

Preparation and Dispersibility of Poly(L-lactide)-Grafted Silica Nanoparticle

Masaaki Takamura,¹ Takeshi Yamauchi,^{1,2} Norio Tsubokawa^{1,2}

¹Graduate School of Science and Technology, Niigata University, 8050, Ikarashi 2-nocho, Nishi-ku Niigata 950-2181, Japan

²Center for Transdisciplinary Research, Niigata University, 8050, Ikarashi 2-nocho, Nishi-ku Niigata 950-2181, Japan

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ABSTRACT: 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) was investigated in the presence of an amidine base catalyst. The ring-opening polymerization of LA successfully initiated in the presence of silica having amino groups (silica-NH₂) and an amidine base catalyst to give PLLA-grafted silica, but not in the presence of untreated silica (silica-OH). In the absence of the amidine base catalyst no ring-opening polymerization of LA even in the presence of silica-NH₂ and no grafting of PLLA onto silica were observed. It became apparent that the amidine base catalyst acts as an effective catalyst for the ring-opening graft poly-

merization of LA from the surface of silica-NH₂. 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-NH₂. Therefore, it was considered that the aggregation structure of silica nanoparticles 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. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 3854–3860, 2012

Key words: silicas; nanoparticle; ring-opening polymerization; L-lactide; surface grafting

INTRODUCTION

The grafting of polymers onto the surface of inorganic nanoparticles, such as silica, carbon black (CB), and ferrite, is effective to improve the dispersibility in solvents and polymer matrices, because the grafted polymer chains on the surface interfere with the aggregation of these nanoparticles and increase the affinity of the surface for solvents and polymer matrices.^{1–4} We have reported the grafting of various polymers onto silica nanoparticle and CB surface by the anionic, cationic, and radical polymerization of vinyl monomers initiated by potassium carboxylate,^{5,6} acylium perchlorate,^{7,8} and peroxyester^{9,10} or azo groups,^{11,12} respectively, previously introduced onto these surfaces.

Recently, attention is very attracted in the field of the biomaterial. For example, L-lactide (LA) or poly(L-lactide) (PLLA) has attracted much attention because it is biodegradable, compostable, producible from renewable resources, and nontoxic to the human body and the environment.^{13–20} PLLA is one of the most important synthetic biodegradable and

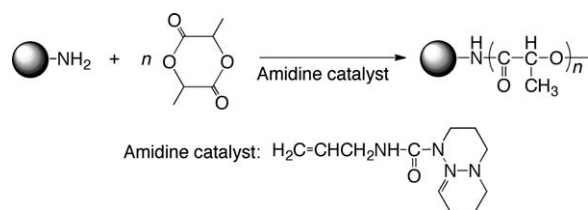
biocompatible polymer investigated for a wide range of biomedical and pharmaceutical applications such as controlled drug delivery, resorbable sutures, medical implants, and scaffolds for tissue engineering.²¹ An effective method for the synthesis of PLLA is the ring-opening polymerization of LA. Owing to the advantages of well-controlled molecular weight and low polydispersity, many metal complexes have been used to initiate/catalyze ring-opening polymerization of LA.²²

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) as catalyst.^{23,24} In addition, Kashio et al. have reported that epoch-making reaction that succeeds in the preparation of PLLA-grafted polysilsesquioxane by ring-opening polymerization of LA in the presence of polysilsesquioxane having amino groups and an amidine base catalyst, which was derived from TBD and allylisocyanate.^{25,26}

In the preceding article, we have successfully achieved the grafting of PLLA onto CB surface by the two methods: (1) polycondensation of L-lactic acid in the presence of CB and (2) grafting reaction of PLLA with CB surface in the presence of Sc(OTf)₃ as catalyst.²⁷

In this article, to improve dispersibility of silica nanoparticles in organic solvents by grafting of biodegradable polymer, the grafting of PLLA onto silica

Correspondence to: N. Tsubokawa (ntsuboka@eng.niigata-u.ac.jp).



Scheme 1 Grafting of PLLA onto silica-NH₂ surface by surface initiated ring-opening polymerization of LA in the presence of amidine base catalyst.

nanoparticle surface by the ring-opening polymerization of LA was investigated in the presence of silica having amino groups using the amidine base catalyst (Scheme 1). In addition, the dispersibility of PLLA-grafted silica in good solvents for PLLA will be discussed.

