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Environmentally Friendly Synthesis of Polymer-Grafted Nanoparticles

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1. Introduction

Inorganic nanoparticles such as silica, and titanium oxide, are widely used industrially as fillers and pigments for polymer materials, because inorganic nanoparticles have excellent properties such as chemical, heat and weather resistance, lightweight, thermal conductivity and low thermal expansion.

On the other hand, nanocarbons, such as carbon black, nanodiamond, and carbon nanotube, are well known as one of the industrially important carbon materials. Carbon materials also have outstanding properties such as electro-conductivity, heat-resistance, biocompatibility, and chemical-resistance. Carbon nanotubes in particular have attracted attention as nanotechnology related materials.

In general, dispersing inorganic nanoparticle and nanocarbons uniformly into a polymer or an organic solvent is very difficult because of aggregation. In addition, the mechanical properties of polymer composite from nanoparticles and nanocarbons are considered to 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 polymers.

The chemical and physical modifications of inorganic nanoparticle and nanocarbon surfaces, therefore, have been extensively studied. The chemical modification of surfaces is permanent, but physical modification is temporary. We have pointed out that the dispersibility of silica nanoparticles and nanocarbons is extremely improved by surface grafting of polymers, namely, chemical binding of polymers, onto nanoparticle and nanocarbon surfaces (Tsubokawa, 1999; Tsubokawa, 2002; Tsubokawa, 2007).

In addition grafting of polymers onto these surfaces interests us for designing new functional composite materials which have the excellent properties both of nanoparticles as mentioned above and of grafted polymers, such as photosensitivity, biorepellent activity, antibacterial activity, and pharmacological activity (Tsubokawa, 2007).

We have succeeded in the grafting of various polymers such as vinyl polymer (Tsubokawa et al., 1988a; Tsubokawa et al., 1990; Fujiki et al., 1990; Tsubokawa et al., 1992a), polyester (Tsubokawa et al., 1982; Tsubokawa et al., 1983), polyether (Tsubokawa et al., 1986; Tsubokawa et al., 1988b), poly(organophosphazene) (Tsubokawa et al., 1992b), and poly(dimethysiloxane) (Tsubokawa et al., 1992c) onto silica nanoparticle and carbon black surfaces using surface functional groups as grafting sites. Furthermore, many experimental attempts by other researchers also have been made to graft polymers onto silica nanoparticle and carbon black surfaces.

For example, it has been reported that controlled grafting of polymers, so called "polymer brush"), from nanoparticles was successfully achieved by atom transfer radical polymerization (ATRP) initiated by a system consisting of surface functional groups and transition metal complexes (Pyun & Matyjaszewski, 2001; Ohno et al., 2002; Lui et al., 2003; Harrak, et al., 2005; Lui et al., 2005). In situ radical transfer addition polymerization (Lui et. al., 2004) [19] and emulsion polymerization from silica nanoparticles also has been reported (Ding et al., 2004). Wang et al. have reported the synthesis of a well-defied organic/inorganic nano-composite *via* reverse ATRP (Wang et. al., 2005a; Wang et al., 2005b).

However, scale-up synthesis of polymer-grafted nanoparticles was hardly achieved, because complicated reaction processes, such as centrifugation, filtration, and solvent extraction, are required for the synthesis and isolation of polymer-grafted nanoparticles, and a lot of waste solvent is generated.

We have reported the scale-up synthesis of polymer-grafted silica nanoparticle in a solvent-free dry-system. In solvent-free dry-system, the isolation and purification after the graft polymerization was easily achieved, because untreated monomer can be removed under high vacuum (Tsubokawa, 2007).

In this Chapter, for the purpose of the prevention of the environmental pollution and the simplification of surface grafting process, the radical graft polymerization of vinyl monomers onto silica nanoparticle and carbon black surfaces by "grafting onto" and "grafting from" process in an ionic liquid will be reviewed. In addition, the grafting of hyperbranched poly(amidoamine) (PAMAM) onto silica nanoparticle surface by dendrimer synthesis methodology in an ionic liquid will be discussed.

2. Advantages of polymer grafting onto nanoparticles in an ionic liquid

Recently, polymer synthesis in an ionic liquid as a solvent for the polymerization has been reported. It is well known that ionic liquids are non-volatile, non-flammable, and thermally stable solvents. These properties promise replacements for the traditional volatile organic solvents for polymer synthesis. Therefore, the number of studies on ionic liquids as polymerization media have increased markedly (Wilkkers, 2002; Harrisson et al., 2002; Carmichael & Haddleton, 2003).

For example, the polymerization of vinyl monomers initiated by benzoyl peroxide (BPO) and 2,2'-azobisisobutyronitrile (AIBN) in ionic liquids has been reported. It is interesting to note that the rate of the radical polymerization and molecular weight of resulting polymer in ionic liquids were much larger than those in a conventional organic solvent.

In addition, Cu^I-*N*-propyl-2–pyridylmethanimine mediated "living" radical polymerization of vinyl monomers by use of 1-butyl-3-methylimidazolium hexafluorophosphate as solvent has been reported (Carmichael et al., 2000). It has been pointed out that the rate of polymerization was enhanced in comparison to other polar/coordinating solvents. Moreover, the polymerization product was made copper free by a simple solvent wash, which avoids the contamination of the polymer product by the catalyst. Other atom transfer radical polymerizations in ionic liquids have recently been reported (Sarbu & Matyjaszewski, 2001; Biendron & Kubisa, 2001).
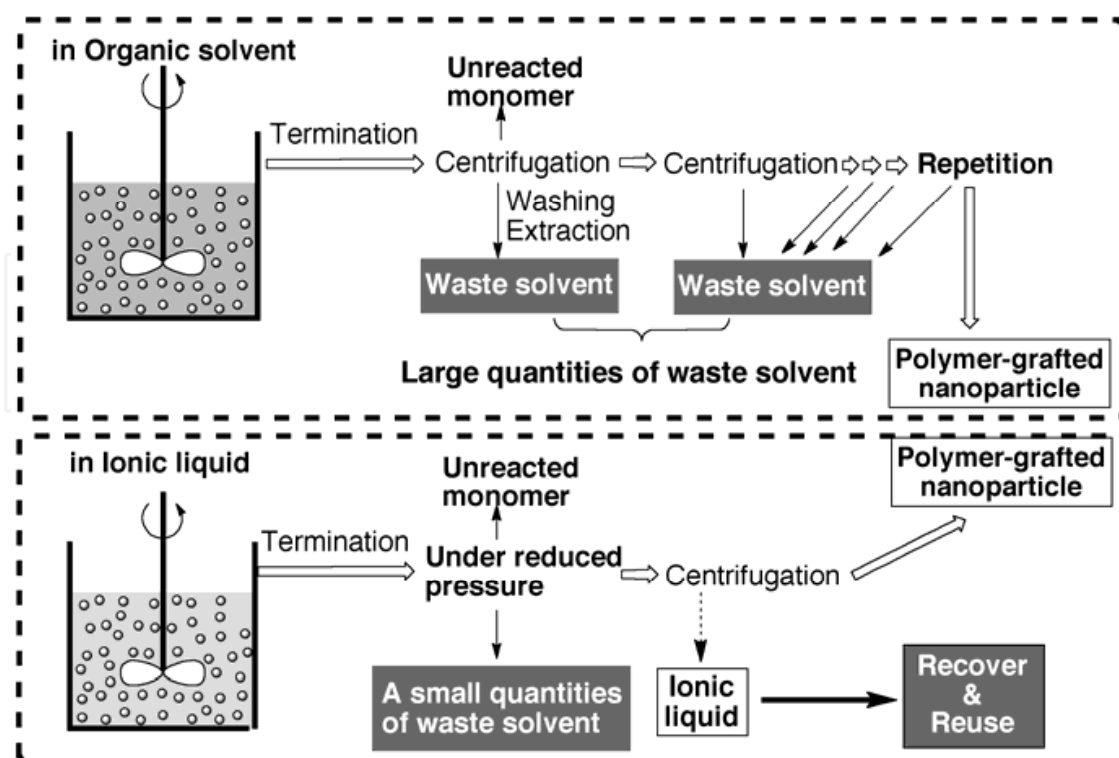
Fig. 1. Graft polymerization in organic solvent system *vs.* in ionic liquid.

Figure 1 shows the comparison of procedures of graft polymerization of various monomers onto nanoparticles, such as inorganic nanoparticles, carbon blacks, and carbon nanotubes, in conventional organic solvents with those in ionic liquids.

In an organic solvent system, after the reaction, the purification and isolation of the resulting nanoparticles was achieved by troublesome procedures, such as filtration and centrifugation as mentioned above. Therefore, the scale-up synthesis of polymer-grafted nanoparticles was hardly achieved and large quantities of waste solvent result.

