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Self-Assembling Siloxane Nanoparticles with Three Phases

Masatoshi Iji
NEC Corporation
Japan

1. Introduction

Inorganic nanometer-sized particles (nanoparticles) are attracting attention as reinforcing fillers for use in polymer-nanoparticle composites (nanocomposites) because they improve key characteristics of these composites at a relatively low content (Hussain et al., 2006, Jordan et al., 2005). For example, clay nanoparticles (Usuki et al, 2005), metal oxide nanoparticles such as silica (Rosso et al 2006) and titania nanoparticles (Zelikman et al., 2006), and carbon nanotubes (Moniruzzaman & Winey, 2006) increase the mechanical properties, especially the elasticity modulus, of many kinds of polymer composites. However, currently available nanoparticles insufficiently improve the tenacity (elongation at breaking point) of nanocomposites, which is necessary if nanocomposites are to be used in durable products such as electronic equipments and automobiles. This is mainly because these nanoparticles lack rubber-like elasticity although they have an affinity for a polymer matrix. Adding a typical elastomer such as rubber or plasticizer (e.g., a long chain alkyl ester) with a high affinity for a polymer matrix, however, reduces the breaking strength and elasticity modulus of the composite due to their lack of rigidity (Li & Turng, 2006, Shibata et al., 2006).

Nanoparticles with multiple-phases, a high-density phase (core) with rigidity and outside phases with rubber-like elasticity and affinity for matrix polymers, should improve the tenacity of nanocomposites without degrading their breaking strength. Metal oxide nanoparticles are typically formed by hydrolysis and condensation reactions of organic metal compounds, mainly silicon alkoxides (Ha & Cho, 2000, Chujo & Saegusa, 1992, Tamaki & Chujo,1999, Li et al., 2001, Kim et al., 2003) and perhydropolysilazane (Yamano, & Kozuka, 2009), in solvents or polymers, i.e., a sol-gel method. However, the formation of multiple-phased nanoparticles using these organic metal compounds is difficult due to their limited chemical structures. Moreover, the use of conventional surface treatment agents such as organic metal alkoxides to uniformly form multiple phases on nanoparticles while preventing their coagulation is practically difficult because such treatment is an extremely complex process.

Poly L-lactic acid (PLLA), a representative mass-produced biopolymer made of biomass (starch), is attractive for use in environmentally sensitive applications because its use prevents petroleum exhaust and reduces plastic waste due to its biodegradability after

disposal. Although it has a relatively high breaking strength, its tenacity is extremely inadequate for it to be used in a variety of applications including durable products like those mentioned above because of its stiff structure, which is due to the hard crystalline region. Studies on PLLA nanocomposites have focused on the usual nanoparticles such as clay and calcium carbonate ones (Li & Turng, 2006, Petersson & Oksman, 2006, Jiang et al.,2007). However, to the best of the authors' knowledge, the use of multi-phased nanoparticles to increase the tenacity of PLLA has not been reported.

In this chapter, self-assembling siloxane nanoparticles with three phases that improve the tenacity of PLLA are reported. The particles consist of a high-density siloxane phase (plural cores), an elastomeric silicone phase, and a caprolactone oligomer phase. Self-assembly by aggregation and condensation of an organosiloxane with three units forms each phase. Testing showed that the use of these nanoparticles increases the tenacity (breaking strain) of PLLA while maintaining its relatively high breaking strength (Iji, 2011).

2. Self-assembling siloxane nano-particle with three phases

2.1 Preparation of siloxane nano-particles with three phases

Figure 1 illustrates the process used to prepare the organosiloxane with three units and the assumed self-assembly of the nanoparticles with three phases through aggregation and condensation of the organosiloxane, which consists of three units: isocyanatepropyltrimethoxysilane (IPTS), polymethylpropyloxysiloxane (PMPS), and a caprolactone oligomer (CLO).

IPTS was selected to form the high-density siloxane phase (plural cores) because it contains methoxy groups, which are highly polar and reactive, at a high molecular ratio, and thus preferentially aggregates and condensates, producing a rigidly cross-linked (high-density) siloxane network that forms more than one core in the particle. PMPS was selected to form the elastomeric silicone phase with an appropriate (nanometer) size around the cores because it contains propyloxy groups, which have moderate polarity and reactivity, at a low molecular ratio in an adequate-length siloxane chain (siloxane number: 8.0). Its use produces a loosely cross-linked (relatively low-density) siloxane network after the core formation. The CLO was selected to form the outside phase due to its low polarity compared with those of IPTS and PMPS and its high affinity for the PLLA matrix (it is highly soluble in melted PLLA).