EXPERIMENTAL

Material and reagents

Silica nanoparticle having amino groups (silica-NH₂) was obtained from Nippon Aerosil, Japan. The specific surface area and average particle size were 460 m² g⁻¹ and 13 nm, respectively. The contents of amino groups were determined to be 0.30 mmol g⁻¹ by titration.²⁸ Silica-NH₂ was dried *in vacuo* for 24 h at room temperature before use. Allylisocyanate (obtained from Aldrich), L-lactide (LA) (obtained from Tokyo Chemical Industry), and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) (obtained from Aldrich) were used without further purification. Amidine base catalyst was prepared by the reaction of TBD with allylisocyanate according to the method of literature.^{25,26}

Grafting of PLLA onto silica surface by surface initiated ring-opening polymerization of LA

In to a flask, 0.30 g of silica-NH₂, 2.70 mmol 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 1.5×10^4 rpm and the supernatant solution was removed by decantation. The resulting silica-NH₂ was dispersed in THF and the dispersion was centrifuged again. The procedures were repeated until no more LA and the amidine base 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.

Determination of conversion of ring-opening polymerization

The conversion of PLLA in the ring-opening polymerization was determined as follows: the reaction

mixture was poured into a large excess of acetone and the precipitate was filtered, washed with acetone, and dried *in vacuo* at 60°C. The conversion of PLLA was determined by the following equation:

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

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

Determination of percentage of grafting and grafting efficiency

The percentage of PLLA grafting onto silica-NH₂ (wt % of PLLA grafted onto silica nanoparticle) was determined by the following equation:

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

where *D* is weight of PLLA grafted onto silica and *E* is weight of silica-NH₂ charged. The weight of PLLA grafted onto silica surface was determined by weight loss when silica-PLLA was heated at 800°C by use of a thermogravimetric analyzer (TGA) (Shimadzu TGA-50).

The grafting efficiency (wt % of grafted polymer to total polymer formed) was determined by the following equation:

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

where *D* is weight of PLLA grafted onto silica as mentioned above and *F* is weight of total PLLA (*A*-*B*) formed.

Characterization of silica-PLLA

Infrared spectra were recorded on a FT-IR spectrophotometer (Shimadzu Manufacturing, FTIR-8400S). The molecular weight and molecular weight distribution of PLLA formed by the ring-opening polymerization of LA in the presence of silica-NH₂ using the amidine base catalyst was estimated by SEC using polystyrene standards. For SEC, a Tosoh CCPD instrument (column: TSK-GEL G2000HHR) was used. Particle size distribution of silica-PLLA in solvents was measured by use of a nanoparticle size analyzer (Shimadzu Manufacturing, SALD-7100).

Dispersibility of silica-PLLA in solvents

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

TABLE I
Grafting Efficiency and Conversion in the Surface Initiated Ring-Opening Polymerization of LA in the Presence of Silica-NH₂ and Amidine Base Catalyst

Silica	Amidine catalyst	Conversion (%)	Grafting (%)	Grafting efficiency (%)
Silica-OH	×	trace	trace	–
	○	3.75	1.45	–
Silica-NH ₂	×	trace	trace	–
	○	37.8	15.5	42.3

Silica-NH₂ (Silica-OH), 0.30 g; amidine base catalyst, 0.15 mmol; LA, 2.70 mmol; THF, 20.0 mL; 40°C; 24 h.

solvent, and decrease of absorbance of the dispersion at 500 nm was recorded by use of UV-vis spectrometer (Shimadzu Manufacturing, UV-1600).

RESULTS AND DISCUSSION

Surface initiated ring-opening polymerization of LA onto silica-NH₂

The surface grafting of PLLA onto silica nanoparticle was carried out by the ring-opening polymerization of LA in the presence of silica-NH₂ using the amidine base catalyst, which was derived by the reaction of TBD with allylisocyanate.^{25,26} The results were summarized in Table I. As shown in Table I, the ring opening-polymerization of LA was successfully initiated in the presence of silica-NH₂ and amidine base catalyst to give PLLA-grafted silica (silica-PLLA), but not in the presence of untreated silica (silica-OH); conversion in the presence of silica-NH₂ and silica-OH was determined to be 37.8 and 3.75%, respectively.