On the contrary, in ionic liquids, the isolation and purification after the graft polymerization was easily achieved, because untreated monomer can be removed under high vacuum as well as solvent-free dry-system. Therefore, it is expected that we can achieve scale-up and environmentally friendly synthesis of polymer-grafted nanoparticles by use of ionic liquid.

3. Methodology of surface grafting of polymers onto nanoparticles

Several methodologies for the preparation of a variety of graft and block copolymers were established. These methodologies can be applied to the preparation of polymer-grafted nanoparticles. The methodology of surface grafting of polymers onto nanoparticle surfaces is summarized in Table 1. We can apply one of the following principles for the surface grafting of various polymers onto inorganic nanoparticles and nanocarbons (Tsubokawa, 1999; Tsubokawa, 2002; Tsubokawa, 2007).

By process (1), although we can obtain polymer-grafted nanoparticles, the percentage of grafting (weight percent of grafted polymer onto nanoparticles) onto nanoparticles is less than 10%, because of the preferential formation of ungrafted polymers. We can obtain polymer-grafted nanoparticles by termination of living polymers with well-defined molecular weight and narrow molecular weight distribution.

	Grafting process	Methodology
1	Grafting onto	Termination 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	Initiation of graft polymerization of various monomers from radical, cationic and anionic initiating groups previously introduced onto nanoparticle surfaces
3	Polymer reaction	Reaction of surface functional groups on nanoparticles with polymers having functional groups, such as hydroxyl, carboxyl, and amino groups
4	Stepwise growth	The growth of hyperbranched polymer chains from surface functional groups on nanoparticles by repeated reaction of low molecular weight compounds by dendrimer synthesis methodology

Table 1. Methodology of surface grafting of polymers onto nanoparticles.

Process (2) is one the most favorable for the preparation of polymer-grafted nanoparticles with a higher percentage of grafting. We can control the molecular weight and number of grafted polymer chains by use of surface initiated living polymerization as mentioned above.

An important characteristic of process (3) is that not only are the molecular weight and the number of grafted chains on the nanoparticle surfaces 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 of steric hindrance. We can include the process (2) with "grafting onto" process.

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 surfaces.

4. Radical grafting of vinyl polymers onto nanoparticles by "grafting onto" process in an ionic liquid

We have pointed out that the radical polymerizations of vinyl monomers initiated by benzoyl peroxide (BPO) and 2,2'-azobisisobutyronitrile (AIBN) were remarkably retarded in the presence of carbon black. It is considered that the competitive reaction of initiator radicals with low molecular weight growing polymer radicals against the carbon black surface proceeds during the radical polymerization (Scheme 1). As a result, a part of polymer formed was grafted onto the surface based on the termination (trapping) of growing polymer radicals by carbon black (Ohkita et al., 1972; Ohkita et al., 1976); but the percentage of grafting was less than 10%. This may be due to preferential trapping of the low molecular weight initiator radicals by the carbon black surface.

Therefore, we have investigated the effect of 1-butyl-3-methylimdazolium hexafluorophosphate as an ionic liquid on the competitive reaction during the radical polymerization in the presence of carbon black (Ueda et al., 2008).
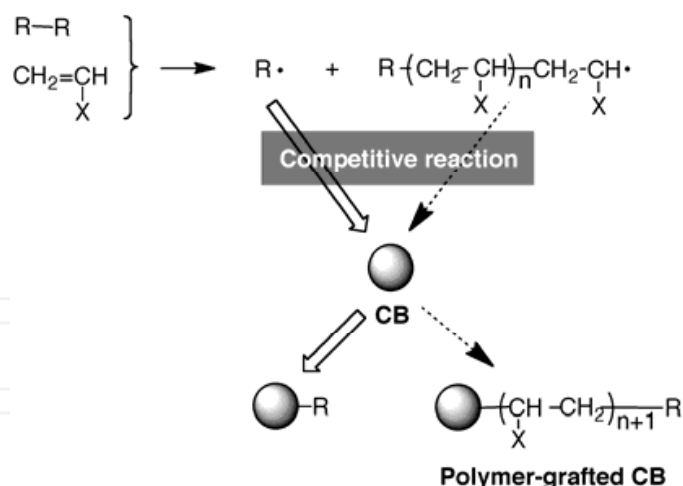
Scheme 1. Competitive reaction of radicals against carbon black surface.

4.1 Radical polymerization of vinyl monomers initiated by BPO in the presence of carbon black

Figures 2 and 3 show the effect of ionic liquid on the radical polymerization of styrene (St) and methyl methacrylate (MMA), respectively, initiated by BPO in the presence of carbon black. As shown in Figures 2 and 3, in toluene as solvent, the polymerization was remarkably retarded. On the contrary, the retardation of polymerization observed in the presence of carbon black was almost eliminated in the initial stage of the polymerization in ionic liquid.

Figures 4 and 5 show the relationship between the reaction time and percentage of polySt and polyMMA grafting, respectively, onto carbon black surface. When toluene was used as solvent, the percentage of polySt grafting onto the carbon black surface was less than 1%. On the contrary, in ionic liquid, the percentage of polySt grafting onto carbon black increased with increasing reaction time and reached to 4.5%.
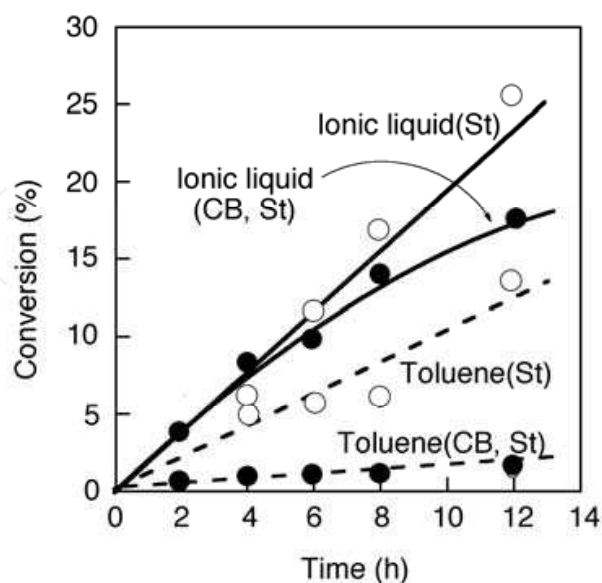

Fig. 2. Effect of ionic solvent on the polymerization of St initiated by BPO in the presence of carbon black. Carbon black, 0.10 g; BPO, 0.10 g; St, 5.0 mL; solvent, 10.0 mL; 60 °C.
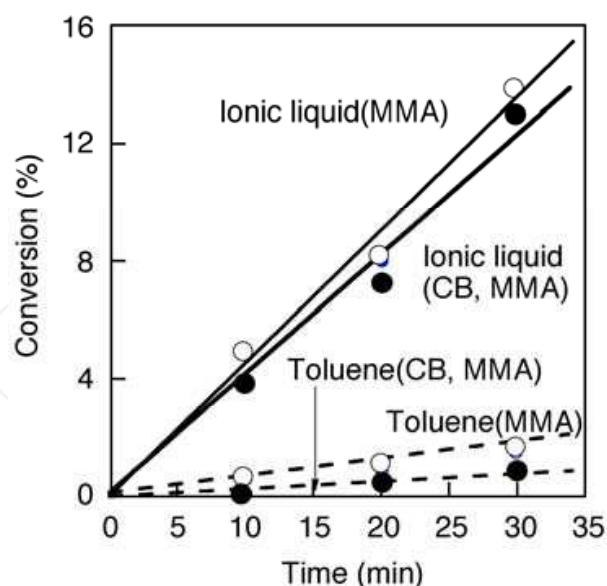
Fig. 3. Effect of ionic liquid on the polymerization of MMA initiated by BPO in the presence of carbon black. Carbon black, 0.10 g; BPO, 0.10 g; MMA, 5.0 mL; solvent, 10.0 mL; 60 °C.
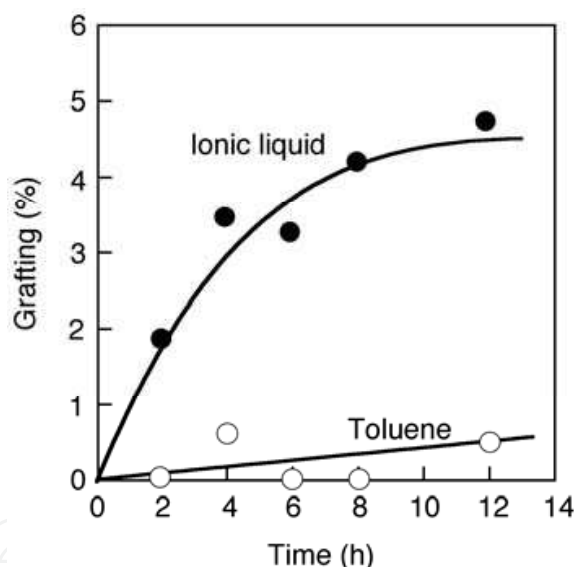

Fig. 4. Relationship between polySt grafting and reaction time. Polymerization conditions are given in Figure 2.