The organosiloxane was synthesized by mixing PMPS with CLO at a molecular ratio of 1:1 and then mixing the resulting compound with IPTS at a molecular ratio of 1:1 (Figure 1 (A)). After the binding reactions had ceased, the unreacted IPTS, PMPS and CLO were removed using a column packed with polystyrene particles. The reactions were confirmed by hydrogen-nuclear magnetic resonance (H-NMR) analysis of the functional groups in the resulting compounds. Moreover, we performed gel permeation chromatography (GPC) analysis to determine the molecular weight, element analysis of carbon, hydrogen, and nitrogen, and Fourier transform infrared spectroscopy (FT-IR) to determine major bonds. These results showed that the IPTS, PMPS, and CLO were combined in almost equal molecular proportions as we intend. The CLO and IPTS were probably randomly located on the PMPS in the final compound but apart to some-extent because of the difference in their polarities. The reference organosiloxanes with two units (IPTS+PMPS or PMPS+CLO) were prepared and determined based on these methods.

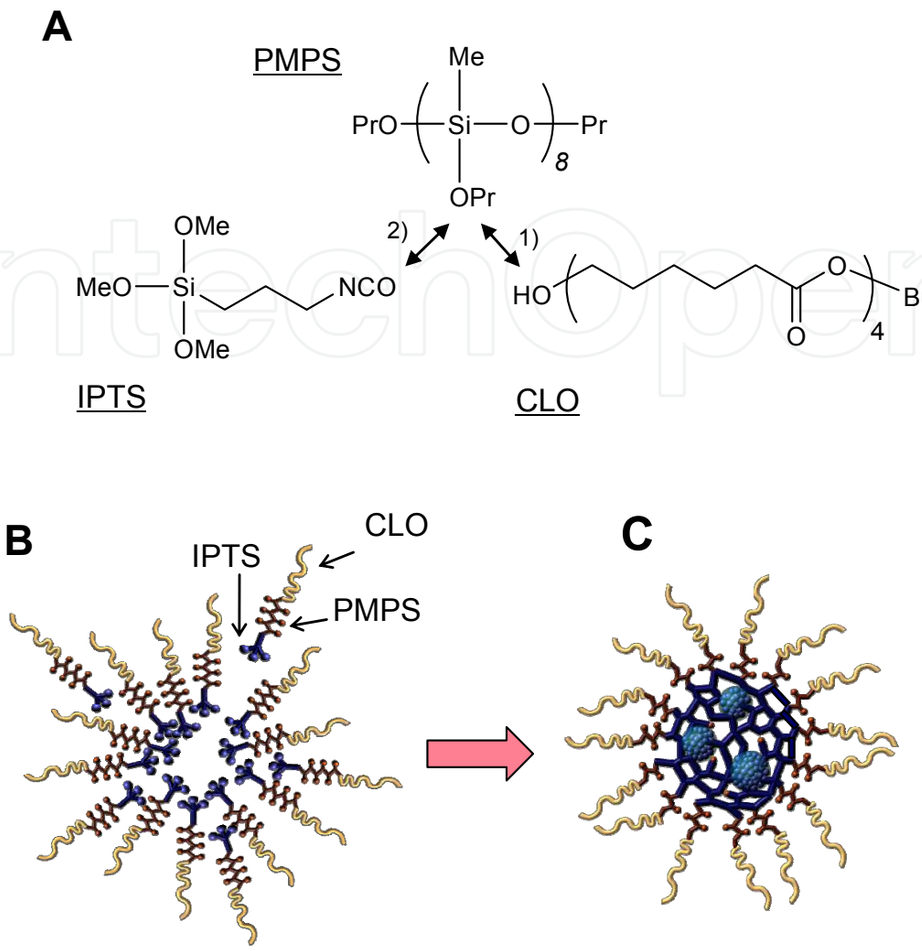


Fig. 1. Preparation of organosiloxane with three units (A) and self-assembly of three-phased nanoparticles through aggregation (B) and condensation (C) of organosiloxane.