It is reported that amidine base catalyst acts as effective catalyst for the ring-opening polymerization of cyclic esters, such as LA and ϵ -caprolactone, in the presence of amines and alcohols, but not silanols.^{23,24} Therefore, it is considered that the ring-opening polymerization of LA was hardly initiated in the presence of silica-OH even in the presence of amidine base catalyst.

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 coexistence of compounds containing amino groups, such as amino group on polysilsesquioxane.²⁵ Therefore, it was found that the amidine base catalyst also acts as effective catalyst of the grafting of PLLA onto silica by the surface initiated ring-opening polymerization of LA from silica-NH₂.

On the other hand, grafting efficiency of PLLA onto silica-NH₂ was found to be 42.3%. This indi-

cates that about half of PLLA formed in the polymerization was grafted onto silica surface. The value of the grafting efficiency was much higher than that in the surface initiated radical polymerization of vinyl monomers.^{9–12}

Figure 1 shows the relationship between reaction time and the percentage of grafting of PLLA onto silica-OH and silica-NH₂ surface by the ring-opening polymerization in the presence of the amidine base catalyst. In the presence of the amidine base catalyst and silica-NH₂, 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 were blocked by grafted PLLA chain on the surface with progress of the grafting. It was found that the percentage of PLLA grafting onto silica surface could be controlled by the polymerization time.

On the other hand, in the presence of silica-OH, the grafting of PLLA onto the surface was negligibly small, because the ring-opening polymerization scarcely initiated even in the presence of the amidine base catalyst.

Confirmation of PLLA grafting onto silica surface by FTIR

The grafting of PLLA onto silica surface was confirmed by FTIR. Figure 2 shows ATR-FTIR spectra of silica-PLLA, silica-NH₂, and PLLA. It was found that FTIR spectra of silica-PLLA show absorption characteristic of ester bond of PLLA at 1759 cm⁻¹. In addition, shoulder absorption at 1650 cm⁻¹ suggests amide bond, by which PLLA is grafted onto silica surface, was also observed. These results show clearly the grafting of PLLA onto silica surface.

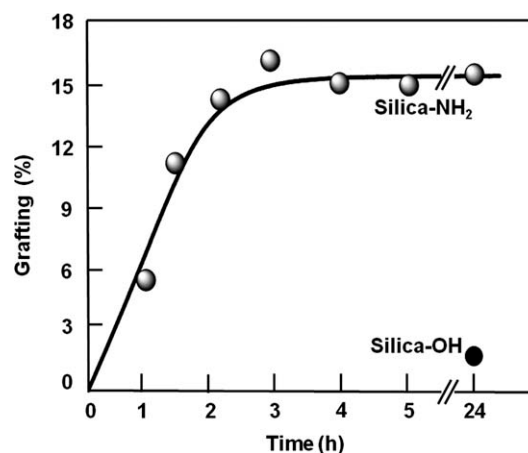


Figure 1 Grafting of LA onto silica surface in the ring-opening polymerization of LA in the presence of silica-NH₂ and silica-OH by use of the amidine base catalyst. silica-NH₂ (silica-OH), 0.30 g; amidine base catalyst, 0.15 mmol; LA, 2.70 mmol; THF, 20.0 mL; 40°C.

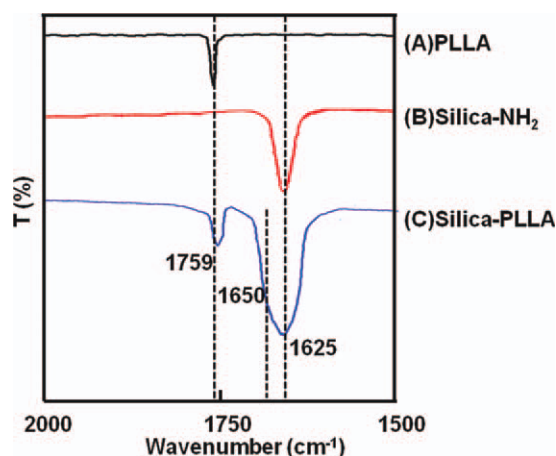


Figure 2 FT-IR spectra of (A) PLLA, (B) silica-NH₂, and (C) silica-PLLA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Effect of the amount of amidine base catalyst on the grafting of PLLA onto silica surface