In addition, it is interesting to note that the effective grafting of polyMMA onto carbon black was achieved in ionic liquid: the percentage of grafting reached 35% after 30 h.

Figure 6 shows relationship between conversion and grafting efficiency [percentage of grafted polymer to total polymer (ungrafted polymer + grafted polymer) formed] during the polymerization shown in Figure 2. It is interesting to note that the grafting efficiency in ionic liquid was larger than that in toluene. These results indicate the formation of ungrafted polymer is inhibited in ionic liquid in comparison with toluene in the initial stage of the polymerization. However, the grafting efficiency in ionic liquid also remarkably decreased with increasing conversion as well as in toluene.
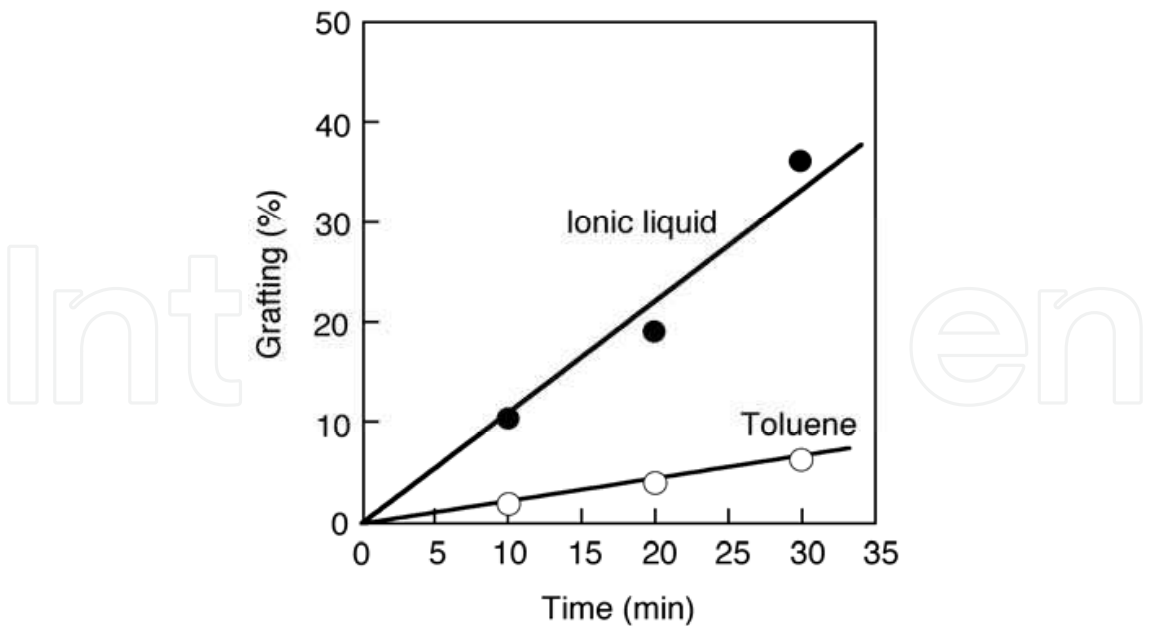
Fig. 5. Relationship between polyMMA grafting and reaction time. Polymerization conditions are given in Figure 3.
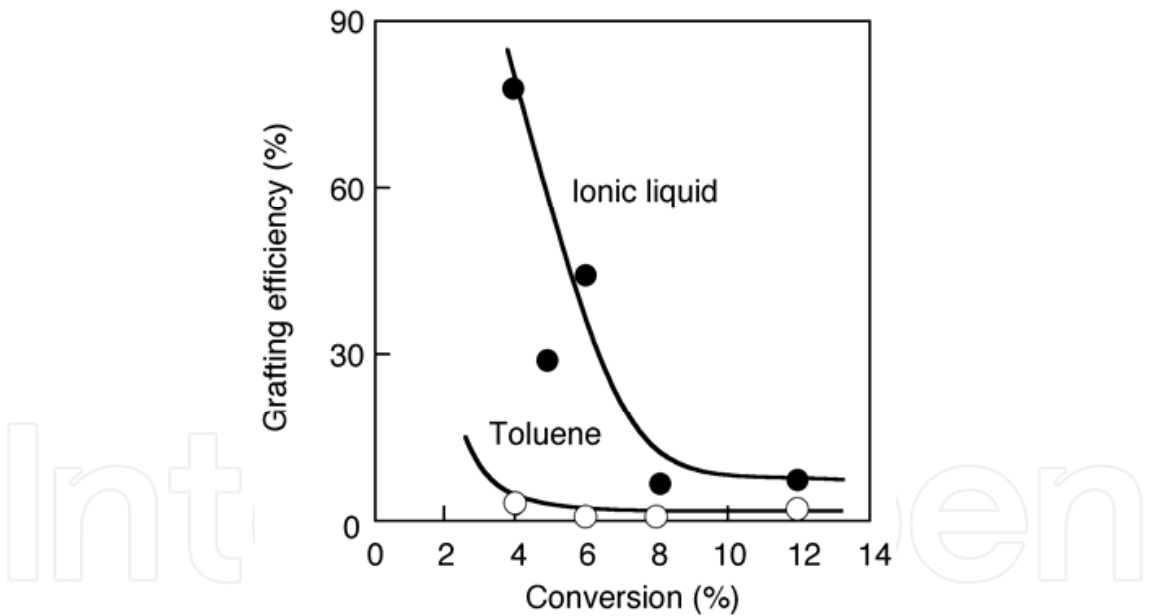

Fig. 6. Relationship between conversion and grafting efficiency of polySt in ionic liquid. Polymerization conditions are given in Figure 2.

The grafting of polySt and polyMMA onto carbon black surface was confirmed by FT-IR and thermal decomposition GC-MS.

These results may be explained as follows: in toluene, initiating radicals (benzoyloxy radicals) were preferentially trapped by carbon black surface and the polymerization is retarded. During the polymerization, a part of growing polySt radicals was trapped by the carbon black surface, the percentage of grafting was very small. This indicates very low molecular weight of polySt was grafted onto the surface in toluene.

On the contrary, in ionic liquid, growing polySt radicals with relatively high molecular weight was trapped by the carbon black surface because of stabilization of polymer radicals in ionic liquid, resulting in higher the percentage of grafting (Scheme 1).

4.2 Radical polymerization of vinyl monomers initiated by AIBN in the presence of carbon black

Figure 7 shows the results of the radical polymerization of MMA in the presence of carbon black initiated by AIBN in ionic liquid and in toluene. It was found that the retardation of the radical polymerization of MMA in the presence of carbon black was also remarkably reduced in ionic liquid. The polymerization behavior of MMA initiated by AIBN shows almost the same tendency as that initiated by BPO in the presence of carbon black.

Figure 8 shows the relationship between reaction time and percentage of polyMMA grafting. As shown in Figure 8, the percentage of grafting increased with increasing reaction time. The percentage of grafting of polyMMA onto carbon black in ionic liquid was also much larger than that in toluene: the percentage of polyMMA grafting was determined to be 40% after 30 h.
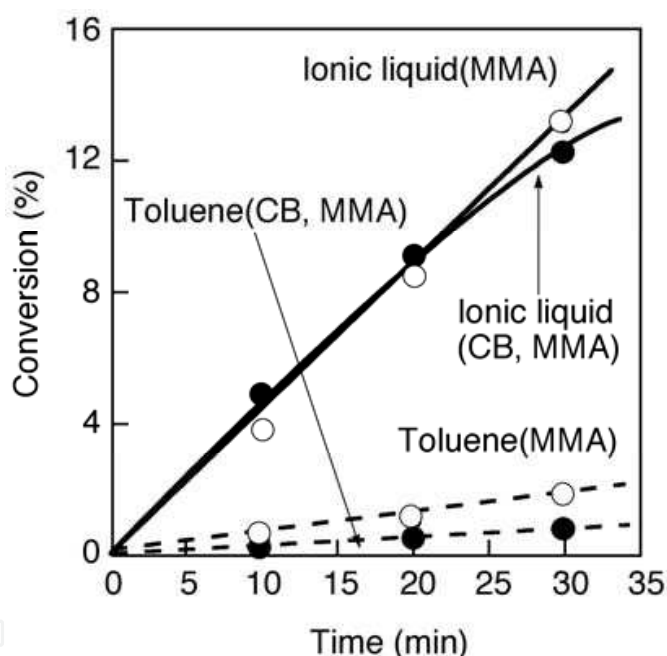

Fig. 7. Effect of ionic liquid on the polymerization of MMA initiated by AIBN in the presence of carbon black. Carbon black, 0.10 g; AIBN, 0.10 g; MMA, 5.0 mL; solvent, 10.0 mL; 60 °C.