We confirmed that the organosiloxane with three units dissolved in tetrahydrofuran (THF) aggregates and forms nanoparticles due to condensation by using water and ammonia as a base catalyst. To avoid confusing the formation of the high-density siloxane cores with the formation of the elastomeric silicone phase around them, we initiated two-step condensation of the organosiloxane by taking advantage of the higher reactivity of the methoxy groups in the IPTS unit than that of the propyloxy groups in the PMPS unit. The first step was core formation through hydrolysis and condensation of the methoxy groups in the IPTS unit at room temperature for 24 hours in THF. The second step was elastomeric silicone phase formation through hydrolysis and condensation of the propyloxy groups in the PMPS unit by heating at a high temperature (180°C) for 20 minutes after replacing the THF with dimethyl sulfoxide, which has a higher boiling point (189°C). These stepwise reactions were ascertained by H-NMR analysis for the methoxy, propyloxy and silanol. After the first step, the methoxy groups in the IPTS were almost completely hydrolyzed and condensed, forming siloxane, while the propyloxy groups in the PMPS unit did not hydrolyzed. After the second step, the propyloxy groups were almost completely hydrolyzed and condensed. These detail methods and results were shown in our paper (Iji, 2011).

2.2 Structures of siloxane nano-particles

As shown in Figure 2, the formed nanoparticles were observed with a scanning electron microscope (SEM). The size distribution, measured by light scattering analysis, indicated a relatively narrow size range, with an average diameter of 13 nm.

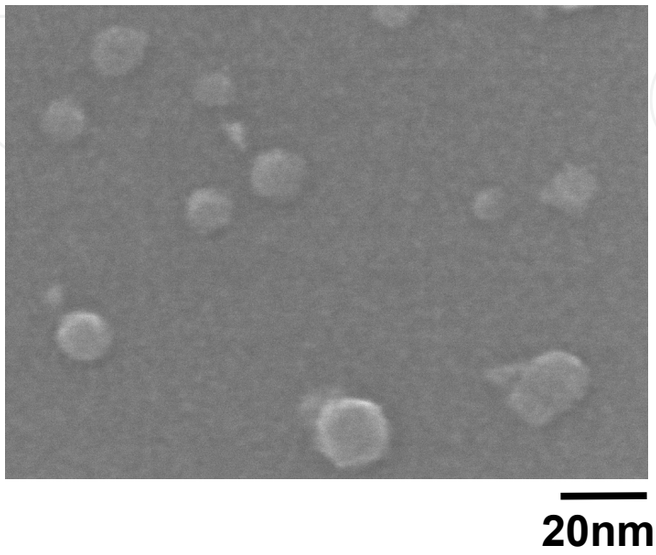


Fig. 2. Observation of three-phased nanoparticles using scanning electron microscope.

The inside structures of the nanoparticles were investigated by scanning electron microscopy and energy dispersive X-ray (SEM-EDX) analysis. Figure 3 shows representative results for the amounts (intensities) of silicon and carbon that were detected along cross-sections of the nanoparticles. The amount of silicon originating from the IPTS and PMPS units was remarkably higher at several points around the center. This indicates that the nanoparticle had plural high-density siloxane cores formed mainly from the IPTS unit and that, around the cores, there was a relatively low-density siloxane phase formed mainly from the PMPS unit. The amount of carbon, which originated from all the units, especially the CLO unit, did not significantly vary throughout the particle. This indicates that there was a relatively high concentration of carbon in the outer layer of the particle, meaning that the CLO unit formed the outside phase fairly well.

Figure 4 shows the thermo-gravity analysis of the nanoparticle formed by the organosiloxane with IPTS, PMPS, and CLO, the reference particle formed by the organosiloxane with PMPS and CLO (through the second step described above), and these organosiloxanes. The results indicated that the nanoparticle showed higher thermo-degradation resistance than the reference particle, which suggests the formation of the high density cross-linking phase to retard the thermo-degradation; we considered the phase to be the cores in the nanoparticle. Furthermore, these particles showed considerably higher thermo-degradation resistances than those of the organosiloxanes. These suggest that not only the high- density cores derived from IPTS but also the relatively low density cross-linking silicone phase derived from PMTS were formed.

