyclohexylcarbodiimide (DCC) as a catalyst [18]. However, *N,N*-dicyclohexylurea (DCU), whose solubility in solvent is very small, was formed during the grafting reaction. Therefore, the isolation of polymer-grafted CB from the reaction mixture containing DCU was hardly conducted as mentioned above.

On the contrary, it is expected that by use of rare-earth triflates as catalyst for the grafting reaction, the polymer-grafted CB can be easily separated from the reaction mixture, because the by-product is water and rare-earth triflates, which is readily soluble in various solvents. Therefore, the grafting reaction of PEG onto CB using rare-earth triflates as catalyst by grafting onto process was investigated.

Figure 2-1 shows the relationship between reaction time and the percentage of grafting onto the CB surface in the presence of rare-earth triflates. The percentage of grafting increased with the progress of the reaction and scarcely increased after 5 h. The percentage of PEG grafting onto CB in the presence of  $\text{Sc}(\text{OTf})_3$  and  $\text{Yb}(\text{OTf})_3$  increased with increasing reaction time and reached 42.1 % and 26.3 %, respectively.

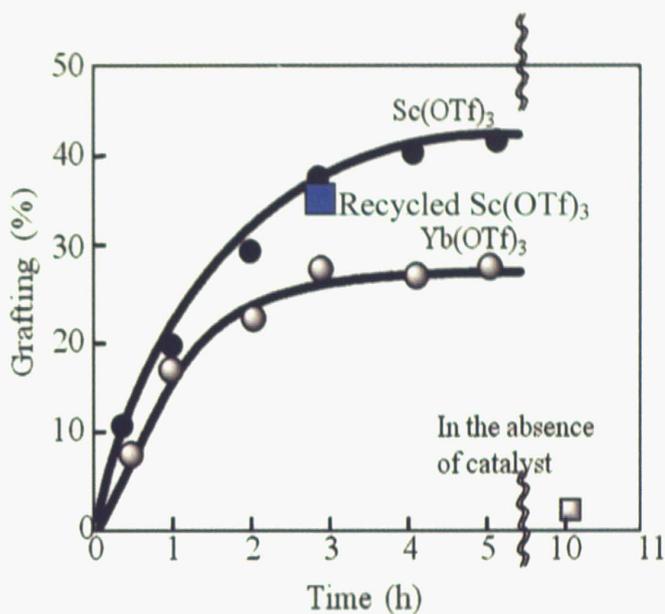
In the absence of rare-earth triflates, the grafting reaction of PEG onto CB was not proceeded.

Therefore, it became apparent that rare-earth triflates act as effective catalysts of the grafting of PEG onto CB surface.

In addition, after the grafting reaction,  $\text{Sc}(\text{OTf})_3$  was readily recovered from the

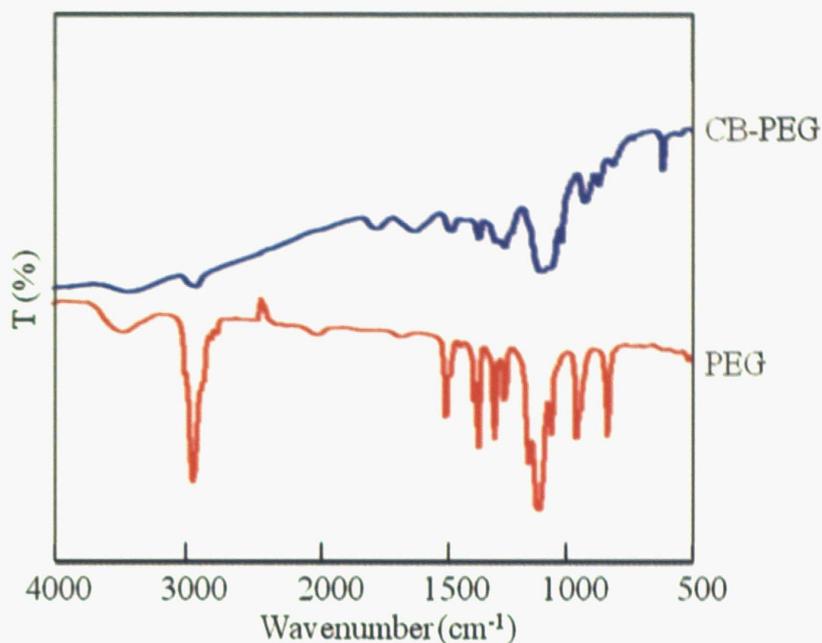
reaction mixture and reused for the grafting reaction: the decrease of percentage of grafting in the presence of reused  $\text{Sc}(\text{OTf})_3$  was scarcely observed as shown in Figure 2-1.

Therefore, it was found that the recovered  $\text{Sc}(\text{OTf})_3$  can be used for the grafting reaction of PEG onto CB.



**Figure 2-1 Grafting of PEG onto CB using rare-earth triflates as catalyst**  
CB, 0.30 g; PEG2000, 0.15 mmol; catalyst, 2.0 mmol; toluene, 15.0 mL; 27 °C.

The grafting of PEG onto CB surface was confirmed by ATR-FTIR. Figure 2-2 shows ATR-FTIR spectra of CB-PEG and PEG. It was found that ATR-FTIR spectra of CB-PEG show absorption characteristic of ether bonds of PEG at  $1100\text{ cm}^{-1}\sim 1250\text{ cm}^{-1}$ . The result shows the grafting of PEG onto CB surface.



**Figure 2-2 ATR-FTIR spectra of PEG and CB-PEG**

### 2.3.2 Effect of the amount of rare-earth triflates on the grafting onto carbon black

Table 2-2 shows the effect of the amount of  $\text{Sc}(\text{OTf})_3$  and  $\text{Yb}(\text{OTf})_3$  on the grafting of the PEG onto CB surface. The percentage of grafting increased with increasing the amount of  $\text{Sc}(\text{OTf})_3$  and  $\text{Yb}(\text{OTf})_3$ . But the percentage of grafting was no longer increased above 0.2 mmol of  $\text{Sc}(\text{OTf})_3$  and  $\text{Yb}(\text{OTf})_3$ .

The ratio of  $\text{Sc}(\text{OTf})_3$  and  $\text{Yb}(\text{OTf})_3$  to phenolic hydroxyl groups and carboxyl groups on CB was exceeded about 1.0 in both catalysts.

Therefore, the results suggest that CB surface was blocked by the grafted PEG chains.

**Table 2-2 Effect of the amount of rare-earth triflates on the grafting of PEG onto carbon black**

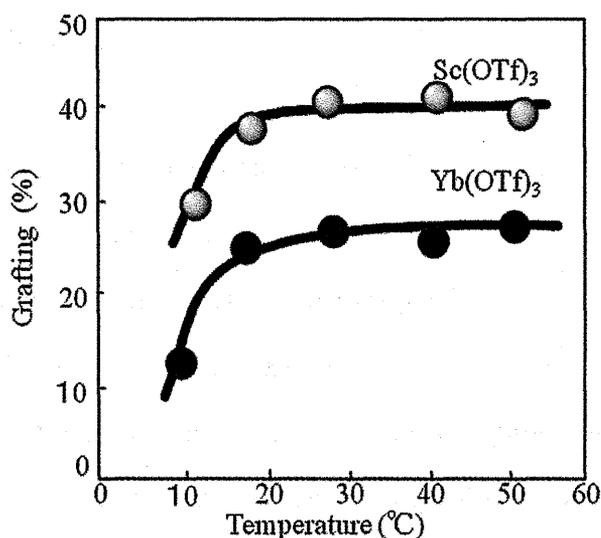
Sc(OTf) <sub>3</sub> (mmol)	Sc(OTf) <sub>3</sub> / -COOH (mol / mol)	Grafting (%)
0.10	0.6	10.2
0.20	1.1	42.9
0.30	1.7	39.7

Yb(OTf) <sub>3</sub> (mmol)	Yb(OTf) <sub>3</sub> / -COOH (mol / mol)	Grafting (%)
0.10	0.6	5.2
0.20	1.1	26.3
0.30	1.7	23.3

### 2.3.3 Effect of temperature on the grafting of poly(ethylene glycol) onto carbon black

Figure 2-3 shows the effect of temperature on the grafting of PEG onto CB in the presence of Sc(OTf)<sub>3</sub> and Yb(OTf)<sub>3</sub>. It became apparent that PEG grafting was scarcely affected by temperature above 27 °C, but decreased below 20 °C. Therefore, it was found that the grafting reaction can be achieved even at room temperature.



**Figure 2-3 Effect of temperature on the grafting of PEG onto CB**  
 CB, 0.30 g; PEG2000, 0.15 mmol; catalyst, 2.0 mmol; toluene, 15.0 mL;  
 24 h.

### 2.3.4 Effect of molecular weight on the grafting of poly(ethylene glycol) onto carbon black

Table 2-3 shows the effect of molecular weight on the grafting of PEG onto CB. As shown in Table 2-3, the percentage of grafting PEG decreased with increasing the molecular weight of PEG. And, the grafted chains on the surface decreased with increasing molecular weight of PEG. The result indicates that steric hindrance increased with increasing molecular weight of PEG.

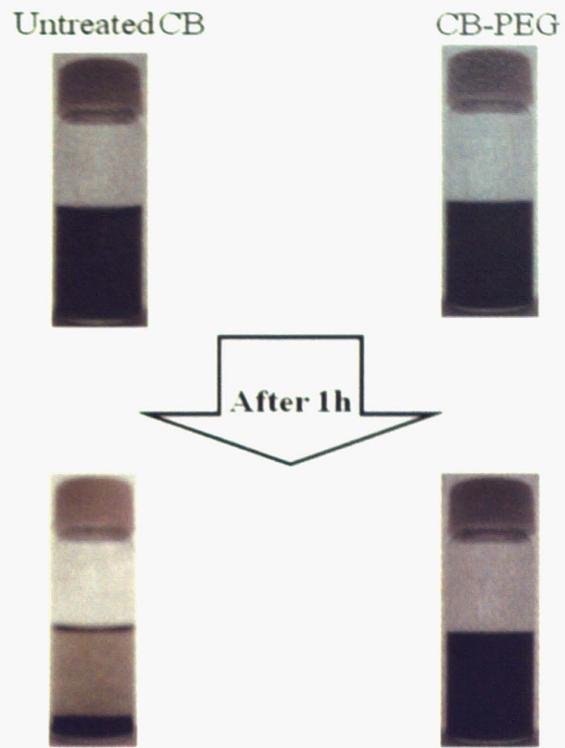
**Table 2-3 Effect of molecular weight on the grafting of PEG onto CB**

Molecular weight of PEG	Grafting (%)	Grafted chain (mmol/g)
2000	38.2	0.19
4000	29.5	0.074
6000	21.1	0.035
8000	14.4	0.018

CB, 0.30 g; PEG, 0.15 mmol; Sc(OTf)<sub>3</sub>, 2.0 mmol ; toluene, 15.0 mL;  
27 °C, 24 h.

### 2.3.5 Dispersibility of CB-PEG

The dispersibility of untreated CB and CB-PEG in methanol was investigated. Figure 2-4 shows images of the dispersibility of untreated CB and CB-PEG in methanol. Untreated CB was found to precipitate within 1 h. On the contrary, CB-PEG gave a stable dispersion in methanol after 1 h. It became apparent CB-PEG gave a stable dispersions in methanol, which is good solvent for PEG. The result suggests that the aggregation of CB particles was considerably destroyed and prevented by surface grafting of PEG onto surface.



**Figure 2-5 Dispersibility of CB-PEG in methanol**

## 2.4 CONCLUSIONS

1. The grafting of the PEG onto CB surface by grafting onto process was achieved by the reaction of hydroxyl groups of the polymer with carboxyl groups on CB using rare-earth triflates as catalyst even at room temperature.
2. It was found that the percentage of grafting decreased with increasing the molecular weight of PEG. And, the number of grafted PEG chains decreased with increasing the molecular weight of PEG.
3. After the reaction,  $\text{Sc}(\text{OTf})_3$  was readily recovered by reprecipitation and successive extraction with water. The recovered  $\text{Sc}(\text{OTf})_3$  was found to be reusable as the grafting catalyst.
4. CB-PEG gave stable dispersions in methanol. The result suggests that the aggregation of CB particles was considerably destroyed and prevented by surface grafting of PEG onto surface.

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## **Chapter 3**

**Grafting and crosslinking reaction of carboxyl-terminated liquid rubber  
with silica nanoparticle and carbon black using Sc(OTf)<sub>3</sub> as catalyst**

## SUMMARY

In the presence of scandium (III) triflate ( $\text{Sc}(\text{OTf})_3$ ) as a catalyst, the grafting of carboxyl-terminated liquid rubbers, polybutadiene (BR-COOH) and nitrile rubber (NBR-COOH), with amino groups on silica nanoparticle and phenolic hydroxyl groups on carbon black (CB) surfaces by grafting onto process was investigated. In the absence of the catalyst, the grafting of the liquid rubbers onto silica nanoparticle and CB hardly proceeded. On the contrary, terminal-carboxyl groups of the liquid rubbers readily reacted with amino groups on silica and phenolic hydroxyl groups on CB in the presence of  $\text{Sc}(\text{OTf})_3$  to give BR-grafted and NBR-grafted silica and CB even at room temperature. The percentage of NBR grafting onto silica and CB increased with increasing reaction time and reached 23.1 % and 66.9 %, respectively. The effects of reaction conditions on the grafting reaction onto silica nanoparticle and CB were discussed. After the grafting reaction,  $\text{Sc}(\text{OTf})_3$  was easily recovered and the recovered  $\text{Sc}(\text{OTf})_3$  could be reused in the grafting of the liquid rubbers onto silica and CB. In addition, when excess of silica nanoparticle and CB was reacted in the absence of solvent (in bulk), the crosslinking reactions of the liquid rubbers by silica nanoparticle and CB proceeded in the presence of  $\text{Sc}(\text{OTf})_3$  to give elastic products (brittle).

### 3.1 INTRODUCTION

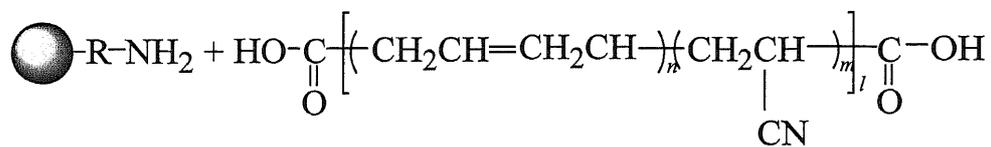
Liquid rubbers are oligomers having terminal amino group, hydroxyl group, carboxyl group, isocyanate group, thiol group, and halogen group, such as polybutadiene rubber (BR), styrene-butadiene rubber (SBR), nitrile rubber (NBR), polyurethane rubber, silicone rubbers, and polysulfide rubbers [1-3].

Liquid rubbers are a kind of rubber. It is well known that liquid rubbers are crosslinking with organic peroxide, metallic oxide, organic amine compound. Liquid rubbers were developed by the depolymerization of the corresponding crude rubber. Recently, liquid rubbers widely used industrially such as a paint, a coating agent, an adhesion bond, and a resinic modifier [4,5].

In Chapter 2, the grafting of the PEG onto CB surface by grafting onto process was achieved by the reaction of hydroxyl groups of the polymer with carboxyl groups on CB using rare-earth triflates as catalyst.

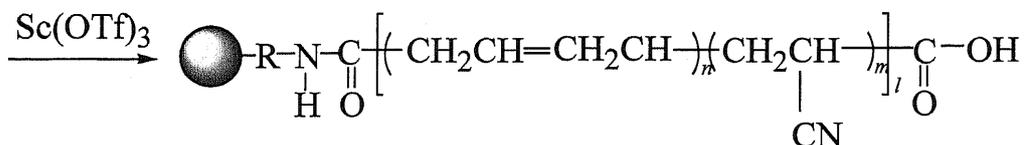
In this Chapter, the grafting reactions of carboxyl-terminated liquid rubbers, mainly polybutadiene (BR-COOH) and nitrile rubber (NBR-COOH), with amino groups on silica nanoparticles (Scheme 3-1) and phenolic hydroxyl groups on CB (Scheme 3-2), were investigated using  $\text{Sc}(\text{OTf})_3$  as catalyst.

In addition, the crosslinking of the liquid rubbers by silica nanoparticles having amino groups and CB using  $\text{Sc}(\text{OTf})_3$  as catalyst will be discussed (Scheme 3-3).