5. Radical grafting of vinyl polymers onto nanoparticles by the "grafting from" process in an ionic liquid

As mentioned above, the radial graft polymerization of vinyl monomers onto silica nanoparticle and carbon black surface was initiated by surface azo groups previously introduced onto the surface, and we can obtain the corresponding polymer-grafted silica nanoparticle and carbon black by the "grafting from" process (Tsubokawa et al., 1990; Fujiki et al., 1990; Tsubokawa et al., 1992a).
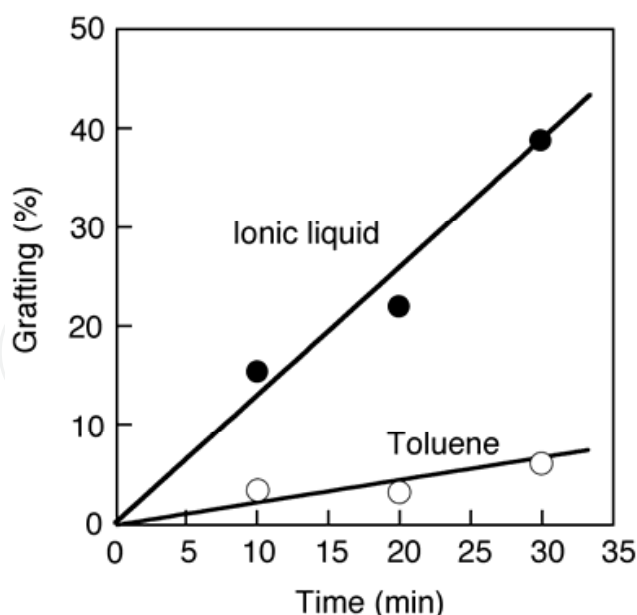
Fig. 8. Relationship between polyMMA grafting and reaction time. Polymerization conditions are given in Figure 7.

Therefore, the effect of ionic liquid on the radical grafting of vinyl polymers onto silica nanoparticle and carbon black by the "grafting from" process was investigated (Ueda et al., 2008).

5.1 Radical graft polymerization of vinyl monomers initiated by azo groups introduced onto silica nanoparticle and carbon black surface in ionic liquid
5.1.1 Radical graft polymerization initiated by CB-Azo

(1) Introduction of azo groups onto the carbon black surface

The introduction of azo groups onto the carbon black surface was readily achieved by the reaction of 4,4'-azobis(4-cyanopentanoic acid) with surface isocyanate groups, which were introduced by the reaction of phenolic hydroxyl and carboxyl groups on the carbon black surface with tolylene-2,4-diisocyanate (TDI) as shown in Scheme 2 (Tsubokawa et al., 1990).
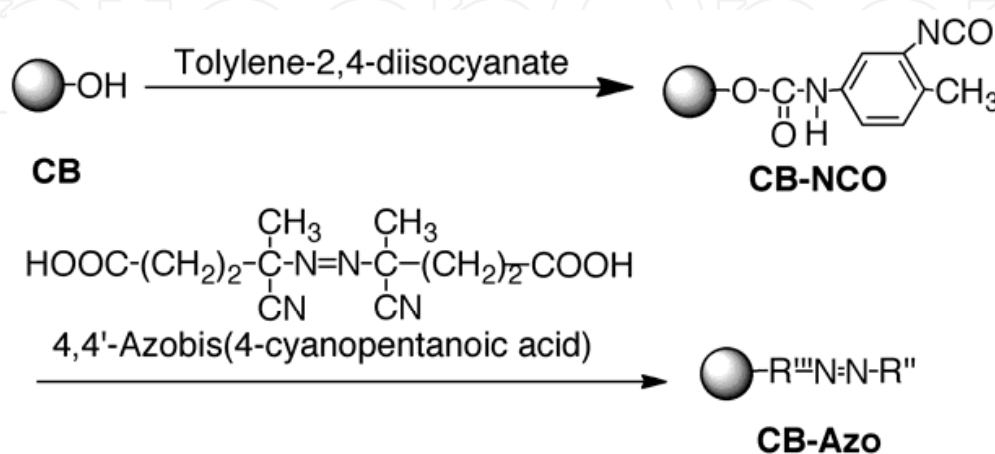
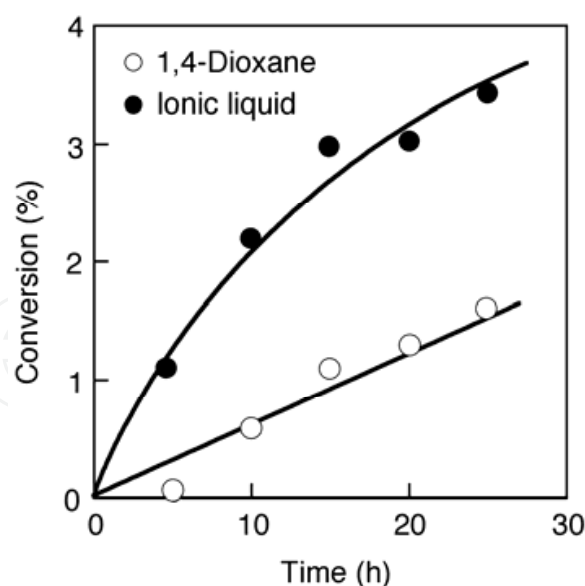Scheme 2. Introduction of azo groups onto carbon black surface.

Fig. 9. Effect of ionic liquid on the graft polymerization of MMA initiated by CB-Azo. CB-Azo, 0.15 g; MMA, 10.0 mL; solvent, 5.0 mL; 70 ˚C.
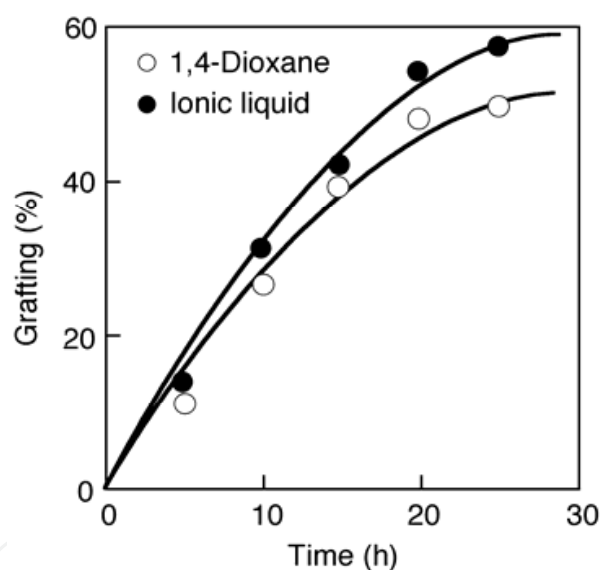

Fig. 10. Relationship between polyMMA grafting and reaction time. Polymerization conditions are shown in Figure 9.

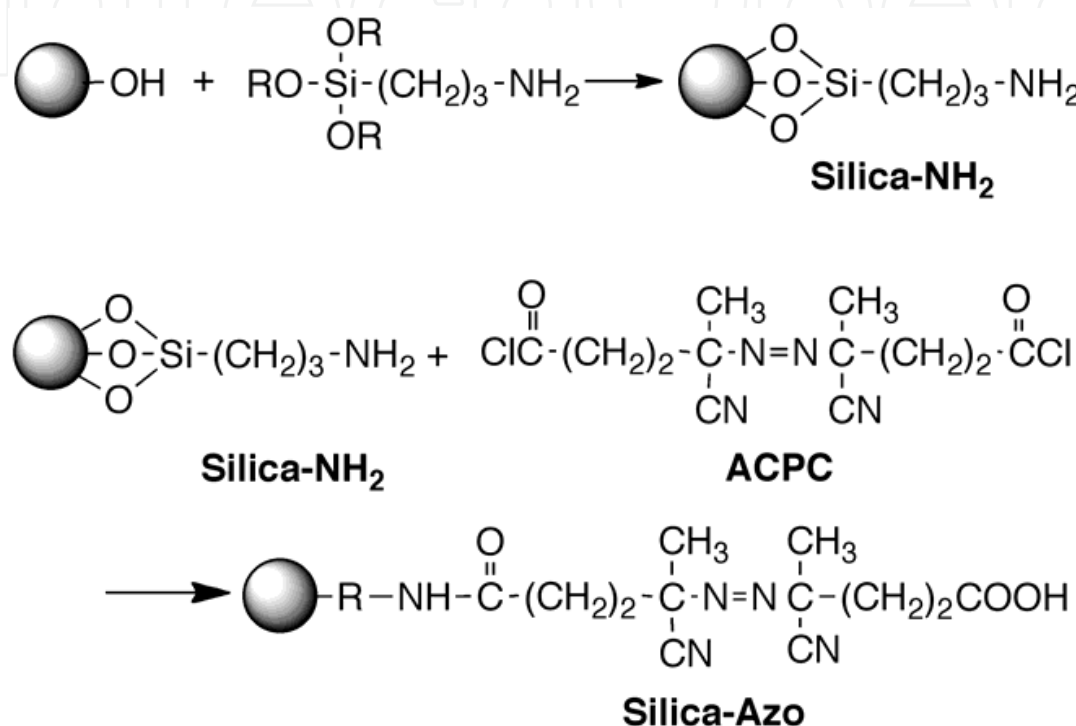(2) Effect of ionic liquid on the graft polymerization of MMA initiated by CB-Azo

The effect of ionic liquid as solvent on the radical graft polymerization of MMA initiated by CB-Azo was investigated. Figure 9 shows the relationship between reaction time and conversion in ionic liquid and 1,4-dioxane. It was found that the rate of the polymerization in ionic liquid was considerably larger than that in 1,4-dioxane.

