Polymer Bulletin 60, 617–624 (2008)
DOI 10.1007/s00289-008-0899-5

Polymer Bulletin

Cationic Graft Polymerization onto Silica Nanoparticle Surface in a Solvent-Free Dry-System

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Received: 9 October 2007 / Revised version: 9 December 2007 / Accepted: 5 January 2008

Summary

For the purpose of the prevention of the environmental pollution and the simplification of reaction process, the scale-up synthesis of polymer-grafted silica nanoparticle by surface initiated cationic ring-opening graft polymerization of 2-methyl-2-oxazoline (MeOZO) in a solvent-free dry-system was investigated. The introduction of iodopropyl groups onto the silica surface as initiating group was carried out by the reaction of silanol groups with 3-iodopropyl- trimethoxysilane in a solvent-free dry-system. The graft polymerization of MeOZO onto silica nanoparticle surface in a solvent-free dry-system was initiated by spraying the monomer onto the surface having iodopropyl groups and the polymerization was conducted in powder fluid system under nitrogen. After the polymerization, unreacted MeOZO was readily removed under high vacuum. It was found that the cationic ring-opening polymerization of MeOZO was successfully initiated in the solvent-free dry-system to give polyMeOZO-grafted silica nanoparticles. The maximum grafting of polyMeOZO obtained from the polymerization initiated by iodopropyl groups on the surface reached 47.7 %. The percentage of grafting and grafting efficiency during the cationic ring-opening graft polymerization in the solvent-free dry-system were considerably larger than those in solution system. This suggests that chain transfer reaction from surface growing cation to monomer was effectively inhibited in the solvent-free dry-system.

Introduction

We have reported the grafting of various polymers onto the surface of nanocarbons, such as carbon black [1,2], and carbon nanotube [3], nanodiamond, and inorganic nanoparticles, such as silica [2,4] and titanium dioxide. Polymer-grafted nanoparticles are known to have excellent properties, such as a good dispersibility in solvents and polymer matrices [1-4].

To obtain polymer-grafted nanoparticles with a high percentage of grafting, it is desirable to initiate the graft polymerization from initiating groups introduced onto the nanoparticle surfaces [1-4]. We have successfully achieved the radical graft polymerization initiated by various initiating groups introduced onto nanoparticles in organic solvents [1-4]. For example, it has been reported that the radical polymerizations of vinyl monomers were initiated by azo and peroxide groups introduced onto silica [5,6] and carbon black [7,8] to give the corresponding polymer-grafted nanoparticles. In the above polymerizations, it was confirmed that the grafted polymer chains are propagated from the surface radicals formed by the thermal decomposition of azo and peroxy groups introduced onto the surfaces in organic solvents. In addition, it was reported that the grafting of polymers onto silica nanoparticle surfaces by the cationic ring-opening polymerization of 2-methyl-2-oxazoline (MeOZO) initiated by surface carboxyl [9] and chloromethyl [10] groups.

However, scale-up production of polymer-grafted nanoparticles was hardly achieved, because complicated procedures, such as centrifugation, filtration, and solvent extraction, are needed for the production of polymer-grafted nanoparticles, and a lot of waste solvent comes out.

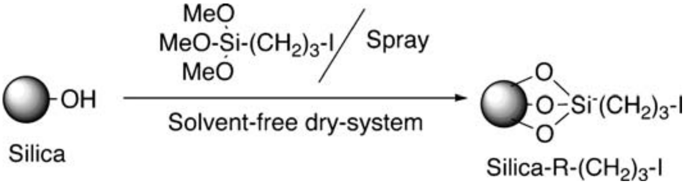
In the previous paper, we have reported a scale-up synthesis of hyperbranched poly(amidoamine)-grafted silica nanoparticle in a solvent free-dry system by using dendrimer synthesis methodology [11]. That is, hyperbranched poly(amidoamine) was allowed to grow from silica surface by repeating two steps, (1) Michael addition of methyl acrylate (MA) to amino groups on the surface and (2) amidation of terminal ester groups with ethylenediamine (EDA). MA was sprayed onto silica having amino groups and the silica was agitated. After the reaction, unreacted MA was removed under vacuum. Then, EDA was sprayed and the reaction was conducted with agitation. After the reaction, unreacted EDA was also removed under vacuum and MA was sprayed again. More recently, we have reported the radical graft polymerization of vinyl monomers onto silica nanoparticle initiated by azo groups previously introduced onto the surface in a solvent-free dry-system [12]. We pointed out that the formation of ungrafted polymer was remarkably depressed in the solvent-free dry-system in comparison with graft polymerization in solution and bulk.