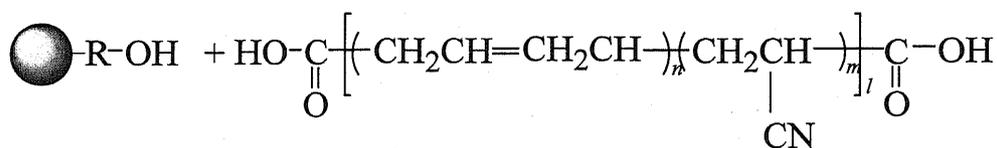


$m=0$ : BR-COOH

$m=0.1$ : NBR-COOH

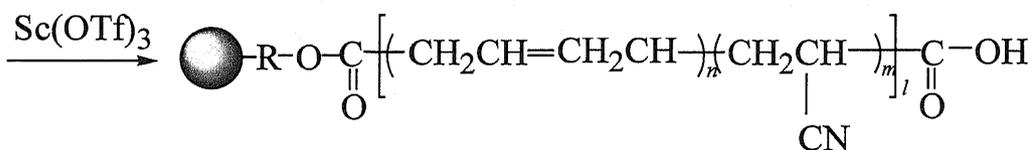


**Scheme 3-1 Grafting of liquid rubbers onto silica nanoparticle using Sc(OTf)<sub>3</sub> as catalyst**

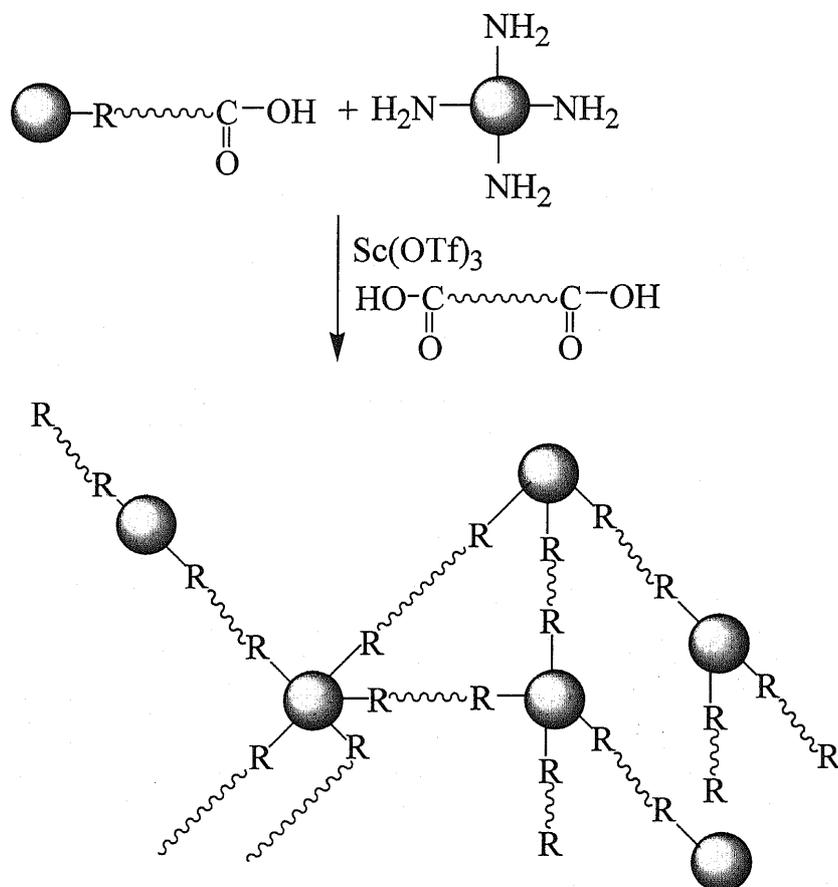


$m=0$ : BR-COOH

$m=0.1$ : NBR-COOH



**Scheme 3-2 Grafting of liquid rubbers onto CB surface using Sc(OTf)<sub>3</sub> as catalyst**



**Scheme 3-3 Crosslinking of liquid rubbers by silica and CB using Sc(OTf)<sub>3</sub> as catalyst**

## 3.2 EXPERIMENTAL

### 3.2.1 Materials and reagents

Silica nanoparticles having amino groups (Silica-NH<sub>2</sub>) were obtained from Nippon Aerosil Co., Ltd., Japan. The properties of Silica-NH<sub>2</sub> are shown in Table 3-1. The carbon black (CB) used was channel black FW200 obtained from Degussa AG as described in Chapter 2 (2.1). The properties of the Silica-NH<sub>2</sub> and CB are also shown in Table 3-1. The CB and Silica-NH<sub>2</sub> were dried *in vacuo* for 48 h before use.

**Table 3-1 Properties of silica and carbon black used**

	Specific surface area	Particle size	Functional group (mmol/g)		
	(m <sup>2</sup> / g)	(nm)	-OH	-COOH	-NH <sub>2</sub>
Silica-NH <sub>2</sub> <sup>a</sup>	200	12	-	-	0.30
Carbon Black <sup>b</sup>	460	13	0.10	0.61	-

<sup>a</sup>Nippon Aerosil Co. Ltd., Japan.

<sup>b</sup>Degussa AG.

Scandium (III) triflate (Sc(OTf)<sub>3</sub>) obtained from Aldrich Chemical Co. Inc. was used without further purification as described in Chapter 2 (2.1). Carboxyl-terminated liquid rubbers, BR-COOH and NBR-COOH (copolymer of polybutadiene with polyacrylonitrile) obtained from Ube Ind. Ltd., Japan were used without further purification. The properties of the liquid rubbers are shown in Table 3-2. Toluene and tetrahydrofuran (THF) obtained from Kanto Chemical Co., Inc. Japan were dried over sodium and distilled before use.

**Table 3-2 Properties of liquid rubber (BR-COOH and NBR-COOH)**

Liquid rubber	Molecular weight	COOH (eq./mol)	Acrylonitril content (mol%)	Viscosity (Pas)
BR-COOH	4800	2.01	0	4.0×10 <sup>3</sup>
NBR-COOH	3500	1.90	10	5.5×10 <sup>5</sup>

### 3.2.2 Grafting of liquid rubbers onto silica nanoparticle and carbon black surface using Sc(OTf)<sub>3</sub> as catalyst

Into a polymerization tube, 0.10 g of Silica-NH<sub>2</sub> (CB, 0.20 g), 0.30 mmol (0.05 mmol) of liquid rubber, 0.10 g of Sc(OTf)<sub>3</sub>, and 20.0 mL of toluene were charged. The mixture was stirred with a magnetic stirrer under nitrogen gas. In order to isolate the resulting silica (CB) from the reaction mixture, after the reaction, the product was dispersed in THF, and the dispersion was centrifuged at 1.5×10<sup>4</sup> rpm. The silica precipitated was dispersed in THF again and the dispersion was centrifuged. These procedures were repeated until no more liquid rubber could be detected in the supernatant solution. The treated silica nanoparticle and CB were dried *in vacuo* at room temperature.

### 3.2.3 Determination of grafting

The percentage of liquid rubber grafting onto the silica nanoparticle and CB was determined by the following equation:

$$\text{Grafting (\%)} = (A / B) \times 100$$

where A is the weight of liquid rubber grafted (g) and B is the weight of the silica nanoparticle (CB) charged (g). The weight of liquid rubber grafted onto the silica and CB surface was determined by the weight loss when liquid rubber-grafted silica and CB were heated at 800 °C by the use of a thermogravimetric analyzer (TGA) (Shimadzu TGA-50).

### 3.2.4 Characterization of liquid rubber-grafted silica and carbon black

The grafting of liquid rubbers onto the silica and CB surface was confirmed by thermal decomposition gas chromatogram–mass spectra (GC–MS). Thermal decomposition GC–MS

was recorded by a GCMS-QP2010 gas chromatograph mass spectrometer (Shimadzu Corporation) equipped with a double shot pyrolyzer (Frontier Laboratories Ltd.).

### **3.2.5 Crosslinking of liquid rubbers by silica nanoparticle and carbon black using Sc(OTf)<sub>3</sub> as catalyst**

Silica-NH<sub>2</sub> (CB), liquid rubber, and Sc(OTf)<sub>3</sub> were uniformly mixed by a rotation and revolution super-mixer (Thinky Model AR-100). The mixture was poured into a polytetrafluoroethylene sheet and cured at 90 °C in an electric oven. The resulting product (gel) was extracted with THF until no more liquid rubber could be detected in the extracting THF. The percentage of gel fraction of the product was determined by the following equation:

$$\text{Gel fraction (\%)} = (C / D) \times 100$$

where C is the weight of gel after extraction with THF (g) and D is the weight of product before extraction (g).

### 3.3. RESULTS AND DISCUSSION

#### 3.3.1 Grafting of liquid rubbers onto silica nanoparticle and carbon black surface using $\text{Sc}(\text{OTf})_3$ as catalyst

Table 3-3 shows the results of the reaction of liquid rubbers with amino groups on a silica nanoparticle and phenolic hydroxyl groups on CB in the presence and in the absence of  $\text{Sc}(\text{OTf})_3$ . Even in the absence of  $\text{Sc}(\text{OTf})_3$ , unextractable liquid rubbers remained on the surface of the silica nanoparticle and CB. This may be due to physical adsorption of liquid rubbers on these surfaces.

On the contrary, in the presence of  $\text{Sc}(\text{OTf})_3$ , the grafting of liquid rubbers onto the silica and CB surface was much larger than those in the absence of  $\text{Sc}(\text{OTf})_3$ . These results indicate that  $\text{Sc}(\text{OTf})_3$  acts as an effective catalyst for the grafting of liquid rubbers onto silica and CB surfaces by grafting onto process. The percentage of grafting onto CB was much larger than that onto silica. This may be due to the fact that the ratio of functional groups to specific surface area of silica nanoparticle and CB effects.

In addition, after the grafting reaction,  $\text{Sc}(\text{OTf})_3$  was readily recovered from the reaction mixture and reused for the grafting reaction: the decrease of percentage of grafting in the presence of reused  $\text{Sc}(\text{OTf})_3$  was scarcely observed as shown in Table 3-3. Therefore, it was found that the recovered  $\text{Sc}(\text{OTf})_3$  can be used for the grafting reaction of liquid rubber onto silica and CB.

Figure 3-1 shows the relationship between reaction time and the percentage of grafting onto the silica and CB surface in the presence of  $\text{Sc}(\text{OTf})_3$ . The percentage of grafting increased with the progress of the reaction and scarcely increased after 5 h.

Therefore, the results suggest that the CB surface was blocked by the grafted liquid rubbers chains.

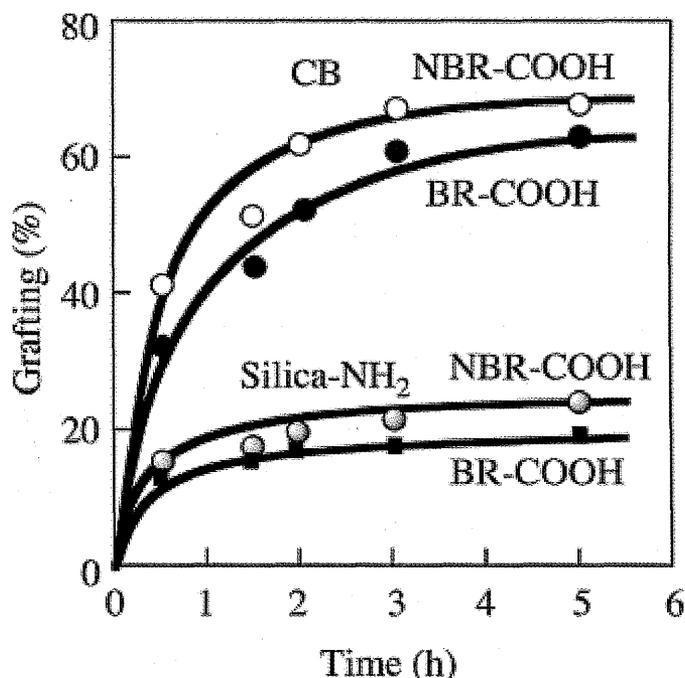
**Table 3-3 Effect of Sc(OTf)<sub>3</sub> on the grafting of liquid rubber onto Silica-NH<sub>2</sub> and CB**

	Liquid rubber	Molecular weight	Sc(OTf) <sub>3</sub> (g)	Grafting(%)	
Silica-NH <sub>2</sub> <sup>a</sup>	BR-COOH	4800	0	3.7	
		4800	0.15	20.2	
		4800	0.15 <sup>c</sup>	17.5	
	NBR-COOH	3500	0	4.2	
		3500	0.15	23.1	
Carbon black <sup>b</sup>	BR-COOH	4800	0.15	16.4	
		4800	0.15	62.9	
	NBR-COOH	3500	0	21.5	
		3500	0.15	66.9	

<sup>a</sup>Silica-NH<sub>2</sub>, 0.10 g; liquid rubber, 0.30 mmol; toluene, 20.0 mL; 27 °C; 5 h.

<sup>b</sup>Carbon black, 0.20 g; liquid rubber, 0.05 mmol; toluene, 20.0 mL; 27 °C; 5 h.

<sup>c</sup>Recovered Sc(OTf)<sub>3</sub> was used as a catalyst.



**Figure 3-1 Grafting of liquid rubber onto Silica-NH<sub>2</sub> and CB using Sc(OTf)<sub>3</sub> as catalyst**

Silica-NH<sub>2</sub>, 0.10 g; liquid rubber, 0.30 mmol; Sc(OTf)<sub>3</sub>, 0.15 g (CB, 0.20 g; liquid rubber, 0.05 mmol; Sc(OTf)<sub>3</sub>, 0.10 g); toluene, 20.0 mL; 27 °C.

Figure 3-2 shows a gas chromatogram of the thermally decomposed gas of NBR-grafted silica (Silica-NBR) and NBR-COOH. The gas chromatogram of the decomposed gas of NBR-grafted silica was in agreement with that of NBR-COOH. The mass spectrum of the decomposed gas of NBR-grafted silica at a retention time of 1.8 min was also in agreement with that of NBR-COOH. These results show that NBR was grafted onto the silica surface.