Figure 10 shows the effect of ionic liquid on the polyMMA grafting onto the carbon black surface obtained from the graft polymerization shown in Figure 9. It was found that the percentage of grafting increased with increasing reaction time in both solvents and the percentage of grafting in ionic liquid was larger than that in 1,4-dioxane.

5.1.2 Radical graft polymerization of St and MMA initiated by azo groups introduced onto silica nanoparticle surface in ionic liquid

(1) Introduction of azo groups onto silica nanoparticle surface

The introduction of azo groups onto silica nanoparticle surface was achieved by the reaction of surface amino groups, which were previously introduced onto the surface by the treatment with 3-aminopropyltriethoxysilane, with 4,4'-azobis(4-cyanopentanoic acid) dichloride (ACPC) as shown in Scheme 3.

Scheme 3. Introduction azo groups onto silica nanoparticle surface.

(2) Effect of ionic liquid on the graft polymerization of St and MMA initiated by Silica-Azo

The effect of ionic liquid as solvent on the radical graft polymerization of St and MMA initiated by Silica-Azo was investigated. Figures 11 and 12 show the effect of ionic liquid on the rate of polymerization of St and MMA initiated by Silica-Azo, respectively. It was found that the rate of the polymerization of both monomers initiated by Silica-Azo in ionic liquid was considerably larger than those in 1,4-dioxane.

Figures 13 and 14 shows the effect of ionic liquid on the grafting of polySt and polyMMA onto the silica nanoparticle surface obtained from the graft polymerization shown in Figures 11 and 12, respectively. It was found that the percentage of grafting onto the silica surface increased with increasing reaction time in both solvents. It is interesting to note that the percentage of grafting in ionic liquid was much larger than those in 1,4-dioxane: the percentage of polySt and polyMMA grafting in ionic liquid were 180% and 300%, respectively.

This may be due to the fact that the lifetime of radical is prolonged because of the high viscosity of the ionic liquid (Wilkkers, 2002; Harrisson et al., 2002; Carmichael & Haddleton, 2003).
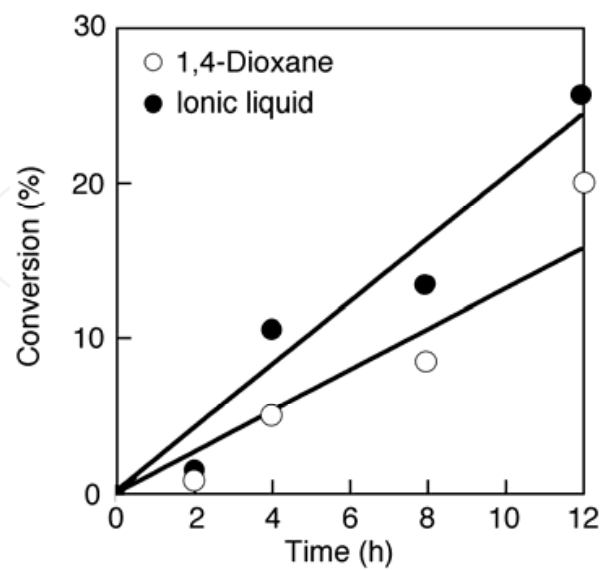
Fig. 11. Effect of ionic liquid on the graft polymerization of St initiated by Silica-Azo. Silica-Azo, 0.20 g; St, 5.0 mL; solvent, 10.0 mL; 70 ˚C.
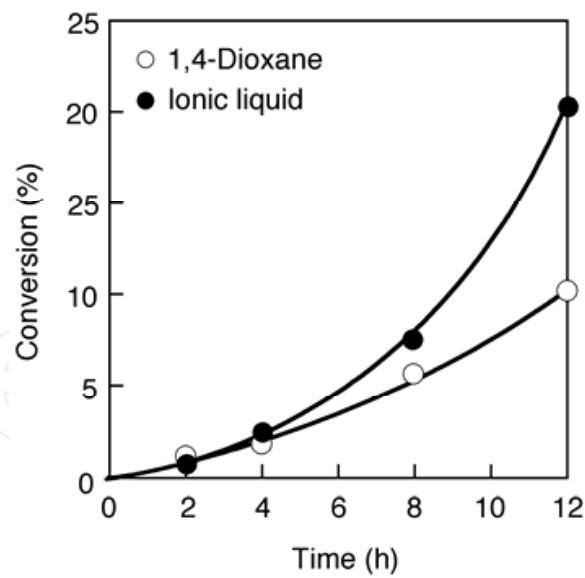

Fig. 12. Effect of ionic liquid on the graft polymerization of MMA initiated by Silica-Azo. Silica-Azo, 0.20 g; MMA, 5.0 mL; solvent, 10.0 mL; 70 ˚C.

Both surface radicals on the nanoparticle surface and fragment radicals formed by the thermal decomposition of surface azo groups initiate the polymerization in the first stage of the polymerization: the surface radicals produce grafted polymer, but the fragment radicals

produce ungrafted polymer as shown in Scheme 4. It is considered that at the last stage of the graft polymerization, the latter reaction preferentially proceeds to give ungrafted polymer, which decreases the grafting efficiency.

On the contrary, it is suggested that in ionic liquid, the propagation of grafted chains from surface radicals formed by the thermal decomposition of azo groups effectively proceeded, because of stabilization of surface radicals and depression of chain transfer reaction.
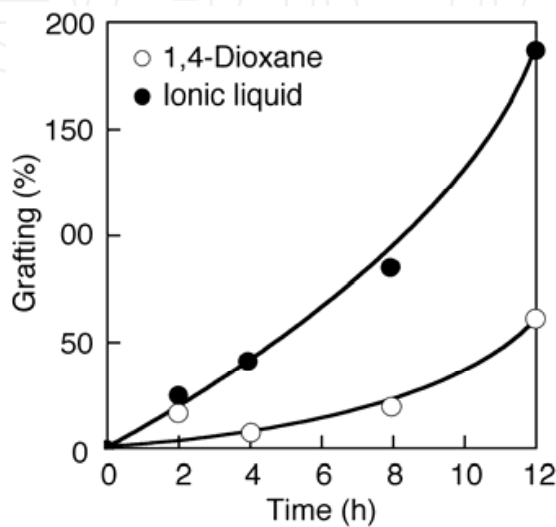

Fig. 13. Relationship between polySt grafting and reaction time. Polymerization conditions are shown in Figure 11.
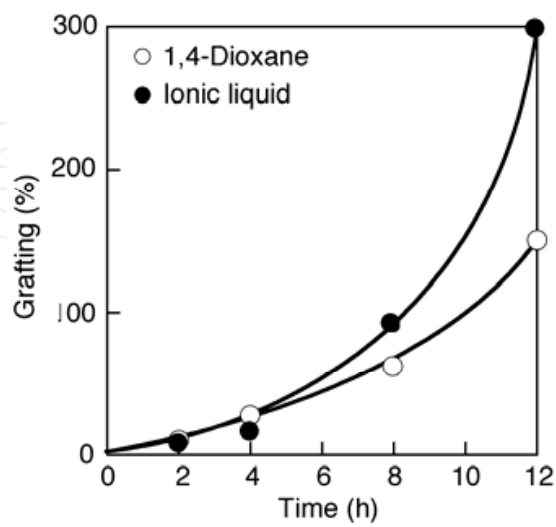

Fig. 14. Relationship between polyMMA grafting and reaction time. Polymerization conditions are shown in Figure 12.