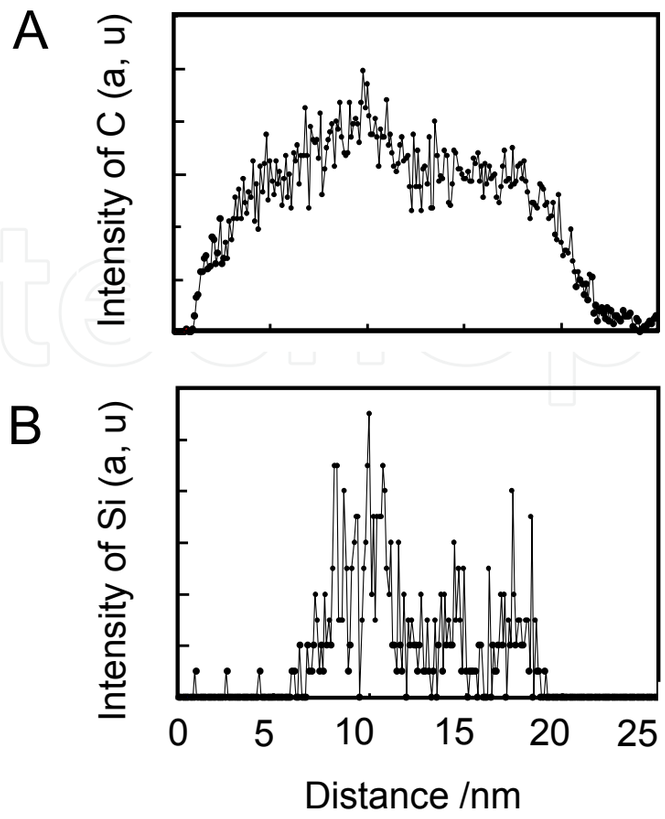


Fig. 3. Analysis of silicon and carbon in a three-phased nanoparticle by SEM-EDX: intensities of silicon (A) and carbon (B) detected along cross-section of the nanoparticle.

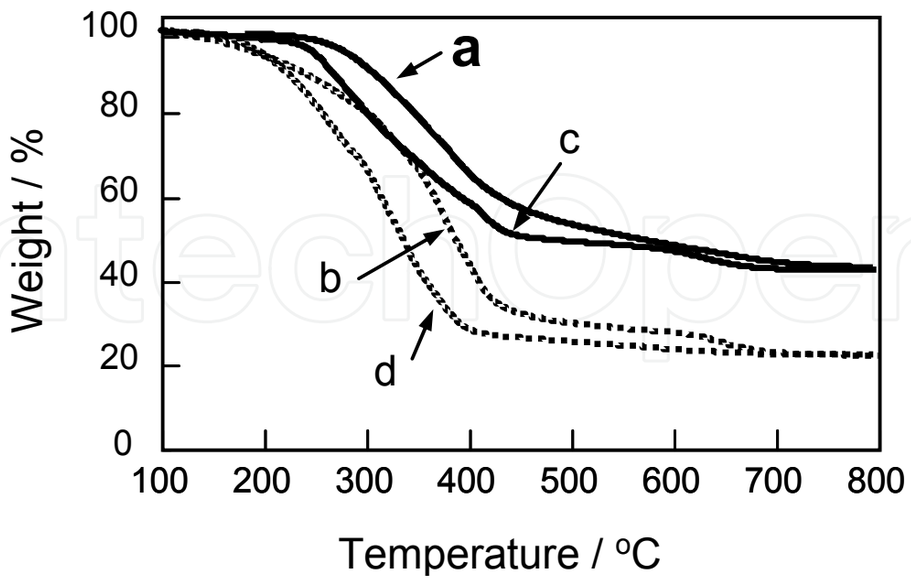


Fig. 4. Thermo-gravimetric analysis of nanoparticles and organosiloxanes (in nitrogen by heating at 10 centigrade per minute)
(a) Three-phased nanoparticle, (b) Organosiloxane consisting of IPTS, PMPS and CLO to

form (a), (c) Two-phased particle consisting of elastomeric silicone and CLO phases, (d) Organosiloxane consisting of PMPS and CLO to form (c)

From these results, it seems reasonable that three-phased nanoparticles can be formed by self-assembly of the organosiloxane with three units, as shown in Figure 1 (B, C). The IPTS unit mainly performs the aggregation of the organosiloxane. The aggregated IPTS unit mainly forms the high-density cross-linked siloxane phase (plural cores) through preferential hydrolysis and condensation reactions of its methoxy groups. After the core formation, the PMPS unit mainly forms the middle phase, the relatively low-density cross-linked siloxane network (elastomeric silicone) around the cores through hydrolysis and condensation reactions of its propyloxy groups. The CLO unit mainly forms the outside phase of the nanoparticles after the organosiloxane has aggregated because of its position and relatively low polarity.