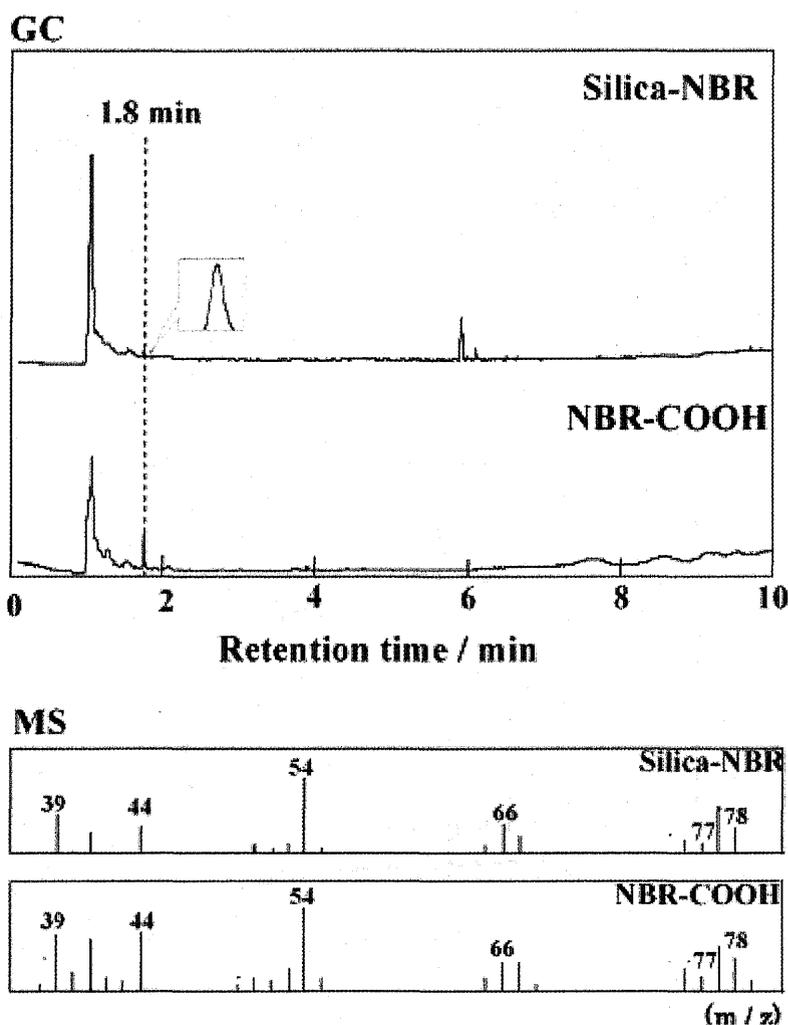
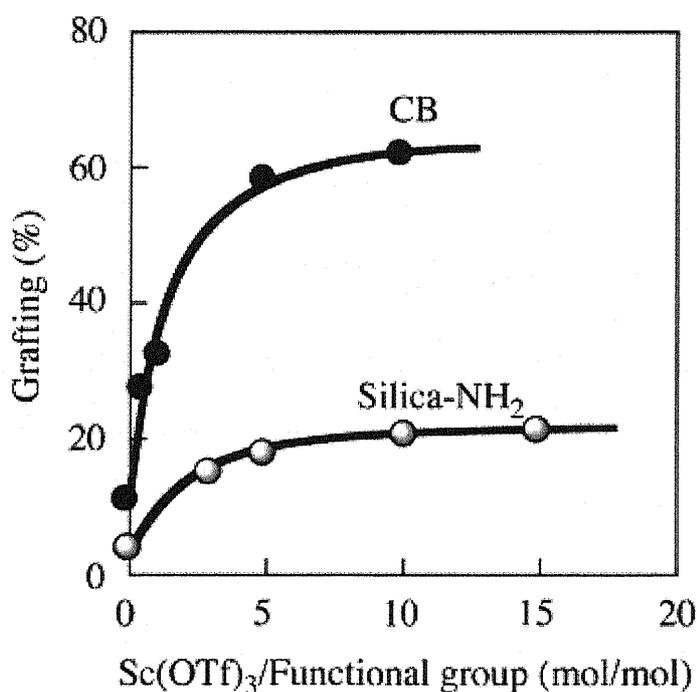


Figure 3-2 Thermal decomposition GC-MS of NBR-grafted silica and NBR-COOH

### 3.3.2 Effect of the amount of $\text{Sc}(\text{OTf})_3$ on the grafting onto silica and carbon black

Figure 3-3 shows the effect of the amount of  $\text{Sc}(\text{OTf})_3$  on the grafting of BR-COOH onto the silica nanoparticle and CB. The percentage of grafting increased with increasing amount of  $\text{Sc}(\text{OTf})_3$ , but the grafting of BR-COOH onto these surfaces no longer increased when the ratio of  $\text{Sc}(\text{OTf})_3$  to amino groups on the silica and phenolic hydroxyl groups on CB exceeded about 10. Therefore, it was found that for the grafting reaction, excess of catalyst is required.

The ratio is much larger than that for the grafting of PEG on to CB surface (Chapter 2, 2.3.2). This may be due to the fact that the amount of functional groups silica and CB effects.

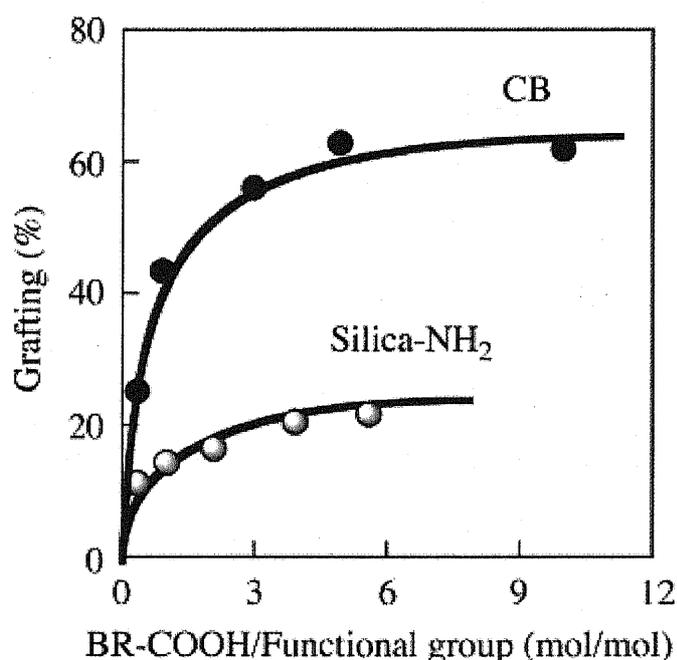


**Figure 3-3 Effect of the amount of  $\text{Sc}(\text{OTf})_3$  on the grafting of BR-COOH onto Silica-NH<sub>2</sub> and CB**

Silica-NH<sub>2</sub>, 0.10 g; BR-COOH, 0.30 mmol; (CB, 0.20 g; BR-COOH, 0.05 mmol); toluene, 20.0 mL; 27 °C, 5 h.

### 3.3.3 Effect of the amount of BR-COOH on the grafting onto silica and carbon black

Figure 3-4 shows the effect of the amount of BR-COOH on the grafting onto the silica nanoparticle and CB. It was found that the percentage of grafting increased with increasing amount of BR-COOH charged, but the grafting no longer increased when the ratio of BR-COOH to amino groups on the silica and phenolic hydroxyl groups on CB exceeded about 4.



**Figure 3-4 Effect of the amount of BR-COOH on the grafting of BR onto Silica-NH<sub>2</sub> and CB**

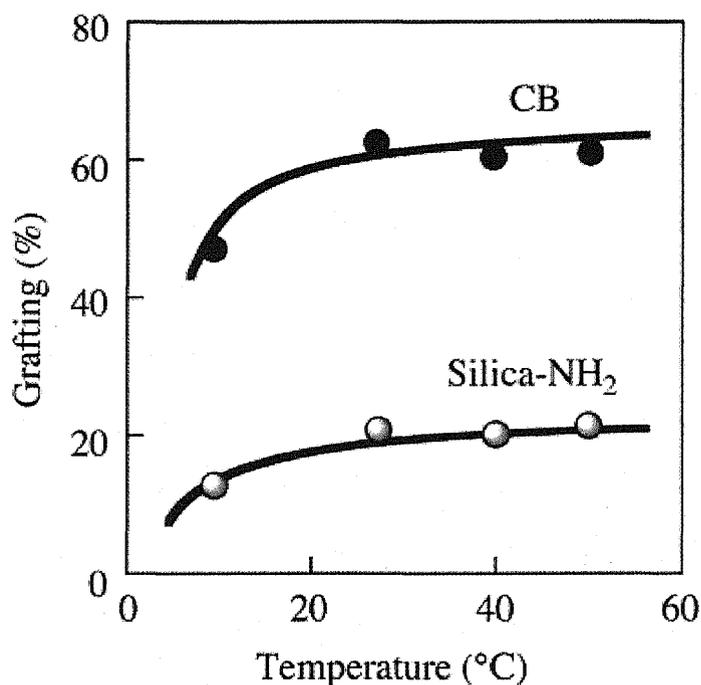
Silica-NH<sub>2</sub>, 0.10 g; Sc(OTf)<sub>3</sub>, 0.15 g (CB, 0.20 g; Sc(OTf)<sub>3</sub>, 0.10 g); toluene, 20.0 mL; 27 °C; 5 h.

### 3.3.4 Effect of temperature on the grafting of BR-COOH onto silica and carbon black

Figure 3-5 shows the effect of temperature on the grafting of BR-COOH onto silica and CB in the presence of Sc(OTf)<sub>3</sub>. It became apparent that BR-COOH grafting was scarcely

affected by temperature above 27 °C, but decreased below 20 °C.

Therefore, the grafting reaction proceeded even at room temperature.



**Figure 3-5 Effect of temperature on the grafting of BR-COOH onto Silica-NH<sub>2</sub> and CB**

Silica-NH<sub>2</sub>, 0.10 g; BR-COOH, 0.30 mmol; Sc(OTf)<sub>3</sub>, 0.15 g (CB, 0.20 g; BR-COOH, 0.05 mmol; Sc(OTf)<sub>3</sub>, 0.10 g); toluene, 20.0 mL; 5 h.

### 3.3.5 Crosslinking of liquid rubbers by silica and carbon black using Sc(OTf)<sub>3</sub> as catalyst

It is expected that the terminal-carboxyl groups of grafted liquid rubber react with amino groups on the silica and phenolic hydroxyl groups on CB, and the crosslinking reactions of NBR-COOH by silica and CB proceeds give gel in the presence of Sc(OTf)<sub>3</sub> as shown in Scheme 3-3.

Therefore, the crosslinking reaction of the NBR-COOH with silica and CB using

Sc(OTf)<sub>3</sub> as catalyst was investigated in the absence of solvent (in bulk). The degree of crosslinking of NBR-COOH was estimated by gel fraction.

Tables 3-4 and 3-5 show the effect of feed ratio of silica having amino groups and CB to NBR-COOH on the gel fraction after the heating at 90 °C for 5 h in bulk, respectively. It was found that no crosslinking reaction was observed when the feed molar ratio of silica to NBR-COOH was less than 0.07, but the grafting of the NBR-COOH onto the surface was proceeded. On the contrary, the crosslinking of NBR-COOH by amino groups on silica was observed when the feed molar ratio exceeded 0.13. The gel fraction increased with increasing feed molar ratio of silica to NBR-COOH.

In the case of CB, no crosslinking reaction by CB was observed when the feed molar ratio of CB to NBR-COOH was less than 0.01, but NBR-COOH was grafted onto the surface. On the contrary, the crosslinking of NBR-COOH by CB was observed when the feed molar ratio exceeded 0.02. The gel fraction also increased with increasing molar ratio of CB to NBR-COOH.

These results suggest that terminal-carboxyl groups of grafted NBR chains on silica and CB surfaces have an ability to react with amino groups on other silica, and phenolic hydroxyl groups on other CB in bulk to give brittle gels, in which silica and CB particles are uniformly incorporated by chemical bonds.

Figure 3-6 shows the relationship between reaction time and gel fraction of NBR-COOH in the presence of silica and CB using Sc(OTf)<sub>3</sub> as catalyst. It was found that gel fraction increased with progress of the reaction.

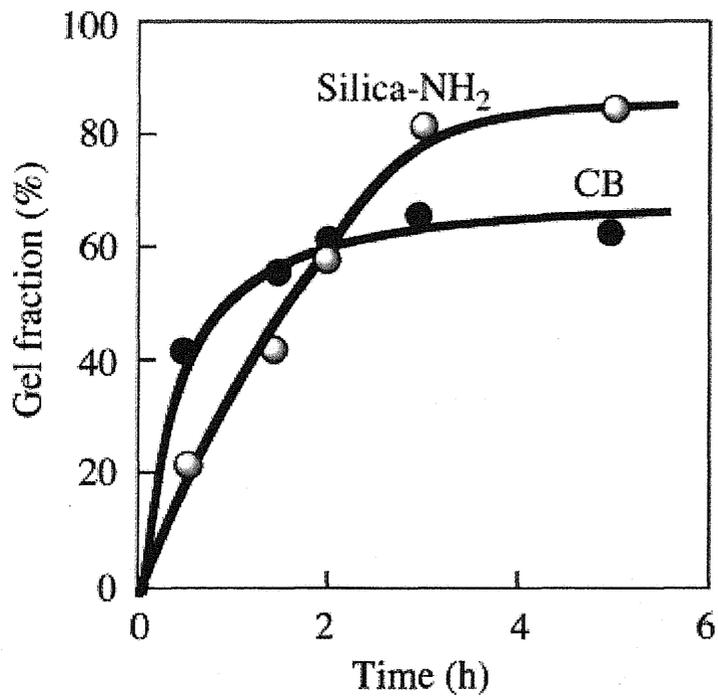
**Table 3-4 Crosslinking of NBR-COOH by Silica-NH<sub>2</sub> using Sc(OTf)<sub>3</sub> as catalyst<sup>a</sup>**

Silica-NH <sub>2</sub> / NBR-COOH (mol/mol)	Gel fraction (%)	Property of product
0.035	No gelation (Grafting)	-
0.06	No gelation (Grafting)	-
0.07	No gelation (Grafting)	-
0.13	55	Brittle
0.16	63	Brittle
0.26	76	Brittle
0.50	87	Brittle
1.00	82	Brittle

<sup>a</sup>90 °C; 5 h.**Table 3-5 Crosslinking of NBR-COOH by CB using Sc(OTf)<sub>3</sub> as catalyst<sup>a</sup>**

CB / NBR-COOH (mol/mol)	Gel fraction (%)	Property of product
0.008	No gelation (Grafting)	-
0.01	No gelation (Grafting)	-
0.02	6	Brittle
0.03	37	Brittle
0.04	59	Brittle
0.05	65	Brittle
0.17	68	Brittle
0.34	69	Brittle

<sup>a</sup>90 °C; 5 h.



**Figure 3-6 Crosslinking reaction of NBR-COOH by Silica-NH<sub>2</sub> and CB using Sc(OTf)<sub>3</sub> as catalyst**  
 Silica-NH<sub>2</sub>, 0.10 g; NBR-COOH, 0.10 g; Sc(OTf)<sub>3</sub>, 0.15 g (CB, 0.10 g; NBR-COOH, 0.10 g; Sc(OTf)<sub>3</sub>, 0.10 g); 90 °C.

### 3.4 CONCLUSIONS

1. The grafting of the liquid rubbers onto a silica nanoparticle and CB surface by grafting onto process was achieved by the reaction of carboxyl groups of the polymer with amino groups on silica and phenolic hydroxyl groups on CB using  $\text{Sc}(\text{OTf})_3$  as catalyst even at room temperature.
2. After the reaction,  $\text{Sc}(\text{OTf})_3$  was readily recovered by reprecipitation and successive extraction with water. The recovered  $\text{Sc}(\text{OTf})_3$  was found to be reusable as the grafting catalyst.
3. The crosslinking reaction of the liquid rubber by amino groups on silica and phenolic hydroxyl groups on CB in the presence of  $\text{Sc}(\text{OTf})_3$  successfully proceeded to give brittle gels, in which silica and CB were uniformly incorporated in the gel matrices.

### 3.5 REFERENCES

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## **Chapter 4**

### **Grafting of poly(*L*-lactic acid) onto carbon black surface**

## SUMMARY

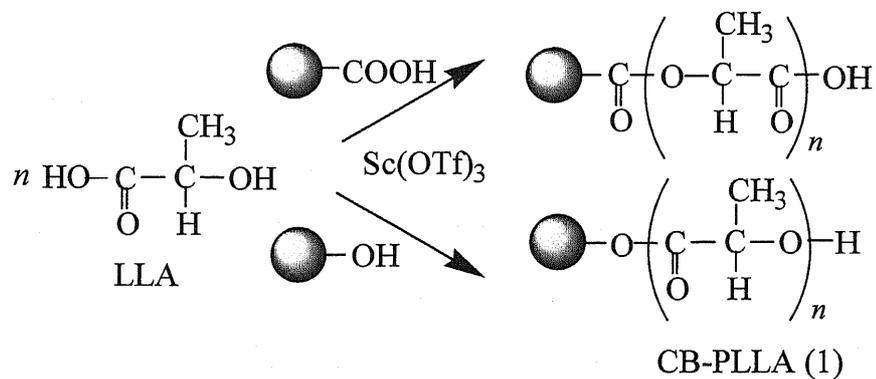
In order to improve the dispersibility of carbon black (CB) in organic solvent, the grafting of poly(*L*-lactic acid) (PLLA) onto CB surface by (1) polycondensation of *L*-lactic acid (LLA) in the presence of CB (grafting onto process and/or grafting from process) and (2) grafting by the reaction of PLLA with CB surface in the presence of catalyst (grafting onto process) was investigated. It was found that, during the polycondensation of LLA in the presence of CB, the grafting of PLLA onto CB surface proceeded both in the absence and in the presence of scandium (III) triflate ( $\text{Sc}(\text{OTf})_3$ ) as catalyst to give PLLA-grafted CB (1), but the percentage of PLLA grafting onto CB in the presence of  $\text{Sc}(\text{OTf})_3$  was higher than that in the absence of  $\text{Sc}(\text{OTf})_3$ . In addition, the reaction of surface functional groups on CB with PLLA was successfully achieved in the presence of  $\text{Sc}(\text{OTf})_3$  to give PLLA-grafted CB (2). The average particle size of CB considerably decreased by grafting of PLLA onto the surface. Therefore, it was concluded that the aggregation of CB particles was considerably destroyed and prevented by grafting of PLLA onto the surface. The PLLA-grafted CBs gave a stable dispersion in polar solvents, such as DMSO and 1,4-dioxane, which are good solvents for PLLA.