5.1.3 Effect of ionic liquid on the molecular weight of grafted polymer

PolySt grafted onto silica nanoparticle was isolated by the alkali treatment of polySt-grafted silica nanoparticle. Table 2 shows the molecular weight (Mw) of grafted polySt on silica nanoparticle surface and ungrafted polySt obtained from the graft polymerization in ionic liquid and 1,4-dioxane. It was found that molecular weight and molecular weight distribution in ionic liquid were almost equal to those in 1,4-dioxane.

Based on the above result, the number of the grafted polymers on the silica surface was calculated. The results are shown in Table 3. The number of grafted polySt on silica obtained from the polymerization in ionic liquid was about 5-times larger than that in 1,4- dioxane as schematically shown in Figure 15. The proportion used for the grafting site to azo group on the surface (R) was about 5 % in 1,4-dioxane, but about 25 % in ionic liquid.
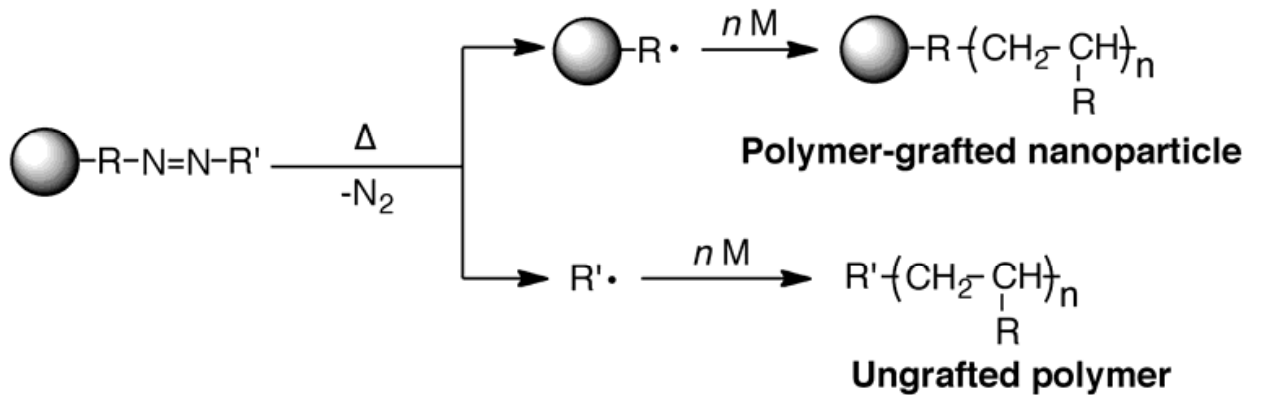
Scheme 4. Graft polymerization initiated by surface azo groups on silica nanoparticle.

Solvent	Mw x10^{-4}		Mw/Mn	
	Ungrafted	Grafted	Ungrafted	Grafted
1,4-Dioxane	5.16	5.45	2.01	1.95
Ionic liquid	5.17	5.47	2.08	2.12

Table 2. Molecular weight of polySt grafted onto silica nanoparticle surface.

Solvent	Number of grafted polymer	R (%)[b]
1,4-Dioxane	2.1 x 10^{18}	5.5
Ionic liquid	9.6 x 10^{18}	25

[a]Silica-Azo, 0.20 g; styrene, 5.0 mL; solvent, 10 mL; 70 °C; 8 h.
[b]R =[Grafted polymer (mmol/g)/ Azo group (mmol/g)] x 100.

Table 3. Number of grafted polySt chain grafted onto silica nanoparticle surface[a].
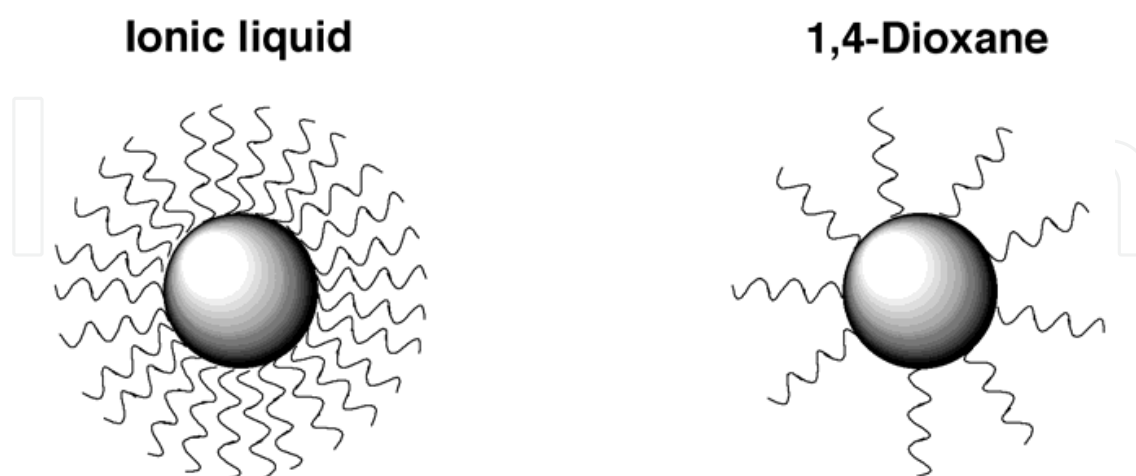
Fig. 15. Polymer chains grafted onto silica nanoparticle surface in ionic liquid and 1,4-dioxane.

The results indicate that in 1,4-dioxane, the growth of the grafted polymer chain from the silica nanoparticle surface is inhibited by the blocking effect of surface radical by grafted polymer chain, but the blocking effect is reduced, because of stabilization of growing polymer radical in ionic liquids.

### 5.2 Recycle of ionic liquid after the radical graft polymerization

Ungrafted polymer precipitated because the polymer is insoluble in ionic liquid. After the graft polymerization, polymerization was terminated by the addition of a small amount of methanol. Therefore, ionic liquid contains polymer-grafted nanoparticles, unreacted monomer, ungrafted polymer, and methanol. The precipitate, containing polymer-grafted nanoparticle and ungrafted polymer, was removed by filtration.

Filtrate contains unreacted monomer and methanol. Methanol and monomer was removed from the filtrate under high vacuum at 70 °C and the resulting ionic liquid could be reused after washing with water followed by drying under high vacuum at 50 °C.

Therefore, the reduction of waste solvent and environmentally friendly scale-up synthesis of polymer-grafted nanoparticles can be achieved by use of ionic liquid as a reaction solvent.

6. Grafting of polymers onto MWCNT in an ionic liquid

1,1-Bis(*t*-butyldioxy)cyclohexane (BDOC) thermally decomposes near 70 °C to give radicals having a peroxyester moiety and a *t*-butoxy radical (Scheme 5). We introduced peroxyester groups onto carbon black surface and MWCNT by the trapping of the radicals having peroxyester moiety. And the radical graft polymerization of vinyl monomers initiated by the peroxyester groups on the surface was achieved (Hayashi et al., 1996).
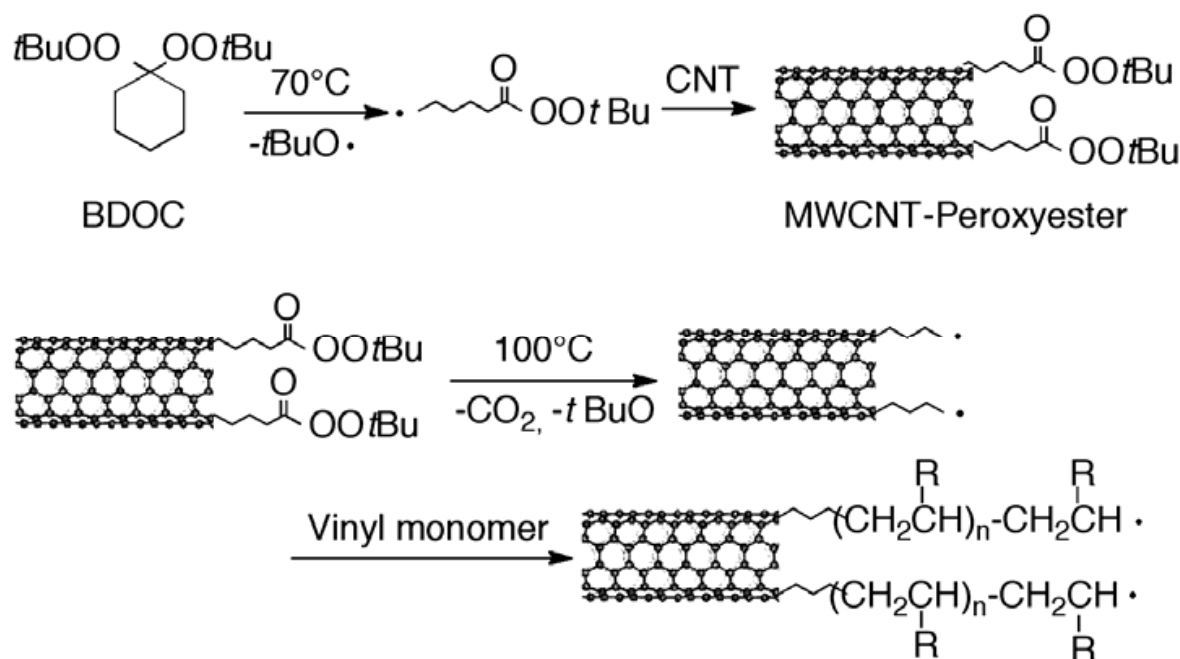
Scheme 5. Introduction of peroxyester groups onto MWCNT surface by the reaction with BDOC.