In the present paper, the cationic ring-opening graft polymerization of MeOZO onto silica nanoparticle surface initiated by iodopropyl groups previously introduced onto the surface in a solvent-free dry-system was investigated (Schemes 1 and 2). In addition, the difference between the cationic ring-opening graft polymerization in solution system and solvent-free dry-system will be discussed.

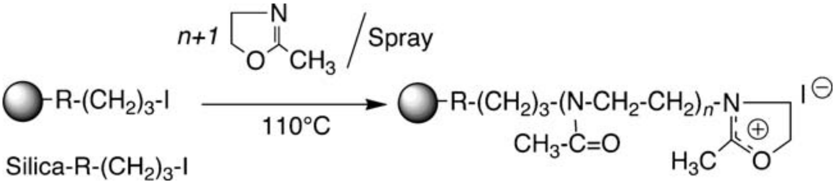
Experimental

Material and reagents

Silica nanoparticle used was Aerosil 200 obtained from Nippon Aerosil Co., Ltd., Japan. The silica was dried *in vacuo* at 110°C for 48 h before use. The specific surface area and particle size were 200 m^2/g and 12 nm, respectively. The content of surface silanol groups was determined to be 1.38 mmol/g by volumetrically measuring the amount of ethane evolved by the reaction with triethylaluminum [13].



Scheme 1. Introduction of iodopropyl groups onto silica nanoparticle by the treatment with 3-iodopropyltrimethoxysilane in a solvent-free dry-system



Scheme 2. Cationic ring-opening graft polymerization of MeOZO initiated by Silica-R-$(CH_2)_3$-I in a solvent-free dry-system

3-Iodopropyltrimethoxysilane (IPTMS) obtained from Chisso Co., Ltd., Japan, was used without further purification. 2-Methyl-2-oxazoline (MeOZO) obtained from Aldrich Chemical Co., Inc. was dried over potassium hydroxide and distilled twice before use. Other solvents and reagents were purified by ordinary methods.

Introduction of iodopropyl groups onto silica nanoparticle surface

The introduction of iodopropyl groups onto silica surface was achieved by the treatment of surface silanol groups with IPTMS in a solvent-free dry-system and in solution system [11,14].

The introduction of iodopropyl groups onto silica surface in a solvent-free dry-system was carried out as follows. Into a 200 mL thee-necked flask (as shown in Figure 1)

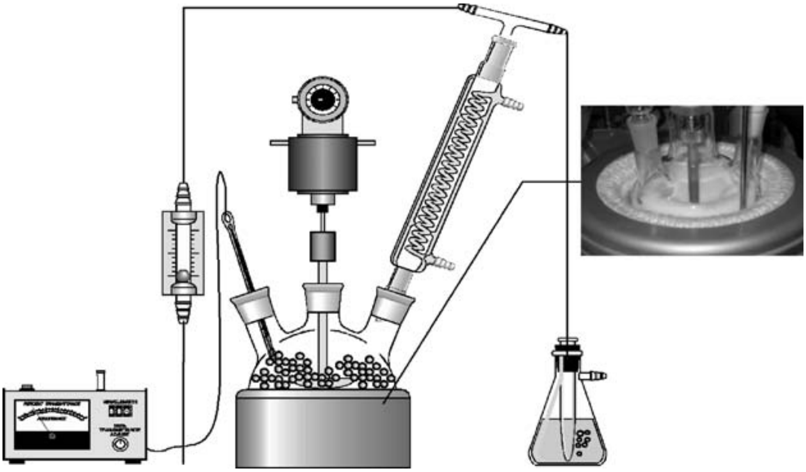


Figure 1. Reaction apparatus for the synthesis of Silica-R-$(CH_2)_3$-I and cationic ring-opening graft polymerization of MeOZO in a solvent-free dry-system

that contained 4.0 g of silica nanoparticle, 8.3 mmol of IPTMS was sprayed and the silica nanoparticle was agitated at 100 rpm at 250°C for 3 h under nitrogen. After the reaction, unreacted IPTMS was completely removed under high vacuum. The silica having iodopropyl groups was abbreviated as Silica-R-$(CH_2)_3$-I.