## 4.1 INTRODUCTION

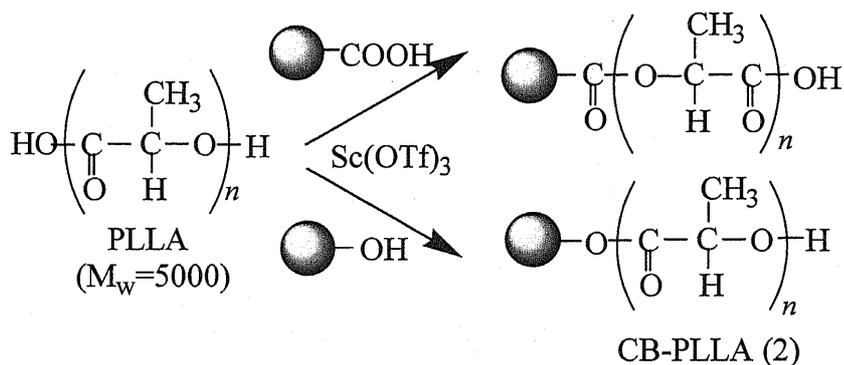
Recently, biodegradable polymers have attracted attention as environmentally friendly materials. The grafting of poly(*L*-lactic acid) (PLLA) onto nanomaterials has been reported [1-11]. For example, Feng et al. have reported the grafting of PLLA onto the surface of magnetic multi-walled carbon nanotubes (m-MWCNTs) by in-situ ring-opening polymerization of lactide [8]. It has been reported by Luo et al. that the surface of TiO<sub>2</sub> was successfully grafted with PLLA layer by in situ melt polycondensation of *L*-lactic acid (LLA) [9]. Moreover, Kim et al. have reported the incorporation of a small amount of PLLA-grafted MWCNTs improved the thermal and electrical properties of PLLA composites [10]. Yan et al. have pointed out that PLLA oligomer was directly grafted onto the surface silanol groups of silica nanoparticles by condensation of LLA without any catalyst [11]. But, no surface grafting of PLLA onto CB was reported.

In Chapter 2 and Chapter 3, it is pointed out that rare-earth catalysts act as effective catalyst for the grafting of the polymers onto a silica nanoparticle and carbon black (CB) surface was achieved at room temperature.

In this Chapter, in order to improve the dispersibility of CB by grafting of biodegradable polymer and to prepare biodegradable conductive composite, the grafting of PLLA onto CB surface by the two methods was investigated: (1) polycondensation of LLA in the presence of CB (Scheme 4-1) (grafting from process and/or grafting onto process) and (2) grafting reaction of PLLA with CB surface (Scheme 4-2) (grafting onto process) in the presence of Sc(OTf)<sub>3</sub>. The dispersibility of PLLA-grafted CB and particle size distribution of PLLA-grafted CB will be discussed.



**Scheme 4-1 Grafting of PLLA onto CB surface during the polycondensation of LLA in the presence of CB**



**Scheme 4-2 Grafting of PLLA by the reaction of PLLA with functional groups of CB in the presence of  $\text{Sc}(\text{OTf})_3$**

## 4.2 EXPERIMENTAL

### 4.2.1 Materials and reagents

Carbon black (CB) used was FW200 obtained from Degussa AG as described as mentioned above. The specific surface area and average particle size were 460 m<sup>2</sup>/g and 13 nm, respectively. The contents of phenolic hydroxyl and carboxyl groups were 0.10 and 0.60 mmol/g, respectively. CB was dried *in vacuo* at 110 °C before use.

*L*-lactic acid (LLA), obtained from Acros Organics Co., Ltd., and poly(*L*-lactic acid) (PLLA) ( $M_n=5.0\times 10^3$ ), obtained from Nacalai Tesque Inc., were used without further purification. Scandium (III) triflate (Sc(OTf)<sub>3</sub>), obtained from Aldrich Chemical Co., Ltd., was used without further purification as mentioned above.

### 4.2.2 Polycondensation of LLA in the presence of carbon black (CB-PLLA (1))

In to a flask, 1.0 g of CB, 0.17 mmol of LLA, 1.6 mmol of Sc(OTf)<sub>3</sub> and 40.0 mL of toluene were charged and the mixture was stirred with a magnetic stirrer at 110 °C. And then, water formed by the polycondensation was removed by azeotropic dehydration with toluene. After the reaction, the mixture was centrifuged at  $1.5\times 10^4$  rpm and the supernatant solution was removed by decantation. The resulting CB was dispersed in THF and the dispersion was centrifuged again. The procedures were repeated until no more LLA and Sc(OTf)<sub>3</sub> could be detected in the supernatant solution. The CB was dried *in vacuo* at 50 °C and stored in a desiccator. The PLLA-grafted CB was abbreviated as CB-PLLA (1).

### 4.2.3 Grafting reaction of PLLA onto carbon black surface (CB-PLLA (2))

In to a test tube, 0.25 g of CB, 0.2 mmol of PLLA, 1.6 mmol of Sc(OTf)<sub>3</sub> and 5.0 mL of THF were charged and the mixture was stirred with a magnetic stirrer at 40 °C. After the reaction, the mixture was centrifuged at 1.5×10<sup>4</sup> rpm and the supernatant solution was removed by decantation. The resulting CB was dispersed in THF and the dispersion was centrifuged again. The procedures were repeated until no more PLLA and Sc(OTf)<sub>3</sub> could be detected in the supernatant solution. The CB was dried *in vacuo* at 50 °C and stored in a desiccator. The PLLA-grafted CB was abbreviated as CB-PLLA (2).

### 4.2.4 Determination of percentage of grafting

The percentage of PLLA grafting onto CB was determined by the following equation:

$$\text{Grafting (\%)} = (A / B) \times 100,$$

where A is weight of PLLA grafted onto CB and B is weight of CB charged. The weight of PLLA grafted onto the surface was determined by weight loss when CB-PLLA was heated at 400 °C by using a thermogravimetric analyzer (TGA) (Shimadzu TGA-50).

### 4.2.5 Characterization of CB-PLLA

Thermal decomposition gas chromatograms and mass spectra were recorded on a gas chromatograph mass spectrometer (GC-MS), (Shimadzu Manufacturing Co., Ltd. GCMS-QP2010) equipped with a double shot pyrolyzer, (Frontier Laboratories Ltd. PY-2020). Infrared spectra were recorded on a FT-IR spectrophotometer (Shimadzu Manufacturing Co., Ltd. FTIR-8400S).

The molecular weight and molecular weight distribution of ungrafted PLLA formed

during the polycondensation of LLA using the  $\text{Sc}(\text{OTf})_3$  were estimated by SEC using polystyrene standards. For SEC, a Tosoh CCPD instrument (column: TSK-GEL G2000HHR) was used.

Particle size distribution of CB-PLLA was measured by use of a nanoparticle size analyzer (Shimadzu Manufacturing Co., Ltd., SALD-7100).

#### **4.2.6 Dispersibility of CB-PLLA in solvents**

CB-PLLA (1.0 mg) was dispersed in 5.0 mL of various solvents under ultrasonic wave irradiation for 10 min and allowed to stand at room temperature.

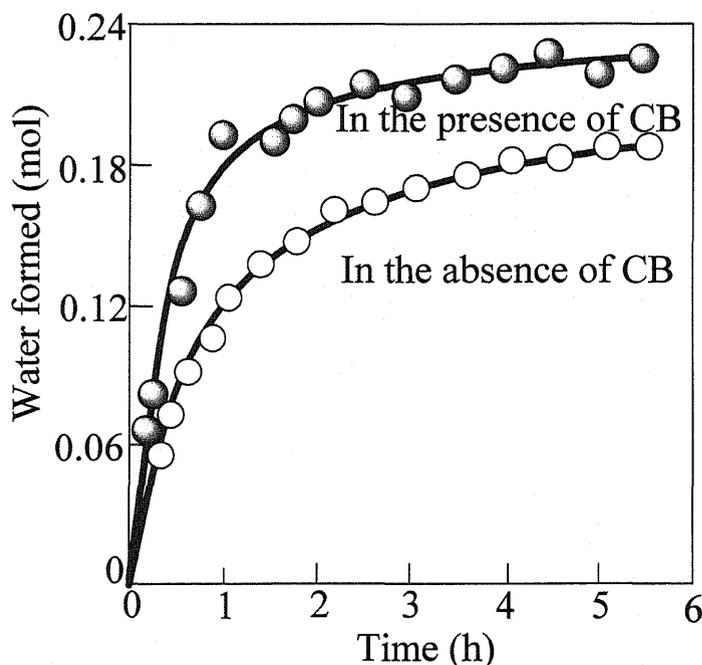
In addition, to estimate dispersibility of CB-PLLA, 1.0 mg of CB-PLLA was dispersed in 10 mL of solvent, and decrease of absorbance of the dispersion at 500 nm was recorded by use of UV-vis spectrometer (Shimadzu Manufacturing Co., Ltd., UV-1600).

## 4.3 RESULTS AND DISCUSSION

### 4.3.1 Polycondensation of LLA in the presence of carbon black (grafting onto process and/or grafting onto process)

Graft polymerization of PLLA onto CB was carried out by polycondensation of LLA in the presence of CB (Scheme 4-1). Figure 4-1 shows the amount of H<sub>2</sub>O formed during the polycondensation of LLA in the presence and in the absence of CB. In the absence of CB, 0.19 mol of H<sub>2</sub>O was formed after 5 h. On the contrary, in the presence of CB, 0.22 mol of H<sub>2</sub>O was formed after 5 h.

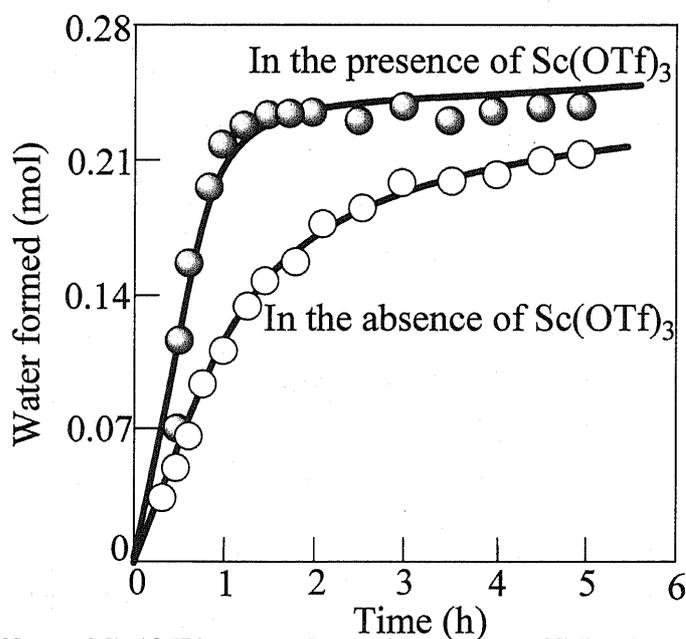
It has been reported that carboxyl group of LLA acts as an effective catalyst for the polycondensation of LLA [12]. Carboxyl groups of CB are well known to act as a strong acid catalyst. Based on the above results, it is suggested that CB acts as a catalyst for the polycondensation of LLA.



**Figure 4-1 Polycondensation of LLA in the presence of CB**  
CB, 1.0 g; LLA, 0.17 mmol; toluene, 40.0 mL; 110 °C.

### 4.3.2 Effect of $\text{Sc}(\text{OTf})_3$ on the polycondensation of LLA in the presence of carbon black

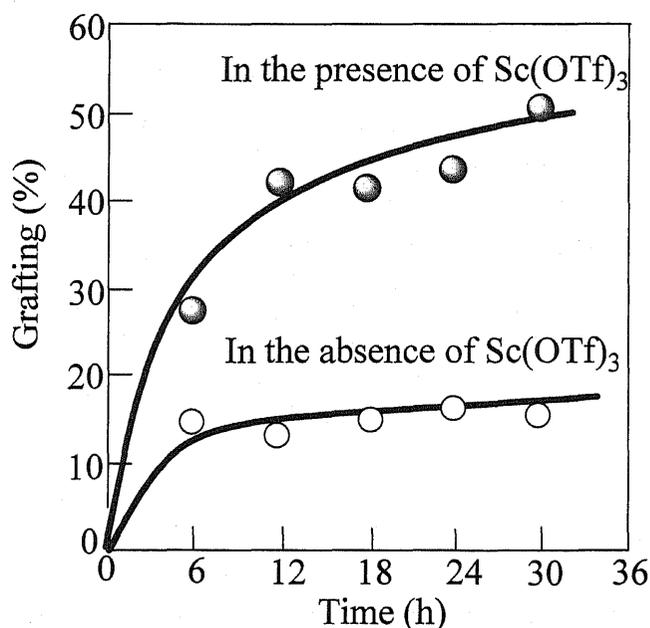
Figure 4-2 shows the effect of  $\text{Sc}(\text{OTf})_3$  on the polycondensation of LLA in the presence of CB. The amount of  $\text{H}_2\text{O}$  formed in the early stage of the polycondensation in the presence of  $\text{Sc}(\text{OTf})_3$  was much more than that in the absence of  $\text{Sc}(\text{OTf})_3$ . Therefore, the results show that  $\text{Sc}(\text{OTf})_3$  promotes the reaction at the initial stage of the polycondensation of LLA.



**Figure 4-2 Effect of  $\text{Sc}(\text{OTf})_3$  on polycondensation of LLA in the presence of CB**  
CB, 1.0 g; LLA, 0.17 mmol;  $\text{Sc}(\text{OTf})_3$ , 1.60 mmol; toluene, 40.0 mL; 110 °C.

### 4.3.3 Grafting of PLLA onto carbon black during the polycondensation in the presence of carbon black

Figure 4-3 shows the percentage of PLLA grafting onto CB surface obtained in the presence and in the absence of  $\text{Sc}(\text{OTf})_3$ . In the absence of  $\text{Sc}(\text{OTf})_3$ , the grafting reached 15.8 % after 30 h. On the contrary, in the presence of  $\text{Sc}(\text{OTf})_3$ , PLLA was successfully grafted onto CB surface to give CB-PLLA (1) and percentage of grafting reached 50 %. As shown in Figure 4-2, the amount of  $\text{H}_2\text{O}$  formed of polycondensation in the presence of  $\text{Sc}(\text{OTf})_3$  increased with increasing the reaction time. But the amount of  $\text{H}_2\text{O}$  formed was no longer increased after 2 h. As shown in Figure 4-3, the grafting of PLLA onto CB promoted after 2 h. It was thought that polycondensation of LLA suspended after 2 h, but grafting of PLLA onto CB promoted for free PLLA after 2 h. Therefore, it was concluded that  $\text{Sc}(\text{OTf})_3$  promotes the grafting reaction of PLLA onto CB surface.



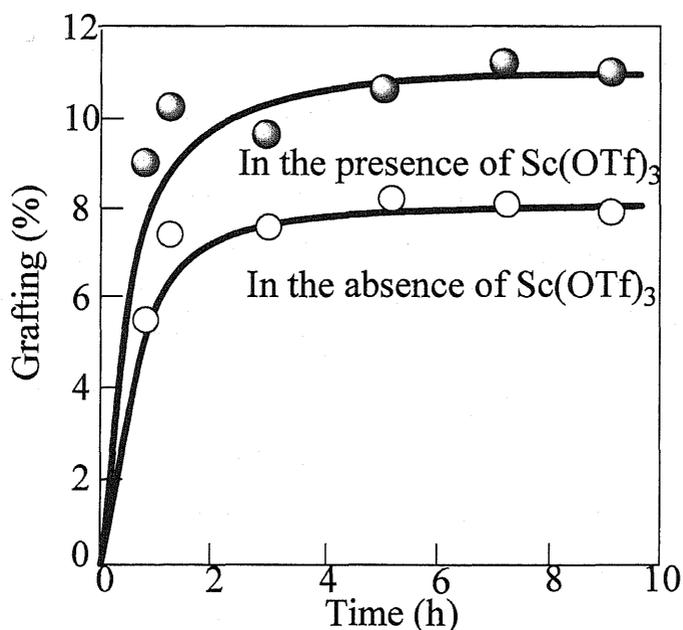
**Figure 4-3 Effect of  $\text{Sc}(\text{OTf})_3$  on the grafting of PLLA onto CB during the polycondensation of LLA**

CB, 1.0 g; LLA, 0.17 mmol;  $\text{Sc}(\text{OTf})_3$ , 1.60 mmol; toluene, 40.0 mL; 110 °C.