6.1 Introduction of peroxyester groups onto MWCNT by radical trapping

The effect of ionic liquid as reaction solvent on the trapping of radicals having peroxyester moiety by MWCNT was investigated. The results are shown in Table 4. The amount of peroxyester groups introduced onto MWCNT by the reaction with BDOC in ionic liquid was much larger than that in hexane, because of the stabilization of free radicals in ionic liquid as mentioned above.

Solvent	Time (h)	Peroxyester group (µmol/g)
Ionic liquid	8	30.1
Ionic liquid	10	34.9
Ionic liquid	12	38.3
Hexane	12	9.8

Table 4. Introduction of peroxyester groups onto MWCNT by the reaction with BDOC. MWCNT, 0.02 g; BDOC, 10.0 mL; solvent 10.0 mL; 70°C.

6.2 Grafting of polymers onto MWCNT initiated by peroxyester groups on the surface

Radical graft polymerization of MMA was successfully initiated by surface radicals formed by the thermal decomposition of peroxyester groups introduced onto MWCNT and grafted chains propagated from the surface to give polyMMA-grafted MWCNT: the percentage of grafting was determined to be 60.2% after 4 h at 100°C.

PolyMMA-grafted MWCNT was found to give stable dispersions in a good solvent for polyMMA: untreated MWCNT precipitated completely in THF within 1 h, but no precipitation of polyMMA-grafted MWCNT in THF was observed even after 1 week.

7. Grafting of hyperbranched poly(amidoamine) onto silica nanoparticles by dendrimer synthesis methodology in an ionic liquid

A great interest has been recently focused on "Dendrimer", because dendrimers have the fundamental building blocks, controlled molecular weight, controlled branching and versatility in modification of terminal groups (Tomalia et al., 1985; Tomalia et al., 1987). We have reported that hyperbranched poly(amidoamine) (PAMAM) can be grown from an amino group on silica nanoparticle, chitosan powder, and carbon black surface using dendrimer synthesis methodology in methanol solvent (Tsubokawa et al., 1988c; Tsubokawa et al., 2000; Fujiki et al., 2000; Tsubokawa et al., 2001).

Grafting of hyperbranched PAMAM onto silica nanoparticle surface was achieved by repeating two steps, (1) Michael addition of methyl acrylate (MA) to amino group on the surface and (2) amidation of terminal methyl ester group with ethylenediamine (EDA) as shown in Scheme 6.
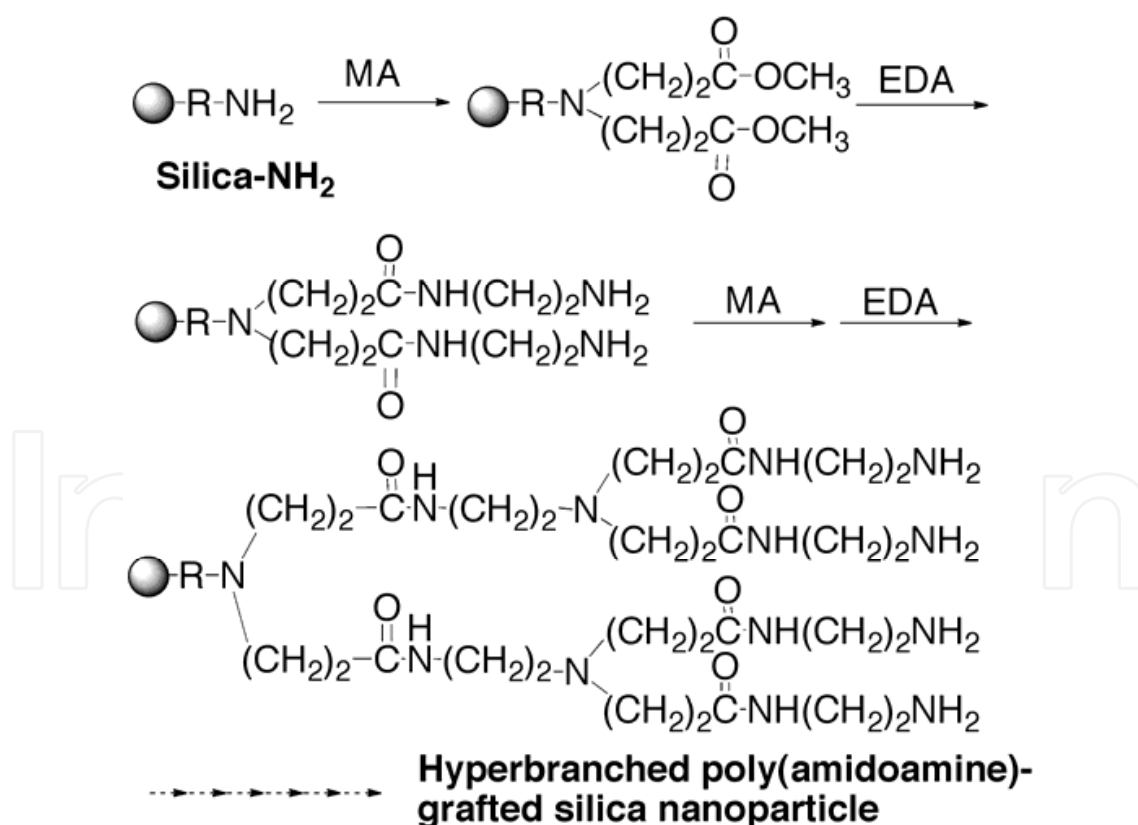
Scheme 6. Grafting of PAMAM onto silica nanoparticle surface by dendrimer synthesis methodology.

The hyperbranched PAMAM-grafted nanoparticle has the possibility of to be utilized as a catalyst support (Hagiwara et al., 2009), biorepellent capsaicin (Yamauchi et al., 2010), and a curing agent of epoxy resin (Ukaji et al., 2008), because hyperbranched PAMAM-grafted nanoparticle has many terminal amino groups.

Therefore, we designed the scale-up synthesis of hyperbranched PAMAM-grafted silica nanoparticle in a solvent-free dry-system (Murota et al., 2002). The preparation of PAMAM-grafted silica in solvent-free dry-system was conducted as follows. MA was sprayed onto silica having amino groups and the silica was agitated at 300 rpm at 50°C. After the reaction, unreacted MA was removed under high vacuum. Then EDA was sprayed and the reaction was conducted at 50°C with agitation. After the reaction, unreacted EDA was also removed under high vacuum at 50°C and MA was sprayed again. The procedures were repeated to grow PAMAM from the surface. The percentage of PAMAM grafting onto the surface was determined to be 141% with repeated reaction cycles of 8-times.

It is considered that by use of ionic solvent as reaction solvent, unreacted MA and EDA can be removed under high vacuum after the reaction as well as solvent-free dry-system. Therefore, we investigated the preparation of hyperbranched PAMAM-grafted silica in ionic solvent.

7.1 Procedures for the grafting of PAMAM onto silica in an ionic liquid

Into a 200-mL four-necked flask, that contained 50 mL of ionic liquid and 5.0 g of silica nanoparticle having amino group, 1.0 g of MA (11.6 mmol; excess of surface amino groups) was added and the reaction mixture was agitated at 300 rpm at 50 °C under argon gas. After 21 h, unreacted MA was removed under high vacuum at 50 °C. After 2 hr, into the flask, 1.0 g of EDA (16.7 mmol; excess of surface ester group) was added and the reaction was conducted at 50 °C with agitation. After 21 h, unreacted EDA was also removed under vacuum at 50 °C for 3 h and MA was added again. Both the Michael addition with MA and the amidation with EDA were repeated to grow PAMAM from the silica surface. After the reaction, PAMAM-grafted silica was isolated by centrifugation.

In order to remove ungrafted PAMAM from PAMAM-grafted silica, the product was dispersed in methanol and centrifuged at 10^4 rpm. The supernatant solution containing ungrafted PAMAM was removed and PAMAM-grafted silica was dispersed in methanol and centrifuged. The procedures were repeated for several times, until no more ungrafted PAMAM was detected in the supernatant solution.