Polymerization procedures in a solvent-free dry-system

After the introduction of iodopropyl groups onto silica surface in a solvent-free dry-system, the cationic ring-opening graft polymerization was carried out without isolation of resulting Silica-R-$(CH_2)_3$-I. Into the thee-necked flask that contained 4.0 g of Silica-R-$(CH_2)_3$-I, MeOZO was sprayed and the silica nanoparticle was agitated at 100 rpm at 110°C (boiling point of MeOZO) under nitrogen. After the reaction, unreacted MeOZO was removed under high vacuum.

Polymerization procedures in solution

Cationic ring-opening graft polymerization of MeOZO onto silica nanoparticle surface initiated by Silica-R-$(CH_2)_3$-I in solution (bulk) was achieved as follows. Into a sealed tube that contained 0.20 g of Silica–$(CH_2)_3$-I and 190 mmol of MeOZO was added. The tube was sealed and the mixture was stirred with a magnetic stirrer at 110°C. After the reaction, the polymerization was terminated by the addition of methanol into the flask.

Determination of iodopropyl group content on silica nanoparticle surface

The amount of iodopropyl groups on silica nanoparticle surface was determined by the following equation,

$$\text{Iodopropyl group (mmol/g)} = (A/B) / C,$$

where A is weight of iodopropyl group introduced onto silica nanoparticle surface (g), B is weight of silica charged (g) and C is molecule weight of iodopropyl groups. The weight of iodopropyl groups introduced onto silica surface was determined by weight loss when the silica was heated at 800°C by use of a thermogravimetric analyzer (TGA) (Simadzu TGA-50).

Determination of percentage of grafting and grafting efficiency

Silica nanoparticle obtained from the grafting reaction was dispersed in methanol, and the dispersion was allowed to centrifuge $1.5\text{x}10^4$ rpm. The silica precipitated was dispersed again in methanol and centrifuged. The procedures were repeated until no more polymer could be detected in the supernatant solution. The percentage of grafting was determined by the following equation,

$$\text{Grafting (\%)} = (D/B) \text{ x } 100,$$

where D is weight of grafted polyMeOZO (g) and B is weight of silica nanoparticle charged (g). The weight of polyMeOZO grafted onto silica surface was determined by weight loss when polyMeOZO-grafted silica was heated at 800°C by use of a thermogravimetric analyzer (TGA) (Simadzu TGA-50).

The grafting efficiency was determined by the following equation,

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

where D is weight of grafted polyMeOZO (g) and E is weight of total polymer formed (grafted polymer + ungrafted polymer) (g). The weight of total polymer formed was determined by weight loss when the product, obtained by the precipitation of reaction mixture, was heated at 800°C.

Characterization of polyMeOZO-grafted silica nanoparticle

The characterization of grafted polymer on silica nanoparticle was identified by FT-IR spectra. FT-IR spectra were recorded on a Simadzu FT-IR Spectrophotometer (Model 8200-A) using KBr pellet.

Results and discussion

Introduction of iodopropyl groups onto silica nanoparticle

Generally, the introduction of iodopropyl groups onto silica surface was achieved by the reaction of surface silanol groups with silane coupling agents in solution. In the present work, the introduction of iodopropyl groups onto silica nanoparticle surface was achieved by the treatment of silica with IPTMS, both in a solution system and a solvent-free dry-system. In a solvent-free dry-system, IPTMS was splayed onto silica nanoparticle surface and the reaction was conducted in powder fluid system. After the reaction, unreacted IPTMS was removed under high vacuum.

Table 1 shows the maximum amount of iodopropyl groups introduced onto the silica nanoparticle surface in a solution (toluene) and a solvent-free dry-system. As shown in Table 1, the maximum amount of iodopropyl groups introduced onto silica nanoparticle surface in the solvent-free dry-system was nearly equal to those in solution system. It was found that in the solvent-free dry-system, the reaction time was considerably shortened, because of higher reaction temperature and higher concentration of IPTMS.