#### 4.3.4 Grafting of PLLA onto carbon black surface (grafting onto process)

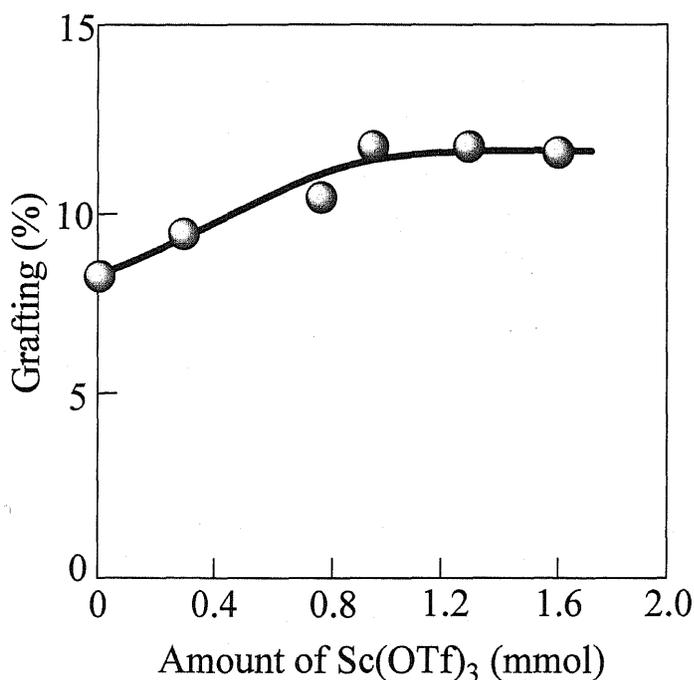
The grafting of PLLA onto CB was carried out by condensation reaction of hydroxyl groups of CB with carboxyl groups of PLLA and carboxyl groups of CB with hydroxyl groups of PLLA (Scheme 4-2). Figure 4-4 shows the relationship between reaction time and the percentage of PLLA grafting onto CB surface (CB-PLLA (2)). In the absence of  $\text{Sc}(\text{OTf})_3$ , the percentage of grafting increased with progress of reaction, but no longer increased after 3 h. On the contrary, in the presence of  $\text{Sc}(\text{OTf})_3$ , the percentage of grafting was reach 11 % after 7 h. Therefore, it became apparent that  $\text{Sc}(\text{OTf})_3$  acts as an effective catalyst for the grafting of PLLA onto surface.

Even in the absence of  $\text{Sc}(\text{OTf})_3$ , the grafting reaction of PLLA onto CB proceeded. This may be due to the fact that PLLA was grafted onto CB by hydrogen bonds between functional groups on CB surface and PLLA.



**Figure 4-4 Effect of  $\text{Sc}(\text{OTf})_3$  on the grafting of PLLA onto CB by the reaction of PLLA with functional groups of CB**  
CB, 0.25 g; PLLA, 0.2 mmol;  $\text{Sc}(\text{OTf})_3$ , 1.60 mmol; THF, 5.0 mL; 40 °C.

Figure 4-5 shows the effect of the amount of  $\text{Sc}(\text{OTf})_3$  on the grafting of the PLLA onto CB surface by condensation of CB with PLLA. The percentage of grafting increased with increasing the amount of  $\text{Sc}(\text{OTf})_3$ . But the percentage of grafting no longer increased above 1.0 mmol of  $\text{Sc}(\text{OTf})_3$ . The ratio of  $\text{Sc}(\text{OTf})_3$  to phenolic hydroxyl groups and carboxyl groups on CB exceeded about 5.6. Therefore, the results suggest that the CB surface was blocked by the grafted PLLA chains.



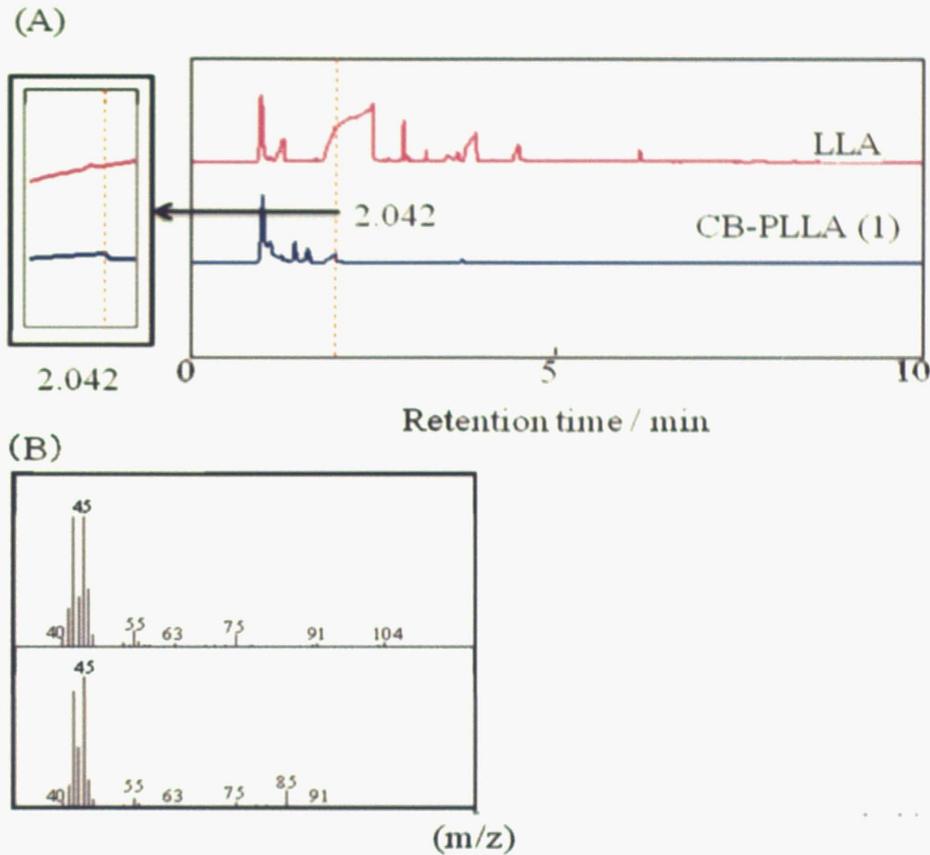
**Figure 4-5 Effect of the amount of  $\text{Sc}(\text{OTf})_3$  on the grafting reaction of PLLA with CB surface**

CB, 0.25 g; PLLA, 0.2 mmol; THF, 5.0 mL; 40 °C; 48 h.

#### 4.3.5 Characterization of CB-PLLA by GC-MS and ATR-FTIR

Figure 4-6 shows gas chromatogram (GC) of thermally decomposed gas of LLA and CB-PLLA (1). GC of decomposed gas of CB-PLLA (1) was in agreement with that of LLA. In addition, Figure 6 shows mass spectra of decomposed gas of LLA and CB-PLLA (1) at

retention time 2.042 min which was also in agreement with that of LLA. These results also show that PLLA was grafted onto CB surface.



**Figure 4-6 (A) thermal decomposition GC of CB-PLLA (1) and LLA, and (B) MS of decomposed gas at retention time 2.042 min**

Figure 4-7 shows ATR-FTIR spectra of PLLA and difference ATR-FTIR spectra of CB-PLLA (2) and CB, which show absorptions characteristic of PLLA. The result shows the grafting of PLLA onto CB surface.

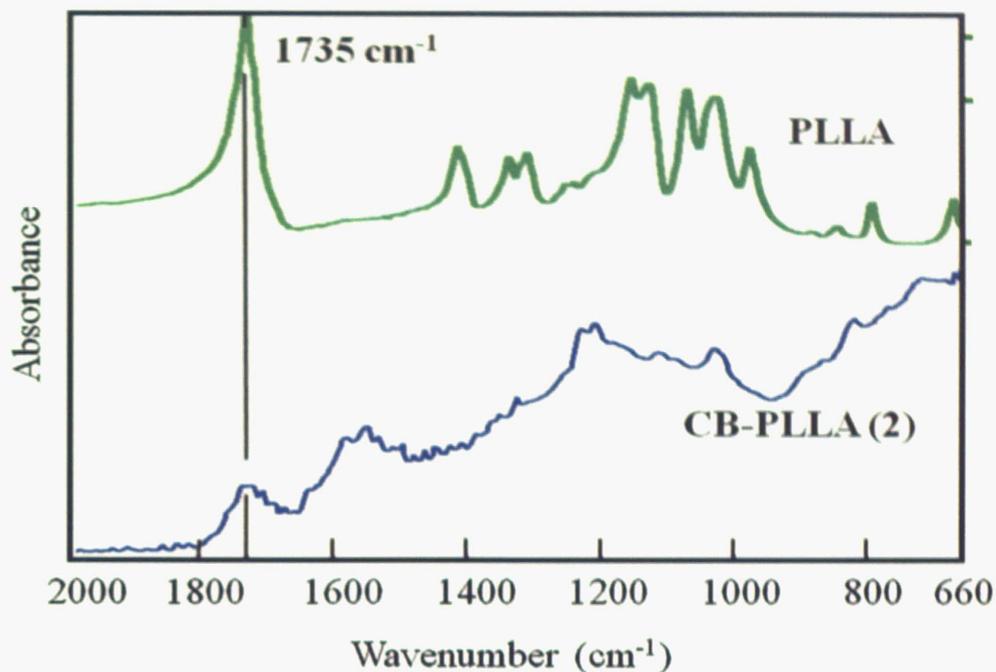


Figure 4-7 ATR-FTIR spectra of PLLA and difference ATR-FTIR spectra of CB-PLLA (2)

#### 4.3.6 Molecular weight of PLLA

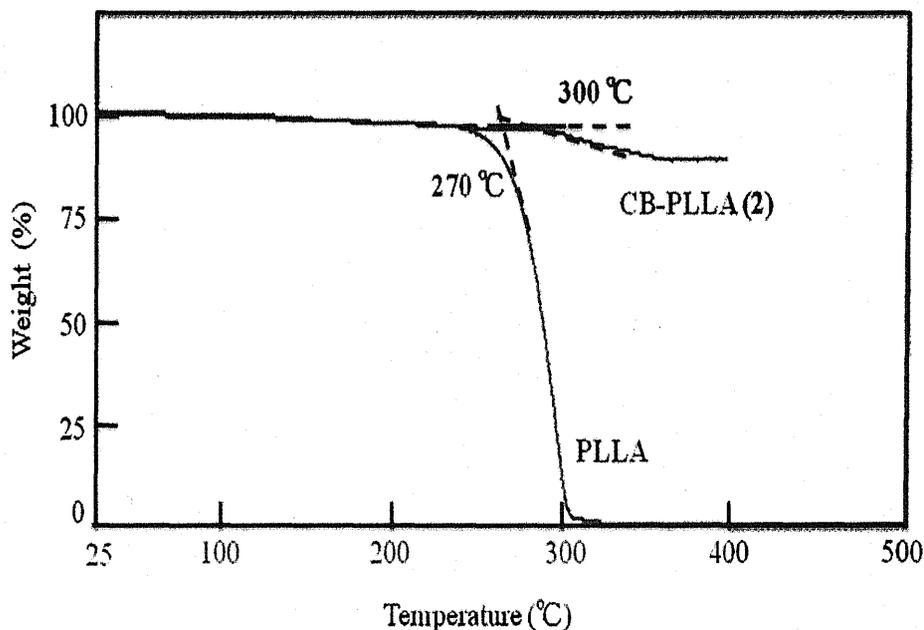
Molecular weight of ungrafted PLLA formed during polycondensation of LLA in the presence of  $\text{Sc}(\text{OTf})_3$  was determined. The results are shown in Table 4-3. The  $M_n$  of ungrafted PLLA was estimated to be 470 by GPC. This indicates that the degree of the polymerization of PLLA is about 5.

Table 4-3 Molecular weight of PLLA

LLA and PLLA	$M_n$	$M_n / M_w$
LLA	90	
PLLA	470	1.1

#### 4.3.7 Thermal stability of CB-PLLA (2)

Figure 4-8 shows TGA curves of CB-PLLA (2) and PLLA. As shown in Figure 4-8, thermal decomposition temperature of CB-PLLA (2) and PLLA was found to be 300 °C and 270 °C, respectively. The result clearly shows that the heat resistance of PLLA was considerably heightened when grafted onto CB surface.



**Figure 4-8 Thermal stability of grafted PLLA on CB surface and ungrafted PLLA**

#### 4.3.8 Particle size distribution of CB-PLLA

Figure 4-9 shows the particle size distribution of untreated CB, CB-PLLA (1), and CB-PLLA (2) after dispersing in 1,4-dioxane under ultrasonic wave irradiation for 10 min. As shown in Figure 4-9, the particle size distribution of CB-PLLA (1) and CB-PLLA (2) was considerably smaller than that of untreated CB. The average particle size distribution of

untreated CB, CB-PLLA (1), and CB-PLLA (2) was found to be 5.0-70  $\mu\text{m}$ , 0.3-4.0  $\mu\text{m}$  and 0.4-4.0  $\mu\text{m}$ , respectively. The average particle size of untreated CB, CB-PLLA (1) and CB-PLLA (2) was summarized in Table 4-2. Therefore, it was concluded that the aggregation of CB particles was considerably destroyed and prevented by grafting of PLLA onto the surface.

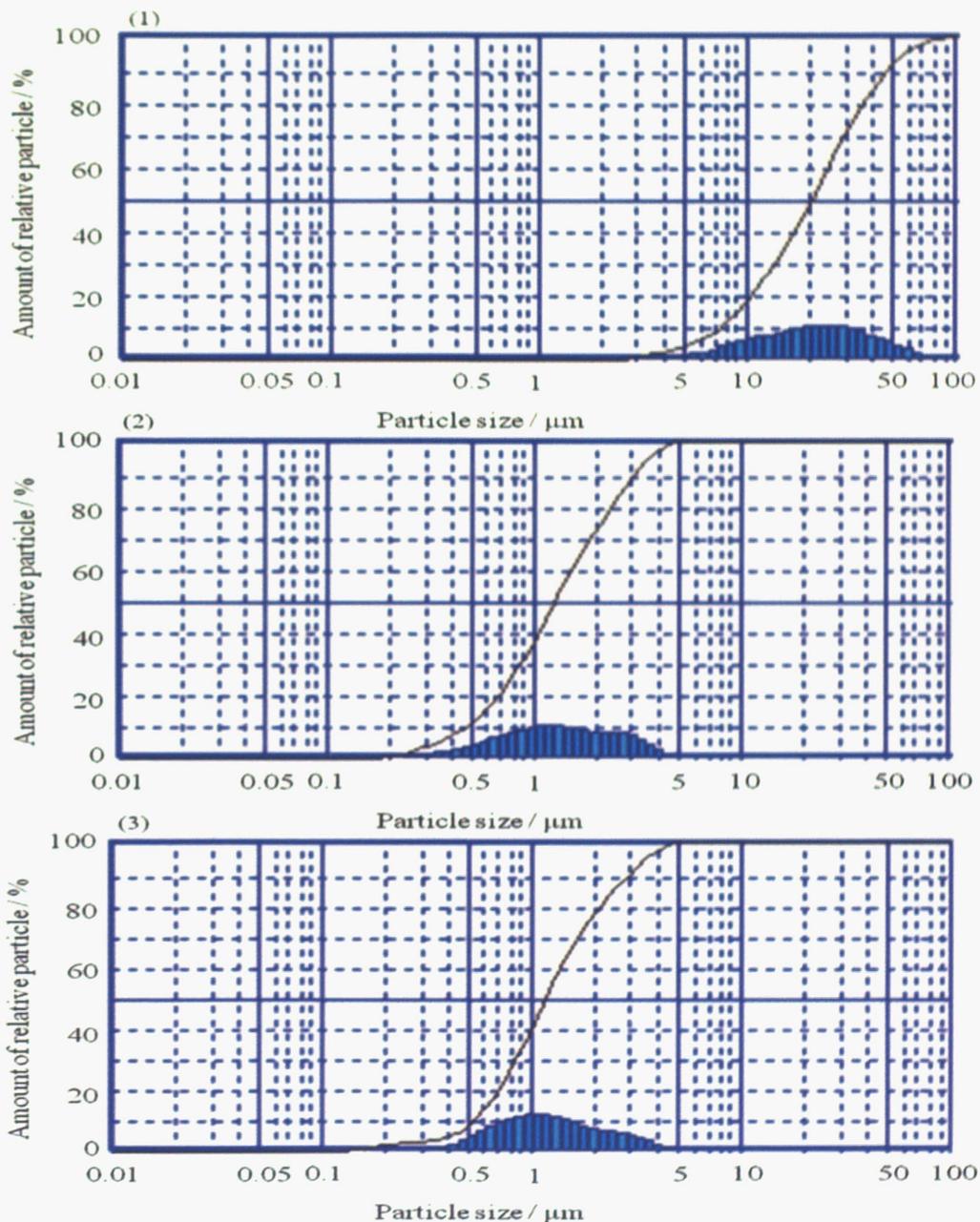


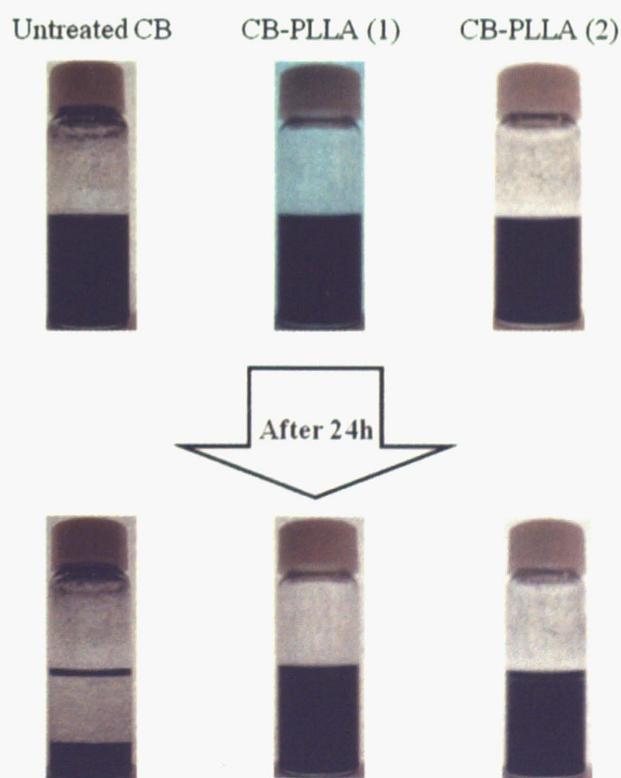
Figure 4-9 Particle size distribution of untreated CB, CB-PLLA (1) and CB-PLLA (2) in 1,4-dioxane