Figure 3 shows the effect of the amount of the amidine base catalyst on the grafting of the PLLA onto silica surface by the ring-opening polymerization of LA in the presence of silica-NH₂ when the amount of silica-NH₂ was fixed. The percentage of grafting increased with increasing the amount of the amidine base catalyst, but no longer increased when the mole ratio of the amidine base catalyst to amino groups on silica exceeded about 1.0. The same tendency was reported in the ring-opening polymerization of LA initiated by amidine base catalyst with amino group of polysilsesquioxane.²⁵

During the polymerization, the formation of ungrafted PLLA was observed. The grafting efficiency [percentage of grafted PLLA to total polymer (ungrafted and grafted PLLA) produced] was about 40%, in spite of the amount of amidine base catalyst and surface amino groups, as also shown in Figure 3. The formation of ungrafted PLLA may be due to the fact that moisture adsorbed on silica-NH₂, which was hardly remove completely from the surface.

Effect of the reaction temperature on the grafting of PLLA onto silica surface

Figure 4 shows the effect of temperature on the grafting of PLLA onto silica by the surface initiated ring-opening polymerization of LA in the presence of silica-NH₂ and the amidine base catalyst. As shown in Figure 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.²⁵

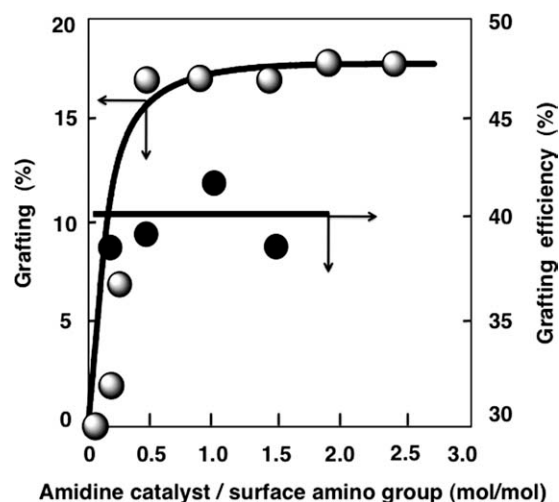


Figure 3 Effect of the amount of amidine base catalyst on grafting of PLLA onto silica surface and grafting efficiency. Silica-NH₂, 0.30 g; LA, 2.70 mmol; THF, 20.0 mL; 40°C; 24 h.

Molecular weight of PLLA formed the ring-opening polymerization

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.²⁹ Therefore, the molecular weight of grafted PLLA chain on the silica surface was estimated from the molecular weight of ungrafted PLLA formed in the ring-opening polymerization of LA in the presence of silica-NH₂ and the amidine base catalyst. The number average molecular weight (M_n) of ungrafted PLLA was estimated to be 5940 by SEC. This indicates that the degree of the polymerization of LA is about 40. The value was much larger than that formed by the polycondensation of L-lactic acid in the presence of CB using Sc(OTf)₃ as catalyst.²⁷

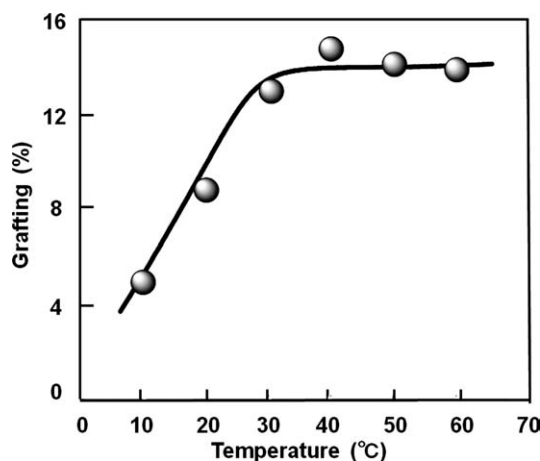


Figure 4 Effect of reaction temperature on the grafting of PLLA onto silica surface. Silica-NH₂, 0.30 g; amidine base catalyst, 0.15 mmol; LA, 2.70 mmol; THF, 20.0 mL; 24 h.