2.3 Characteristics of nanocomposites consisting of siloxane nano-particles and polylactic acid

Using these three-phased siloxane nanoparticles at 5wt%, we prepared a molded PLLA nanocomposite to measure its tenacity by flexural and tensile testing. After the first step (core formation), the THF, water, and ammonia were removed by evaporation. The nanoparticles were mixed with PLLA in chloroform, followed by removing the solvent by evaporation. The resulting composite was extruded at 180°C for 10 minutes using a screw-type mixer and then molded by pressing while heating at 180°C for 10 minutes, followed by crystallization of the PLLA in the composite by heating at 100°C for 4 hours. It is likely that the condensation reaction to form the elastomeric silicone phase in the particle was mostly finished during the extruding and molding of the PLLA composite because the same heating condition as that for the solvent in the second step above resulted in the same condensation reaction.

As shown in Figure 5 (A, B), the three-phased nanoparticles greatly increased the PLLA's tenacity without degrading its high breaking strength. The elongation of the PLLA nanocomposite was more than twice that of PLLA while the elasticity modulus and breaking (maximum) strength were comparable to those of PLLA.

As references, PLLA composites containing commercial silica nanoparticles, two-phased nanoparticles (cores and elastomeric silicone phase), or the organosiloxane consisting of PMPS and CLO units were prepared using the method described above. The composite containing the commercial silica nanoparticles, average diameter 12 nm, showed a slight increase in the modulus, but its strength and elongation were less than those of PLLA (Figure 5A (c)). The two-phased nanoparticles, average diameter of 10 nm, were formed using the organosiloxane with IPTS and PMPS units through the same core formation step described above. The composite containing the nanoparticles showed only a slight increase in elongation compared with that of PLLA (Figure 5A (d)). The composite containing the organosiloxane with PMPS and CLO (PMPS might be cross-linked when mixing with PLLA during heating) showed substantial increase in elongation compared with that of PLLA, but its strength and modulus were less (Figure 5A (e)). The composite containing CLO alone decreased the elasticity modulus of the PLLA composite and insufficiently increased its elongation (Figure 5A (f)). The amount of CLO alone in the composite was 2 wt%, which is

near to the amounts of the CLO parts of the three-phased nanoparticles and the organosiloxane with PMPS and CLO. Increasing the amount of CLO further decreased both the modulus and also the strength while it increasing the elongation. These mean that each phase in the three-phased nanoparticles is necessary to increase the PLLA's tenacity while maintaining its breaking strength and modulus.

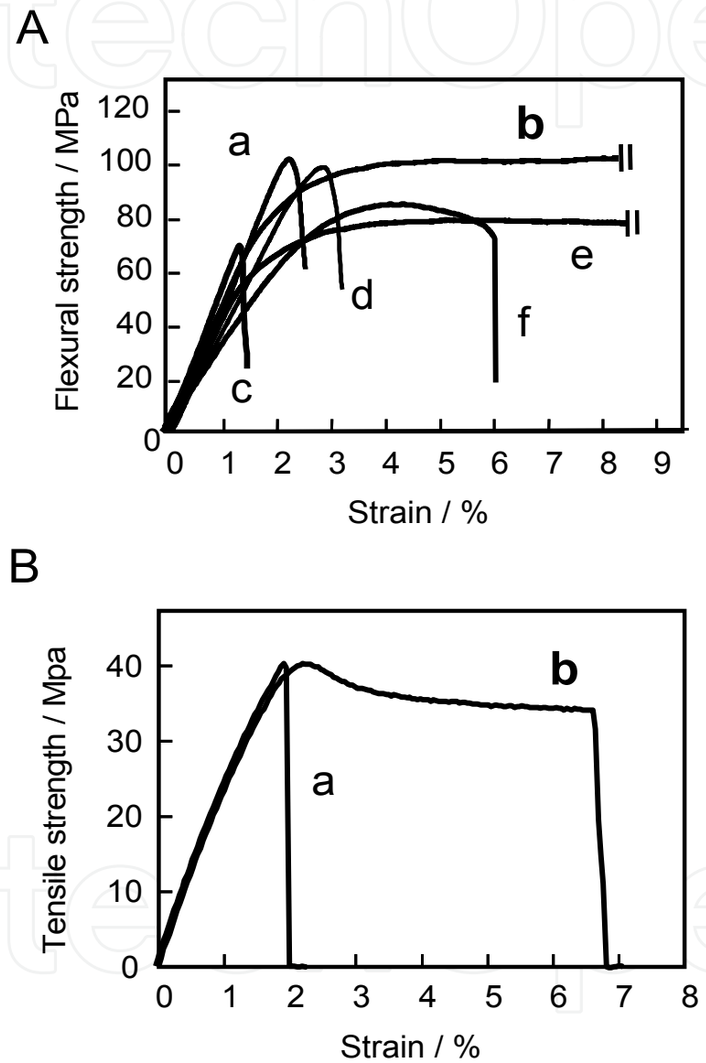


Fig. 5. Flexural (A) and tensile (B) testing of PLLA composites
(a) PLLA, **(b) PLLA nanocomposite with three-phased nanoparticles (5 wt%)**, (c) PLLA nanocomposite with silica nanoparticles (5 wt%), (d) PLLA nanocomposite with two-phased nanoparticles consisting of cores and elastomeric silicone phase (5 wt%), (e) PLLA composite with organosiloxane consisting of PMPS and CLO (5 wt%), and (f) PLLA composite with CLO (2 wt%).