**Table 4-2 The average particle size of untreated CB and CB-PLLA in 1,4-dioxane**

CB	The average particle size ( $\mu\text{m}$ )
Untreated CB	19.5
CB-PLLA (1)	1.23
CB-PLLA (2)	1.18

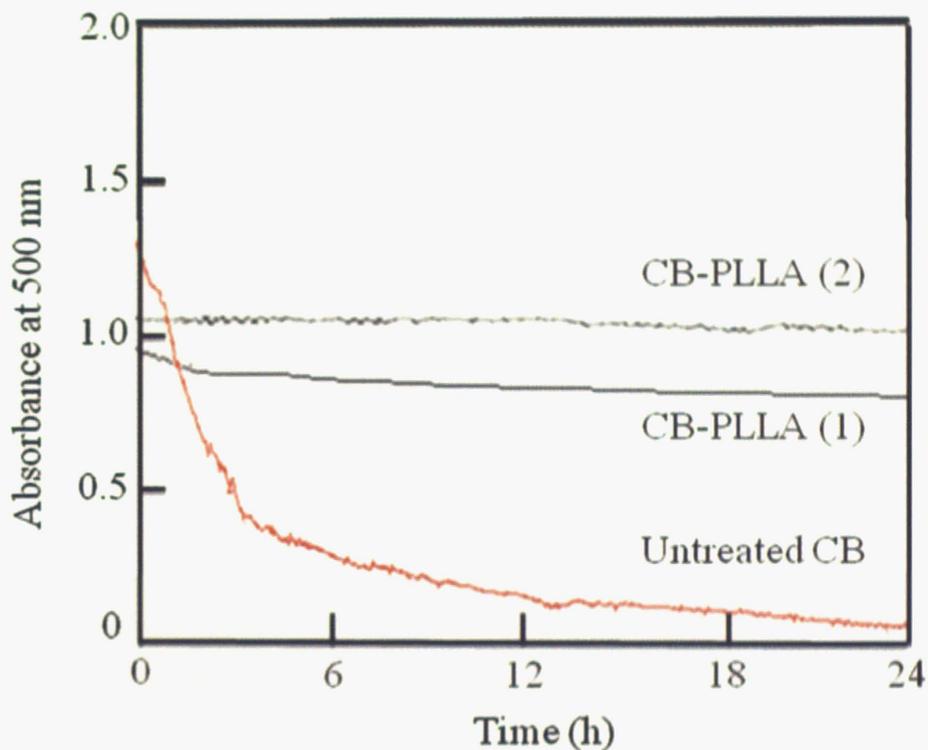
#### 4.3.9 Dispersibility of CB-PLLA

The dispersibility of untreated CB, CB-PLLA (1) and CB-PLLA (2) in various solvents was investigated. Figure 4-10 shows images of the dispersibility of untreated CB, CB-PLLA (1) and CB-PLLA (2) in 1,4-dioxane. Untreated CB was found to precipitate within 6 h. On the contrary, CB-PLLA (1) and CB-PLLA (2) gave a stable dispersion in 1,4-dioxane after 24 h.



**Figure 4-10 Images of dispersibility of untreated CB, CB-PLLA (1) and CB-PLLA (2) in 1,4-dioxane**

Figure 4-11 shows the absorption of the dispersion of untreated CB, CB-PLLA (1), and CB-PLLA (2) in 1,4-dioxane at 500 nm. The results shown in Figure 4-11 also show that the dispersibility of CB was remarkably improved by grafting of PLLA onto CB surface.



**Figure 4-11 Dispersibility of untreated CB, CB-PLLA (1) and CB-PLLA (2) in 1,4-dioxane**

The dispersibility of CB-PLLA (1) and CB-PLLA (2) in various solvents was summarized in Table 4-3. It became apparent CB-PLLA (1) and CB-PLLA (2) gave stable dispersions in polar solvents, such as DMSO, DMF, and 1,4-dioxane, which are good solvents for PLLA.

It is interesting to note that CB-PLLA (1) gave a stable dispersion in water, but not CB-PLLA (2). This may be due to the fact that the molecular weight of grafted PLLA on CB-PLLA (1) is smaller than that of CB-PLLA (2): it is known that low molecular weight

PLLA is soluble in water, but the solubility of PLLA in water gradually decreases with increasing molecular weight of PLLA [13].

**Table 4-3 The dispersibility of CB-PLLA (1) and CB-PLLA (2) in various solvents**

Permittivity	Solvent	Dispersibility after 24 h	
		CB-PLLA (1)	CB-PLLA (2)
High	Water	Good	Poor
	DMSO	Good	Good
	DMF	Good	Good
	1,4-Dioxane	Good	Good
Low	Hexane	Precipitated	Precipitated

#### 4.4 CONCLUSIONS

1. PLLA was successfully grafted onto CB surface during the polycondensation of LLA in the presence of CB. The percentage of PLLA grafting onto CB obtained in the presence of  $\text{Sc}(\text{OTf})_3$  was higher than that in the absence of  $\text{Sc}(\text{OTf})_3$ .
2. The grafting of PLLA onto CB was also achieved by the condensation reaction of hydroxyl groups of CB with carboxyl groups of PLLA and carboxyl groups of CB with hydroxyl groups of PLLA.  $\text{Sc}(\text{OTf})_3$  acts as an effective catalyst for the grafting of PLLA onto CB surface by grafting onto process and/or grafting process.
3. CB-PLLA (1) and CB-PLLA (2) gave stable dispersions in various organic solvents. The results suggest that the aggregation of CB particles was considerably destroyed and prevented by surface grafting of PLLA onto the surface.

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## **Chapter 5**

### **Grafting of poly(*L*-lactide) onto silica surface by ring-opening polymerization of *L*-lactide**

## SUMMARY

In order to improve dispersibility of silica nanoparticle in organic solvents, the grafting of poly(*L*-lactide) (PLLA) onto silica nanoparticle surface by ring-opening polymerization of *L*-lactide (LA) in the presence of silica having amino groups (Silica-NH<sub>2</sub>) was investigated in the presence of an amidine base catalyst. The ring-opening polymerization of LA successfully initiated in the presence of Silica-NH<sub>2</sub> and the amidine catalyst to give PLLA-grafted silica, but not in the presence of untreated silica (Silica-OH). In the absence of the amidine catalyst no ring-opening polymerization of LA even in the presence of Silica-NH<sub>2</sub> was initiated and no grafting of PLLA onto silica was observed. Therefore, it was concluded that the amidine catalyst acts as effective catalyst for the ring-opening graft polymerization of LA from the surface of Silica-NH<sub>2</sub>. In addition, it was found that the percentage of PLLA grafting onto silica could be controlled according to the reaction conditions. The average particle size of PLLA-grafted silica was smaller than that of Silica-NH<sub>2</sub>. Therefore, it was found that the aggregation structure of silica nanoparticle was considerably destroyed by grafting of PLLA onto the surface. The PLLA-grafted silica gave a stable dispersion in polar solvents, which are good solvents for PLLA.

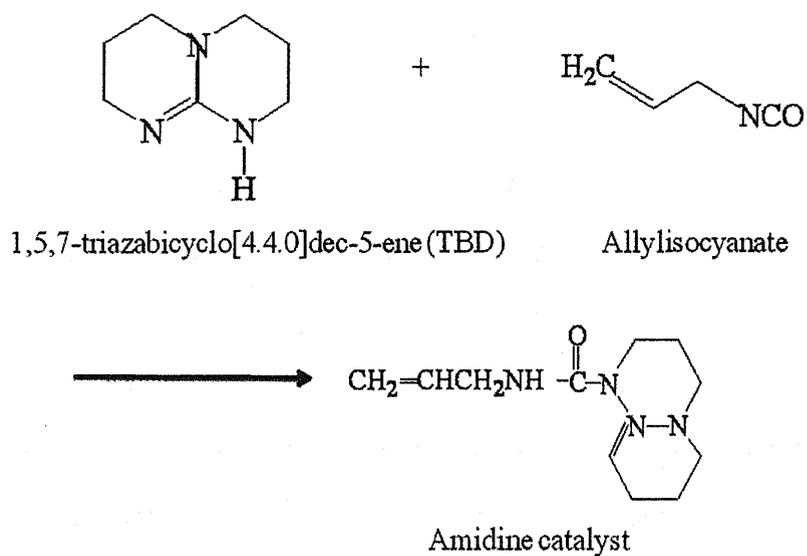
## 5.1 INTRODUCTION

In Chapter 4, the grafting of PLLA onto CB surface by the two methods ((1)grafting onto process and/or grafting onto process. (2)grafting onto process) was achieved. However, no grafting of poly(*L*-lactic acid) (PLLA) onto silica nanoparticle surface proceeded by same methods.

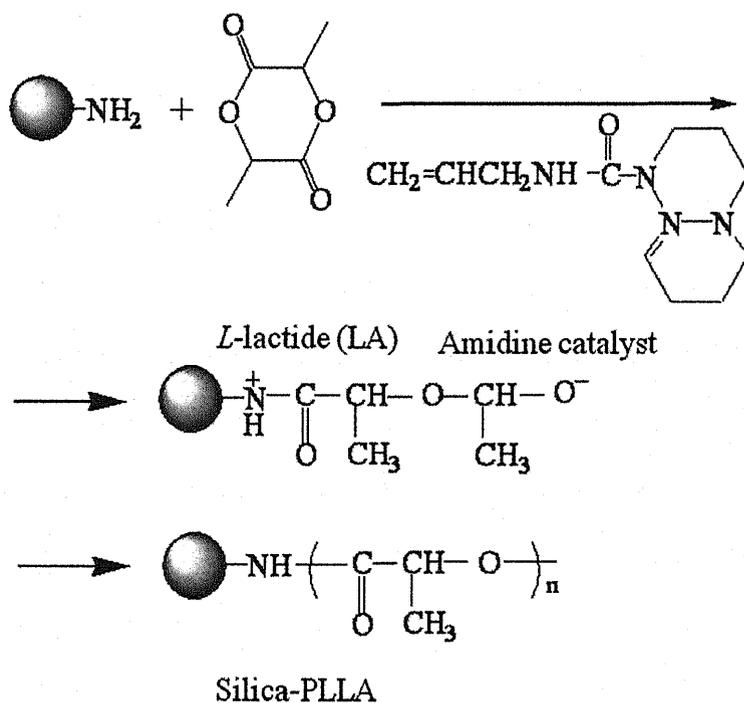
An effective method for the synthesis of PLLA is the ring-opening polymerization of lactides. Owing to the advantages of well controlled molecular weight and low polydispersity, many metal complexes have been used to initiate/catalyze ring-opening polymerization of *L*-lactide (LA) [1].

On the other hand, it has reported that ring-opening polymerization of LA in the presence of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) [2,3]. In addition, Kashio et al have reported that epoch-making reaction that succeeds in the ring-opening polymerization of LA in the presence of amidine base catalyst derived from TBD and allylisocyanate (Scheme 5-1) [4,5]. They prepared the block copolymer of PEG with PLLA by the ring-opening polymerization of LA in the presence of PEG-NH<sub>2</sub> and the amidine catalyst.

In this Chapter, in order to improve dispersibility of silica in organic solvents, the grafting of PLLA onto silica surface by the ring-opening polymerization of LA in the presence of silica having amino groups (Silica-NH<sub>2</sub>) using the amidine catalyst by grafting from process was investigated (Scheme 5-2). In addition, the dispersibility of PLLA-grafted silica in good solvents of PLLA chain was investigated.



**Scheme 5-1 Synthesis of amidine catalyst**



**Scheme 5-2 Grafting of PLLA onto silica surface by the ring-opening polymerization of LA in the presence of silica having amino groups using the amidine catalyst**

## 5.2 EXPERIMENTAL

### 5.2.1 Material and reagents

Silica nanoparticles having amino groups (Silica-NH<sub>2</sub>) were obtained from Nippon Aerosil Co., Ltd., Japan as mentioned above. The specific surface area and average particle size were 460 m<sup>2</sup>/g and 13 nm, respectively. The contents of amino groups were 0.30 mmol/g. Silica-NH<sub>2</sub> was dried *in vacuo* for 24 h at room temperature before use.

*L*-lactide (LA), obtained from Tokyo Chemical Industry Co., Ltd., Allylisocyanate and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), obtained from Aldrich, were used without further purification. The amidine catalyst was prepared by the reaction of TBD and allylisocyanate according to the method of literature [4].

### 5.2.2 Grafting of PLLA onto silica surface by ring-opening polymerization of *L*-lactide

In to a flask, 0.30 g of Silica-NH<sub>2</sub>, 0.40 g of LA, 0.15 mmol of the amidine base catalyst and 20.0 mL of THF were charged and the mixture was stirred with a magnetic stirrer at 40 °C. After the reaction, the mixture was centrifuged at 1.5×10<sup>4</sup> rpm and the supernatant solution was removed by decantation. The resulting Silica-NH<sub>2</sub> was dispersed in THF and the dispersion was centrifuged again. The procedures were repeated until no more LA and the amidine catalyst could be detected in the supernatant solution. The PLLA-grafted silica was dried *in vacuo* and stored in a desiccator. The PLLA-grafted silica was abbreviated as Silica-PLLA.

### 5.2.3. Determination of monomer conversion

When the conversion of PLLA was determined, the reaction mixture was poured into large excess of acetone and the precipitate was filtered. The conversion of PLLA was determined by the following equation:

$$\text{Conversion (\%)} = (A-B/C) \times 100,$$

where A is weight of precipitate (product) obtained, B is weight of silica charged, and C is weight of LA used.

### 5.2.4. Determination of percentage of grafting

The percentage of PLLA grafting onto Silica-NH<sub>2</sub> was determined by the following equation:

$$\text{Grafting (\%)} = (D / E) \times 100,$$

where D is weight of PLLA grafted and E is weight of Silica-NH<sub>2</sub> charged. The weight of PLLA grafted onto the surface was determined by weight loss when Silica-PLLA was heated at 800 °C by using of a thermogravimetric analyzer (TGA) (Shimadzu TGA-50).