Table 1. Introduction of iodopropyl groups onto silica nanoparticle by the treatment with IPTMS in solution and in solvent-free dry-system

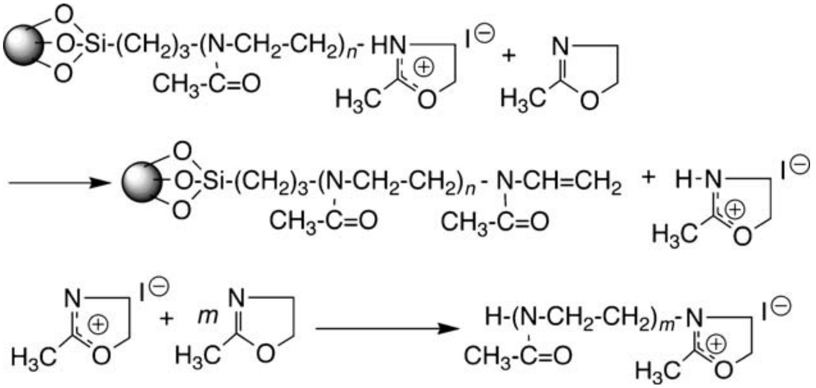
System	Temperature (°C)	Time (h)	Iodopropyl group (mmol/g)
Solvent-free dry$^{1)}$	250	3	0.19
Solution$^{2)}$	110	24	0.16

$^{1)}$ Silica, 4.0 g; IPTMS, 8.3 mmol.
$^{2)}$ Silica, 4.0 g; IPTMS, 33.5 mmol: toluene, 90 mL.

Cationic ring-opening graft polymerization of MeOZO onto silica nanoparticle

It is well known that methyl iodide have an ability to initiate the cationic ring-opening polymerization of MeOZO [15]. We have reported the cationic ring-opening polymerization of MeOZO initiated by chloromethyl groups previously introduced onto carbon black surface to give polyMeOZO-grafted carbon black [12]. However, the grafting efficiency was less than few percent because of preferential chain transfer reaction of growing polymer cation to monomer in solution (Scheme 3).

In the previous paper, we reported that surface radicals are stabilized and the chain transfer reaction of growing polymer radicals from solid surface to monomer remarkably depressed in solvent-free dry-system because of low monomer concentration in gas phase [12]. Endo and his coworkers also reported the living nature of free radical polymerization on solid surface in the presence of monomer vapors [16-18].



Scheme 3. Chain transfer reaction during the cationic ring-opening polymerization of MeOZO initiated by Silica-R-$(CH_2)_3$-I

It is expected that the chain transfer reaction of growing polymer cation form the surface is also inhibited in a solvent-free dry-system. Therefore, the cationic ring-opening graft polymerization of MeOZO onto silica nanoparticle surface initiated by Silica–$(CH_2)_3$-I in a solvent-free dry-system was investigated.

After the introduction of iodopropyl groups onto silica surface in the solvent-free dry-system, without isolation of resulting Silica–$(CH_2)_3$-I, MeOZO was sprayed onto the Silica–$(CH_2)_3$-I and the graft polymerization was conducted in powder fluid system.

Table 2 shows the result of the cationic ring-opening graft polymerization of MeOZO in the presence of Silica–$(CH_2)_3$-I in the solvent-free dry-system. It was found that even in the solvent-free dry-system, Silica–$(CH_2)_3$-I have an ability to initiate the cationic ring-opening polymerization of MeOZO to give polyMeOZO-grafted silica nanoparticles. The percentage of polyMeOZO grafting onto the surface of silica nanoparticle increased to nearly 100 % with increasing MeOZO monomer concentration.

On the other hand, the grafting efficiency tends to decrease with increasing of MeOZO monomer concentration. The results suggest that chain transfer reaction was accelerated with increasing MeOZO monomer concentration. However, the grafting efficiency was considerably high, that is 20% even after the conversion reached 99%.

Table 2. Cationic ring-opening graft polymerization of MeOZO initiated by Silica-R-$(CH_2)_3$-I in a solvent-free dry-system

Silica	MeOZO (mmol)	Conversion (%)	Grafting (%)	Grafting efficiency (%)
Untreated	43.8	0	0	-
Silica-R-$(CH_2)_3$-I	43.8	48.3	17.4	40.0
Silica-R-$(CH_2)_3$-I	80.0	87.8	47.7	26.5
Silica-R-$(CH_2)_3$-I	126.7	99.0	44.3	19.2

Silica-R-$(CH_2)_3$-I, 4.0 g; 110°C; 24 h.