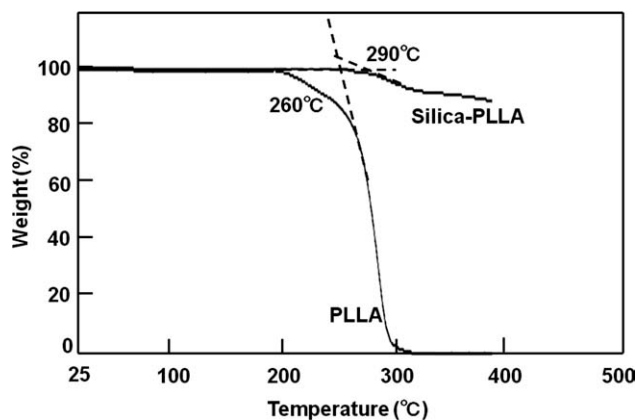


Figure 5 TGA curves of PLLA and silica-PLLA.

Thermal stability of silica-PLLA

Figure 5 shows TGA curves of silica-PLLA and PLLA. As shown in Figure 5, thermal decomposition temperature of silica-PLLA and PLLA was found to be 290 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 grafting reaction of PLLA with CB surface using $\text{Sc}(\text{OTf})_3$ as catalyst.²⁷ This may be due to the fact that terminal groups of PLLA were immobilized onto the silica surface by amide bonds.

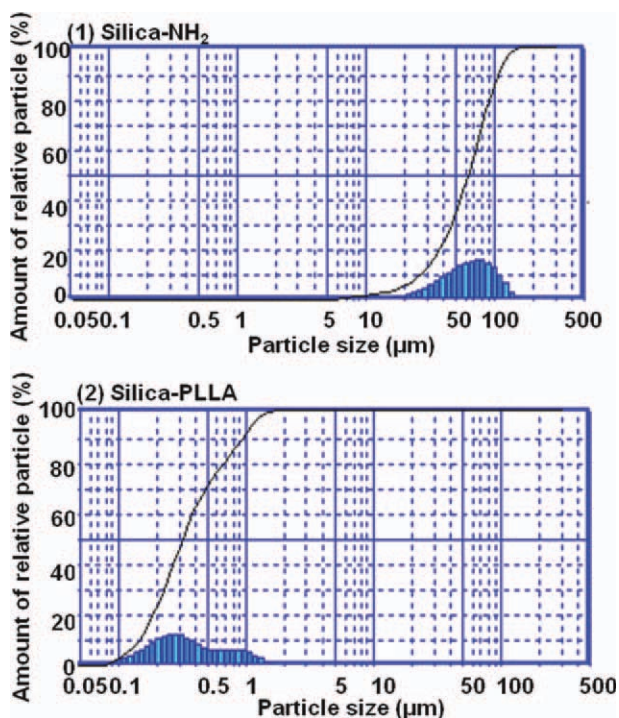


Figure 6 Particle size distribution of ungrafted silica (silica-NH₂) and silica-PLLA in 1,4-dioxane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
Average Particle Size of Ungrafted Silica (Silica-NH₂) and Silica-PLLA in 1,4-dioxane

Silica	The average particle size (μm)
Silica-NH ₂	55.4
Silica-PLLA	0.39

Average particle size of silica-PLLA in solvent

Figure 6 shows the particle size distribution of ungrafted silica (silica-NH₂) and silica-PLLA. The particle size distribution was determined after the dispersing in 1,4-dioxane under ultrasonic wave irradiation for 10 min. As shown in Figure 6, the particle size distribution of silica-PLLA was considerably smaller than that of silica-NH₂: the particle size distribution of silica-NH₂ and silica-PLLA was found to be 20–150 μm and 0.1–1.5 μm, respectively.

Table II shows the average particle size of silica-NH₂ and silica-PLLA in 1,4-dioxane. It was found that the average particle size of silica-NH₂ and silica-PLLA was estimated to be 55.4 and 0.39 μm, respectively.

Based on these results, it was concluded that the aggregation of silica nanoparticles could be considerably destroyed by grafting of PLLA onto the surface.