### 5.2.5. Determination of grafting efficiency

The grafting efficiency was determined by the following equation:

$$\text{Grafting efficiency (\%)} = (F / G) \times 100,$$

where F is weight of PLLA grafted and G is weight of total PLLA formed.

### **5.2.6. Characterization of Silica-PLLA**

Infrared spectra were recorded on a FT-IR spectrophotometer (Shimadzu Manufacturing Co., Ltd. FTIR-8400S).

The molecular weight and molecular weight distribution of ungrafted PLLA formed during the ring-opening polymerization of LA in the presence of Silica-NH<sub>2</sub> using the amidine catalyst were estimated by SEC using polystyrene standards. For SEC, a Tosoh CCPD instrument (column: TSK-GEL G2000HHR) was used.

Particle size distribution of Silica-PLLA was measured by use of a nanoparticle size analyzer (Shimadzu Manufacturing Co., Ltd., SALD-7100).

### **5.2.7. Dispersibility of Silica-PLLA**

Silica-PLLA (2.0 mg) was dispersed in 5.0 mL of various solvents under ultrasonic wave irradiation for 10 min and allowed to stand at room temperature. In addition, to estimate dispersibility of Silica-PLLA, 1.0 mg of Silica-PLLA was dispersed in 10 mL of solvent, and decrease of absorbance of the dispersion at 500 nm was recorded by use of UV-vis spectrometer (Shimadzu Manufacturing Co., Ltd., UV-1600).

## 5.3 RESULT AND DISCUSSION

### 5.3.1 Ring-opening polymerization of *L*-lactide onto Silica-NH<sub>2</sub> surface

The surface grafting of PLLA onto silica nanoparticle was carried out by surface initiated ring-opening polymerization of LA in the presence of Silica-NH<sub>2</sub> using the amidine base catalyst by grafting from process. These results were summarized in Table 5-1. As shown in Table 5-1, the ring opening-polymerization of LA was successfully initiated in the presence of Silica-NH<sub>2</sub> and amidine base catalyst to give PLLA-grafted silica, but not in the presence of Silica-OH; conversion in the presence of Silica-NH<sub>2</sub> was found to be 37.8 %. On the other hand, conversion in the presence of Silica-OH was not proceeded. The grafting efficiency of PLLA onto Silica-NH<sub>2</sub> was found to be 42.3 %. These results indicate that amino groups on silica surface play an important role on the initiation of the ring-opening polymerization of LA and grafting of PLLA onto silica surface.

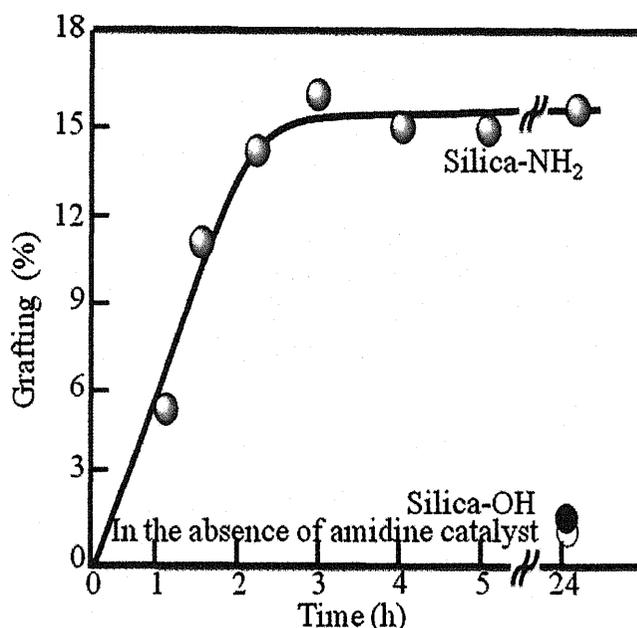
It has been reported that the amidine base catalyst acts as effective catalyst in the co-existence of compounds containing amino groups, such as amino group terminated poly(ethylene glycol) [5]. Therefore, it was found that the amidine base catalyst also acts as effective catalyst of the grafting of PLLA onto silica by the ring-opening polymerization of LA from Silica-NH<sub>2</sub> surface.

**Table 5-1 Ring-opening polymerization of *L*-lactide onto Silica-NH<sub>2</sub> surface**

Silica	Amidine catalyst	Time (h)	Conversion(%)	Grafting (%)	Grafting efficiency(%)
Silica-OH	×	24	trace	trace	-
	○	24	trace	trace	-
Silica-NH <sub>2</sub>	×	24	trace	trace	-
	○	24	37.5	15.5	42.3

Figure 5-1 shows the relationship between reaction time and the percentage of grafting of PLLA onto Silica-NH<sub>2</sub> surface in the presence and absence of the amidine base catalyst. As mentioned above, in the absence of the amidine base catalyst, the ring-opening polymerization reaction of LA was scarcely initiated. On the other hand, in the presence of the amidine base catalyst, the ring-opening polymerization of LA was successfully initiated in the presence of the amidine base catalyst to give Silica-PLLA.

In the presence of the amidine base catalyst and Silica-NH<sub>2</sub>, the percentage of grafting onto silica increased with increasing reaction time, and no longer increased after 3 h. This may be due to the fact that amino groups on silica surface blocked by grafted PLLA chain on the surface with progress of the grafting. In Chapter 4, the grafting of PLLA onto carbon black surface by the condensation of poly(lactic acid) (PLLA) using Sc(OTf)<sub>3</sub> as catalyst. The percentage of PLLA grafting onto silica by the ring-opening polymerization of LA in the presence of the amidine catalyst was slightly higher than that by condensation of PLLA.



**Figure 5-1** The relationship between reaction time and the percentage of grafting of PLLA onto Silica-NH<sub>2</sub> surface in the presence and absence of the amidine catalyst

Silica-NH<sub>2</sub>, 0.30 g; amidine catalyst, 0.15 mmol; LA, 2.70 mmol; THF, 20.0 mL; 40 °C.

### 5.3.2 Confirmation of PLLA grafting onto silica surface by ATR-FTIR

The grafting of PLLA onto silica surface was confirmed by ATR-FTIR. Figure 5-2 shows ATR-FTIR spectra of Silica-PLLA, Silica-NH<sub>2</sub> and PLLA. It was found that ATR-FTIR spectra of Silica-PLLA show absorption characteristic of ester bond of PLLA at 1759 cm<sup>-1</sup>. In addition, shoulder absorption at 1650 cm<sup>-1</sup> suggests amide bond, by which PLLA is grafted onto silica surface, was observed. These results show clearly the grafting of PLLA onto silica surface.

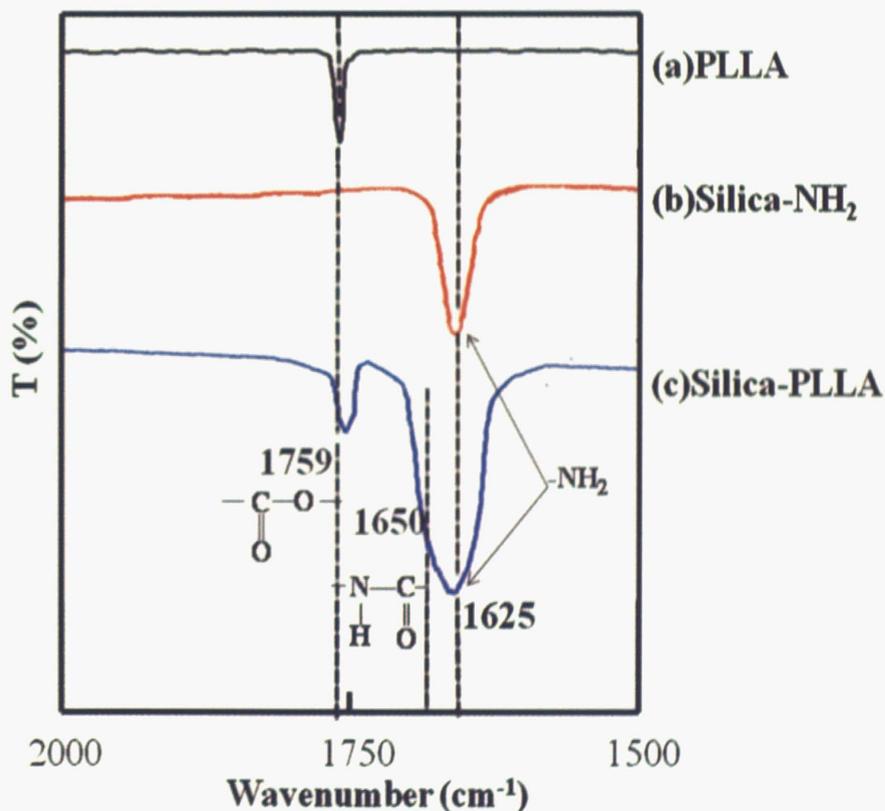
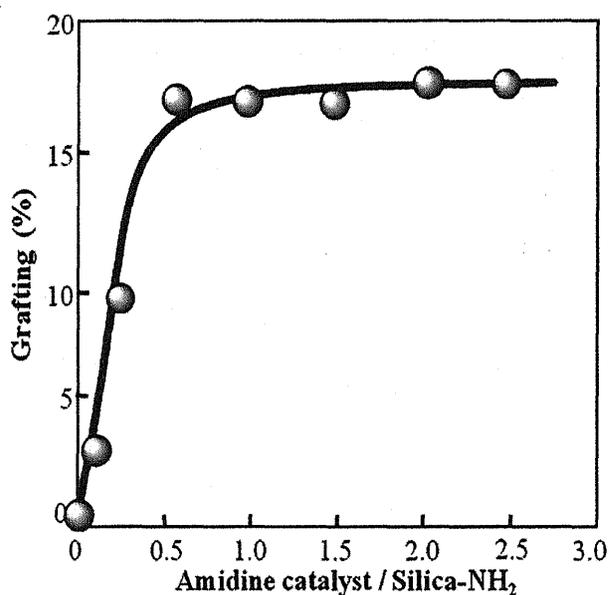


Figure 5-2 ATR-FTIR spectra of Silica-PLLA, Silica-NH<sub>2</sub> and PLLA

### 5.3.3 Effect of the amount of amidine catalyst on the grafting reaction

Figure 5-3 shows the effect of the amount of the amidine catalyst on the grafting of the PLLA onto silica surface by the ring-opening polymerization of LA in the presence of Silica-NH<sub>2</sub>. The percentage of grafting increased with increasing the amount of the amidine base catalyst. But the percentage of grafting was no longer increased above 0.15 mmol of the amidine catalyst. The mole ratio of the amidine catalyst to amino groups on silica exceeded about 1.0.



**Figure 5-3 Effect of the amount of the amidine catalyst on the grafting of the PLLA onto silica surface**  
Silica-NH<sub>2</sub>, 0.30 g; amidine catalyst, LA, 2.70 mmol; THF, 20.0 mL; 40 °C; 24 h.

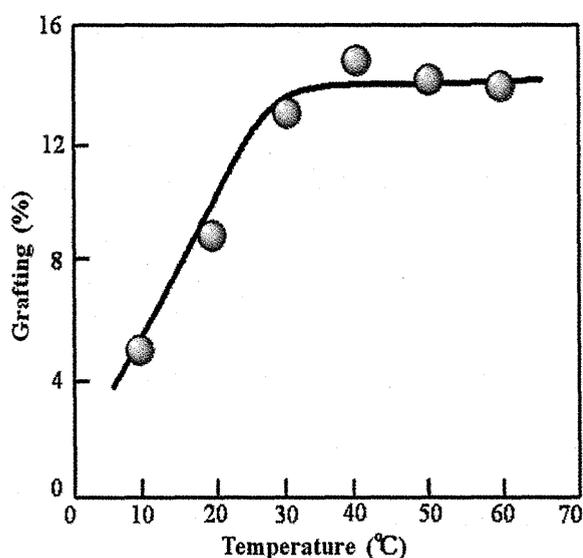
The effect of the amount of amino groups on the grafting efficiency was investigated. The grafting efficiency of PLLA onto silica surface was summarized in Table 5-2. The grafting efficiency of PLLA onto silica surface was high. It was found that no effect of the amount of amidine base catalyst on the grafting efficiency of PLLA was scarcely observed.

**Table 5-2 The grafting efficiency of PLLA onto silica surface**

Amidine catalyst / -NH <sub>2</sub>	Time (h)	Grafting (%)	Grafting efficiency (%)
0.3	24	7.7	38.9
0.5	24	15.0	39.5
1.0	24	15.5	42.3
1.5	24	14.8	38.9

### 5.3.4 Effect of the reaction temperature of the grafting of PLLA onto silica surface

Figure 5-4 shows the effect of temperature on the grafting of PLLA onto silica by the ring opening polymerization of LA in the presence of Silica-NH<sub>2</sub> and the amidine base catalyst. As shown in Figure 5-4, it became apparent that PLLA grafting was scarcely affected by the polymerization temperature above 30 °C, but decreased below 30 °C. The same tendency was reported in the ring-opening polymerization of LA in the presence of amino compounds and the amidine base catalyst [5].



**Figure 5-4 Effect of the reaction temperature of the grafting of PLLA onto silica surface**

Silica-NH<sub>2</sub>, 0.30 g; amidine catalyst, 0.15 mmol; LA, 2.70 mmol; THF, 20.0 mL; 24 h.

### 5.3.5 Molecular weight of PLLA

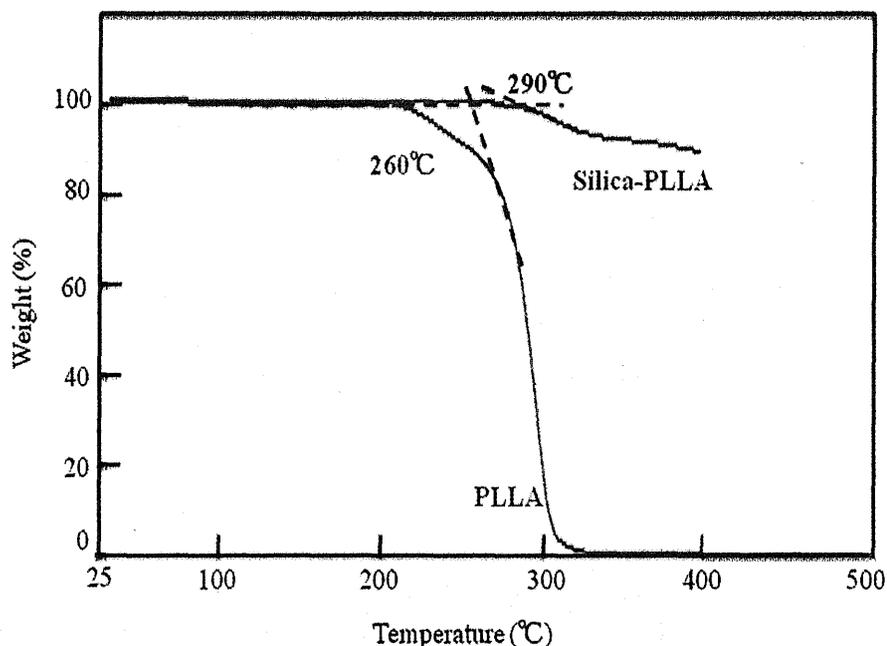
It is known that molecular weight of grafted polymer on nanoparticle surface is almost equal to that of ungrafted polymer during the graft polymerization initiated by surface initiating groups [6]. Therefore, the molecular weight of grafted PLLA chain on the silica surface was estimated from the molecular weight of ungrafted PLLA formed during the ring-opening polymerization of LA in the presence of Silica-NH<sub>2</sub> and the amidine catalyst. The results are shown in Table 5-3. The number average molecular weight (*M<sub>n</sub>*) of ungrafted PLLA was estimated to be 5940 by GPC. This indicates that the degree of the polymerization of PLLA is about 40. The value was much larger than the formed by the polycondensation of LLA in Chapter 4.

**Table 5-3 Molecular weight of PLLA**

LA and PLLA	<i>M<sub>n</sub></i>	<i>M<sub>n</sub> / M<sub>w</sub></i>
<i>L</i> -lactide	144	
Poly( <i>L</i> -lactide)	5940	1.14

### 5.3.6 Thermal stability of grafted PLLA on silica surface PLLA

Figure 5-5 shows TGA curves of Silica-PLLA and PLLA. As shown in Figure 5-5, thermal decomposition temperature of Silica-PLLA and PLLA was found to be 290 °C and 260 °C, respectively. Therefore, it was found that the heat resistance of PLLA considerably increased by the grafting onto silica surface. The same tendency was observed for PLLA-grafted carbon black obtained during the condensation of PLLA in Chapter 4. This may be due to the fact that terminal groups of PLLA was immobilized onto the silica surface by amide bonds.