Figure 2 shows FT-IR spectra of untreated silica nanoparticle, polyMeOZO-grafted silica nanoparticle, and polyMeOZO. FT-IR spectra of polyMeOZO-grafted silica nanoparticle show new absorptions at 1630 cm^{-1}, 2860 cm^{-1}, and 2930 cm^{-1}, which are

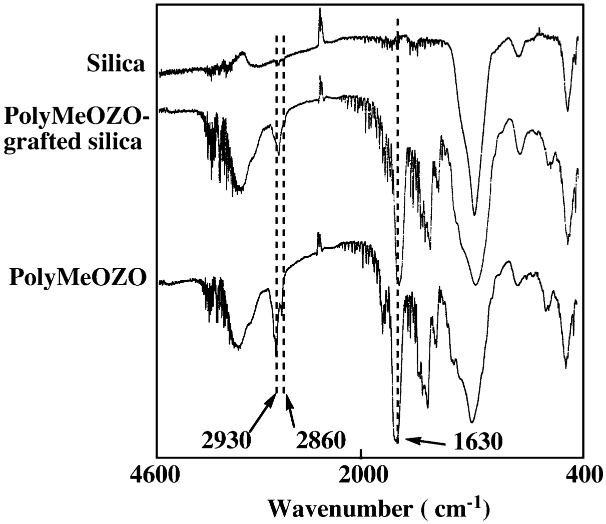


Figure 2. FT-IR spectra of untreated silica, polyMeOZO-grafted silica, and polyMeOZO

characteristic of polyMeOZO. These results clearly indicate that polyMeOZO was grafted onto silica nanoparticle surface.

Comparison of grafting and grafting efficiency in solution with those in solvent-free dry system

Table 3 shows the comparison of the cationic ring-opening polymerization of MeOZO initiated by Silica–$(CH_2)_3$-I in the solvent-free dry-system with those in solution system: the polymerization in solution was carried out in bulk to prevent the chain transfer to solvent. It became apparent that the conversion, grafting, and grafting efficiency in the solvent-free dry-system were much larger than those in solution system. In addition, the grafting efficiency in the solvent-free dry-system didn't decrease with progress of the polymerization.

Table 3. Cationic ring-opening graft polymerization of initiated by Silica-R-$(CH_2)_3$-I in the solvent-free dry-system and in solution (bulk)

System	Time (h)	Conversion (%)	Grafting (%)	Grafting efficiency (%)
Solvent-free dry[1)]	2	98.8	44.0	22.0
Solvent-free dry[1)]	6	94.0	44.5	26.2
Solution[2)]	2	0.5	9.7	25.0
Solution[2)]	6	2.1	8.6	6.4

[1)] Silica-R-$(CH_2)_3$-I, 4.0 g; MeOZO, 87.7 mmol; 110°C.
[2)] Silica-R-$(CH_2)_3$-I, 0.2 g; MeOZO, 190 mmol; 110°C.

The result suggests that in solvent-free dry-system, growing polymer cations on the silica surface was stabilized and the chain transfer reaction of growing polymer cation on the silica surface to monomer was depressed because of low monomer concentration in vapor phase. The same tendency was observed during the radical graft polymerization initiated by azo groups introduced onto silica surface [12] and the living nature of the free radical polymerization on solid surface in the presence of monomer vapors [16-18].

Conclusions

1. The introduction of isopropyl groups and graft polymerization in solvent-free dry-system were achieved by splaying coupling agent and monomer, respectively, onto silica nanoparticle surface and the reaction was conducted in powder fluid system under nitrogen. After the reaction, unreacted coupling agent and monomer were removed under high vacuum.
2. The introduction of iodopropyl group onto silica nanoparticle surface was successfully achieved by the treatment with IPTMS in the solvent-free dry-system.
3. The cationic ring-opening graft polymerization of MeOZO onto silica nanoparticle surface was successfully initiated by iodopropyl group introduced onto the surface in solvent-free dry-system to give polyMeOZO-grafted silica nanoparticle.
4. The maximum grafting of polyMeOZO obtained from the polymerization initiated by iodopropyl group on the surface reached 47.7 %.
5. The conversion, grafting, and grafting efficiency in the solvent-free dry-system were considerably larger than those in solution system because of depression of chain transfer reaction of growing polymer cation to monomer.
6. The solvent-free dry-system is suitable for the scale-up synthesis of polymer-grafted silica, because the complicated operation is not required, furthermore, the environment loading is small to diminish the waste solvent.

Acknowledgements. This study was partly supported by a Grant in Aid for Scientific Research from the Ministry of Education, Culture, Sport, Science and Technology of Japan (No. 19560691), which is gratefully acknowledged.

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