Dispersibility of silica-PLLA in solvents

The dispersibility of ungrafted silica (silica-NH₂) and silica-PLLA in various solvents was estimated. Figure 7 shows images of the dispersion of silica-NH₂ and silica-PLLA in 1,4-dioxane. The dispersions of silica-NH₂ and silica-PLLA in 1,4-dioxane were

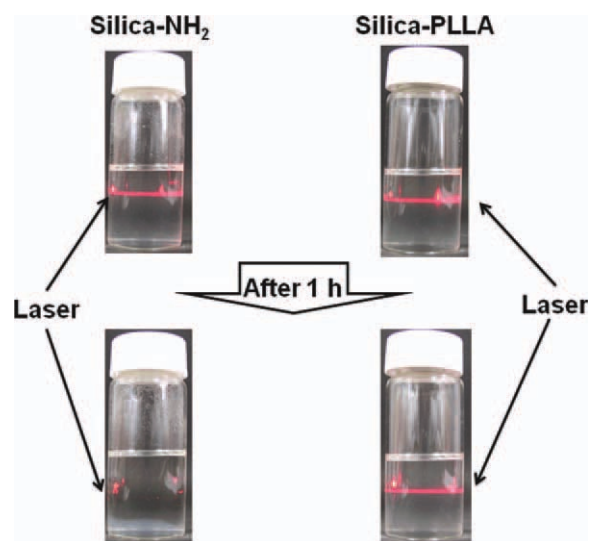


Figure 7 Images of dispersibility of ungrafted silica (silica-NH₂) and silica-PLLA in 1,4-dioxane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

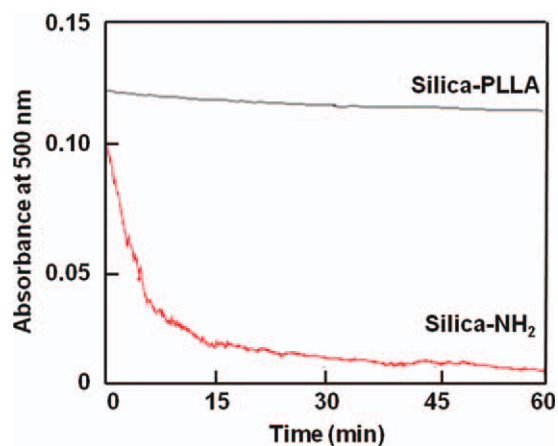


Figure 8 Dispersibility of ungrafted silica (silica-NH₂) and silica-PLLA in 1,4-dioxane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

transparent. Therefore, the dispersibility of silica nanoparticle in 1,4-dioxane was confirmed by the observation of a laser beam through the dispersions. As shown in Figure 7, a path of laser light through the dispersion of silica-PLLA and silica-NH₂ in 1,4-dioxane immediately after the ultrasonic irradiation was clearly observed: these based on the light scattering caused by nanoparticles in solvent, which shows that nanoparticles disperse in solvent.

On the contrary, after 1-h standing at room temperature, the pass of laser light through the dispersion of silica-NH₂ was not observed, indicating the precipitation of silica nanoparticle, 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-NH₂ precipitated.

Figure 8 shows the absorption change of the dispersion of silica-NH₂ and silica-PLLA in 1,4-dioxane at 500 nm during the standing at room temperature. Figure 8 also shows that the stability of silica nanoparticle dispersion was remarkably improved by grafting of PLLA onto the surface.

The dispersibility of silica-PLLA in various solvents was summarized in Table III. It became apparent that silica-PLLA gave stable dispersions in polar

TABLE III
Dispersibility of Silica-PLLA and Solubility of PLLA in Various Solvents

Permittivity	Solvent	Solubility of PLLA	Dispersibility of silica-PLLA after 1 h
High	Water	Poor	Poor
Low	DMSO	Good	Good
	DMF	Good	Good
	1,4-Dioxane	Good	Good
	Hexane	Bad	Precipitated

solvents, such as DMSO, DMF, and 1,4-dioxane, which are good solvents for PLLA, but not nonpolar solvent, which are nonsolvent for PLLA. Silica-PLLA scarcely dispersed in polar solvent water, which is poor solvent for PLLA.

This may be due to the fact that grafted PLLA chains on the silica surface spread out from the silica surface in good solvents and effectively interfere with the aggregation of silica particles. On the contrary, in poor solvents, grafted chains on the surface are unable to spread out and therefore, interfere with the aggregation.

CONCLUSIONS

1. The ring-opening polymerization of LA was successfully initiated from silica-NH₂ 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 (silica-OH) having no amino groups 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-NH₂).
4. Silica-PLLA gave stable dispersions in various organic solvents, such as DMSO, DMF, and 1,4-dioxane, which are good solvents for PLLA, but not in nonsolvent for PLLA. The results suggest that the aggregation of silica nanoparticles was considerably destroyed by surface grafting of PLLA onto the surface.

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