7.2 Grafting of PAMAM in an ionic liquid

The treatment of silica nanoparticle having amino group with MA and EDA in ionic liquid was repeated for *n*-times to obtain PAMAM-grafted silica nanoparticle as shown in Scheme 6 (Murota, et al., 2002).

Table 4 shows the amino group content of silica nanoparticle and the percentage of PAMAM grafting onto silica nanoparticle surface after the grafting reaction. As shown in Table 4, the amino group content and percentage of PAMAM grafting of the resulting silica nanoparticle increased with increasing repeated reaction cycles.

On the other hand, when untreated silica nanoparticle was used, no increase of surface amino group and no grafting of PAMAM onto the surface were observed even with repeated reaction cycles of 8-times.

The percentage of grafting and amino group content of PAMAM-grafted silica obtained in ionic liquid was slightly smaller than those in methanol.

During the grafting reaction, the formation of a small amount of ungrafted polymer was observed: methanol soluble part (major product) was hyperbranched PAMAM and THF soluble part (minor product) was a mixture of polyMA and unknown viscous materials. This indicates that the removal of unreacted monomer in each step was incomplete.

Cycle of repeated reactions	Amino group (mmol/g)		Grafting (%)		R^b
	Found	Calcud.	Found	Calcud.	
2-times	1.5	1.3	13.5	22.6	0.60
6-times	6.8	21.1	90.1	474.0	0.19
8-times	7.7	84.5	99.8	1918.6	0.05

[a]Amino group content of grafting site, 0.33 mmol/g
[b]R =Experimental value/Calculated value

Table 4. Grafting of hyperbranched PAMAM onto silica nanoparticle surface in ionic liquid[a]

The amino group content of silica nanoparticle and percentage of PAMAM grafting, however, were considerably smaller than those of the calculated value. The ratio of experimental value for calculated value, R, remarkably decreased with increasing repeated reaction cycles. The same tendency was observed in the grafting of PAMAM onto silica nanoparticle in methanol solvent system (Tsubokawa et al., 1988; Tsubokawa et al., 2000; Fujiki et al., 2000; Tsubokawa et al., 2001).
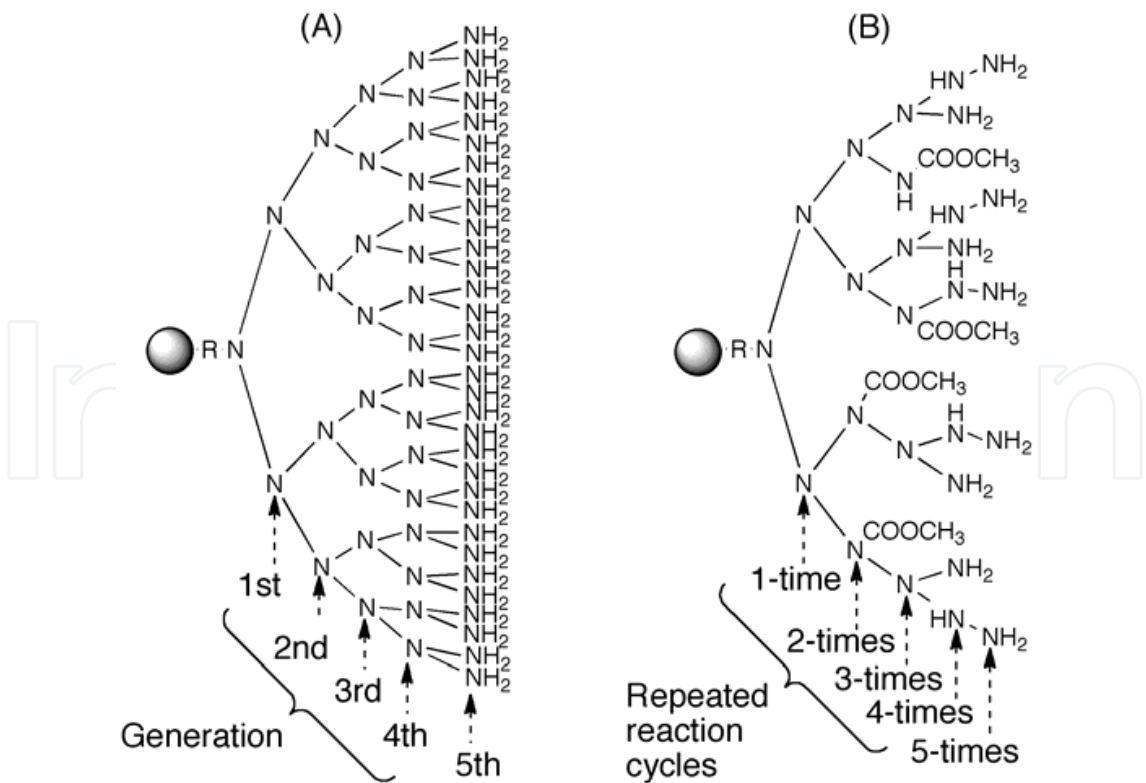

Fig. 16. Illustration of (A) theoretical structure of PAMAM-grafted and (B) hyperbranched PAMAM-grafted silica nanoparticle.

Based on the above results it is concluded that the theoretical propagation of PAMAM from silica nanoparticle surface was hardly achieved and hyperbranched PAMAM was grafted onto the surface: Figure 16 shows illustration of (A) theoretical PAMAM-grafted silica nanoparticle and (B) hyperbranched PAMAM-grafted silica nanoparticle.

This may be due to the fact that (1) complete Michael addition and the amidation with surface amino and ester group hardly proceeded because of aggregation of silica nanoparticles and (2) the grafted chains on the silica surface interfere with the propagation of PAMAM from the surface because of steric hindrance (Tsubokawa et al., 1988; Tsubokawa et al., 2000; Fujiki et al., 2000; Tsubokawa et al., 2001).

8. Conclusion

1. The effect of ionic liquid on the radical polymerization of St and MMA in the presence of carbon black initiated by BPO and AIBN was investigated. When a conventional organic solvent was used as solvent, the polymerization was remarkably retarded by carbon black. On the contrary, the retardation of polymerization was almost eliminated in the initial stage of the polymerization in ionic liquid. It is interesting to note that the percentage of grafting of polySt and polyMMA onto carbon black in ionic liquid was much larger than those in organic solvent.

2. The radical graft polymerizations of vinyl monomers initiated by azo groups introduced onto silica nanoparticle and carbon black surfaces in ionic liquid were investigated. The percentage of grafting in ionic liquid was mach larger than those in 1,4-dioxane. The molecular weight of polySt grafted onto the silica nanoparticle surface in ionic liquid was almost equal that in 1,4-dioxane. The result indicates that the number of grafted polySt in ionic liquid is 5-times that in 1,4-dioxane. This may be due to the fact that lifetime of the surface radical formed by the thermal decomposition of azo groups is prolonged because of the high viscosity of ionic liquid. Therefore, the surface azo groups were effectively used as initiating sites for the graft polymerization.

3. Peroxyester groups were successfully introduced onto MWCNT surface by the trapping of radicals containing peroxyester moieties formed by the thermal decomposition of BDOC. The number of peroxyester groups introduced onto MWCNT in ionic liquid was much larger than those in conventional organic solvent. The radical graft polymerization of MMA was initiated by peroxyester groups on the surface to give polyMMA-grafted MWCNT.

4. Grafting of hyperbranched PAMAM onto silica nanoparticle surface was achieved by repeating two steps in ionic liquid: (1) Michael addition of MA to amino group on the surface and (2) amidation of terminal methyl ester group with EDA. The reaction procedures are considerably simplified by use of ionic liquid as solvent, because unreacted MA and EDA can be removed under high vacuum.

5. The reduction of waste solvent was achieved by use of ionic liquid as reaction solvent, because unreacted monomer could be removed under high vacuum after the reaction and the reuse of ionic liquid was easily achieved. Therefore, the graft polymerization onto nanoparticle surface in ionic liquid enables environmentally friendly scale-up synthesis of polymer-grafted nanoparticles.

9. Acknowledgment

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This volume, of a two volume set on ionic liquids, focuses on the applications of ionic liquids in a growing range of areas. Throughout the 1990s, it seemed that most of the attention in the area of ionic liquids applications was directed toward their use as solvents for organic and transition-metal-catalyzed reactions. Certainly, this interest continues on to the present date, but the most innovative uses of ionic liquids span a much more diverse field than just synthesis. Some of the main topics of coverage include the application of RTILs in various electronic applications (batteries, capacitors, and light-emitting materials), polymers (synthesis and functionalization), nanomaterials (synthesis and stabilization), and separations. More unusual applications can be noted in the fields of biomass utilization, spectroscopy, optics, lubricants, fuels, and refrigerants. It is hoped that the diversity of this volume will serve as an inspiration for even further advances in the use of RTILs.