**Figure 5-5 Thermal stability of grafted PLLA on silica surface and ungrafted PLLA**

### 5.3.7 Average particle size of Silica-PLLA

Figure 5-6 shows the particle size distribution of Silica-NH<sub>2</sub> and Silica-PLLA. The particle distribution was determined after the dispersing in 1,4-dioxane under ultrasonic wave irradiation for 10 min. As shown in Figure 5-6, the particle size distribution of Silica-PLLA was considerably smaller than that of Silica-NH<sub>2</sub>: the average particle size distribution of Silica-NH<sub>2</sub> and Silica-PLLA was found to be 20-150 μm and 0.1-1.5 μm, respectively. The average particle size of Silica-NH<sub>2</sub> and Silica-PLLA was summarized in Table 5-4. Based on the results of Table 5-4, it was concluded that the aggregation of silica particles was considerably destroyed and prevented by grafting of PLLA onto the surface.

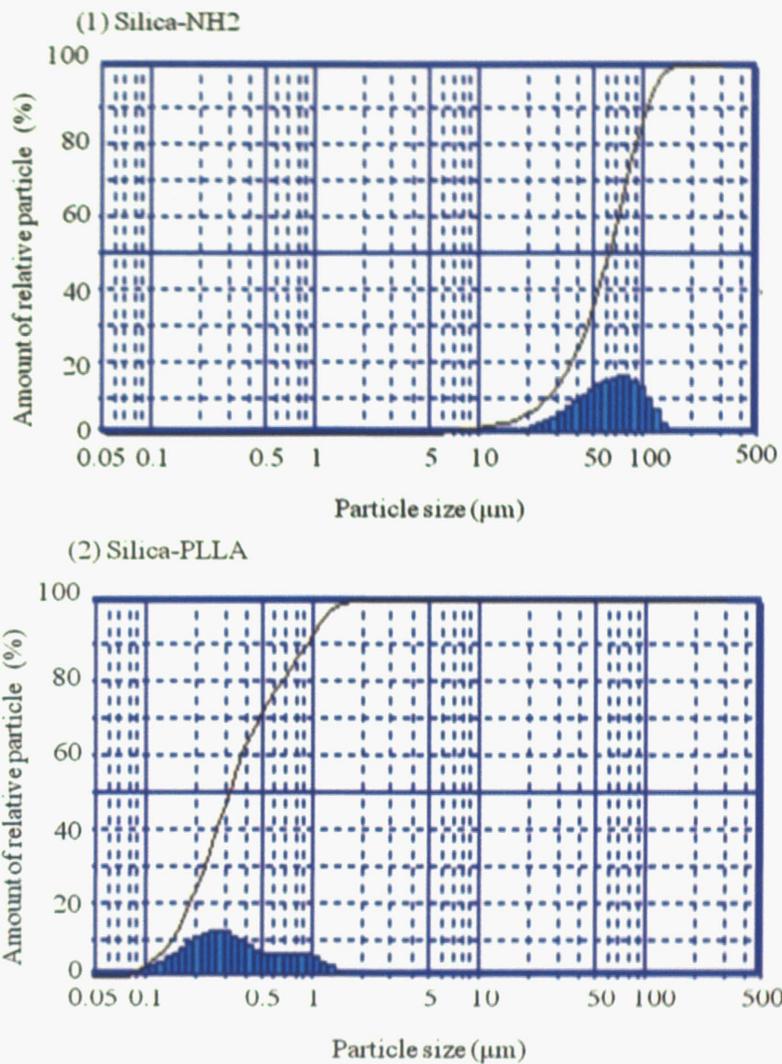


Figure 5-6 Particle size distribution of Silica-NH<sub>2</sub> and Silica-PLLA in 1,4-dioxane

Table 5-4 The average particle size of untreated silica and Silica-PLLA in 1,4-dioxane

Silica	The average particle size (μm)
Silica-NH <sub>2</sub>	55.4
Silica-PLLA	0.39

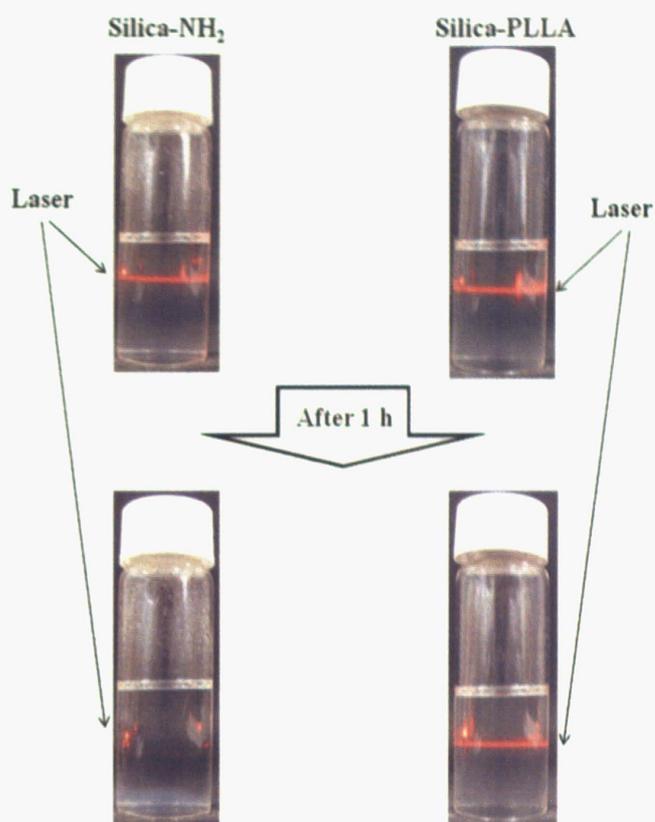
### 5.3.8 Dispersibility of Silica-PLLA

The dispersibility of Silica-NH<sub>2</sub> and Silica-PLLA in various solvents was investigated. Figure 5-7 shows images of the dispersibility of Silica-NH<sub>2</sub> and Silica-PLLA in 1,4-dioxane. The dispersibility of silica particle in 1,4-dioxane was confirmed by the observation of a laser beam through the dispersions. As shown in Figure 5-7, a path of laser light through the dispersion of Silica-PLLA and Silica-NH<sub>2</sub> in 1,4-dioxane was observed immediately after the ultrasonic irradiation: this is based on the light scattering caused by particles in solvent, which shows that particles disperse in solvent.

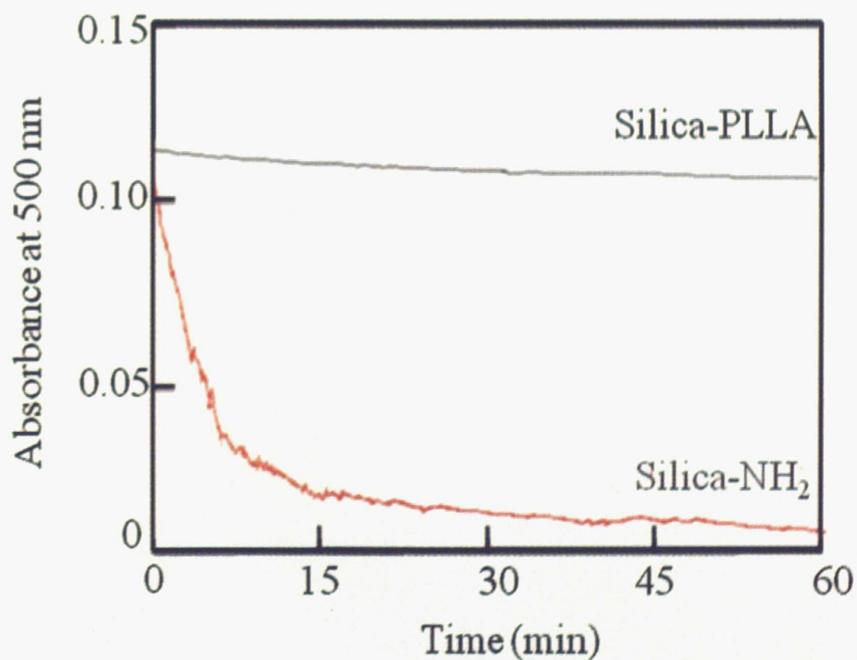
On the contrary, after 1 h standing at room temperature, the pass of laser light through the dispersion of Silica-NH<sub>2</sub> was not observed, but that of Silica-PLLA was clearly observed. These results show that Silica-PLLA gave a stable dispersion in 1,4-dioxane over 1 h, but Silica-NH<sub>2</sub> precipitated.

Figure 5-8 shows the absorption change of the dispersion of Silica-NH<sub>2</sub> and Silica-PLLA in 1,4-dioxane at 500 nm during the standing at room temperature. Figure 5-8 also shows that the dispersibility of silica was remarkably improved by grating of PLLA onto the surface.

The dispersibility of Silica-PLLA in various solvents was summarized in Table 5-5. It became apparent Silica-PLLA gave stable dispersions in polar solvents, such as DMSO, DMF, and 1,4-dioxane, which are good solvents for PLLA.



**Figure 5-7 Images of the dispersibility of untreated silica and Silica-PLLA in 1,4-dioxane**



**Figure 5-8 The absorption of the dispersion of untreated silica and Silica-PLLA in 1,4-dioxane**

**Table 5-5 The dispersibility of Silica-PLLA in various solvents**

Permittivity	Solvents	Dispersibility after 1 h Silica-PLLA
High	Water	Poor
	DMSO	Good
	DMF	Good
	1,4-Dioxane	Good
Low	Hexane	Precipitated

## 5.4 CONCLUSIONS

1. The ring-opening polymerization of LA was successfully initiated from Silica-NH<sub>2</sub> in the presence of amidine base catalyst to give PLLA-grafted silica. On the contrary, no grafting of PLLA onto silica surface in the presence of untreated silica having no amino groups (Silica-OH) even in the presence of the amidine base catalyst proceeded.
2. The heat resistance of PLLA considerably increased by grafting of PLLA onto silica nanoparticle surface.
3. The average particle size of PLLA-grafted silica nanoparticle in 1,4-dioxane was much smaller than that of ungrafted silica (Silica-NH<sub>2</sub>).
4. Silica-PLLA gave stable dispersions in various organic solvents, such as DMSO, DMF, and 1,4-dioxane, which are good solvents for PLLA. The results suggest that the aggregation of silica nanoparticles was considerably destroyed by surface grafting of PLLA onto the surface.

## 5.5 REFERENCES

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## **Chapter 6**

### **CONCLUDING REMARKS**

In general, dispersing nanoparticles, such as silica and carbon black, uniformly into a polymer or organic solvent is difficult because of aggregation of the nanoparticles. The mechanical properties of nanocomposite with these nanoparticles are considered to depend not only on the mechanical properties of the polymer matrix, but also properties of interfacial regions between surface of nanoparticles and matrix polymer.

In this thesis, the surface modification nanoparticles is summarized. Modification of nanoparticles surfaces will become more and more important for the design of high performance composite materials. Surface-modified nanoparticle by grafting of polymers have a large potential as high performance nano-composites.

On the other hand, environmental problems attract attention. This problem is what should be paid attention for the field of chemistry.

In this thesis, the surface grafting of several polymers onto nanoparticles by using an environment-friendly catalyst was investigated to improve dispersibility of silica nanoparticles and CB in organic solvents.

The results and conclusions are as follows.

(1) The grafting of the PEG onto CB surface was achieved by the reaction of hydroxyl groups of the polymer with carboxyl groups on CB in the presence of rare-earth triflates by grafting on to process. When the ratio of rare-earth triflate to phenolic hydroxyl groups and carboxyl groups on CB exceeded about 1.0, PEG-grafted CB with the highest grafting was obtained. It was found that the percentage of grafting decreased with increasing the molecular weight of PEG. And, the number of grafted PEG chains decreased with increasing the molecular weight of PEG. CB-PEG gave stable dispersions in methanol. The result suggests that the aggregation of CB particles was considerably destroyed and prevented by surface grafting of PEG onto surface.

After the reaction,  $\text{Sc}(\text{OTf})_3$  was readily recovered by reprecipitation and successive

extraction with water. The recovered  $\text{Sc}(\text{OTf})_3$  was found to be reusable as the grafting catalyst. (Chapter 2)

(2) The grafting of the liquid rubbers onto a silica nanoparticle and CB surface by grafting onto process was achieved by the reaction of carboxyl groups of the polymer with amino groups on silica and phenolic hydroxyl groups on CB using  $\text{Sc}(\text{OTf})_3$  as catalyst. After the reaction,  $\text{Sc}(\text{OTf})_3$  was readily recovered by reprecipitation and successive extraction with water. The recovered  $\text{Sc}(\text{OTf})_3$  was found to be reusable as the grafting catalyst. In addition, the crosslinking reaction of the liquid rubber by amino groups on silica and phenolic hydroxyl groups on CB in the presence of  $\text{Sc}(\text{OTf})_3$  successfully proceeded to give brittle gels, in which silica and CB were uniformly incorporated in the gel matrices. (Chapter 3)

(3) PLLA was successfully grafted onto CB surface during the polycondensation of LLA in the presence of CB (CB-PLLA (1)) (grafting onto process and/or grafting from process). The percentage of PLLA grafting onto CB obtained in the presence of  $\text{Sc}(\text{OTf})_3$  was higher than that in the absence of  $\text{Sc}(\text{OTf})_3$ . The grafting of PLLA onto CB was also achieved by the condensation reaction of hydroxyl groups of CB with carboxyl groups of PLLA and carboxyl groups of CB with hydroxyl groups of PLLA (CB-PLLA (2)) (grafting onto process).  $\text{Sc}(\text{OTf})_3$  acts as an effective catalyst for the grafting of PLLA onto CB surface. It was found that CB-PLLA (1) and CB-PLLA (2) gave stable dispersions in various organic solvents. The results suggest that the aggregation of CB particles was considerably destroyed by surface grafting of PLLA onto the surface. (Chapter 4)

(4) The ring-opening polymerization of LA was successfully initiated from Silica- $\text{NH}_2$  in the presence of amidine base catalyst to give PLLA-grafted silica. On the contrary, no grafting of PLLA onto silica surface in the presence of untreated silica having no amino groups

(Silica-OH) even in the presence of the amidine base catalyst proceeded. The heat resistance of PLLA considerably increased by grafting of PLLA onto silica nanoparticle surface. The average particle size of PLLA-grafted silica nanoparticle in 1,4-dioxane was much smaller than that of ungrafted silica (Silica-NH<sub>2</sub>). Silica-PLLA gave stable dispersions in various organic solvents, such as DMSO, DMF, and 1,4-dioxane, which are good solvents for PLLA. The results suggest that the aggregation of silica nanoparticles was considerably destroyed by surface grafting of PLLA onto the surface. (Chapter 5)

Based on the experimental results, the methodologies can be decrease organic waste was for the preparation of polymer-grafted nanoparticles. This method is environment-friendly. Industrial applications of polymer-grafted nanoparticles may likely be expanded in the future. For example, the PEG-grafted CB may be able to use as novel sensor materials. The liquid rubber-grafted silica (CB) can be used as new rubber materials. The PLLA-grafted silica (CB) can be used as filler of PLLA materials. I hope that polymer-grafted nanoparticles can be used industrially in the future.

## List of Publications

(1) M. Takamura, T. Yamauchi and N. Tsubokawa, Grafting and crosslinking reaction of carboxyl-terminated liquid rubber with silica nanoparticle and carbon black in the presence of  $\text{Sc}(\text{OTf})_3$ , *React. Funct. Polym.*, **68**, 1113 (2008).

(Chapter 3)

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(Chapter 4)

(3) M. Takamura, T. Yamauchi and N. Tsubokawa, Grafting reaction of poly(ethylene glycol) with carbon black using rare-earth triflates as catalyst, in prepared.

(Chapter 2)

(4) M. Takamura, T. Yamauchi and N. Tsubokawa, Grafting of poly(*L*-lactide) onto silica surface by ring-opening polymerization *L*-lactide, in prepared.

(Chapter 5)

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Masaaki Takamura

Doctoral Program in Advanced Materials Science and Technology,  
Graduate School of Science and Technology,  
Niigata University,  
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