These results suggest that the mechanism of the improved tenacity due to the use of the three-phased nanoparticles is as follows. During the initial period of the PLLA nanocomposite deformation, the nanoparticles create a high elasticity modulus and maximize the strength because of their core rigidity and the high affinity of the outside CLO phase for the PLLA matrix. This idea is supported by the results that the reference organosiloxane with PMPS and CLO, not forming cores and also, the nano-silica, which aggregated in the PLLA composites due to its low affinity with PLLA, did not maintain such a high modulus and strength, simultaneously. In the middle and final periods of the deformation, the three-phased nanoparticles elongated the composite due to the rubber-like elasticity of the elastomeric silicone phase derived from PMPS and the plasticity of the outside CLO phase. While the nano-silica, the reference two-phased particles without the CLO phase, and CLO alone did not perform such elongation of the PLLA composites, the organosiloxane with PMPS and CLO elongated the composite, which can supports the proposed mechanism.

Furthermore, we have cleared that the influence of adding the three-phased nanoparticles on the heat resistance of PLLA (Table 1). The glass transition temperature and heat distortion temperature of the PLLA composite with the nanoparticles (5wt%) slightly decreased comparing with PLLA, but these levels were fairly kept. The decomposition temperature measured by TGA increased. Adding typical elastomers such as rubber or plasticizer reduces heat resiatance of the composites. However, the nanoparticles maintained the heat resistance because of its core rigidity and its higher thermo-degradation resistance as above mentioned.

	Glass transition temp. (°C)	Heat distortion temp.(°C) Load: 0.45MPa / 1.80MPa	Decomposition temp.(°C) / 10% weight loss
PLLA	63	124 / 66	337
PLLA with three-phased nanoparticle (5wt%)	59	119 / 64	344

Table 1. Heat resistance of PLLA and PLLA composites with three-phased nanoparticle

3. Conclusion

In conclusion, we developed self-assembling siloxane nanoparticles with three phases: a high-density cross-linked siloxane phase (plural cores), an elastomeric silicone phase around the cores, and an outside CLO phase with a high affinity for the PLLA matrix. These nanoparticles self-assemble by aggregation and condensation of the organosiloxane with three units, IPTS, PMPS, and CLO that respectively form each phase. Adding these nanoparticles to PLLA increases the tenacity of the PLLA while maintaining its high breaking strength. Their use will expand the use of PLLA in durable product applications and other new applications. These nanoparticles can also be applied to various other brittle polymers by modifying the structure of the outside phase to achieve a high affinity with these polymers.

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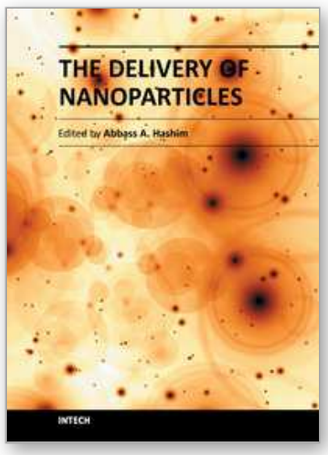
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The Delivery of Nanoparticles
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Nanoparticle is a general challenge for today's technology and the near future observations of science. Nanoparticles cover mostly all types of sciences and manufacturing technologies. The properties of this particle are flying over today scientific barriers and have passed the limitations of conventional sciences. This is the reason why nanoparticles have been evaluated for the use in many fields. InTech publisher and the contributing authors of this book in nanoparticles are all overconfident to invite all scientists to read this new book. The book's potential was held until it was approached by the art of exploring the most advanced research in the field of nano-scale particles, preparation techniques and the way of reaching their destination. 25 reputable chapters were framed in this book and there were alienated into four altered sections; Toxic Nanoparticles, Drug Nanoparticles, Biological Activities and Nano-Technology.

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InTech Europe
University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China
Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
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